Handbook of Environmental Engineering 22

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Integrated Natural Resources Research

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Series Editors

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The past 30 years have seen the emergence of a growing desire worldwide to take positive actions to restore and protect the environment from the degrading effects of all forms of pollution: air, noise, solid waste, and water. The principle intention of the Handbook of Environmental Engineering (HEE) series is to help readers formulate answers to the fundamental questions facing pollution in the modern era, mainly, how serious is pollution and is the technology needed to abate it not only available, but feasible. Cutting-edge and highly practical, HEE offers educators, students, and engineers a strong grounding in the principles of Environmental Engineering, as well as providing effective methods for developing optimal abatement technologies at costs that are fully justified by the degree of abatement achieved. With an emphasis on using the Best Available Technologies, the authors of these volumes present the necessary engineering protocols derived from the fundamental principles of chemistry, physics, and mathematics, making these volumes a must have for environmental pollution researchers.

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Preface

The past 75 years have seen the emergence of a growing desire worldwide that positive actions should be taken to restore and protect the environment from the degrading effects of all forms of pollution—air, water, soil, thermal, radioactive, and noise. Since pollution is a direct or indirect consequence of waste, the seemingly idealistic demand for "zero discharge" can be construed as an unrealistic demand for zero waste. However, as long as waste continues to exist, we can only attempt to abate the subsequent pollution by converting it to a less noxious form. Three major questions usually arise when a particular type of pollution has been identified: (1) How serious are the environmental pollution and natural resources crisis? (2) Is the technology to abate them available? and (3) Do the costs of abatement justify the degree of abatement achieved for environmental protection and natural resources conservation? This book is one of the volumes of the Handbook of Environmental Engineering series. The principal intention of this series is to help readers formulate answers to the above three questions.

The traditional approach of applying tried-and-true solutions to specific environmental and natural resources problems has been a major contributing factor to the success of environmental engineering and has accounted in large measure for the establishment of a "methodology of pollution control." However, the realization of the ever-increasing complexity and interrelated nature of current environmental problems renders it imperative that intelligent planning of pollution abatement systems be undertaken. Prerequisite to such planning is an understanding of the performance, potential, and limitations of the various methods of environmental protection available for environmental scientists and engineers. In this series of handbooks, we will review at a tutorial level a broad spectrum of engineering systems (natural environment, processes, operations, and methods) currently being utilized, or of potential utility, for pollution abatement, environmental protection, and natural resources conservation. We believe that the unified interdisciplinary approach presented in these handbooks is a logical step in the evolution of environmental engineering.

Treatment of the various engineering systems presented will show how an engineering formulation of the subject flows naturally from the fundamental principles and theories of chemistry, microbiology, physics, and mathematics. This emphasis on fundamental science recognizes that engineering practice has in recent years become more firmly based on scientific principles rather than on its earlier dependency on empirical accumulation of facts. It is not intended, though, to neglect empiricism where such data lead quickly to the most economic design; certain engineering systems are not readily amenable to fundamental scientific analysis, and in these instances we have resorted to less science in favor of more art and empiricism.

Since an environmental natural resources engineer must understand science within the context of applications, we first present the development of the scientific basis of a particular subject, followed by exposition of the pertinent design concepts and operations, and detailed explanations of their applications to natural resources conservation or environmental protection. Throughout the series, methods of mathematical modeling, system analysis, practical design, and calculation are illustrated by numerical examples. These examples clearly demonstrate how organized, analytical reasoning leads to the most direct and clear solutions. Wherever possible, pertinent cost data or models have been provided.

Our treatment of environmental natural resources engineering is offered in the belief that the trained engineer should more firmly understand fundamental principles, be more aware of the similarities and/or differences among many of the engineering systems, and exhibit greater flexibility and originality in the definition and innovative solution of environmental system problems. In short, the environmental and natural resources engineers should by conviction and practice be more readily adaptable to change and progress.

Coverage of the unusually broad field of environmental natural resources engineering has demanded an expertise that could only be provided through multiple authorships. Each author (or group of authors) was permitted to employ, within reasonable limits, the customary personal style in organizing and presenting a particular subject area; consequently, it has been difficult to treat all subject materials in a homogeneous manner. Moreover, owing to limitations of space, some of the authors' favored topics could not be treated in great detail, and many less important topics had to be merely mentioned or commented on briefly. All authors have provided an excellent list of references at the end of each chapter for the benefit of interested readers. As each chapter is meant to be self-contained, some mild repetition among the various texts was unavoidable. In each case, all omissions or repetitions are the responsibility of the editors and not the individual authors. With the current trend toward metrication, the question of using a consistent system of units has been a problem. Wherever possible, the authors have used the British system (fps) along with the metric equivalent (mks, cgs, or SIU) or vice versa. The editors sincerely hope that this redundancy of units' usage will prove to be useful rather than being disruptive to the reader.

The goals of the *Handbook of Environmental Engineering* series are: (1) to cover entire environmental fields, including air and noise pollution control, solid waste processing and resource recovery, physicochemical treatment processes, biological treatment processes, biotechnology, biosolids management, flotation technology, membrane technology, desalination technology, water resources, natural control processes, radioactive waste disposal, hazardous waste management, and thermal pollution control; and (2) to employ a multimedia approach to environmental conservation and protection since air, water, soil, and energy are all interrelated.

This book (Volume 22) and its three sister books (Volumes 17, 19, and 20) of the *Handbook of Environmental Engineering* series have been designed to serve as a natural resources engineering reference books as well as supplemental textbooks. We hope and expect they will prove of equal high value to advanced undergraduate and graduate students, to designers of natural resources systems, and to scientists and researchers. The editors welcome comments from readers in all of these categories. It is our hope that the four natural resources engineering books will not only provide information on natural resources engineering, but will also serve as a basis for advanced study or specialized investigation of the theory and analysis of various natural resources systems.

This book, *Integrated Natural Resources Research, Volume 22,* covers the topics on Fenton oxidation and biological activated carbon treatment for recycling biotreated coking plant wastewater; composting for food processing wastes; treatment of wastewaters from chemical industries; agricultural waste as a low-cost adsorbent; waste vegetable oils, fats, and cooking oils in biodiesel production; physicochemical treatment consisting of chemical coagulation, precipitation, sedimentation, and flotation; water quality control of tidal rivers and estuaries; first wave of flotation technology evolution; once the world's largest DAF-filtration plant; hydroelectric facility; cationic surfactant analysis with good laboratory practice and waste management; treatment of laundry wastewater by physicochemical processes including flotation; book review; and glossary of water quality, treatment, and recovery.

This book's first sister book, *Natural Resources and Control Processes, Volume 17*, covers the topics on the management of agricultural livestock wastes for water resources protection; application of natural processes for environmental protection; proper deep well waste disposal; treating and managing industrial dye wastes; health effects and control of toxic lead in the environment; municipal and industrial wastewater treatment using plastic trickling filters for BOD and nutrient removal; chloride removal for recycling fly ash from municipal solid waste incinerator; recent evaluation of early radioactive disposal and management practice; recent trends in the evaluation of cementitious material in radioactive waste disposal; extensive monitoring system of sediment transport for reservoir sediment management; and land and energy resources engineering glossary.

This book's second sister book, *Environmental and Natural Resources Engineering, Volume 19*, covers the topics on understanding, conservation, and protection of precious natural resources—bees; waste reclamation for reuse; biological processes for water resources protection and water reuse; removal of endocrine disruptors for environmental protection; cooling and reuse of thermal discharges; basic hydrology, water resources, and DAF boat plant for lake restoration; cadmium detoxification by sintering with ceramic matrices; treatment of vegetable oil refining wastes; environmental engineering education; environmental control of pests and vectors; new book reviews; and glossary of environmental and natural resources engineering.

This book’s third sister book, *Integrated Natural Resources Management, Volume 20*, covers the topics on the effect of global warming and climate change on glaciers and salmons; village-driven latrines with “engineers without borders—USA”; surface water quality analysis; treatment of electrical and electronic components manufacturing wastes; geographic information systems and remote sensing applications in environmental and water resources; investigation and management of water losses from wet infrastructure; lake restoration and acidic water control; biohydrogen production through mixed culture dark anaerobic fermentation of industrial waste; agricultural wastes-derived adsorbents for decontamination of heavy metals; removal of heavy metal ions using magnetic materials; and biohydrogen production from lignocellulosic biomass by extremely halotolerant bacterial communities from a salt pan and salt damaged soil.

The editors are pleased to acknowledge the encouragement and support received from Mr. Aaron Schiller, Executive Editor of the Springer Nature Switzerland, and his colleagues, during the conceptual stages of this endeavor. We wish to thank the contributing authors for their time and effort and for having patiently borne our reviews and numerous queries and comments. We are very grateful to our respective families for their patience and understanding during some rather trying times.

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Lawrence K. Wang has served the society and the humanity as a professor, inventor, chief engineer, chief editor, and public servant for 30+ years, with experience in facility design, environmental sustainability, natural resources, resources recovery, global pollution control, construction, plant operation, management, STEM/STEAM education, and analytical chemistry. He is a licensed NY-MA-NJ-PA-OH Professional Engineer, a certified NY-MA-RI Water Quality Laboratory Director, a MA-NY Water Operator, and an OSHA Train-the-Trainer Instructor. He has special passion, talent, and expertise in developing various innovative technologies, educational programs, licensing courses, international projects, academic publications, and humanitarian organizations, all for his dream goal of promoting world peace. He is a retired Acting President/Engineering Director/VP of the Lenox Institute of Water Technology (LIWT), Krofta Engineering Corporation (KEC), and Zorex Corporation, respectively, in the USA, a Senior Advisor of the United Nations Industrial Development Organization (UNIDO) in Vienna, Austria, and a professor in the USA and Taiwan. Dr. Wang is the author of over 750 papers and 50 books and is credited with 24 US invention patents and *5* foreign patents. He received his BSCE degree from National Cheng-Kung University, Taiwan, ROC, his two MS degrees from the University of Missouri and the University of Rhode Island, USA, and his PhD degree from Rutgers University, USA. Currently he is the Chief Series Editor of the *Advances in Industrial and Hazardous Wastes Treatment* series (CRC Press of Taylor & Francis Group), the *Handbook of Environmental Engineering* series (Springer), the *Evolutionary Progress in Science, Technology, Engineering, Arts, and Mathematics series* (Lenox Institute Press), and the *Environmental Science, Technology, Engineering and*

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Mu-Hao Sung Wang has been an engineer, an editor, and a professor serving private firms, governments, and universities in the USA and Taiwan for over 25 years. She is a licensed Professional Engineer and a Diplomate of American Academy of Environmental Engineers. Her publications have been in the areas of water quality, modeling, environmental sustainability, waste management, NPDES, flotation, and analytical methods. Dr. Wang is the author of over 50 publications and an inventor of 14 US and foreign patents. She received her BSCE from National Cheng Kung University, Taiwan, ROC, her MSCE from the University of Rhode Island, RI, USA, and her PhD from Rutgers University, NJ, USA. She is the Co-Series Editor of the *Handbook of Environmental Engineering* series (Springer), Coeditor of the *Advances in Industrial and Hazardous Wastes Treatment* series (CRC Press of Taylor & Francis Group), and the Coeditor of the *Environmental Science, Technology, Engineering and Mathematics series* (Lenox Institute Press). She is a member of AWWA, NEWWA, WEF, CIE, and OCEESA.

Yung-Tse Hung has been Professor of Civil Engineering at Cleveland State University, Cleveland, Ohio, USA, since 1981. He is a Fellow of the American Society of Civil Engineers, Professional Engineer in Ohio and North Dakota, Diplomate of American Academy of Environmental Engineers. He has taught at 16 universities in eight countries. His research interests and publications have been in the field of biological treatment processes and industrial waste treatment. Dr. Hung is credited with over 470 publications and presentations, 28 books, 159 book chapters, in water and wastewater treatment. He received his BSCE and MSCE from National Cheng-Kung University, Taiwan, and his PhD from the University of Texas at Austin, USA. He is the Editor-in-Chief of

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Chapter 1
Fenton Oxidation and Biological Activated Carbon Treatment for Recycling Biotreated Coking Plant Wastewater

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Abstract Fenton oxidation, coagulation/flocculation/sedimendation plus Fenton oxidation, and Fenton oxidation plus activated carbon adsorption were conducted to develop the effective processes for recycling a biologically treated coking plant effluent. Fenton oxidation enhanced adsorptive capacities of activated carbon for the residual organics and also made them more biodegradable. The Fenton oxidation followed by adsorption and biodegradation in a biological activated carbon (BAC) adsorber was the most cost-effective treatment process to recycle the final effluent for in-plant reuses while meeting the much more stringent discharge limits of the future. Batch experiments were also conducted to determine the effects of copper-loading and fixing methods on the capacity of granular activated carbon (GAC) for removing cyanide from KCN (pH = 11), $K_3Fe(CN)_6$ solutions and several Shanghai Coking Plant (SCP) effluent samples. KI-fixed carbon (Cu/KI-GAC) was the best GAC samples tested. Adsorption was the primary mechanism of cyanide removal; catalytic oxidation of the adsorbed cyanide on carbon surface contributed a minor amount of the observed removal. Four small adsorbers containing the base GAC and 0–100% of Cu/KI-GAC were employed for treating a Fenton-oxidized/precipitated SCP effluent sample. After the start-up period (<3 weeks) to establish the effective BAC function in the adsorbers, the effluents became stable and met the discharge limits ($COD_{Cr} < 50$ mg/L and TCN < 0.5 mg/L); with >30% Cu/KI-GAC in the adsorber, the effluent would meet the discharge limits during the start-up phase. The BAC function of the adsorber substantially reduced the carbon replacement cost, making the combined Fenton oxidation and BAC treatment process a cost-effective alternative for recycling the biotreated coking plant effluent.

Keywords Cyanide-containing coking wastewater · Fenton oxidation · Carbon adsorption · BAC · Copper-loaded GAC

Abbreviations

BAC	Biological activated carbon
CFC	Coagulation flocculation and sedimentation
DO	Dissolved oxygen
GAC	Granular activated carbon
POP	Persistent organic pollutants
SCP	Shanghai coking plant
SMP	Soluble microbial products

1 Introduction

1.1 Coking Plant Wastewater

A typical coking plant wastewater contains a wide variety of organic contaminants from coking, coal gasification, many other production and maintenance operations; some of the contaminants are present in high concentrations and/or are not removed by the conventional biological wastewater treatment processes. In China today, most existing chemical industry wastewater treatment plants are hard pressed to meet increasingly more stringent effluent discharge limits. There is also an urgent need to recycle well-treated effluents for many beneficial reuse purposes. Relative to more highly developed countries, a much smaller fraction of industrial effluents is being recycled and/or reused [1]. Development of innovative cost-effective processes for recycling chemical plant effluents is essential to ensure a sustainable development in China.

Shanghai Coking Plant (SCP) is one of the largest chemical plants in the city with capacities to produce 3.2 million m^3/a of manufactured gas, 1.9 million ton/a of coke, 350,000 ton/a of methanol, and more than 100 additional products. About 7000 m^3/day of wastewater from chemical production, cleaning, washing and other operations is treated in the anaerobic and aerobic biofilm reactors as depicted in Fig. 1.1. Because the wastewater composition is highly variable and many of its many organic constituents are not readily biodegradable, the biotreated SCP effluent often does not meet the existing discharge limits for residual organic constituents and total cyanide ($COD_{Cr} < 50$ mg/L and TCN < 0.5 mg/L) [2]. Cost-effective post treatment of the SCP effluent is desired to produce a final effluent that may not only be directly discharged but also can be recycled for many in-plant reuse functions.

1.2 Treatment Processes for Coking Plant Wastewater

Granular activated carbon (GAC) is commonly employed for removing persistent organic pollutants (POPs) of biologically treated chemical plant effluents [3, 4]. Fenton oxidation is highly effective for breaking up large organic molecules and has thus become a popular pretreatment step to improve biodegradability of organic constituents of biotreated effluent consisting of relatively small amounts of POPs, large amounts of metabolic intermediates and soluble microbial products (SMPs)

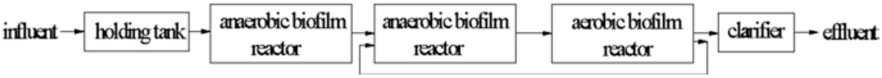

Fig. 1.1 Flow diagram of the coking wastewater treatment plant

[5–7]. The Fenton reactions are dependent on the highly reactive $^{\bullet}OH$ radicals according to the following mechanisms [8]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \tag{1.1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot OOH + H^+ \tag{1.2}$$

$$\cdot OH + H_2O_2 \rightarrow HO_2\cdot + H_2O \tag{1.3}$$

$$\cdot OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \tag{1.4}$$

$$\cdot OOH + H_2O_2 \rightarrow O_2 + H_2O + \cdot OH \tag{1.5}$$

$$RH + \cdot OH \rightarrow R\cdot + H_2O \tag{1.6}$$

$$R\cdot + O_2 \rightarrow ROO\cdot \rightarrow CO_2 + H_2O \tag{1.7}$$

The Fe^{3+} produced in the Fenton oxidation is a powerful coagulant for removing high-molecular-weight constituents of the feed by adsorption on the new $Fe(OH)_3$ flocs formed at a neutral pH [9]. Combining Fenton oxidation with coagulation-flocculation-sedimentation (CFS) and/or carbon adsorption are attractive for advanced treatment for recycling coking plant effluents.

Alkaline chlorination, ozonization, and wet-air oxidation are chemical oxidation methods effective for treating cyanide-containing wastewater [10, 11]. The high degree of chlorination required to meet the effluent objectives often requires excessive doses of caustic and chlorine or sodium hypochlorite [12] which, in addition to the need for neutralization, would create a safety concern due to the large amounts of residual chemicals and by products [13]. Ozonization is expensive because it is not selective, while wet-air oxidation is only a viable alternative for small-scale applications because of the high temperature and pressure requirements. Other reported treatment methods, such as Caro's acid, copper-catalyzed hydrogen peroxide, electrolytic oxidation, ion exchange, acidification, AVR (acidification, volatilization, and re-neutralization) process, lime-sulfur, reverse osmosis, thermal hydrolysis, and INCO process (by SO_2/air) [10, 11, 14, 15] are either too costly or unable to produce an effluent that would meet the discharge limits on both cyanide and organic.

Depending on the influent composition and season of the year, the SCP effluent contains variable concentrations COD_{Cr} (100–200 mg/L) and TCN (0.5–7 mg/L) of complex cyanides since any free cyanide would have been stripped by aeration (p*K*a of HCN = 9.3). Granular activated carbon (GAC) adsorption has been employed for removing both free and complex cyanides present in many industrial wastewaters and that its adsorptive capacities for $Cu(CN)_4^{2-}$ were much greater than for CN^- [16, 17]. Activated carbon functioned both as an adsorbent and as a carrier of catalyst for cyanide oxidation [18–21]. In the presence of dissolved oxygen (DO), the adsorbed cyanide may be oxidized to CNO^- (Eq. 1.8), which was hydrolyzed to NH_4^+ (Eq. 1.9); further oxidation of CNO^- to form N_2 (Eq. 1.10) is not expected since about the same total nitrogen concentrations were found in an SCP effluent before and after the copper/sulfite catalyzed oxidation treatment [22]:

$$CN^- + 0.5O_2 \rightarrow CNO^- \tag{1.8}$$

$$CNO^- + 2H_3O^+ \rightarrow CO_2 + NH_4^+ + H_2O \tag{1.9}$$

$$2CNO^- + 1.5O_2 + H_2O \rightarrow N_2 + 2CO_2 + 2OH^- \tag{1.10}$$

Fenton oxidation (Fe^{2+}-catalyzed oxidation by H_2O_2) is effective for breaking up large organic molecules and complex cyanides of the SCP effluent [6, 23, 24] making it possible for their long-term removal in GAC adsorbers, which in effect function as biological activated carbon (BAC) systems, capable of removing both residual organic (COD and UV_{254}) and TCN, in the SCP effluent [25]. Recently, Dash has found the BAC process is more effective than adsorption and biodegradation alone for removing iron cyanide in batch reactors [26].

Loading a transitional metal, such as copper and silver, on the GAC has improved its adsorptive capacity for cyanide due to chemisorption resulting from the interaction between complex ions and the surface groups of GAC and the catalytic oxidation of cyanide by adsorbed oxygen with metal compounds adsorbed on carbon surface as the catalyst [27–29]. To further improve the capacity of Fenton-BAC system in removing TCN, metal impregnation (loading) of GAC was investigated in this study.

2 Materials and Methods

2.1 Chemicals and Activated Carbons

Since $K_3Fe(CN)_6$ is likely the major TCN constituent of a coking plant effluent [30], it was employed to prepare the test solutions and also to maintain a desired TCN concentration of the SCP effluent in the long-term treatment runs. Several batches of SCP effluent samples ($pH = 6–7$, $COD_{Cr} = 100–150$ mg/L, TCN = 1.0–6.5 mg/L) were brought in from the plant during the study period and employed as the feed to the carbon adsorbers after pretreatment by coagulation/flocculation using polymeric ferric sulfate ($Fe^{3+} = 58$ mg/L at $pH = 7.0$ maintained by NaOH) or Fenton oxidation/precipitation using hydrogen peroxide, $FeSO_4$ and NaOH solutions (oxidation: $Fe^{2+} = 56$ mg/L, $H_2O_2 = 27.2$ mg/L, followed by neutralization with NaOH to $pH = 7.0$).

Commercial polymeric ferric sulfate (PFS, Fe^{3+} 19% by weight) was dissolved, and the solution (20 g/L) was employed as the coagulant. $FeSO_4$ solution (6 g/L, $FeSO_4 \cdot 7H_2O$) and hydrogen peroxide (30% H_2O_2) were employed as the Fenton reagents. All other chemicals employed for pH adjustment and analytical measurements were reagent grades. Three fresh GACs made from coal, apricot nut and walnut (fruit) shell, and coconut shell, and a spent coconut carbon after 1 year of dechlorination service were employed in the study. All GAC samples were provided by Shanghai Activated Carbon Co.

Cyanide removal effectiveness of 11 different activated carbons was compared in the batch treatment runs. The activated carbon samples included base coal activated carbon (Coal) and ten metal-loaded activated carbons of which 7 were prepared in the lab: Ag-GAC-1 (1.62% Ag), Ni-GAC (0.89% Ni), Fe-GAC (0.84% Fe), Cu-GAC-1 (0.96% Cu) and 3 Cu loaded and fixed carbon: Cu/$NaHCO_3$-GAC, Cu/Na_2CO_3-GAC, Cu/KI-GAC-1, and 3 others provided by Shanghai Activated Carbon Co.: Ag-GAC (0.1% Ag), Cu-GAC (3.1% Cu) and Cu/KI-GAC (3.1% Cu and fixed by KI). The home-made metal loaded carbons were prepared by mixing a fixed amount of Coal with an aliquot of metal sulfate/nitrate solution enough to cover the carbon and then drying the mixture in an oven (at 105 °C) to remove the water. Cu/KI-GAC was prepared by mixing Cu-GAC with KI solution and then dried; $NaHCO_3$ and Na_2CO_3 solutions were employed in place of KI for preparing the other two Cu fixed carbons. All carbon samples were crushed using a coffee grinder, sieved for the proper size fractions, washed, dried, and stored before the test.

2.2 Coagulation Flocculation and Sedimentation (CFS) Experiments

The use of PFS as the coagulant and the CFS treatment procedure were established in a side-by-side study [31]. Two hundred milliliter of the biotreated coking plant effluent was poured to series of 500-mL glass beakers; a fixed volume of the PFS stock solution (10% of the commercial grade) was added to each beaker. The beaker content was mixed rapidly (200 rpm) for 1 min and then slowly (20 rpm) for 30 min; pH was kept at 7.0 using 1 M NaOH. The supernatant after 3 h of settling was the CFS-treated effluent sample.

2.3 Fenton Oxidation Experiments: Effects of pH and Chemical Doses

Two hundred milliliters of the biotreated coking plant effluent was poured to series of 500-mL glass beakers; a fixed volume of each reagent solution ($FeSO_4$ and H_2O_2) was added to every beaker under moderate mixing (50 rpm); pH was adjusted to the test level using 1 M NaOH. After 20 min of reaction, the pH was adjusted back to 7, and the mixing was continued at a reduced speed (20 rpm) for another 10 min to achieve good flocculation of the newly formed $Fe(OH)_3$ precipitates before stopping. The supernatant after 3 h of settling was taken as the Fenton-oxidized effluent sample. The Fenton oxidation pretreatment runs were performed using a 4-L or larger glass beaker to produce more samples for the adsorption capacity and column breakthrough experiments.

2.4 DO Decay Experiments: Effect of Fenton Oxidation on Biodegradability of the Residual Organics

A mixed liquor sample of the coking plant's aerobic biofilm reactor was washed and then aerated in dechlorinated tap water for 24 h; the settled sludge was transferred to 1 L of Fenton-oxidized effluent for 48 h of acclimation. The DO decay experiments were conducted using water/effluent samples after they were aerated for 10 min to raise their DOs to near-saturation levels and supplemented with a fixed amount of the acclimated sludge (250 mL with 50 mg/L of sludge); the DO of each sample was monitored for biodegradability assessment.

2.5 Carbon Adsorptive Capacity Experiments: Capacity Indicators and Freundlich Isotherms

The batch adsorption isotherm experiments were performed to determine the four adsorptive capacity indicators of the activated carbon samples and their effectiveness in removing the organic constituents, measured as COD, UV_{254} (for aromatic organic compounds) and VIS_{380} (for color ingredients), and total cyanide of the effluent samples. The detailed procedures are described in a related paper [32].

2.6 BAC Treatability Study: GAC Presaturation and Inoculation of the Carbon Columns

About 15 g of the GAC sample was placed in a 4-L beaker containing 3 L of Fenton-oxidized effluent sample under moderate mixing. After several hours of contact to allow adsorption of the residual organic and cyanide constituents, the mixing was stopped for replacement of the liquid with another volume of Fenton-treated effluent; the liquid exchange continued many times until there were no significant changes in concentrations of the organics and cyanide. The presaturated carbon was filled in a small glass column, which was then inoculated with the supernatant of the acclimated sludge employed in the DO decay experiments after further acclimation with more of the Fenton-oxidized effluent in a 4-L beaker. The inoculation was conducted for 24 h to allow retention of the acclimated bacteria on the four columns (Col. A–D of Table 1.5), while the fifth column was filled new coal carbon and operated without inoculation. To simulate the full-scale adsorption treatment, the five columns were in the upflow manner at an empty bed contact time (EBCT) of 40 min. The BAC treatability study was conduct to verify the BAC functions in the adsorbers and to compare the BAC treatment effectiveness of different GACs.

2.7 Batch Experiments of Cyanide Removal

Five series of batch experiments were conducted to determine the effects of metal loading, the metal-fixing method, contact time and DO on the removal of free and complex cyanides by adsorption and/or catalytic oxidation on carbon surface. A series of six 40-mL glass bottles were filled with 20–100 mg of pulverized (45–75 μm) carbon and the cyanide-containing sample; the bottles were then capped with no headspace and mixed in a rotating drum for 1–6 h. The amount of cyanide removed was calculated for each test sample: X/M (mg/g) = $(C_0 - C_f) \times V/m$, where C_0: the initial cyanide concentration (mg/L), C_f: the residual cyanide concentration (mg/L), V: sample volume (0.04 L), and m: carbon weight (g). The pairs of X/M & C_f were correlated by the Freundlich adsorption isotherm model: $X/M = k\, C_f^{1/n}$. The experimental data and the model best fit straight lines were plotted as the isotherms in log-log scale [32, 33].

2.8 Continuous-Flow Carbon Column Breakthrough Experiments

Three series of continuous-flow carbon column breakthrough experiments were conducted for removing TCN from $K_3Fe(CN)_6$ solution, coagulated/precipitated SCP effluent, and Fenton-oxidized/precipitated SCP effluent samples. The breakthrough experiments employed both the conventional method (using 10–13 g of un-sieved carbon) and the efficient MCRB (0.5 g of 80–120 μm carbon) to verify the TCN removal capacities of Coal and Cu/KI-GAC, to confirm the effectiveness of the MCRB technique, and to obtain long-term treatment performance of the small Coal column in removing TCN from the SCP effluent. The MCRB method is described in earlier papers [34, 35].

3 Development of the Effective Treatment Process

3.1 Feasibility Study Employing Coagulation and Flocculation

Results of previous experiments showed that the coagulation and flocculation treatment employing 2 min of high-speed mixing (200 rpm) followed by 30 min of low-speed mixing (20 rpm) was most effective for removing organic constituents of the effluent. Although the coagulation and flocculation treatment was capable of producing an effluent with a COD of <50 mg/L (Table 1.1) required for recycling as a cooling water make-up, the treatment, even at a much higher dose of Fe^{3+}, was unable to lower the total cyanide concentration below the present discharge limit of 0.5 mg/L as shown in Fig. 1.2.

Table 1.1 Results of CFS, Fenton oxidation, and CFS + Fenton oxidation for pretreating a coking plant effluent sample[a]

	Raw sample	CFS	Fenton oxidation	CFS + Fenton
UV_{254} (abs)	1.789	0.983	0.888	0.503
VIS_{380} (abs)	0.411	0.152	0.174	0.098
COD (mg/L)	88.9	49.0	48.8	35.7
Total cyanide (mg/L)	5.07	1.131	0.236	0.13

[a] Average chemical doses of multiple test runs. CFS: PFS (Fe^{3+} = 57 mg/L), Fenton.Oxidation: (Fe^{2+} = 56 mg/L and H_2O_2 = 27.2 mg/L), and CFS + Fenton: PFS (Fe^{3+} = 57 mg/L) followed by Fe^{2+} = 28 mg/L and H_2O_2 = 13.6 mg/L

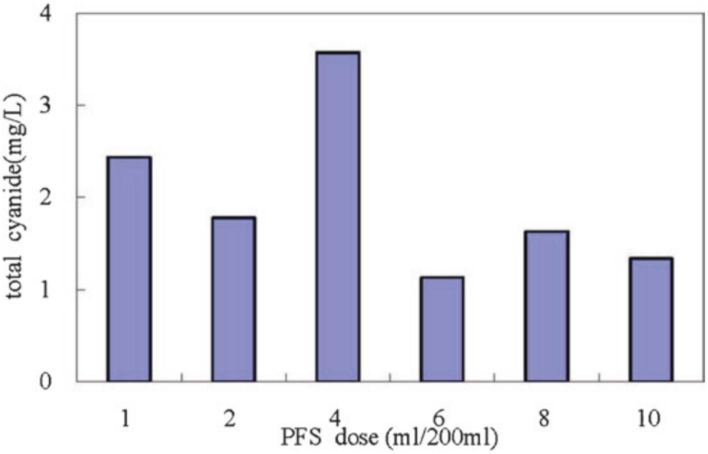

Fig. 1.2 Effect of PFS dose on the residual total cyanide after coagulation and flocculation

3.2 Feasibility Study Employing Fenton Oxidation

The effectiveness of Fenton oxidation is pH dependent as illustrated in Eqs. (1.1) and (1.2). The production of active radicals would be inhibited at a pH lower [36] or higher [37] than the optimum. The basic pH also would reduce the effectiveness of Fe^{2+} as a catalyst [38]. Figure 1.3 presents the effect of pH adjustment on removal of organic constituents, as measured by COD, UV_{254}, and VIS_{380}, by Fenton oxidation of the raw coking plant effluent. Therefore, in the subsequent study, Fenton oxidation was performed directly on the raw effluent without pH adjustment as its pH (6.8–7.0) was very close to the best initial pH. The actual oxidation took place at an acidic pH of about 3.0–5.0 after the desired amount of $FeSO_4$ solution was added. The results were consistent with the literature report that an acidic pH 2–4 was preferred for Fenton oxidation [39].

The organic removal increased with the amounts of Fenton reagents (H_2O_2 and $FeSO_4$, Figs. 1.4 and 1.5). A much larger-than-desired dose of H_2O_2 would consume •OH (Eq. 1.3) reducing the oxidation potential [40], while too much Fe^{2+} also consumes •OH (Eq. 1.4) to form Fe^{3+}, which would result in excessive amount of sludge after neutralization. Based on the results of many test runs and considering the cost of chemicals and sludge disposal [41], 27.2 mg/L of H_2O_2 and 56 mg Fe^{2+}/L were selected for treating the biotreated coking plant effluent samples.

H_2O_2 may oxidize both free and complex cyanide stepwise to CNO^- [42] and finally to N_2 [43]. Most of the total cyanide present in the coking plant effluent was removed in 20 min by the Fenton oxidation; the total cyanide concentration was easily reduced <0.5 mg/L using a range of H_2O_2 doses as shown in Fig. 1.6.

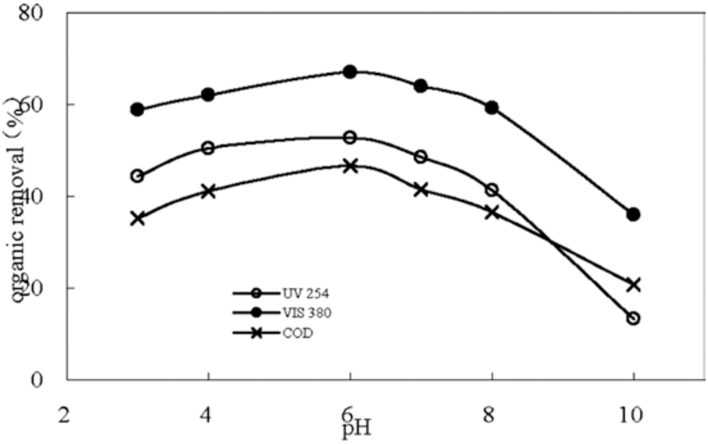

Fig. 1.3 Effect of pH adjustment on organic removal by Fenton oxidation

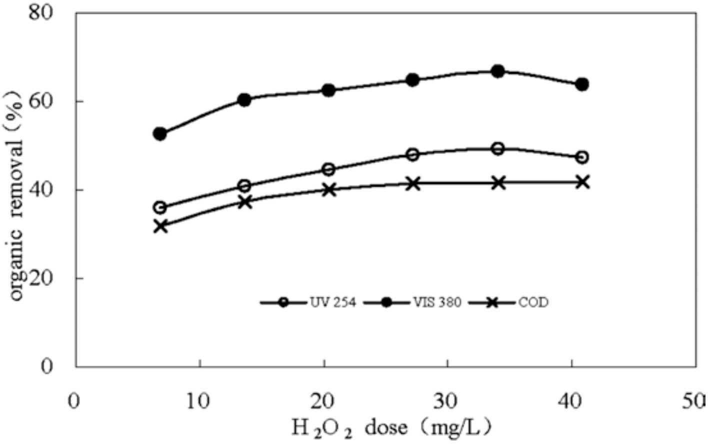

Fig. 1.4 Effect of H_2O_2 dose on organic removal by Fenton oxidation

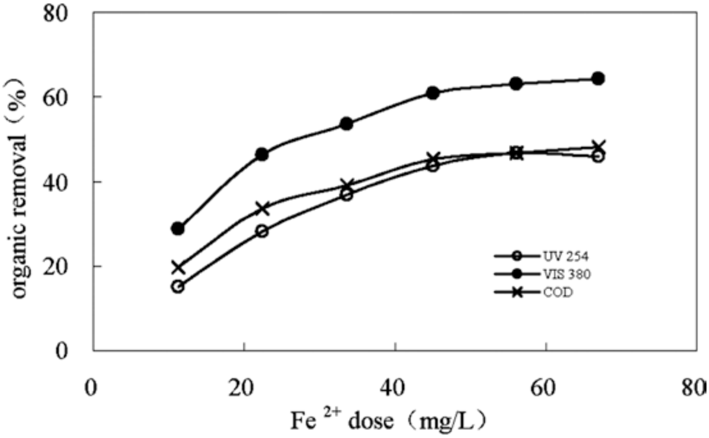

Fig. 1.5 Effect of Fe^{2+} dose on organic removal by Fenton oxidation

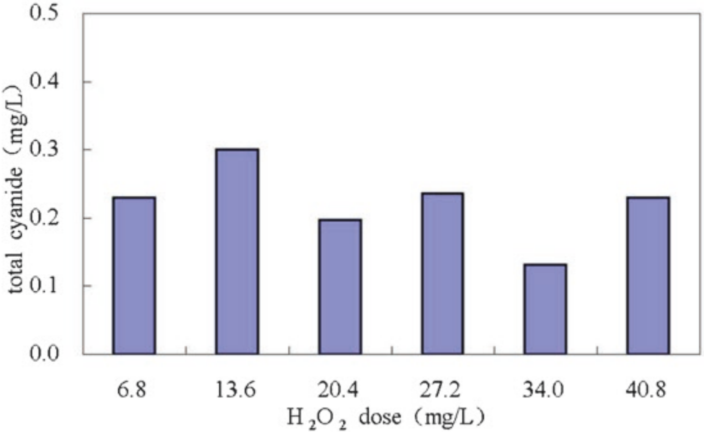

Fig. 1.6 Effect of H_2O_2 dose on the residual total cyanide after Fenton oxidation

Results of multiple treatment runs, employing CFS, Fenton oxidation, and CFS followed by a polishing Fenton oxidation step, performed on a biotreated coking plant sample are summarized in Table 1.1. Both the optimized Fenton oxidation and the CFS plus the polishing Fenton oxidation at much reduced chemical doses achieved the objectives of <50 mg/L of COD and <0.5 mg/L required for reusing the final effluent as cooling water make-up water; at about the same treatment cost, the latter alternative (CFS + Fenton) is the preferred simple solution to produce a directly dischargeable effluent since the simple Fenton was unable to do so when the raw effluent sample quality was much worse as illustrated in the example of the treatability study.

3.3 Effect of Fenton Oxidation on Biodegradability of Residual Organic Constituents

Figure 1.7 depicts the DO decay curves for the raw and Fenton-oxidized coking plant effluents and the dechlorinated tap water after they were first aerated to raise the DOs. The data have demonstrated that some organic ingredients of the raw coking plant effluent were slowly biodegraded [44] and that Fenton treatment made the residual organics more biodegradable. Continued acclimation of the bacteria in the seeding solution was demonstrated by the higher oxygen utilization rates of the Fenton-oxidized samples of more aeration.

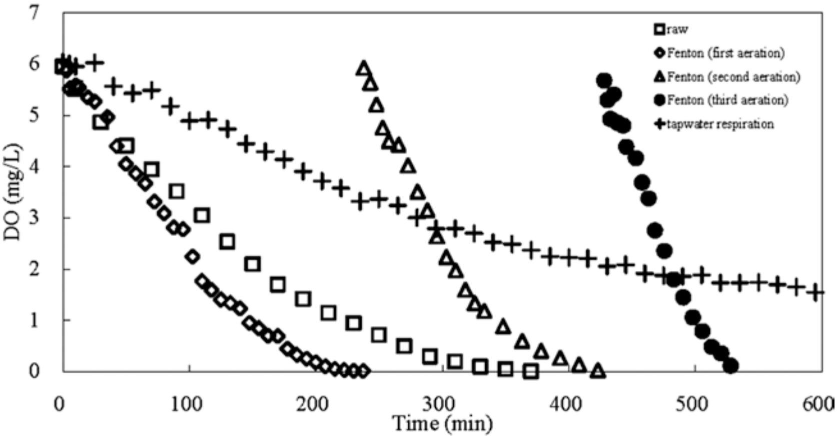

Fig. 1.7 DO decay curves for the raw and Fenton-oxidized coking plant effluents and tapwater

3.4 Feasibility Study Employing Carbon Adsorption (GAC, CFS + GAC, and Fenton + GAC)

Activated carbon's BET surface area and pore volume for pore diameters of <10, 10–15, 15–28, and >28 Å are properly disclosed by its phenol, iodine, methylene blue, and tannic acid numbers [33]. Table 1.2 data show that the four carbons had highly different adsorptive properties; Coconut carbon was effective for removing small size pollutants but ineffective for removing large adsorbates that Coal and Fruit carbons were effective for removing water pollutants of all sizes and that the spent Coconut carbon had the lowest capacities of all. The adsorptive capacities of the lower cost coal carbon for the organic constituents of the raw, CFS-treated, and the Fenton-oxidized effluent samples were represented by the Freundlich isotherms as summarized in Table 1.3. To allow a fair estimate of the coal carbon's capacity for total cyanide, the removal capacities vs. residual cyanide data for four series of experiments (1- and 2-h of contact with 10 m/L solutions of free cyanide and Fe complexed cyanide) were plotted as the Freundlich isotherms (Fig. 1.8). The isotherm-based requirements for the coal carbon are listed in Table 1.4 in which the

Table 1.2 Adsorptive properties of the activated carbon samples

Activated carbon	Phenol no.	Iodine no.	Methylene blue no.	Tannic acid no.
Coal	81	1114	313	42.3
Coconut	126	1154	303	16.7
Fruit	111	1033	307	105.0
Spent coconut	67.0	837	<150	8.2

(a) mg of phenol adsorbed by 1 g of carbon at an equilibrium phenol conc. of 20 mg/L
(b) mg of iodine adsorbed by 1 g of carbon in at an equilibrium iodine conc. of 0.02 N
(c) mg of methylene blue adsorbed by 1 g of carbon at an equilibrium methylene blue conc. of 1 mg/L
(d) mg of tannic acid adsorbed by 1 g of carbon in at an equilibrium tannic acid conc. of 2 mg/L

Table 1.3 Freundlich isotherm parameters for the coal carbon

Effluent sample	Organic	K^a	$1/n^a$	R^{2b}
Raw effluent	UV_{254}	2.563	1.194	0.9905
	VIS_{380}	1.727	0.976	0.9738
	COD	0.065	1.873	0.9950
CFS-treated effluent	UV_{254}	7.422	0.979	0.9776
	VIS_{380}	7.292	1.058	0.9685
	COD	0.309	1.792	0.9868
Fenton oxidized	UV_{254}	6.420	0.938	0.9996
	VIS_{380}	8.734	0.994	0.9739
	COD	0.002	3.252	0.9862

[a] X/M (mg/g) = $K\,C_f^{1/n}$
[b] R^2 correlation coefficient

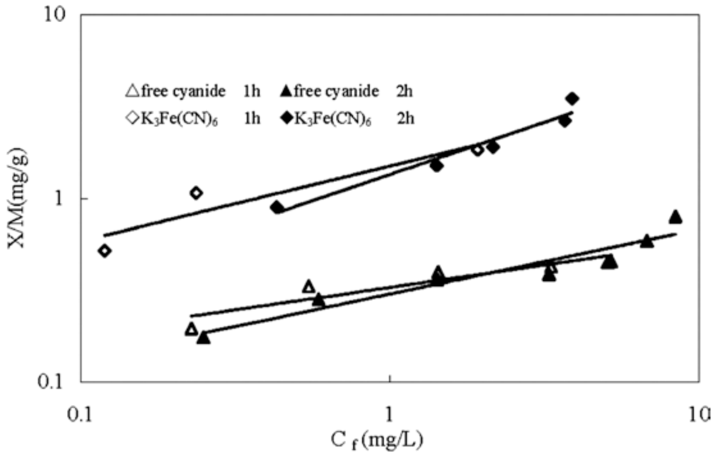

Fig. 1.8 Adsorption isotherms of free and complex cyanide for the coal carbon

Table 1.4 Isotherm-based requirements for the coal carbon

Contaminants	Effluent	C_{in}[a]	GAC[b]
UV_{254} (abs)	Raw	1.723	0.35
	CFS	0.983	0.20
	Fenton	0.888	0.15
VIS_{380} (abs)	Raw	0.411	0.57
	CFS	0.152	0.15
	Fenton	0.174	0.11
COD (mg/L)	Raw	88.9	0.29
	CFS	49.0	0.15
	Fenton	48.8	0.07
Total cyanide (mg/L)	Raw	5.03	1.30
	CFS	1.13	0.78
	Fenton	0.236	0.398

[a] C_{in} feed concentration

[b] $\mathrm{GAC}(g/L) = C_{in}/(X/M)_{C_{in}}$, $(X/M)_{C_{in}}$: the capacity at C_{in}; for organics, use Table 1.2 isotherms; for CN, use CN in $K_3Fe(CN)_6$, X/M (mg/g) = 1.346 $C_f^{0.569}$ ($R^2 = 0.949$)

coal carbon's capacity for total cyanide was its 2-h isotherm of CN in the $K_3Fe(CN)_6$ solution. In addition to having accomplished the removals of organics and total cyanide, the Fenton oxidization made the residual organics more highly adsorbed on activated carbon as evidenced by the greater reduction in carbon requirements than the corresponding concentration reductions.

3.5 BAC Treatability Study

Five small carbon columns were operated at the same time for 70 days treating H_2O_2 supplemented (40 mg/L) Fenton-oxidized effluent; four columns filled with presaturated carbons were inoculated with the acclimated bacteria originated from the coking plant's aerobic biofilm reactor, while the fifth column filled with new Coal carbon was not inoculated. The operating conditions and the treatment performance are summarized in Table 1.5. The column performance data for removing organic constituents and total cyanide of the feed are depicted in Figs. 1.9, 1.10, 1.11, and 1.12. Immediate breakthrough of organic constituents, measured as, UV_{254} (Fig. 1.9), VIS_{380} (Fig. 1.10) and COD (Fig. 1.11), and total cyanide (Fig. 1.12) was observed in the effluents of Col. A–D since the presaturated carbons had virtually no adsorptive capacities available at the start up; the effluent concentrations began to decline, as the inoculated acclimated bacteria started to grow actively, until they stabilized at steady low values in about 30 days. The data for the new carbon column without inoculation (Col. E) show almost total removal of the organics and total cyanide initially and their increasing presence in the effluent as breakthrough occurred; bacteria present in the feed were retained in the column and began to grow resulting in the stable effluent in 35–40 days when it also functioned as a BAC adsorber.

Table 1.5 Summary of the BAC treatment performance. EBCT = 40 min, run time = 70 day; Col. A–D were inoculated[a] columns charged with presaturated carbons[b]. Feed: H_2O_2 (40 mg/L) supplemented Fenton-oxidized coking plant effluent, COD = 68 mg/L, $UV_{254} = 1.08$, $VIS_{380} = 0.217$ abs, CN = 0.75 abs. Total amount fed: COD = 5480 mg, $UV_{254} = 87.3$ abs-L, $VIS_{380} = 17.0$ abs-L, total CN = 60.5 mg

		Amount removed[c]	Total capacity[d]	Removal[e]	Capacity utilization[f]
No.	Carbon/ weight (g)	COD/UV_{254}/VIS_{380}/ CN (mg or abs-L)	COD/UV_{254}/VIS_{380}/ CN (mg or abs-L)	COD/UV_{254}/VIS_{380}/ CN (%)	COD/UV_{254}/VIS_{380}/ CN (%)
A	Fruit, 14.1	2840/41.1/8.37/		51.9/47.0/49.2/—	
B	Coconut, 10.5.	2860/43.6/8.01/		52.1/49.9/47.1/—	
C	Coal, 14.0.	2780/42.4/8.37/25.7		50.7/48.4/49.2/42.5	
D	Spent coconut, 10.7	2780/40.8/8.24/		50.6/46.8/48.5/—	
E	New coal, 13.7	3370/61.6/11.3/41.0	9020/79.0/21.4/15.7[g]	61.6/70.5/66.5/67.8	37.4/77.9/53.9/262

[a] Presaturated by the Fenton-oxidized effluent

[b] Inoculated with the acclimated culture

[c] Calculated from the BAC data (Fig. 1.9, 1.10, 1.11, and 1.12)

[d] Adsorptive capacity (Table 1.2 & g) × carbon weight

[e] Amount removed/amount fed

[f] Amount removed/total capacity

[g] Capacity for CN in $K_3Fe(CN)_6$, X/M (mg/g) = $1.346\ C_f^{0.569}$ ($R^2 = 0.949$)

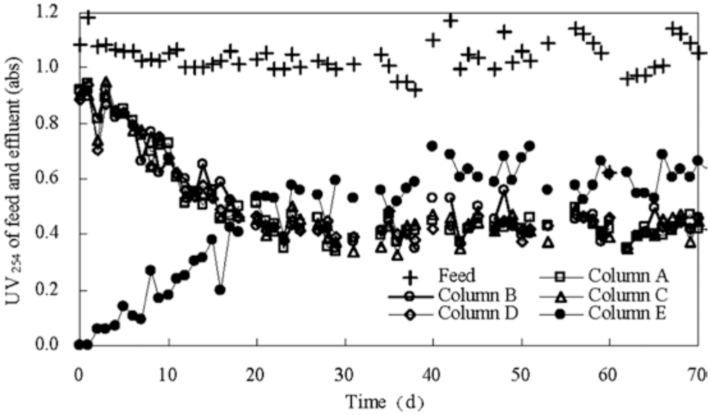

Fig. 1.9 Performance of the BAC treatment of the Fenton-oxidized effluent sample: UV_{254}

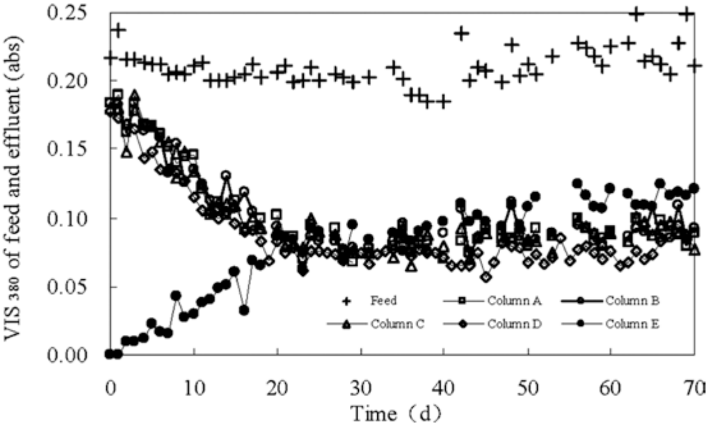

Fig. 1.10 Performance of the BAC treatment of the Fenton-oxidized effluent sample: VIS_{380}

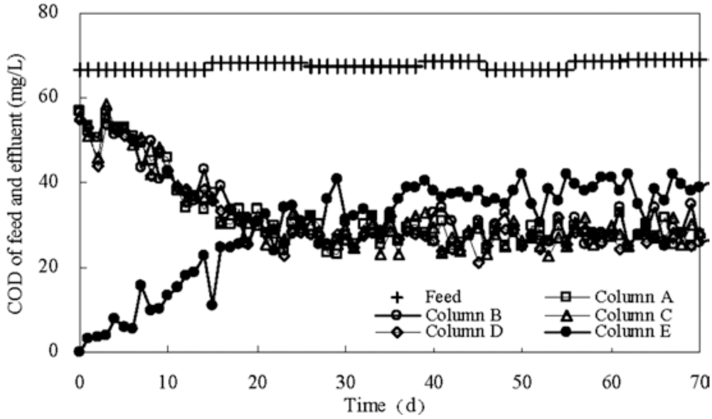

Fig. 1.11 Performance of the BAC treatment of the Fenton-oxidized effluent sample: COD

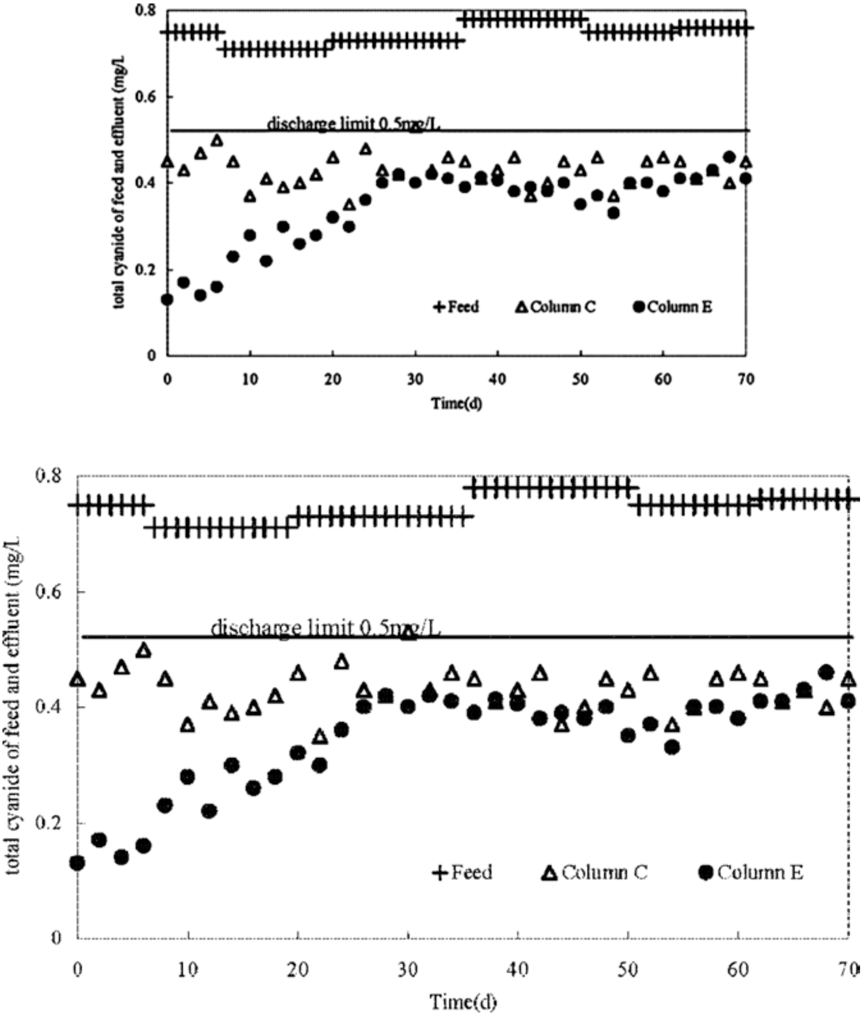

Fig. 1.12 Performance of the BAC treatment of the Fenton-oxidized effluent sample: total cyanide

The effect of BAC is illustrated by the large amount of total cyanide removed in Col. E (262% of the comparable adsorptive capacity) as a result of its biodegradation [45]. The long-term steady removal of organics and total cyanide in carbon columns demonstrates that the BAC function would be established naturally although the inoculation made it happen faster [34].

Although total cyanide was not as well adsorbed on activated carbon as the residual organics (Table 1.4) and had indeed broken through the carbon column much faster, its concentration of Col. E effluent remained significantly below the discharge limit of 0.5 mg/L as the result of biodegradation. The findings of cyanide biodegradation are consistent with the literature reports [35]; the following mechanism has been proposed [46]:

$$\mathrm{M}_x\mathrm{CN}_y + 4\mathrm{H_2O} + \mathrm{O_2} \xrightarrow{\text{bacteria}} \mathrm{M}\ \ \text{biofilm} + 2\mathrm{HCO_3^-} + 2\mathrm{NH_4^+}$$

$$\mathrm{NH_4^+} + \frac{3}{2}\mathrm{O_2} \xrightarrow{\text{bacteria}} \mathrm{NO_2^-} + 2\mathrm{H^+} + \mathrm{H_2O}$$

$$\mathrm{NO_2^-} + \frac{1}{2}\mathrm{O_2} \xrightarrow{\text{bacteria}} \mathrm{NO_3^-}$$

It is significant to note that the long-term treatment performance of a fully established BAC adsorber was not dependent on the carbon's adsorptive capacities [47] as contaminants were primarily removed by biodegradation and bacterial utilization.

4 Enhanced BAC Treatment Employing Copper-Loaded GAC to Ensure Cyanide Removal

4.1 Batch Experiments of Cyanide Removal

Figure 1.13 presents the 1-h TCN removal capacities of five carbons (Coal, Ag-GAC-1, Cu-GAC-1, Ni-GAC, and Fe-GAC); the data clearly show that metal loading significantly enhanced the TCN removal capacity of the base carbon, consistent with literature reports [18, 27, 28, 48] and that, considering the % loading and cost of metal, copper was the best metal of the four studied. Figure 1.14 presents the same comparative removal capacities of six Cu-loaded carbons with and without chemical fixing; the data have demonstrated that fixing loaded Cu on the carbon enhanced its TCN removal capacity and that KI was the best fixing chemical, as CuI was less water soluble than $\mathrm{CuCO_3}$ and $\mathrm{Cu(HCO_3)_2}$ [49, 50]. Similar batch runs were performed on KCN solutions; the results show the GACs' removal capacities for free cyanide were much less than those for $\mathrm{K_3Fe(CN)_6}$-based TCN.

The TPR intensity profiles (Fig. 1.15) show a peak at 288 °C for the Cu-GAC ample and a delayed peak at 510 °C for the Cu/KI-GAC sample; such a shift suggests that the KI-fixing treatment enhanced the interaction of CuO and GAC, making the loaded copper more difficult to be reduced in the TPR procedure, which might have been the reason for the higher TCN removal capacity of Cu/KI-GAC, relative to Cu-GAC, because its loaded copper is more tightly bound and thus less likely to be removed from GAC. Higher copper loading of Cu-GAC and Cu/KI-GAC and more effective loading/fixing procedures employed in the preparation of the commercial copper-loaded carbon (Cu-GAC and Cu/KI-GAC) were the reasons for their higher TCN removal capacities relative to those of the home-made Cu-loaded carbons.

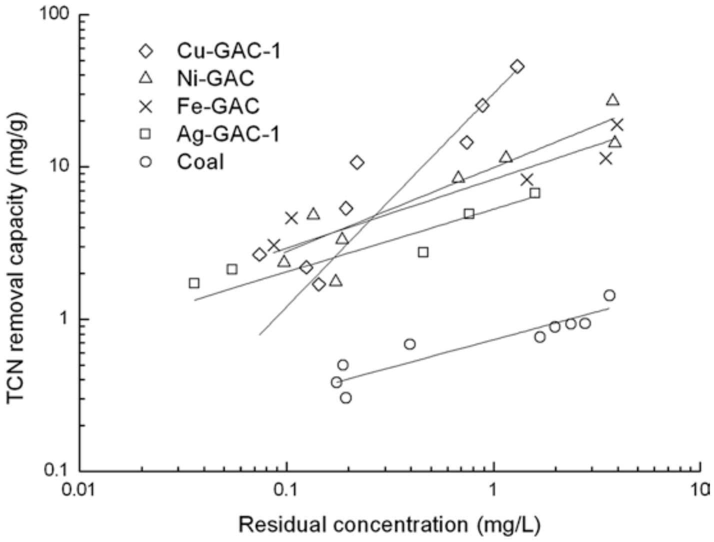

Fig. 1.13 Effect of metal loading on TCN removal

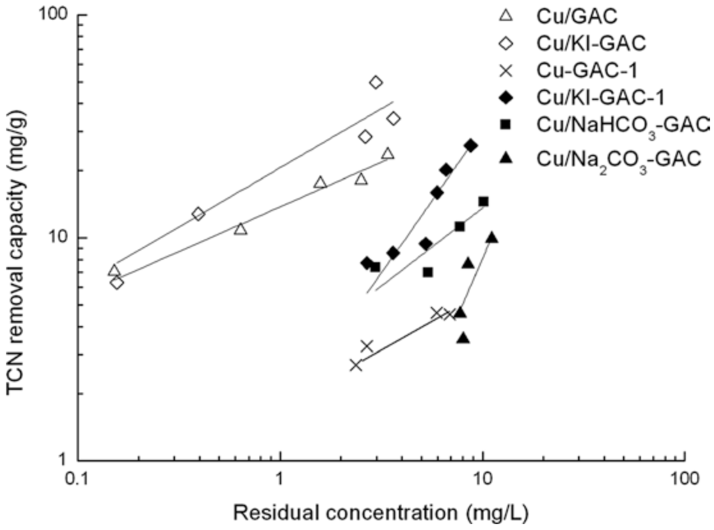

Fig. 1.14 Effect of Cu fixing on TCN removal

Figure 1.16 illustrates the effects of contact time (1 and 5 h) and DO (2 and 7 mg/L) on TCN removal capacities of Coal and Cu/KI-GAC from an SCP effluent. The higher removal capacities observed with a longer contact time and a higher DO were the result of catalytic oxidation of adsorbed cyanide on carbon surface. The catalytic oxidation was not strongly dependent on cyanide concentration and that its contribution to the total observed cyanide removal was not as noticeable for Cu/

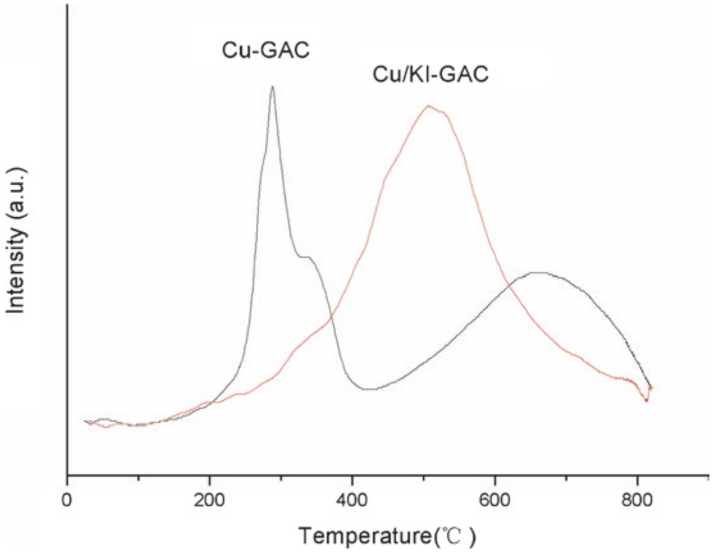

Fig. 1.15 TPR patterns of copper-impregnated GAC composites

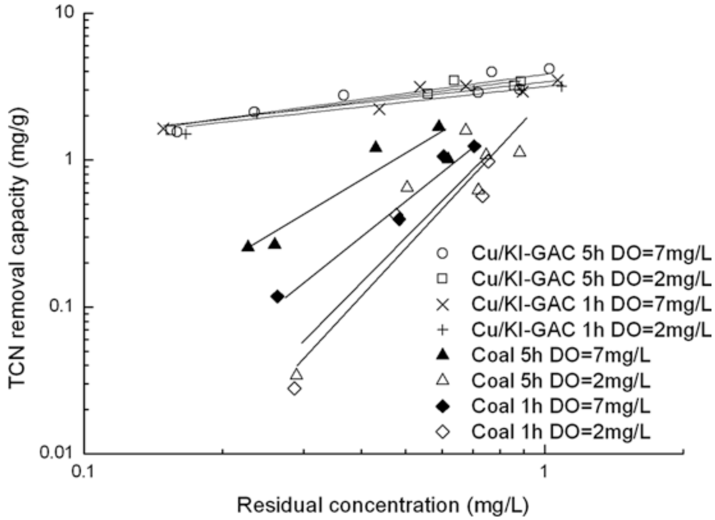

Fig. 1.16 Effects of contact time and DO on TCN removal

KI-GAC due to its much higher TCN removal capacity relative to Coal. Such results have suggested that adsorption of cyanide species is fast and that the observed 1-h removal capacity of a carbon may be considered as its adsorptive capacity for cyanide.

Figure 1.17 presents the adsorptive capacities of four carbons for TCN in $K_3Fe(CN)_6$ solution, showing the expected order of Cu/KI-GAC > Cu-GAC > Ag-GAC > Coal. The observed cyanide removal capacities were dependent on factors

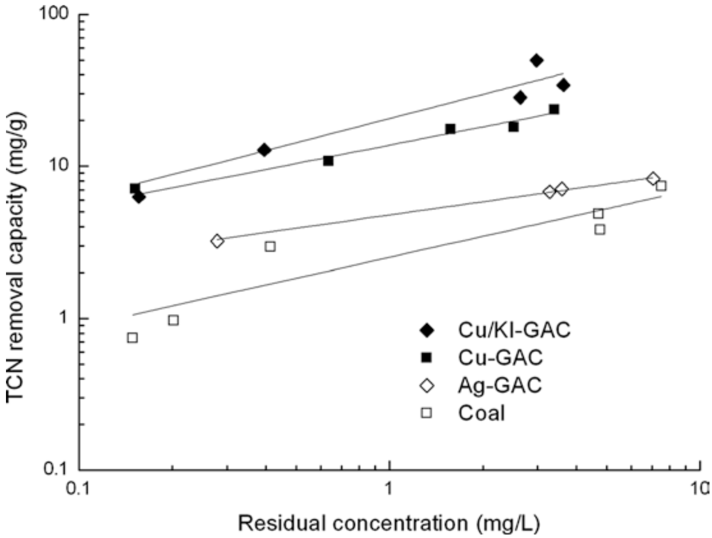

Fig. 1.17 Effect of Cu fixing on TCN removal

that affect adsorption and catalytic oxidation, such as carbon type, cyanide form/source (free and total cyanides of a solution and effluent), contact time, and DO.

4.2 Breakthrough Experiments

Figure 1.18 presents TCN breakthrough curves of six columns employing both the conventional method (b, d, and f) and the MCRB method (a, c, and e); Col. a and Col. b were fed by $K_3Fe(CN)_6$ solutions, while other columns were fed by the coagulated/precipitated SCP effluents. Table 1.6 summarizes the performance data of those columns. The results demonstrate that Cu/KI-GAC had a much larger TCN removal capacity than Coal and that catalytic oxidation of adsorbed TCN on Coal resulted in >100% removal ratio of Col. a and Col. b where the longer contact time enhanced removal even more [28]. The MCRB curves of Col. c and Col. e are similar to the corresponding small conventional columns (Col. d and Col. f) in the common ranges of bed volumes treated; such results have validated using the MCRB method to obtain a full breakthrough curve in a small fraction of time that would be necessary for the conventional method using a small carbon column.

The third series of breakthrough experiments involved the long-term treatment of an SCP effluent sample containing higher than usual TCN (6.5 mg/L). To ensure the GAC treatment would produce an acceptable final effluent, the SCP effluent was first pretreated by Fenton oxidation/precipitation to produce the feed ($COD_{Cr} < 80$ mg/L and TCN < 3.5 mg/L) to the four small conventional adsorbers

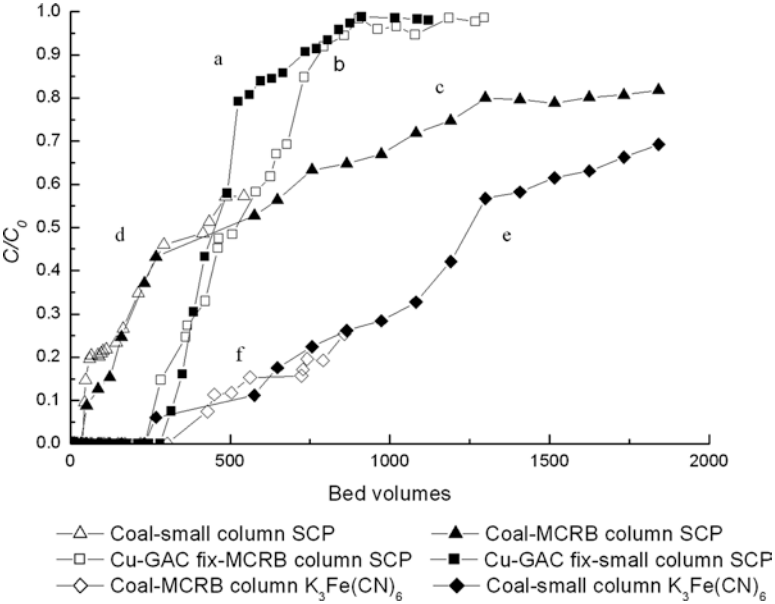

Fig. 1.18 Breakthrough curves for activated carbon adsorbers

Table 1.6 Summary of breakthrough runs for treating $K_3Fe(CN)_6$ solution and coagulated SCP effluent

Carbon/ column (Fig. 1.7)	Flow rate (mL/ min)	Carbon charged (g)	EBCT (s)	Feed TCN (mg/L)	Contact (run) time (h)	Batch removal capacity (mg/g)[a]	TCN removed (mg/g)[b]	Removal ratio (%)[c]
Coal (a)[d]	3.1	0.51	17	2.5	15	2.3	2.5	109
Coal (b)[e]	1.0	10.3	1530	2.1	551	2.0	3.2	160
Coal (c)[d]	3.1	0.51	17	1.9	9	2.4	2.5	104
Coal (d)[e]	0.9	10.2	1668	1.9	254	2.4	1.6	67
Cu/KI-GAC (e)[d]	3.3	0.50	15	1.9	9	5.8	3.8	66
Cu/KI-GAC (f)[e]	0.9	11.7	1608	1.9	383	5.8	3.2	55

[a] 1-h removal capacity at the feed concentration from Figs. 1.5 and 1.6

[b] Cumulative TCN removal at the end

[c] b/a

[d] MCRB runs

[e] Small column conventional breakthrough runs

filled with the base coal and varying account of Cu/KI-GAC (0%, 10%, 30%, 100% in Col. g, h, i, j, respectively). Figure 1.19 presents their TCN breakthrough curves and Fig. 1.9 shows their COD removal performance of the last 4 days of the 57-d study.

TCN concentration of the Col. g–i effluent samples increased quickly, exceeding the discharge limit (0.5 mg/L) in 2–5 days. While TCN of Col. j, the column with all Cu/KI-GAC, effluent samples were well below <0.5 mg/L during the entire 57-day study. After 10 days, the TCN concentrations of Col g–i effluent samples began to decrease gradually and dropped below the discharge limit by the 20th day. After this start-up period (the first 3–4 weeks of the column runs), the treatment performance of all columns became stable; TCN of all effluent samples remained below 0.5 mg/L even when the feed concentration was increased to 3.5 mg/L (with less intensive Fenton pretreatment). Figure 1.20 shows that Col g–j were still effective for COD removal that COD of all effluent samples were below the discharge limit of 50 mg/L).

Table 1.7 summarizes the performance data of TCN removal in the four columns. The cumulative TCN removals in the four columns were 280–383% of their respective TCN adsorptive capacities, and furthermore, there was no need for any of them to replace GAC. Those GAC columns exhibited such long-term TCN and COD removal capabilities because they became fully functional BAC systems, which resulted from the fact that organic and TCN constituents of the feed were made more biodegradable by the Fenton oxidation pretreatment and that the GAC columns were ideal for establishing highly acclimated biomass during the start-up period [26, 30, 51, 52]. The data of this study have demonstrated that partial filling

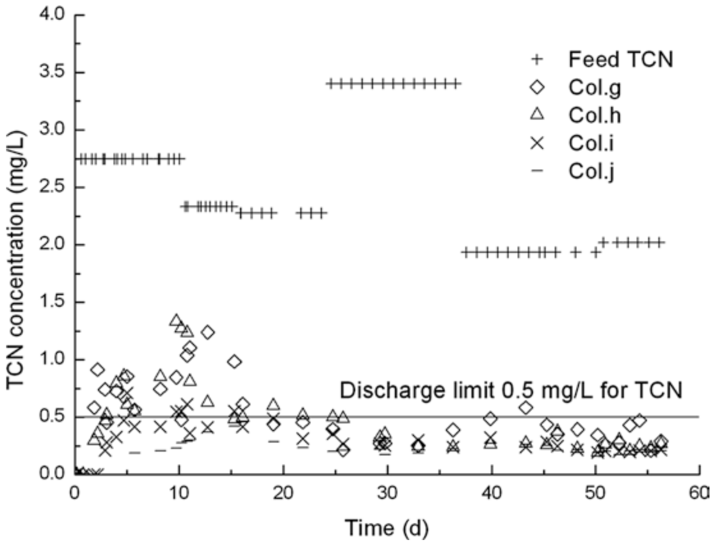

Fig. 1.19 Performance of the Fenton-BAC process: TCN removal

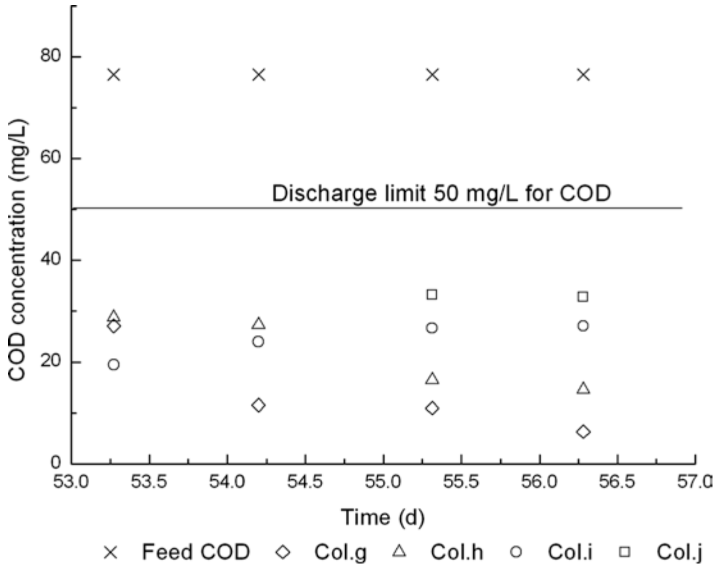

Fig. 1.20 Performance of the Fenton-BAC process: COD removal

Table 1.7 Summary of 57 d breakthrough runs for Fenton-pretreated SCP effluent samples (feed pH = 6.5, DO = 7 mg/L)

Carbon/column (Fig. 1.8)	Flow rate (mL/min)	Carbon charged (g)	EBCT (min)	Batch removal capacity (mg/g)[a]	TCN removed (mg/g)[b]	Removal ratio (%)[c]
100%coal (g)	0.94	10.0	26	3.9	14.0	359
10%cu/ KI-GAC +90%coal (h)	1.00	10.2	25	4.1	15.7	383
30%cu/ KI-GAC +70%coal (i)	0.92	10.2	26	4.6	15.3	333
100%cu/ KI-GAC (j)	0.98	10.1	22	6.1	17.1	280

[a] 1-h removal capacity at the feed concentration from Fig. 1.5
[b] Cumulative TCN removal at the end
[c] b/a

of Cu/KI-GAC did not prevent the BAC function and that a sizable amount of it (>30% in this study) would ensure the final effluent meeting the stringent TCN discharge limit at all times. These results suggest that Fenton oxidation pretreatment followed by the BAC treatment in the adsorber is a cost-effective advanced treatment of the SCP effluent for direct discharge and/or reuse and that partial filling of the adsorber with Cu/KI-GAC will furthermore ensure meeting the effluent discharge limits during the start-up phase of the adsorber operation [30, 51–55].

5 Summary

Fenton oxidation, coagulation/flocculation/sedimendation (CFS) plus Fenton oxidation, and Fenton oxidation plus activated carbon adsorption experiments were conducted to develop the most practical and the best advanced treatment processes for treating a biologically treated coking plant effluent. Both Fenton oxidation and CFS were effective for removing many organic constituents, measured as UV_{254} (aromatic organics), VIS_{380} (color ingredients), and COD_{Cr}; Fenton oxidation, in addition, was capable of removing most total cyanide present in the sample. Fenton oxidation enhanced adsorptive capacities of activated carbon for the residual organics and also made them more biodegradable. The CFS followed by Fenton oxidation was the most practical advanced treatment process to ensure meeting the existing effluent discharge limits and to recycle the final effluent for cooling water make-up. The Fenton oxidation followed by adsorption and biodegradation in a biological activated carbon (BAC) adsorber was the best advanced treatment process to recycle the final effluent for many more reuses while meeting the much more stringent discharge limits of the future.

Batch experiments were also conducted to determine the effects of metal loading and fixing methods on the capacity of granular activated carbon (GAC) for removing cyanide from KCN (pH = 11), $K_3Fe(CN)_6$ solutions and several SCP effluent samples. KI fixed carbon (Cu/KI-GAC) was the best GAC samples tested. Adsorption was the primary mechanism of cyanide removal; catalytic oxidation of the adsorbed cyanide on carbon surface contributed a minor amount of the observed removal. Four small adsorbers containing the base GAC and 0–100% of Cu/KI-GAC were employed for treating a Fenton-oxidized/precipitated SCP effluent sample. After the start-up period (<3 weeks) to establish the effective biological activated carbon (BAC) function in the adsorbers, the effluents became stable and met the discharge limits ($COD_{Cr} < 50$ mg/L and TCN < 0.5 mg/L); with >30% Cu/KI-GAC in the adsorber, the effluent would meet the discharge limits during the start-up phase. The BAC function of the adsorber substantially reduced the carbon replacement cost making the combined Fenton oxidation and BAC treatment process a cost-effective alternative for recycling the biotreated coking plant effluent.

Glossary

Biodegradation Biodegradation is the decomposition of organic material by microorganisms.

Biological activated carbon The combination of ozonation and GAC is commonly referred to as the biological activated carbon (BAC) process, or biologically enhanced active carbon process.

Carbon adsorption Activated *Carbon Adsorption* is the act of an accumulation of a gas or liquid onto the surface of the activated carbon.

Coking wastewater treatment Removal of suspended solids and chemicals that are toxic to biological systems, followed by biological treatment.

Fenton reaction *Fenton* reaction is a catalytic process that converts hydrogen peroxide, a product of mitochondrial *oxidative* respiration, into a highly toxic hydroxyl free radical.

Granular activated carbon *Granular activated carbon* is defined as the activated carbon being retained on a 50-mesh sieve.

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Chapter 2
Composting for Food Processing Wastes

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Contents

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Abstract Composting of food processing waste was analyzed as a biological process and an engineered system. The goal is to establish fundamental principles and design criteria that would aid its adoption as waste management practice. Characteristics of the inflow, reactor, and outflow were evaluated. Success of the bioreactor was found to be largely dependent on microbial community structure, physical properties of biodegradable waste (BW), aeration, and time required for maturation. Vermicomposting, electric field induction, maggot farming, microbial fuel cells, energy production, air pollution reduction, and leachate treatment were explored.

Keywords Compost · Bioreactor · Biodegradation · Porous media · Food processing waste · Vermicomposting · Electric field induction · Maggot farming · Microbial fuel cells · Constructed wetlands

1 Introduction: We Cannot Decompose

Composting is an exciting industry, where study of microbiology and natural cycles is applied to the operation of biological reactors to reduce pollution, aid degraded lands, and improve agricultural sustainability.

Disposal of material deemed no longer useful is excessive and growing at alarming rates. “The generation of municipal solid waste per capita was 2.68 pounds per day in 1960. By 1970, it had grown to 3.25 pounds per day and by 1980 it was 3.66 pounds per day. By 2010, the daily generation of municipal solid waste per capita had reached 4.44 pounds” [1]. Food and other biodegradable wastes are an essential concern. The availability of better technology and the perishability of valuable resources is strong support for a change of industry standard. An understanding of biological systems and the environmental impact of engineered systems is leading to positive change in waste management and this chapter will analyze composting as a critical means. Composting of biodegradable waste (BW) is largely dependent on favorable conditions for microbial populations. I would like to consider Landfills, Landfill Bioreactors, Composting, and Natural wastewater treatment as a continuum on the treatment of labor/ecosystems in biodegradation and the pollution generated. It is evident that favorable conditions for decomposers produce greater rates of decomposition and greater utilization of effluent material. We rely greatly on microorganisms, and a symbiotic relationship proves to be the most beneficial to our ecosystem’s success.

Natural systems work in natural cycles. Biodiversity and symbiotic reliance have occurred for billions of years and have established ideal systems for the transfer and utilization of energy. Ecosystems and earth cycles alike rely on the amazing process of decomposition and biodegradation, which is achieved through the abundance of microorganisms. Bacteria, fungi, and countless feeding species are the means of decomposition and their study is the most critical to compost engineering. Ecosystem populations and system dynamics will be discussed in this study. The nitrogen and carbon cycle are dependent on continual material exchange and symbiotic relationships between auto and heterotrophs. One of the largest evolutionary advancements was the terrestrialization of plants, which was dependent on symbiotic bacterial populations. Decomposition of organic matter into soluble forms is essential for the production of energy and even in complex organisms, such as ourselves, impossible without the aid of decomposers. Mitochondria generates the majority of ATP through cellular respiration and does not share the DNA of its Eukaryote. Popular opinion is that mitochondria has bacterial ancestry and the evolution of eukaryotic cells was through symbiosis of prokaryotic bacteria and archaea. One may look down to their gut microbiome for evidence of the incredible reliance on microbial decomposition of organic material and the sustenance of life, and even find contributions to waste management.

In composting, engineers need understand they cannot decompose and thus shall seek to only serve those that can. Adoption is necessary to improve the environmental impact and sustainability of waste management. Matured compost can leave our home, find partners with beautiful plants, rescue degraded lands, produce food, reduce pollution, and further life on earth. The alternative for our food waste is degradation without air, without light, filled with noxious methane, pollutants, and heavy equipment. Comparisons can be made between composting and wastewater treatment to aid in design and operation. As a biological system, inflow, reaction, and outflow characteristics summarize the process criteria and will be evaluated.

In this chapter, the principles and practicum of composting will be explored. Guidelines and recommendations for a low-energy practice will be determined. First, Influent composition will be discussed, then reactor characteristics, followed by a review of natural cycles, analysis of microbial community structure, metabolism and microbial nutrition, and lastly, reaction effluents.

Throughout analysis, comparisons to the natural decomposition of organics will be reviewed to ensure engineering design does not stray due to miseducation and incomplete understanding of natural process. Organic material has decayed in natural environments for eons and mimicry shall be essential for design. Alongside accordance with natural systems and low-energy input, diversity will be a fundamental goal in all aspects of composting design; in this system, its importance is equivalent to that of any other field. Adoption of compost engineering will only further as waste management practice, for aiding soil ecosystems and countless others is a righteous practice. “Earth knows no desolation; she smells regeneration in the moist breath of decay” [2].

2 Influent Composition

Food waste composted alone is inferior to a mixed influent. The addition of Bulking agents improves porosity and physical structure, plant materials improve carbon quantity, manure, oil, and sludge improve energy content and early growth, and countless other additives improve countless other aspects. Living cells have complicated chemical structures and rely on a diverse array of nutrients. Elemental composition of substrate is key to successful degradation, and analyzing the elementary composition of microbial cells offers insight into ideal feed ratios. Most microbial cells have about 50% carbon, 20% oxygen, 10–15% nitrogen, 8–10% hydrogen, 1–3% phosphorus, and 0.5–1.5% Sulfur considering dry weight [3].

2.1 C/N Ratio

An important parameter for input material is the carbon nitrogen (C/N) ratio. An experiment consisting of five initial C/N ratios of 12.81, 21.37, 24.66, 29.22, and 37.41 was compared and "CO_2 concentrations, compost temperature, dry matter loss, organic matter loss, electrical conductivity, and pH were measured" [4] to determine an ideal ratio. Triplite samples of each ratio were placed in identical insulated batch reactors and the "results of regression analysis indicated that the actual maximum decomposition had a peak value at [C/N] mix of 30.39" [4]. C/N ratio impacts degradation efficiency because microbial cell composition, composed of both material and provision, is needed for growth and biological success, while different ratios also impact microbial succession. Nitrogen present in manure and being ideally 1/30th the quantity of carbon makes carbon often limit the quantity of treated waste. The cost of sawdust bulking agent was 40% in total costs in an aerated static pile composting plant in USA [5]. A study to test the viability of lower C/N ratio was performed by the South China University of Technology. Results determined that temperature and pH varied little among 20/1 and 25/1 ratios with thermophilic temperatures obtained in both mixes. Greater nitrogen losses by ammonification and longer maturity times (about 2 weeks) with lower C/N ratios were discovered [5]. From this experiment, it was concluded that low C/N ratios are feasible and beneficial to the economy of composting.

Low C/N ratios also have an advantage in some pathogen suppression. Accumulation of ammonia is the most common mechanism to kill pathogens in soils treated with nitrogenous material. Tenuta and Lazarovitis found ammonia and nitrous acid, rather than their ionized counterparts of ammonium and nitrite, were lethal to microsclerotia of *V. Dahlia* [6]. Verticillium Dahlia is an ascomycete fungus responsible for billions of dollars in crop losses every year [7]. I imagine the application of nitrogenous waste acts as a fungicide and should not be pursued for pathogen control. Microbial diversity and limited interference in soil dynamics have shown to decrease survival of invading and possibly pathogenic species, "as global richness increased, E. coli survival decreased. Moreover, the effect was magnified over time" [8].

The success of another pathogen, F. oxysporum, was studied in soil communities with varying microbial diversities. Cao et al. discovered the survival (or growth) of F. oxysporum sp. radicis-cucumerinum was strongly suppressed by microbial communities with high diversity. Second, disease severity index was much higher ($P < 0.05$) in the 10^9 and 10^6 dilution treatments than in the 10^3 dilution treatment [9].

As mentioned in the nitrogen cycle chapter, ammonia is produced more than ammonium in basic environments. Ammonium, being only slightly acidic, will likely donate a hydrogen to surrounding basic compounds leading to a transformation into ammonia. Zhang et al. discovered high C/N ratios lead to lower nitrogen losses, and low C/N ratios lead to volatilization of ammonia increasing the pH of the product. C/N ratios of 30/1 observed the lowest percentages of losses compared to 20/1 and 25/1 [10].

Zhang et al. hypothesized that variation in nutrient losses can be explained by changes in microbial succession [10]. 30/1 CN ratios increased and decreased faster slightly faster due to different successional patterns. Gao et al. concluded a C/N ratio of 28 maintained thermophilic temperatures for pathogen destruction, enhanced stability and maturity, and had a lower environmental impact by analyzing cation exchange capacity, germination index, and SOUR uptake [11].

It is hypothesized that ammonia and nitrous acid likely penetrate the outer membrane of the cells; ammonia killing through disruption of cell membranes [12], and nitrous acid destroying vital compounds as a strong oxidizing agent. Ammonia is believed to eliminate proton gradients across membranes [13], assimilate into glutamine-depleting citrate and malate [14], and exhaust chemical energy through removal of cytosolic ammonia across a concentration gradient [15]. While nitrous acid acts as an oxidizing agent, destroying vital compounds in organisms such as glycosaminoglycans, porphyrins, free amino groups, and ascorbic acid. Nitrous acid also undergoes reactions with secondary amines yielding carcinogenic nitrosamines. Unlike ammonia, nitrous acid is not volatile and it is questionable how the presence of nitrous acid at lower soil levels kills suspended microsclerotia.

Low C/N ratios are not recommended for composting. Volatilization of ammonia is a leading cause of acid rain and is inversely related to C/N ratio values. Ammonia and nitrous acid are fatal to some fungal populations and species richness is proven to be the greatest attribute time and again to ecosystem health and viability. In high C/N piles, the percentage of nitrogen accumulation is considerably higher, producing greater nutrient content in compost piles and reduced emissions.

2.2 Moisture Content

Water is necessary for composting. Microbial activity including Hydrolysis reactions are dependent on the presence of H_2O. Sharma and Poulsen studied oxygen uptake in porous media using yard waste compost as a test medium. Water content from air dry to field capacity was analyzed under gas flow ranging from 0.2 to 2 L*min^{-1} [16]. Increased water content improves nutrient supply to organisms and biological activity but decreases the quantity of air-filled pores. Increased water content produced inactive zones with little or no gas movement and hindered microbial activity. Ideal moisture content is dependent on balancing these effects and is controlled by pore size distribution, organic matter content, water flow velocity, water content, and influent air flow.

$$\psi = \frac{2\gamma\cos\theta}{r}$$

The equation above was used to estimate the pore size distribution in a porous media, where ψ is water potential (Pa), γ is the surface tension of water (j*m^{-2}), θ is the contact angle of the porous medium solids with water, and r is the maximum contact angle.

$$\psi_s = \frac{3000}{r}$$

The simplified equation above represent applied suction (ψ_s) (in cm of H_2O).

$$q = -\frac{k_a}{\eta}\frac{\Delta P}{L}$$

Airflow for porous media can be assumed to follow Darcy's law for laminar flow. The equation states that q, the specific air flow rate (m*s^{-1}) is equal to k_a, air permeability (m^2), divided by η the dynamic air viscosity (kg*m^{-1}*s^{-1}), multiplied by the pressure difference in pascals over the length of the sample. Stated simply, airflow in a porous media is driven by an enthalpy difference generated by different pressures inside the reactor and in the environment, Viscosity is typically the controlling variable and in porous media is adjusted by a permeability coefficient.

Air permeability was determined using samples and air permeameters. Samples were packed into 100 cm^3 sample rings at a dry bulk density of 0.8 g*cm^{-3} at water contents of 5.52, 12.19, 23.3, 32.8, 45.8, 48.6, and 51.8% volume. O_2 uptake rates were measured using wetted 50 g samples wetted to 0.069, 0.150, 0.248, 0.292, 0.410, 0.573 g water/g dry compost and samples of 25 g compost wetted with 0.608 and 0.647 g water/g dry compost [16].

Rate of oxygen consumption increased until approximately 40% volumetric water content. Likely, rate-limiting factor switched from nutrient limiting to oxygen limiting. There is no optimal moisture content in compost science; composting is highly variable and a balance between rate limitations must be pursued. Sharma and Poulsen also discovered that the compost used had large pores with radii greater than 30 μm (>90%), which were air filled above suction range (p*F*) values of 2. Results also showed that many air-filled pores were not likely well connected and available for gas flow at porosities below 0.4 cm^3*cm^{-3} [16].

3 Reactor

3.1 Aeration

Critical to aerobic degradation of solid waste is oxygen supply, for an adequate oxygen supply is essential for catabolism and maturation of biodegradable waste. Insufficient supply increases gaseous emissions, including the emission of odorous compounds and greenhouse gases. Inadequate oxygen supply also promotes anaerobic degradation and the altering of environmental conditions, which become unable to house as diverse as a microbial population. Inadequate supply also reduces the ability to reach thermophilic phase, reduces the capability of pathogen control, and increases the time to reach maturity.

Windrows attempt to supply oxygen demand through molecular diffusion and natural draft ventilation with periodic mechanical turning. If influent feedstock has a high C/N ratio, an addition of mature compost is incorporated, or if odor and gaseous emission are not of great concern, this method may be used solely to aerobically degrade organic waste. The oxygen supply for biological decomposition (stoichiometric demand) often needs windrow turning or alternative methods for oxygen supply. Peak oxygen demand occurs early in processing and decreases after thermophilic phase, windrow maturation after the thermophilic phase is reached is common practice.

Stoichiometric oxygen is entirely dependent on feedstock. COD-based stoichiometry is a useful means of determining oxygen requirement, in composting substrates are heterogeneous and simplifications are necessary to determine oxygen requirements.

3.2 Electron Field Induction

Oxygen supply is critical in composting and often rate limiting for aerobic degradation of biodegradable waste. Increasing porosity and tortuosity aids aeration but reduces temperature rise due to convective heat loss and increases energy demand. An alternative attempt to aid the supply of oxygen and reduce the production of methane is through enhancement of O_2 utilization. Increasing gas-liquid interface or air retention time are common methods [17]. A fluidic oscillator has been used to reduce the size of air bubbles tenfold and improve volumetric mass transfer coefficient by 55% [18]. Compost layered with bamboo charcoal to extend air retention time was studied by Li et al. Results showed increased air retention time, but restricted and nonuniform air supply remained problematic [19]. Tang et al., who are responsible for the compiling of these attempts to improve oxygen supply, state that due to the high solids and low moisture content of influent raw material, the use of fluidic oscillator and bamboo charcoal is greatly limited [20].

Oxygen is the terminal electron acceptor in aerobic degradation of biological degradation. The absence of O_2 is likely to lead to an accumulation of electric charge. Generated electrons remain static until the presence of O_2 is supplied. This is a passive process, resulting in a low O_2 utilization due to uneven distribution of O_2 in the compost pile [20]. Gaseous flow in porous media will develop pathways of least resistance and will produce many areas void of activity. It is well known that electrons can move under an electric field. Reimers et al. placed one electrode in the seafloor sediment and another in upper sea water and demonstrated the flow of electrons from anaerobic regions to aerobic regions via an external circuit [21]. Microbial fuel cells also demonstrate this ability and is a fascinating approach to energy production; a brief introduction is provided in a later chapter. Tang et al. experimented with two groups of reactors (volume 200 L) with triplicate samples. One reactor was used for electric-field-assisted aerobic composting (EAC), a DC voltage was applied, the other reactor was used as a control. A sheet of stainless steel was placed around the inside of the reactor to act as a positive electrode, and a graphite rod was inserted in the center of the reactor to act as a negative electrode. Chicken manure, dewatered sewer sludge, rice hulls, and mature compost were mixed 5:2:2:1 and moisture content were adjusted to 65–70%. Intermittent aeration was supplied at air flow rate 1.5 L min^{-1} for 24 h then off for 24 h for days 1–13. No aeration was supplied from days 14 to 30, with days 10 and 20 being turning days [20].

The effect of electric field on the physicochemical properties of compost was analyzed. Self-potential was used to determine soil charge distribution, for the control pile (CAC) it is was distributed between −2.0 and +2.0 V, and for the EAC pile it was between −0.2 and +0.2 V. The data support the use of DC current in composting to force the flow and acceptance of electrons. The rate of temperature increase in the EAC was higher than control, the moisture content lower, the volume loss, and reduction in volatile solids greater.

EEM spectroscopy was used to obtain data on peak wavelengths from the compost pile. Peak wavelengths associated with humic and fulvic acid–like substances had higher intensities with EAC piles indicating enhanced biodegradation. Peak wavelengths related to tyrosine or tryptophan class substances had disappeared in both types of reactors, which are strong indicators of maturity. The increment rate of HA-like substances (in relation to the initial sample) reached 363 ± 36% (region V), which was 144 ± 16% higher than that of CAC (219 ± 20%) [20]. This chapter also demonstrated the effectiveness of EEM spectroscopy in determination of maturity.

Maximum CO_2 emission rates were approximately 1.6 times higher in EAC indicating enhanced oxidation of organic matter by electric field induction. CH_4 emissions only continued after the period of aeration in the control pile suggesting the EAC pile had completed the main humification process. N_2O emissions occurred in both reactors and was released as an intermediate product of nitrification, denitrification, or ammoxidation [22, 23]. N_2O emissions were considerably lower in the EAC, suggesting that oxygen accepted the majority of electrons. The germination index was also considerably higher in EAC compared to CAC reactors [20].

Microbial community structure varied among reactor types. Electroactive bacteria are capable of transporting electrons in bioelectrochemical systems. Typical bacteria include *Tepidimicrobium, Corynebacterium, Bacillus,* and *Alcaligenes*. In EAC, the abundance of electroactive bacteria was greater than 7.9% with increased abundance of *Bacillus*, *Corynebacterium*, and *Tepidimicrobium*. The generation of electroactive bacteria may become marketable if wastewater treatment begins adopting microbial fuel cell technology [20].

It can be concluded that the electric field enhanced the flow of electrons from biological redox processed to oxygen, enhancing maturation and GHG emissions. It is theorized that the addition of biochar and ferric acid would further optimize O_2 utilization.

3.3 Porous Media

The physical structure of biological reactor is a key variable in operation. Air- and water-filled pores, permeability, pore tortuosity, hydraulic conductivity, moisture content, water-holding capacity, matric potential, and thermal conductivity are all effected by the compost environment [24]. Biodegradable solid waste is heterogeneous and thus is the physical structure. Agostini reviewed the main properties of the porous physical characteristics, phenomena, and simulation models for the management of biodegradable waste [25]. The initial microbial community, moisture content, oxygen availability, physical availability to degradation, temperature, and chemical composition determine the overall biodegradation rate.

Oxygen demand can be calculated stoichiometrically assuming some homogeneity in organic chemical composition. At low concentrations, changes in oxygen concentration are highly influential on reaction rates. Beck-Friss et al. noticed a larger rate difference from 1 to 2.5% than from 2.5 to 16% O_2 [26].

Temperature in compost is affected by outside temperature, the type of reactor, and mainly the dynamics of the microbial community. Chemical composition is extremely influential for it is the food of the microbial community.

Porous materials are distinguished by the diameter of its pores—those with diameter greater than 10^{-7} m and those having a diameter less than 10^{-7} m. Capillary porous material has suction and adsorption forces generated by the surface tension of water and its contact angle with the matrix. Bulk density (mass/volume) is used to define a porous material and varies with water content. To analyze mass/volume ratios without water content variations, a term known as particle density is used. Particle density is used to define the solid matrix but is difficult to obtain due to volume entrapped gases. The size of the particles determines the size of pores and is an easily altered parameter; internal friction and cohesion are dependent on particle dimensions.

Compost is a macroporous environment–containing waste that also possess a porous structure. Food waste, manure, biological tissue, etc. all are porous and affect fluid and mass transfer as well as biodegradation rate. In compost environments, the porosity determines air permeability and gas transfer. Microbial reactions are dependent on the supply of oxygen for reduction oxidation reactions, as well as the removal of excessive heat, carbon dioxide, and other gases. A 30% air/gas-filled porosity is considered by many the minimum for the composting process. Richard et al. established a linear decrease of air permeability with dry bulk density, holding water content constant. Increasing water content exaggerated this relationship [27]. It was concluded that tortuosity had a greater impact on air flow than porosity due to process compaction, reactions, and changes of flow pathways [27].

Air-filled porosity and water content are dependent variables; many studies conclude that water content under a certain amount aids in particle aggregation and gains in air permeability. Liquid and gases in a porous solid matrix compete for void space. Microbial catabolism requires the presence of both gases and liquids and thus void balance is critical in design. The presence of water is required for microbial reactions and transport of microbial populations. Too low a moisture content is rate limiting due to minimal microbial movement, and too high a moisture content is inhibiting on microbial reactions for hampering colonization.

Flow is controlled by molecular diffusion for gases, capillary diffusion for liquids, and convection driven by pressure gradients. In liquids, the pressure is of two sources, one intrinsic to the fluid and the other capillary pressure caused by contact with capillary pores. The capillary pressure is caused by molecular affinity, dependent on polar or a polar nature. Polarity defines the separation of charge of a molecule. Polar molecules have positive and negatively charged ends and result in partial positively and negatively charged ends. Water is a polar molecule, which contributes to the ability to act as a universal solvent [28].

Nonpolar molecules have no dipole moment. Fluids with a high affinity for the waste surface are considered wetting, those with less affinity are nonwetting [29].

Preferential pathways for fluid flow, structural changes due to degradation and compaction, and heterogenous material make it difficult to model phenomena. Consider the variations depicted below in the everchanging environment of a biological reactor for solid waste. Heat will conduct through solid, liquids, and gases, it will conduct through some material at greater rates, driven by temperature gradient and desire for maximum enthalpy [25].

Pressure and velocity are the state variables in the study of porous media fluid dynamics. Predicted values increase in complexity from the basic Darcy equation to Naiver Stokes momentum equations. Simulations of flow are complex and recently the use of modeling software has contributed to its study. Complex Multiphysics simulation software (MTDATA, FEMlab, COMSOL multi physics, KARDOS ANSYS, PHYSICA) is available but is so complex dedicated training and specialized knowledge of programming languages is required. Agostini analyzed the applicability of computational fluid dynamics (CFD) software that use mathematical techniques to describe Navier stokes equations [25]. The commonly used CFD packages are [30]:

CFX capable of modeling multiphase flow, porous media transport, and heat transfer.

FLUENT software tailored for food engineering.
FIDAP software that is finite element based for modeling non-Newtonian fluids and free surface flows.
POLYFLOW general-purpose finite element CFD designed for material engineering.
PHOENICS general-multipurpose CFD package.

Similar software exists for specific porous media problems that are simplified and more easily accessible. TOUGH2 Petrasim for hydrogeology and HYDRUS for vadose transport, both of which include a graphics user interface.

Composting is not homogeneous; transport gradients and solute concentrations occur within the mass. Heat transfer in composting is extremely difficult to model, countless parameters affect flow and there exist few data sets applicable to the industry. Particle size, reaction rates, microbial community dynamics, etc. are all influential parameters and there exist few to no data sets for application. Further research and usage into CFD modeling will likely first proceed in landfill and landfill bioreactor studies. TOUGH2/PETRASIM combined with a biodegradation module has been suggested as the standard tool for transport phenomena in landfills [31].

In conclusion, computational fluid dynamics have not been used extensively in compost science but could provide physically sound and effective simulation.

4 Natural Cycles

4.1 Carbon Cycle

4.1.1 Biosynthesis

Atmospheric carbon exists in two main forms, carbon dioxide and methane. Fixation into organic forms is dependent on synthesis reactions. Photosynthesis is the most prominent and well-known form of fixation, while chemosynthesis is lesser known and occurs in the absence of light. The reaction equation for the production of glucose is provided here.

$$6CO_2 + 12H_2O \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O$$

An understanding of further utilization of carbon in plants and the production of organic carbon-based compounds will aid in the design of biodegradation. Flowering plants cell walls are complex matrices composed of cellulose and are commonly described as type 1 or type 2 walls [32]. Type 1 cell walls are found in dicots, non-commelinoid monocots, and gymnosperms. Type 2 are found only in commelinid monocots. In flowering plants exist grasses, which are among the most important crops worldwide; these species contain type 2 walls. Cellulose content is similar in type 1 and 2, but type 2 has greater concentrations of hemicellulose [33]. The cell walls of grasses are used as one of the foremost energy sources for heterotrophs and deserve considerable attention in compost design. Composition of cell walls has great variance in their degradability and thus the study of their composition is essential to the field of composting.

Annual carbon fixation is estimated to be $2.34*10^{17}$ g year^{-1} [34], and 45% destined for incorporation into plant cell walls [35]. Carbon is necessary for soil ecosystems due to the numerous species of heterotrophs essential for ecosystem health. In undisturbed carbon cycles, plant litter provides soil ecosystems with carbon-rich organic compounds, but agriculture has yet to develop this practice to aid soil sustenance. Cellulose is one of the most common polymers on earth and the main constituent of plant cell walls [36]. At the molecular level, cellulose has a simple repeating structure of β-1,4-linked glucopyranosyl residues [37]. Glucan chains are polysaccharides derived from glucose monomers; these chains then link to a crystalline cellulose microfibril. The formation of larger macrofibrils comprises polysaccharides and lignin to produce secondary plant walls. Lignin is a phenolic polymer derived from monolignols synthesized via the phenylpropanoid pathway [38]. The science of plant biosynthetic pathways is important to compost science because the organic material formed will be the object of degradation. Application into compost science would be highly beneficial, but time must be devoted to a new field of science for application into a field with the incorporation of so many.

4.1.2 Biodegradation

Heterotrophic organisms receive carbon and energy from the oxidation of organic compounds. Many microorganisms can survive on a single organic compound, but some must be with specific compounds known as growth factors. Biodiversity of microbial communities often fulfill the growth factors for all species through ecosystem interactions. Cellular respiration is the common form for transformation of organic carbon–based compounds into inorganic CO_2 and the release of energy; members of the plant, animal, and protist kingdom all share this reaction. Provided below is the reaction equation.

$$C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O + ATP$$

The goal of composting coincides with the biodegradation of organic compounds and production of humic substances. Humic substances are resistant to biodegradation and an essential addition to improve soil properties.

4.2 Nitrogen Cycle

Nitrogen is expressed in molecular form as N_2. In this inorganic state, the majority of nitrogen is present in our atmosphere and unavailable to most living forms. Nitrogen fixed into organic compounds is essential for most life and its production dependent on nitrogen fixation.

Nitrogen fixation is a unique ability and few processes allow for the synthesize of organic nitrogenous compounds. Lightning converts N_2 to reactive nitrogen (i.e., NO), but the majority of organic compounds are produced through microorganisms capable of converting N_2 into reactive nitrogen—otherwise known as biological nitrogen fixation.

$$\mathrm{N_2 + 8H + 8}e^{-} \rightarrow \mathrm{2NH_3 + H_2}$$

Nitrogen-fixing microorganisms are named diazotrophs. The equation above summarizes this reaction, nitrogen fixation is a catalytic reaction dependent on the enzyme nitrogenase [39]. Diazotrophs can be further categorized into free-living diazotrophs, symbiotic nitrogen-fixing bacteria, and associative nitrogen-fixing bacteria. Through these relationships, soil food webs intake atmospheric, inorganic nitrogen and produce organic forms. Composting looks to amend nitrogen depletion in soils through an alternative means. Organic nitrogen present in decaying matter will instead be mineralized by biological reactions for application to agricultural soils.

Decomposition or mineralization of organic nitrogen produces ammonia (NH_3). Ammonia or ammonium can produce one another and are dependent on the environmental ph. Ammonium is mildly acidic and is nontoxic to fungi unlike its basic counterpart ammonia. If environmental pH is low, more ammonia molecules will be converted to ammonium; both reaction equations are provided here.

$$\mathrm{H^+ + NH_3 \rightarrow NH_4{}^+}$$

$$\mathrm{NH_4{}^+ + B^- \rightarrow HB + NH_3}$$

Hydrogen acts as a proton donor and if the environment is more basic than ammonium, the fourth hydrogen atom will be lost to a Bronsted base (B^-) to produce the uncharged ammonia acid. Ammonium is not very mobile in soils compared to nitrogen in the form of nitrates ($NO_3{}^-$). The strong adsorption quality of ammonium causes uptake by plants to be less common than that of Nitrates. Nitrates must be reduced prior to utilization for amino acid construction, but ammonium can be immediately incorporated [40]. Therefore, both forms of nitrogen are incredibly important to plant growth and subsequently the science of composting.

The production of nitrates results from the nitrification of ammonia into nitrite, then an addition of an oxygen ion to form nitrate. In the pollution chapter, biofiltration with mature compost is discussed. Biofiltration with adequate oxygen supply may cause a great production of nitrates and improve quality as a biofertilizer.

Plants differ in their nitrogen preference. Investigation into ammonium and nitrate uptake was performed in four tree species, Pinus, Larix, Quercus, and Juglans [40]. Contribution of glycine, ammonium, and nitrate by different plant organs is shown later. A multitude of variables affect these rates, primarily the mobility of the soil, but incorporation into this study is to display the dependency of all forms for plant growth and importance incorporation into composting. Uptake mechanisms of N in roots are specific and rely on high-affinity and low-affinity transport systems

[41]. Many plant species that normally use NO_3^- also have an efficient system for absorbing NH_4^+, identified as AMT, which is constitutively expressed at high NH_4^+ levels [42].

5 Community

5.1 Bacteria

Several methods of microbial analysis have been employed in the investigation of composting environments.

Only a small fraction of the microbes present in compost can be cultured and therefore understanding of compost ecosystems requires alternative methodology. Culture-independent methods have been employed; examples include analyses of extracted phospholipid fatty acid patterns. Molecular biology techniques such as denaturing gradient gel electrophoresis (DGGE) may also be significant.

Zhang conducted an experiment to analyze the effects of C/N ratios on the abundance of nitrogen-transforming bacteria [10]. Different ratios were used, total losses of N and C were investigated, and microbial succession was analyzed by 16S rDNA sequencing. Chicken manure and corn stover were mixed to obtain C/N ratios of 20/1, 25/1, and 30/1 (A, B, C, respectively). Different successional patterns were observed in each pile. At initial stage, all three piles exhibited predominant populations at phylum level of Firmicutes, Bacteroidetes, Proteobacteria, Tenericutes, and Actinobacteria. Firmicutes hydrolyze polysaccharides, Bacteroidetes contribute to degrading cellulose, tenericutes are significant in proteolysis [10]. These populations seem significant in degrading macromolecules. Temperature rises due to microbial activity and environmental conditions change rapidly as the compost enters the thermophilic temperature stage. The predominant populations drop to far below 1% and differences in community structure among C/N ratios emerge [10].

Some of the most important bacteria involved in composting emerge from the digestive tracts of chickens, these include Bacteroides, Enterococcus, and Bacillus [43, 44]. Redundancy analysis was performed to investigate relations between top 15 genera and losses. Highlighted in red are populations positively correlated with nitrogen losses. Zhang et al. stated "Thermoactinomyces, Planifilum, Flavobacterium, Bacillaceae, Pseudomonas, Sphingobacterium, Paenibacillus, Bacillus and Thermobifida were all found to be nitrogen fixing bacteria, and their relative abundance could be boosted by increasing the C/N ratio to 30:1, while Pusillimonas, Ignatzschineria, Alcanivorax, Cerasibacillus, Truepera and Erysipelothrix were all denitrifying bacteria, and their relative contents decreased with the increase of C/N ratio."

Cao experimented with microbial community diversity and its effect on pathogenic control in mature compost [9]. Compost of chicken manure and straw with a C/N ratio of 25, and water content of 60% (of wet weight) was mixed weekly and matured for 113 days. Germination indexes for both lettuce and radish were above 90%. The piles were then sterilized, suppressing 99.1% bacteria and 98.5% fungi. Inoculation with suspensions of the same compost were completed at four different dilutions. After seed germination, inoculation of plant pathogen, *F. oxysporum* sp. *radicis-cucumerinum* was performed in select samples. Results showed no difference in cucumber plant growth and health (analyzed by shoot and root weight and disease severity index, respectively) among dilutions without the presence of *F. oxysporum* sp. *radicis-cucumerinum.* In the presence of *F. oxysporum* sp. *radicis-cucumerinum*, significant differences in plant growth and health were observed ($p < 0.0001$). Plant growth and health were inversely related to the amount of dilution [9].

Proteobacteria and *Bacteroidetes* were the two most abundant phyla in almost all samples. Cao et al. [9] stated "the genera Asticcacaulis (Proteobacteria), Novosphingobium (Proteobacteria), Rhodanobacter (Proteobacteria), Cellvibrio (Proteobacteria), and Flavobacterium (Bacteroidetes) were identified as the most dynamic taxa associated with disease suppression in compost." Below is a graph representing the number of disease-suppressant populations among dilution levels [9].

Szekely analyzed the relationship between microbial community structure and the amount of button mushroom (*Agaricus Bisporus)* harvested [45]. *Agaricus Bisporus,* along with several other *Basidiomycetes,* is grown in matured compost substrate. 16S rDNA DGGE and terminal restriction fragment-length polymorphism molecular fingerprinting methods were used to track microbial succession, Relevance to this chapter stems from the compost undergoing a short heat treatment stage after temperatures begin to decline from the thermophilic range. This practice is performed for the preparation of a pathogen-free growth media. *Agaricus Bisporus* growth is promoted by the presence of growth-promoting fungi, such as the well-known *Syctalidium thermophilum.*

Thousand kilograms wheat straw, 890 kg broiler chicken manure, 200 kg horse manure, and 80 kg gypsum were mixed and wetted with approximately 5 m^3 of water for a moisture content of approximately 75%. The windrow was turned, mixed, and wetted every second day for 5 days. After the sixth day, the compost was placed in an open-air bunker with forced aeration. Every second day, the compost was put into a new bunker. On day 15, the compost was rested for a day after removal from bunker, then placed in an indoor composting tunnel where heat treatment occurred. 58 °C for 8 h, 48 °C until ammonium content fell below 10 ppm, approximately 3 days. After heat treatment, moisture content, fell below 70%, and TKN raised to 2.1% indicating maturity.

DGEE results showed microbial sequences in three groups*: Deinococcus-Thermus, Firmicutes*, and γ*Proteobacteria.* Dominant DGEE bands until day 4 were related to γ*Proteobacteria* and *Firmicutes*. Thermophilic temperatures were related to *Deinococcus-Thermus* and *Firmicutes,* winter bands were often related to the anaerobic species *Thermacetogonium,* and final mature composts were related to species, Pseudoxanthomanas taiwanensis.

T-RFLP screening was performed on mature compost in summer conditions, the recordings resulted in recordings of seven different phylogenetic groups. *Actinobacteria, Fimicutes, Germmatimonadetes, αProteobacteria, βProteobacteria, γProteobacteria,* and *δProteobacteria*. Fifty-five precent of the community belonged to Proteobacteria, 73% of which corresponded to *Xanthomonadaceae* phylotype. Eighteen percent of the community belonged to *Actinobacteria, with* 12% *Thermobifida,* and 5% *Thermomonospora*. Firmicutes were the third most frequent accounting for 4%, followed by *Germmatimonadetes,* and *Bacteriodetes*. Twenty-eight percent of the data did not have a previously isolated relative, these readings belonged to *Bacteriodetes, Firmicutes, Germmatimonadetes,* and *Protobacteria* [45].

Neher analyzed bacterial and fungal communities among variations in composting procedure. Populations are compared among windrow, aerated static pile, and vermicomposting [46].

Treatment after the temperature declines from the thermophilic range was believed to have a great impact on the emergence of microbial communities in mesophilic environments. Windrows had a high number of *Bacteroides* and *Chloroflexi,* Aerated Static Pile, *Protobacteria,* and Vermicompost, had the greatest amount of *Bacteroides, Proteobacteria,* and *Verrucomicrobia,* with the lowest amount of *Chloroflexi and Chlorobi.* Vermicompost had the greatest bacterial diversity and was assumed to be caused by avoiding thermophilic temperatures. Neher conducted an experiment where vermicompost was exposed to thermophilic temperature prior to worm inoculation. The diversity was still higher than windrow or ASP furthering an argument that earthworms promote the growth of bacteria. The temperature was 21–27 °C and 0.6 m thick compared to 55 °C piles in windrow and ASP; therefore, I do not support this conclusion due to the multitude of variables left unaccounted for. Neher also compared different carbon source and their effect on microbial communities but did not use constant C/N ratios, which have been proven to effect microbial community dynamics. Neher's study is most useful to show microbial communities are highly dynamic and environmental conditions are very influential.

In conclusion, community succession is highly dynamic and populations are often replaced in changing environmental conditions. Zhang proposed high C/N ratios promoted the growth of nitrogen-fixing bacteria and suppressed denitrifying populations. Cao demonstrated the effectiveness of microbial diversity on pathogen suppression, and Neher demonstrated how composting methods change community dynamics. All three experiments incorporated manure as a feedstock, which provided *Bacteroides* and *firmicutes* in abundance. Provided Composting is the best waste management practice for manure and natural decomposition originally : involved manure by large heterotrophs. The digestive of heterotrophs is also a highly evolved biological reactor to degrade food, so incorporation into composting may aid time of maturity. The amount of manure added to soils is unnatural but nutrient rich, as an abundant waste it should be incorporated into agriculture, but it will probably further the mistreatment of soils. As a readily available solution, it will prolong the acceptance and advocation of soil care, minimal disturbance, and the return to agriculture as a community responsibility.

5.2 Fungi

Much like bacteria, there is succession in fungal communities and prominent populations are dependent on environmental conditions and influent feedstock.

Research into compost fungal communities is less prominent than that of bacteria and a study was conducted to elucidate the prominent populations [47]. A compost mixture of mushroom residue and chicken manure was mixed at 1:1 and samples were collected using a DNA isolation kit. Not all populations are recorded through this method, although as an incredible tool for scientific analysis one should recognize the potential for incomplete recording of taxonomy. DNA samples were taken at different depths on days 1, 3, 5, 7, 10, 14, and 21; these are denoted as T1, T2, T3,…, respectively [47].

Saccharomycetales was dominant in early composting. *Saccharomycetales* are in the phylum *Ascomycota* and multiply by budding. *Saccharomycetales* are believed to be dominant due to spore-like cellular structure that can withstand high temperatures and low initial moisture contents. *Acremonium alcalophilum* and S*ordariales* were dominant at $t = 3$ days, *Saccharomycetales* was dominant at $t = 5$ days, at $t = 7$ days *Scedosporium, minutuisporum (32.65%), Aspergillus cibarius (16.89%),* and *Thermomyces lanuginosus (9.42%)* were the most abundant [47].

Bonito provides great information on fungal communities present in a compost with no addition of nitrogenous waste. Samples from 0-, 210-, and 410-day-old composts were assessed using denatured gradient gel electrophoresis (DGGE) [48].

As shown, Ascomycota dominated starting composts and by day 210, Basidiomycota grew from 13 to 51%. Day 410 showed a diverse community structure with no one population contributing more than 43% of the total population. Many yeast sequences were recovered from initial stages; these included *Candida* varieties that are opportunistic pathogens. Few pathogens were recorded in 210-day and 410-day samples, demonstrating compost is effective at the removal of fungal pathogens. Zygomycetes are associated with composting but are unable to be represented using (DGEE). Therefore, DGGE methodology is a great tool in assessing microbial community structure but is like all sampling, somewhat incomplete.

Ascomycota, Basidiomycota, Zygomycota, with five other phylas, make up the kingdom fungi. *Ascomycota* and *Basidiomycota* form the subkingdom *Dikarya,* which represent most of the "higher fungi." Ascomycota are sac fungi and form spores in a sac known as an ascus. Common ascomycetes include species used for the production of bread, alcohol, penicillium, as well as many pathogenic species. Pathogen is not necessarily bad; it only means the species is capable of causing infection. Basidiomycota encompass common fungi we all know and love. Basidiomycota include mushrooms, puffballs, chanterelles, boletes, bracket fungi, stinkhorns, smuts, bunts, rusts, and some yeasts. Basidiomycota are composed of hyphae and reproduce sexually with specialized end cells called basidia. Underneath a mushroom cap is an example of Basidiomycota reproduction. Ectomycorrhiza (EM) is a common plant symbiont that does not penetrate the host cells, unlike another symbiont, arbuscular mycorrhiza (AM) [49].

Ectomycorrhizal fungi often belong to phylum *Basidiomycota* but unlike the common populations in composting are not saprotrophic. A presence in compost would aid degraded land and I hypothesize incorporation could be beneficial to aid lands where fungicides are commonly used.

5.3 Vermicomposting

> It may be doubted if there are any other animals which have played such an important part in the history of the world as these lowly organized creatures.–Charles Darwin

Darwin's final book, *The Formation of Vegetable Mould, Through the Action of Worms,* leads us to believe that the "father of evolution" in his most educated and wisest state found himself studying earthworms. Vermicomposting is a biological reaction dependent on earthworms and microorganisms for the degradation of biodegradable organic waste and the production of humic substances.

5.3.1 Earthworm Species

Many earthworm species can be found in vermicomposting operations, including Eudrilus eugeniae Kinberg, Perionyx excavatus Perrier, Lampito mauritii Kinberg, Lumbricus rubellus [50]. Vermicompost products are used as a soil amendment, and native species of earthworms should be prioritized. Raphael and Velmourougane compared the vermicomposting rated of exotic (Eudrilus eugeniae) and a native earthworm (Perionyx ceylanesis) from a coffee farm for decomposition of coffee pulp. 1 m × 1 m × 0.75 m brick tanks were smeared with cow dung slurry, filled with a layer of dried coffee husk (15 cm) over which cow dung slurry was sprinkled and weed biomass was spread (10 cm) [51]. Partially composted coffee pulp was added, sprinkled with cow slurry, and lastly composted pulp mixed with partially composted weeds finished the influent loading. Three boxes of each population were constructed. The tanks were covered, moisture was maintained, and final quality was analyzed by visual observation and sieving. Results concluded the exotic species were able to degrade the pulp faster (112 days) compared to (165 days); however, compost yields were significantly higher among native earthworm populations. Microflora, except fungi, were found to be significantly higher among native populations, as well as recordings of functional microbial groups. Pedersen and Hendriksen reported that in the guts of earthworms there is an increase in the number of vegetative cells as well as germination of the spores of the bacterial community [52]. Bacteria, fungi, and yeast populations were found to be significantly higher in native vermicast as well as the abundant presence of macro and micronutrients.

There exist three main categories of earthworms, *epigeics, anecics,* and *endogeics. Epigeics* are surface dwellers and feed on humus, *anecics* are a geophytophagous, soil-dwelling species that construct vertical tunnels, and *endogeics* are a geophagous, soil-dwelling species that construct horizontal branching burrows [51].

5.3.2 Vermicomposting vs. Composting

Most species are unable to endure temperatures that exceed 40 °C, which are below the thermophilic range commonly associated with composting. Vermicomposting requires no mixing or agitation for the worms accomplish the same task as engineered machinery and labor. This has been their life far before the emergence of our own. The mesophilic state following thermophilic decline is a well-suited environment for worm populations. Large aggregates are broken down by agitation and made more readily available for worms, and hazardous materials are stabilized that would be hostile to worms. Food waste, slaughterhouse waste, and poultry waste have a large proportion of the material undergoing rapid biodegradation, anaerobic zones of decomposition as well as the production of volatile fatty acids severely stress and kill worm populations. Stabilization of waste through composting as a prior stage has significant positive effects in the field of vermicomposting.

5.3.3 Vermicompost Continuous

Composting of solid wastes is considered only feasible as a batch reactor [53]. Due to the necessary rise of thermophilic temperature, new material cannot be added to an ongoing reactor. Common windrow operations involve layering of compost material 15 cm thick and manure or sludge in 5-cm-thick layers, wetting with approximately 60% of the reactant mass, means of aeration either through passive or active means, covering with cohesive clays or open plastic sheets, in forced aeration systems. Once temperature exceeds 55 °C, aeration is stopped and blowers are used to push away hot gases, turning of the pile and prior procedure is repeated. Typically, after 50–70 days, maturity is reached under optimal environmental conditions and is demonstrated by constant pile temperature [53]. Compost then is left to cure for 2–4 weeks and then production is considered complete.

Vermicomposting, unlike normal composting, can be considered a batch, semi-batch, and even a continuous reaction. The product sold is the excretion of the earthworm, which is performed on a continuous basis. There are no thermophilic criteria and little biodegradation occurs to vermicast after production. Vermicast by epigeic and anecic species is typically deposited at the top of the reactor (Eudrilus *eugeniae and Eisenia Fetida do)*. This contributes to a possible continuous design. Regardless of reactor design, a solids retention time of at least 1 month but more commonly 2–6 months. Design can be optimized as any bioreactor can, by controlling access to food for earthworm species. Earthworm density can be increased to a rate-limiting value where competition becomes restrictive. Optimal design is considered high surface-area-to-volume ratios.

5.3.4 Food and Vegetable Processing Waste

Along with the gross production of food waste from consumers, the production of fruit and vegetable products produces processing waste, skins, tops, bottoms, unwanted pieces. Vermicomposting following precomposting may be an economical and productive practice.

Sharma and Garg investigated vermicomposting of processing waste with buffalo dung with earthworm species *Eisenia fetida.* Unlike Abbasi, Sharma and Garg manually tuned the pile to avoid anaerobic conditions [54]. Twenty worms were placed in 12-cm-deep vermibins at 25 ± 3 °C with moisture maintained at 60–80%, earthworms were sorted and counted after 90 days. Ca and NH_4-N were secreted by earthworms and neutralized humic acids, which helped maintain a neutral ph. Four ratios of dung to processing wastes were conducted, these being 100% dung, 75–25%, 50–50%, and 25–75%. Trials are named VB1, VB2, VB3, VB4, respectively.

When TOC and OM decreased, TKN increased significantly. High TKN values lead to favorable environmental conditions to reduce nitrogen loss in vermicomposting process by earthworms. Sharma hypothesizes high TKN values are a result of earthworm activities, nitrogenous excreta and mucus, secretion of polysaccharides, growth-stimulating hormones and enzymes [55]. C/N reduction was greatest in 100% buffalo dung and lowest in 25–75% ratio. Increases in heavy metal concentrations are synonymous with vermicomposting but are assumed to result from the reduction of biodegradable waste. Worm growth and reproduction increased with the proportion of buffalo dung.

5.3.5 Vermicompost Diversity

Vermicomposting's effect on microbial diversity was researched [56]. Four Hundred grams OF 1:1 cow dung and sewage sludge were mixed with 100 g of sawdust and inoculated with 150 *Eisenia fetida* earthworms, while another was used as control without inoculation. Vermicomposting was compared to composting without inoculation, results showed enhanced microbial diversity in general, with enrichment of fungi and protozoa, and in some cases increases in bacterial abundance.

PLFA analysis showed higher ratios of mono: bran phospholipid fatty acids with the maximum quantity of earthworm biomass. High ratios are associated with aerobic degradation, this and the abundance of protozoa establish that vermicomposting improves aerobic conditions in static piles. Increased aerobic conditions, increased microbial diversity, and increased stabilization of excess sludge in vermicomposting prove its effectiveness in the management of organic wastes.

5.4 Maggots

Sustainable Farming is of equal importance to sustainable waste management. In composting, nutrients are produced for application in farming, but what if during composting one could farm at with the pile. The production of maggots is a profitable industry, with demand from commercial fish and poultry production.

Batches of fresh pig manure (200 kg) 7-cm thick were placed in cement trays under greenhouse emissions with maggot inoculum at weight ratios of 0, 0.25, 0.5, 0.75, 1, and 1.5%. Maggots were harvested id day 7 and dried using microwave equipment. The manure residue was then composted, the pile was covered by a plastic film for 24 h to kill residual maggots.

Results showed that the temperature of the manure rose more rapidly with increasing levels of maggot inoculum. Moisture content decreased with increasing levels of inoculum; nitrogen followed a similar pattern. Crawling and digestion produces heat and increases the porosity of the material aiding further microbial degradation. Harvested maggots also met national standards for fish meal in China when analyzing protein, Met, Lys, As, Pb, Hg, Cd, Cr.

6 Metabolism

To determine the efficiency, duration, composition, specifications of compost, one must analyze energy metabolism. Food waste consists of the macronutrients: carbohydrates, fats, and proteins. Carbohydrate catabolism is performed through glycolysis, protein catabolism by proteolysis, and fats by lipolysis. Energy metabolism in aerobic conditions often depends on the intensity of oxygen consumption (rate of oxygen consumption per unit mass of the organism) and the glycolytic intensity [57].

$$\psi = \dot{q}_{\mathrm{o}_2} + \dot{q}_{\mathrm{gl}} \tag{2.1}$$

Glycolytic intensity in comparison to oxygen consumption intensity is considered minimal under aerobic conditions for the majority of organisms and neglected with expression simplification following:

$$\psi = \dot{q}_{\mathrm{o}_2} \tag{2.2}$$

If glycolytic intensity is negligible, it seems we can assume energy metabolism and microbial growth is most directly influenced by oxygen availability given there is no limiting reagent. Glycolytic and oxygen consumption intensity help determine rate-limiting reactants and products formed but offer little insight into reaction kinetics. Reaction rates are described using reaction rate constants. Rate constants for composting substrates are significantly less compared to municipal sewage.

Composting is a heterogeneous system where suspended microbes are separated from the substrate in solid form. Energy metabolization requires a complicated series of events. First, hydrolytic enzymes are produced and transported to the surface of the substrate, then hydrolysis of substrate molecules into soluble fractions, diffusion transport to the cell, then through biological membranes. The same series of events is required for the transport of oxygen into the microbial cell, floc, or mycelia. Many biochemical reactions are nonelementary homogeneous reactions, "those whose rate expressions cannot be written from inspection of stoichiometric equation" [58]. Stoichiometric equations do not produce reaction rate expression in many nonelementary reactions due to the presence of enzymes, biological catalysts, which remains as free enzymes after the formation of a product. These are known as Catalytic reactions.

$$S + E \leftrightarrow ES \rightarrow P + E$$

Biodegradation and the energy metabolism are considered autocatalytic reactions. Microbial cells contain and will produce the necessary enzymes without aid to "generate more cells, energy, and metabolic products" [58]. Hydrolysis can be described as follows:

Kinetics of solubilization

$$E + A \leftrightarrow EA \leftrightarrow P + E$$

Oxygen uptake rate (OUR) helps us define the required oxygen demand for organic decomposition (stoichiometric demand). Oxygen is supplied by aeration and comprises 20.95% of dry air volume. The aeration of BW is essential for decomposition (stoichiometric demand), as well as moisture and heat removal. Air transport regulates drying and heat removal demands, which will also be considered in design.

6.1 Nutrition

I owe all credit to Biological Waste Treatment by Grady & Lim for the content provided in this chapter, the textbook *Biological Principles* is incredible and I would like to give thanks for the information provided.

Organic substrate biodegradation releases energy and simple molecules used for cell synthesis. The study of its breakdown is an investigation into the metabolism of cellular heterotrophic functions. Cellular chemical composition of living things contains nucleic acids, lipids, proteins, and carbohydrates. The synthesis of these compounds requires building blocks of carbon, nitrogen, phosphorus, etc. and are easily provided by similar organic material.

6.1.1 CHONPS

The synthesis of proteins and amino acids is dependent on nitrogen and sulfur. Sulfur reacts with the amino acid serine and forms cysteine—one of the four amino acids present in DNA coding. Phosphorus is necessary for synthesis of nucleic acids and phospholipids and is important in energy transfer. Enzymes known as phosphatases are able to incorporate phosphorus from degraded organic compounds into cell synthesis. Oxygen is incredibly important in metabolism. Organic compounds contain oxygen as a basic constituent, the oxygen present in cell synthesis is obtained from organic substrates and water. Molecular oxygen acts as the terminal oxidizing agent in aerobic respiration. Anaerobes and facultative microorganisms are capable of respiration in the absence of oxygen, using an alternative oxidizing agent.

6.1.2 Mineral Nutrition

Potassium activates many enzymes, while calcium aids cell wall stability and bacterial spore heat stability. Iron is a dominant electron carrier in redox reactions. Cobalt is required to produce vitamin B-12, which is necessary for single-carbon transfer reactions. Zinc is a structural component of enzymes. Molybdenum is essential for nitrate reduction. Lastly, Copper is involved in redox reactions.

6.2 ATP Generation

Metabolism releases energy. This energy would be lost to entropy if not for energetic coupling. The most important coupling compound is known as adenosine triphosphate, or ATP. Its composition is depicted below and highlights the importance of phosphorus as a critical nutrient.

The entry of many nutrients into the cell is driven by active transport. Active transport is an endergonic reaction requiring external energy input, it is the transfer of nutrients pass the cell wall driven by concentration differences and aided by cellular enzymes. Another form of transport occurs in eukaryotic cells, phagocytosis, which uses transport vessels like lysosomes to engulf nutrients. The second time ATP will be needed is in the conversion of nutrients into intermediate metabolites of low-molecular weight. Intermediate metabolites include proteins, polysaccharides, nucleic acids, and lipids. Lastly, ATP will be required to synthesize new macromolecules through polymerization.

ATP is produced via substrate-level phosphorylation or reactions associated with the electron transfer chain. NAD and NADP are major hydrogen acceptors.

7 Effluent

7.1 Estimation of Maturation

Maturity assessment for composting is critical for the removal of phytotoxic substance that can delay germination and cause plant injury. If anaerobic decomposition continues to occur in compost, plant will suffer from the production of such substances.

The plant seed germination index (GI) is a frequently cited, low-cost method to assess compost maturity. A liquid obtained from the compost samples is used for germination and growth of seeds, phytotoxity prevents successful germination and makes the GI index a useful tool in maturity assessment. Spectroscopy, total nitrogen and carbon analysis, and other more intensive methods are commonly used for maturity assessment, but the GI index retains a prominent practice in the field [59].

7.2 Pollution

As a green waste management practice, pollution should be of primary concern. Gaseous emissions and leachate pollutants are key issues and pollution prevention is discussed here.

7.3 Gaseous Emissions

Compost operation success as sustainable waste management is dependent on the quality of all effluent. Odorous gas emissions and air pollution are necessary criteria for design. Odor is a main cause for the closing of industrial operations and reduced pollution is crucial for all engineered systems. It is understood that emissions are best under aerobic conditions and since the alternative waste management practice is anaerobic, emission from CO_2, N_2O, $CH_{4,}$, which contribute to global warming, shall be considered.

Sulfur compounds, and most of the volatile organic compounds (VOCs) emission causes undesirable and other odor nuisances [60, 61]. VOCs emitted are often biodegradable due to biogenic origin, water soluble, and have adsorption potential, which allows the use of psuedofilters or biological processes for control of emissions. Proper C/N ratios aid in porosity, tortuosity, and microbial populations that reduce the volatilization of ammonia. pH control and vermicomposting also enhance nitrogen fixation.

In-vessel composting enables faster treatment and greater control over emissions. Windrows are commonly associated with anaerobic zones due to the inability for oxygen to access the middle portions of the pile resulting in methane production.

Many odor emissions produced from windrow operations are released in turning and disturbance of the piles releasing trapped gases.

7.3.1 VOC and Treatment

High concentrations of VOCs are released during the initial stages of composting, i.e., hydrolytic stage [62]. There are more than 100 volatile organic compounds studied during composting, aldehydes, alcohols, carboxylic acids, esters, ketones, sulfides, terpenes, organosulfur compounds, ammonia, etc. [62].

7.3.2 Biofiltration

Biofiltration is treatment of air pollution by means of diffusion in a biological material. Mature compost is used to eliminate and reduce most of the potent odors [63].

Air flow rate is the adjustable variable for control of reactor dynamics. Humidified air is used as influent, the bed comprises compost, soil, peat, chipped brush, bark, etc. and may include additives to improve porosity such as gravel [63]. Much like composting, biofilter pH control, moisture content, and pollutant influent concentration must be monitored. Temperature and moisture content are critical; unlike compost biofilters lack a high concentration of organic material to generate heat, temperature is recommended to range from 20 to 40 °C, moisture content is recommended to be 40–60% or until oxygen inhibition. Biological processes are dependent on microbial catabolism and are dependent on many micronutrients. In biofilters, the influent material is not a complete feed; often nitrogen, phosphates, minerals, and trace elements are necessary. Mature compost has higher concentrations of these materials that support microbial growth [63].

Biotrickling Filter

Concurrent liquid and gas flow are used to remove volatized pollutants. Contaminated air flows through an inert medium where continuous supply of liquids containing nutrients for microorganisms flows concurrently. Biotrickling filters are primarily used to remove gases with acidic compounds [64]. Bedding materials such as structured plastics, random dump plastics, resins, ceramics, celite, polyurethane foam, and lava rock are suggested [63]. Microbial inoculation of these inert materials is essential for operation. Recommended trickling velocities range from 0.01 to 10 m h^{-1} and recirculation is fundamental for optimal degradation of polluted gases. Following is an example of a biotrickling filter.

Bioscrubber

Bioscrubbers are common in industrial applications for the degradation of vaporizing solvent pollutant from coating facilities, carboxyl acids, esters, heterocyclic sulfur and nitrogen components, mercaptans, phenols, and sulfides [63]. Influential parameters include pH, nutrient concentration, and operational parameters such as low-pressure drop, which can be controlled [65]. Scrubbers are capable of treating higher concentrations of polluted gases compared to alternative biofilter systems; capacity ranges from 3000 to 4000 $m^3\ m^{-2}\ h^{-1}$ [66].

7.3.3 Use of Mature Compost

Yang conducted research on the incorporation of mature compost into kitchen waste composting and its effect on gaseous emissions [67]. Mature compost is on site, porous, and a microbial-rich material well suited for biofiltration. Incorporation into composting is done is via direct mixing, used as a covering agent, or used as a separate filtering process. Research was conducted through experimentation of three reactors, one with directly mixed mature compost, one with mature compost cover, and one with no incorporation. Results showed no difference in reactor temperatures in insulated forced aeration reactors. $NH_{3,}$ N_2O, and CH_4 emissions varied greatly among the three reactors [68].

The greatest reduction in NH_3 emission was in the reactor with mixed compost, a 58% reduction over 35 days was observed. Reduction in ammonia loss may be contributed to physiochemical absorption of NH_4^+, urea, and uric acid. The covered pile witnesses a 21% reduction in NH_3 emission [68].

CH_4 emissions were significant in the first 10 days of operation, then decreased gradually to undetectable levels in all treatments. Due to high presence of initial organics, resources and environmental conditions aided the growth of anaerobic bacteria. During the thermophilic phase (days 3–20), CH_4 emissions were considerable where O_2 content decreased significantly. In the reactor of mixed mature compost, CH_4 emissions were reduced by 44.8%. In the covered reactor, a 36.2% reduction was observed. The increased porosity and ventilation are considered responsible for reduced emissions.

N_2O emission was a concern at initial composting and greatest in the thermophilic phase. Initial emissions are a result of denitrifying microbial populations, under environmental conditions of O_2 scarcity and NO_x^- abundance. In the thermophilic phase, high temperatures(>40 °C) inhibit nitrifiers and increase N_2O emission due to NH_4^+ oxidation by methanotrophs [67]. A 73.6% reduction was observed in the mixed reactor, and a 37.6% reduction in the covered reactor. Mature compost from manure or sewer sludge could considerably enhance N_2O emissions. High nitrate and nitrite levels could result in intense nitrous oxide emissions stemming for denitrification [69, 70].

Conclusion

Mature compost greatly reduces gaseous emissions during composting. Mixed Compost provides the greatest results for increased duration of filtration from forced aeration inlet. Mature compost also decreased the C/N ratio considerably more during treatment. Enhanced biodegradation of organic matter, accelerated succession of microbial communities, maintenance of microbial diversity, and increased physical structure may be the responsible [68].

7.4 Leachate

Generation of leachate from composting occurs in large quantities. Compost leachate contains high concentrations of dissolved biodegradable and nonbiodegradable compounds and therefore poses a potential risk to local streams and aquifers. Shu et al. state the most common technique for leachate treatment is biological degradation [71]. Anaerobic digester–activated sludge, anaerobic sequencing batch reactors, and up flow anaerobic sludge blankets have been used in leachate treatment. Leachate effluent often cannot meet stringent discharge regulations. Shu et al. propose membrane filtration as a prominent solution [71].

7.4.1 Membrane Filtration

Membrane filtration uses semipermeable skins and is subject to serious fouling. Chemical coagulation is sued to remove suspended solids, colloid particles, nonbiodegradable organic compounds, and heavy metals. Ferrous or aluminum salts are used for coagulation, flocculation with organic components, or colloid particles produce bulky floccules that settle. Shu et al. conducted an experiment where 15 L of compost leachate was coagulated in a beaker and allowed to settle for 2 h, then filtered through a manufactured nanofiltration membrane.

Chemical coagulation and nanofiltration proved to be a successful method to for leachate treatment. Removal efficiencies for turbidity (75.3%) and COD (62.8%) were observed in chemical coagulation. The removal efficiency for nanofiltration process was about 89.7% of COD, 78.2% of TOC, 72.5% of TN, 83.2% of TP, and 78.6% of NH_3–N. Effluent concentration of COD, NH_3–N, TOC, and SS was 92, 21, 73, and 23 mg L^{-1}, respectively [71].

7.4.2 Constructed Wetlands

Treatment for leachate treatment could be the construction of wetlands that mimic their natural counterpart. Low maintenance, low energy, and benefits to our natural ecosystem help support this method. High influent concentrations are problematic for all treatments and pretreatment can be used. Constructed wetlands are commonly used for tertiary treatment, but on large scale could be used solely. Leachate for watering compost windrows [72], settling basins [73], or stabilization lagoons [74] to more advanced processes like sludge digesters [75], usage of coagulants, or biofilters [76] have been studied. Leachate dilution is also a method to reduce high concentration.

Bakshoodeh et al. experimented with 1.5 m*0.5 m*0.5 m stainless steel boxes, filled with fine gravel to provide a uniform flow distribution at inlet and outlet areas. Fine sand and vetiver plants made the treatment zone [77].

Final concentrations of the contaminants, even in the Vetiver CW with removal efficiencies of 53.7%, 74.5%, 69.9%, 73.5%, and 73.4% for COD, BOD5, NH_3–N, NO_3–N, and TN, respectively, are still too high for release to the environment [77]. Exploration into various wetlands plants for application and pretreatment methods should be analyzed for further improvement. Initial costs of a constructed wetlands could be minimal, operational costs and maintenance low, and benefits large for leachate treatment and natural ecosystems. I recommend constructed wetlands for all tertiary treatment especially in the composting industry.

8 Decentralized Composting

The greatest contribution a compost engineer can make would be furthering decentralized composting. Immeasurable benefits would arise from individuals being responsible for their own waste management. Composting may reduce waste production, garner support for greener waste management, instill passions for gardening, bring families together, reduce the most nonpoint fertilizer and pesticide pollution, and compost the most waste.

Industrial food waste, manure, and sludge must be composted on a large scale. A balance between both residential, community, and industrial practices would bring the most reduction to the dependency on landfills to decompose biodegradable waste.

9 Applications

9.1 Microbial Fuel Cells

Electricity is often generated from an electron-rich anode to an electron acceptor, cathode. Oxygen is the strongest electron acceptor. Therefore, most energy transformations are aerobic oxygen is the strongest electron acceptor and therefore causes most energy transformations to be aerobic. Nitrates, sulfates, Iron, and manganese are prominent electron acceptors when oxygen is not present. MFCs are bioelectrochemical transducers that convert microbial reducing power into electric energy, while electrons released from anaerobic degradation could flow toward greater enthalpy when oxygen is present in abundance. Say, an anode in a hydrophobic rhizosphere to a cathode in the atmosphere. It is the most direct form of energy production from autotrophs, which results in no carbon emission, and depends on plants and soil ecosystems.

Moqsud 2014 investigated compost in plant microbial fuel cells for bioelectricity generation. Mosqud concluded that compost added plant growth and enhanced voltage generation [78]. The power density became three times more when compost was added.

9.2 Compost Solar Tower

Heat is generated from microbial decomposition of organic material. Anderson et al. proposed and constructed a solar tower/waste to energy facility [79].

Turbines, placed in a solar chimney above a composting pile, offer a very green solution to both waste management and energy production. Incorporated with alternative methods of energy production will help if ever a transformation from nonrenewable sources occurs.

10 Bioeconomy

Global annual generation of food loss and waste amounts to 4.4 Giga tonnes equivalent of carbon dioxide, which is about 8% of total anthropogenic GHG emissions and only slightly less than that of global road transportation [80].

Food waste produces only methane and landfills. The three R's applied to food waste offer exciting possibilities for alternative waste management. First, food waste should be reduced. Disposal behavior is based on culture and personal choice; one could hope for improved attitudes, but waste generation per capita per day is always increasing. Then we are left to reuse and recycle. Food waste is generated from agriculture and meat production (chickens, pigs, and cows). With demand increasing for these industries, especially the latter, resource depletion will worsen. Waste management should look to aid these industries or be used as a free resource to compete against gross industrial agriculture and meat production.

10.1 Food Waste Industry

Food waste is a very valuable resource and should be used for applications with less stringent regulation. The Swine Health Protection Act stipulates food waste containing animal parts must be heat-treated at 100 °C for 30 min at licensed operations to qualify for swine feeding [81]. It is illegal to feed mammalian protein to ruminant animals for concern of bovine spongiform encephalopathy (mad cow disease). Alternative uses for food waste begin very high on the commercial food chain and continue until the production of humic substances. Uses for livestock feed, insect production, algae production, worm production, biofuel production, and other bio-based products could be researched.

11 Summary

Composting is an exciting industry, where study of microbiology and natural cycles are applied to the operation of biological reactors to reduce pollution, aid degraded lands, and improve agricultural sustainability.

Disposal of material deemed no longer useful is excessive and growing at alarming rates. "The generation of municipal solid waste per capita was 2.68 pounds per day in 1960. By 1970, it had grown to 3.25 pounds per day and by 1980 it was 3.66 pounds per day. By 2010, the daily generation of municipal solid waste per capita had reached 4.44 pounds" [1]. Food and other biodegradable wastes are an essential concern. The availability of better technology and the perishability of valuable resources are strong support for a change of industry standard. An understanding of biological systems and the environmental impact of engineered systems is leading to positive change in waste management and this chapter analyzed composting as a critical means. Composting of biodegradable waste (BW) is largely dependent on favorable conditions for microbial populations. I would like to consider Landfills, Landfill Bioreactors, Composting, and Natural wastewater treatment as a continuum on the treatment of labor/ecosystems in biodegradation and the pollution generated. It is evident that favorable conditions for decomposers produce greater rates of decomposition and greater utilization of effluent material. We rely greatly on microorganisms, and a symbiotic relationship proves to be the most beneficial to our ecosystem's success.

Low C/N ratios are not recommended for composting. Volatilization of ammonia is a leading cause of acid rain and is inversely related to C/N ratio values. Ammonia and nitrous acid are fatal to some fungal populations and species richness has proven to be the greatest attribute time and again to ecosystem health and viability. In high C/N piles, the percentage of nitrogen accumulation is considerably higher, producing greater nutrient content in compost piles and reduced emissions.

Water is necessary for composting. Microbial activity, including Hydrolysis reactions, is dependent on the presence of water. Sharma and Poulsen studied oxygen uptake in porous media using yard waste compost as a test medium [16]. Water content from air dry to field capacity was analyzed under gas flow ranging from 0.2 to 2 L*min^{-1}. Increased water content improves nutrient supply to organisms and biological activity but decreases the quantity of air-filled pores. Increased water content produces inactive zones with little or no gas movement and hindered microbial activity. Ideal moisture content is dependent on balancing these effects and is controlled by pore size distribution, organic matter content, water flow velocity, water content, and influent air flow.

Critical to aerobic degradation of solid waste is oxygen supply. Adequate oxygen supply is essential for catabolism and maturation of biodegradable waste. Insufficient supply increases gaseous emissions, including the emission of odorous compounds and greenhouse gases. Inadequate oxygen supply also promotes anaerobic degradation and the altering of environmental conditions, which become unable to house a diverse microbial population. Inadequate supply also reduces the ability to reach thermophilic phase and pathogen control, and increases the time to reach maturity.

Windrows attempt to supply oxygen demand through molecular diffusion and natural draft ventilation, with periodic mechanical turning. If influent feedstock has a high C/N ratio, an addition of mature compost is incorporated, or if odor and gaseous emission are not of great concern, this method may be used solely to aerobically degrade organic waste. The oxygen supply for biological decomposition (stoichiometric demand) often needs windrow turning or alternative methods for oxygen supply. Peak oxygen demand occurs early in processing and decreases after thermophilic phase, windrow maturation after the thermophilic phase is reached is common practice.

Stoichiometric oxygen is entirely dependent on feedstock. Oxygen is the terminal electron acceptor in aerobic degradation of biological degradation. The absence of O_2 is likely to lead to an accumulation of electric charge. Generated electron remains static until the presence of O_2 is supplied. This is a passive process, resulting in a low O_2 utilization due to uneven distribution of O_2 in the compost pile [20]. Gaseous flow in porous media will develop pathways of least resistance and will produce many areas void of activity. It is well known that electrons can move under an electric field. Electric field induction enhanced the flow of electrons from biological redox processed to oxygen, enhancing maturation and GHG emissions. It is theorized that the addition of biochar and ferric acid would further optimize O_2 utilization.

The physical structure of biological reactor is a key variable in operation. Air- and water-filled pores, permeability, pore tortuosity, hydraulic conductivity, moisture content, water-holding capacity, metric potential, and thermal conductivity are all affected by the compost environment [24]. Biodegradable solid waste is heterogeneous and thus is the physical structure. Agostini reviewed the main properties of the porous physical characteristics, phenomena, and simulation models for the management of biodegradable waste [25]. The initial microbial community, moisture content, oxygen availability, physical availability to degradation, temperature, and chemical composition determine the overall biodegradation rate. Computational fluid dynamics have not been used extensively in compost science but could provide physically sound and effective simulation.

The science of plant biosynthetic pathways is important to compost science because the organic material formed will be the object of degradation. Application into compost science would be highly beneficial, but time must be devoted to a new field of science for application into a field with incorporation of so many. The goal of composting coincides with the biodegradation of organic compounds and production of humic substances. Humic substances are resistant to biodegradation and an essential addition to improve soil properties.

Ammonium is not very mobile in soils compared to nitrogen in the form of nitrates (NO_3^-). The strong adsorption quality of ammonium causes uptake by plants to be less common than that of Nitrates. Nitrates must be reduced prior to utilization for amino acid construction, but ammonium can be immediately incorporated [40]. Therefore, both forms of nitrogen are incredibly important to plant growth and subsequently the science of composting. Decomposition or mineralization of organic nitrogen produces ammonia (NH_3). Ammonia or ammonium can produce one another and are dependent on the environmental ph. Ammonium is mildly acidic and is nontoxic to fungi unlike its basic counterpart ammonia. If environmental pH is low, more ammonia molecules will be converted to ammonium.

Community succession is highly dynamic, populations are often replaced in changing environmental conditions. Zhang proposed high C/N ratios that promoted the growth of nitrogen-fixing bacteria and suppressed denitrifying populations. Cao demonstrated the effectiveness of microbial diversity on pathogen suppression [10], and Neher demonstrated how composting methods change community dynamics [46]. All three experiments incorporated manure as a feedstock, which provided *Bacteroides* and *firmicutes* in abundance. Provided composting is the best waste management practice for manure and natural decomposition originally involved manure by large heterotrophs, I am happy for its incorporation. The digestive of heterotrophs is also a highly evolved biological reactor to degrade food, so incorporation into composting may aid time of maturity. The amount of manure added to soils is unnatural but nutrient rich, as an abundant waste it should be incorporated into agriculture but it will probably further the mistreatment of soils. As a readily available solution, it will prolong the acceptance and advocation of soil care, minimal disturbance, and the return to agriculture as a community responsibility. For fungi, *Saccharomycetales* was dominant in early composting. *Saccharomycetales* are in the phylum *Ascomycota* and multiply by budding. *Saccharomycetales* are believed to be dominant due to spore-like cellular structure that can withstand high temperatures and low initial moisture contents. *Acremonium alcalophilum* and S*ordariales* were dominant at $t = 3$ days, *Saccharomycetales* was dominant at $t = 5$ days, at $t = 7$ days *Scedosporium, minutuisporum (32.65%), Aspergillus cibarius (16.89%),* and *Thermomyces lanuginosus (9.42%)* were the most abundant.

Most species are unable to endure temperatures that exceed 40 °C, which are below the thermophilic range commonly associated with composting. Stabilization of waste through composting as a prior stage has significant positive effects to the field of vermicomposting.

Moqsud investigated compost in plant microbial fuel cells for bioelectricity generation and concluded that compost added plant growth and enhanced voltage generation [78]. The power density became three times more when compost was added.

Glycolytic intensity, in comparison to oxygen consumption intensity, is considered minimal under aerobic conditions for the majority of organisms. Energy metabolization requires a complicated series of events. First, hydrolytic enzymes are produced and transported to the surface of the substrate, then hydrolysis of substrate molecules into soluble fractions, diffusion transport to the cell, then through biological membranes. The same series of events is required for the transport of oxygen into the microbial cell, floc, or mycelia. Many biochemical reactions are nonelementary homogeneous reactions, “those whose rate expressions cannot be written from inspection of stoichiometric equation” [58]. Stoichiometric equations do not produce reaction rate expression in many nonelementary reactions due to the presence of enzymes, biological catalysts, which remain as free enzymes after the formation of a product. These are known as Catalytic reactions. Microbial nutrition is dependent on CHONPS and minerals. There may be other necessary nutrients, but carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulfur are essential for cellular functions and microbial growth. Minerals such as potassium, calcium, iron, molybdenum, cobalt, zinc, and copper are needed for various reactions; for instance, potassium activates many enzymes.

Compost maturity is required for the presence of phytotoxic substances that can cause plant injury. The plant seed germination index (GI) method is common for maturity assessment. Alternatives exist to estimate maturity, but none as low cost and easy to complete as the GI method. Pollution is a concern in the composting industry, gaseous emissions and leachate are released from aerobic biodegradation and must be considered in design. CO_2, N_2O, $CH_{4,}$ contribute to global warming, while $NH_{3,}$ Sulphur compounds, and most of the volatile organic compounds (VOCS) emission cause undesirable and other odor nuisances. Ideal physical and chemical characteristics can greatly reduce emissions, proper C/N ratio, tortuosity, and pH control are only a few important parameters that influence gaseous emissions. High concentrations of VOCs are released during initial stages, biofiltration is a BMP for treatment. Mature Compost is ideal as an additive to compost or as a filter for gaseous emissions. Leachate is an industrial wastewater. Treatment operations can include membrane filtration but serious fouling is a continuous problem. Constructed wetlands offering tertiary treatment for COD removal rates aren’t high enough to deal with high concentrations of organic material.

Decentralized composting offers the greatest solution to the waste management crisis. Microbial fuel cells increase productivity under the addition of compost to wetland plants. A lot of heat is generated from composting and a potential source of green energy [79].

11.1 Conclusion

In conclusion, producing food for plants makes composting an incredible field. Food waste has many uses when it is disposed of, most of it probably still fit for human consumption. Reducing waste production is ideal, but trends point to waste management being responsible to improve food wastage. I believe the best waste management practice for food waste is starting product reuse with high eukaryotic organisms and transcending down the food web. Farming and compost engineering could make a grand team to combat the disgraceful practices in both industries today. Food waste can be fed to livestock. Early domestication of pigs relied on food waste as feed but vesicular exanthema, a viral swine disease, led state laws mandating heating of food waste material before refeeding [82]. Manure produced and rotting food waste could be used for the production of maggots. Maggot farming is an established industry and research will need to be completed for the establishment of proper growth mediums and harvesting larvae. Then a biological reactor could serve to mix influent materials, collect leachate, and allow for escalation to thermophilic temperatures with electric field induction. Mature compost should be used for recirculation and as a static pile for biofiltration. Once temperature declines to mesophilic ranges, vermicomposting could be used to complete maturation. Leachate can be treated through common wastewater treatment operations; organic loading is high and may need dilution. Trickling filters are recommended for low-energy consumption. Tertiary treatment and energy production could stem from constructed wetlands and microbial fuel cells. Microbial fuel-cell proton-exchange membranes (PEM) are expensive and single-chamber reactors without PEMs are being improved upon. Gaseous emissions are treated via biofiltrations and if odor is a strong concern could be released at high elevations, and turbines may generate energy through temperature differences with the outside environment. No one method of composting is best, everyone should educate themselves and do as they please, for all composting is good practice and in need of adoption.

Glossary

Biological process Biological processes are those processes that are vital for an organism to live, and that shape its capacities for interacting with its environment.

Composting This process recycles various organic materials otherwise regarded as waste products and produces a soil conditioner (the compost).

Constructed wetlands A constructed wetland is an engineered sequence of water bodies designed to filter and treat waterborne pollutants found in sewage, industrial effluent, or storm water runoff.

Electric field induction The production of an electromotive force (i.e., voltage) across an electrical conductor in a changing magnetic field.

Food-processing waste Food-processing wastes contain a high amount of organic components that could be converted into energy and then recovered in the form of heat or electricity.

Maggot farming Maggot farming is the act of growing maggots for industry.

Microbial fuel cells A microbial fuel cell (MFC) is a bioelectrochemical system that drives an electric current by using bacteria and a high-energy oxidant such as O_2, mimicking bacterial interactions found in nature.

Vermicompost Vermicompost is the product of earthworm digestion and aerobic decomposition using the activities of micro- and macroorganisms at room temperature.

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Chapter 3
Treatment of Wastewaters from Chemical Industries

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Contents

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Abstract Chemical industry wastewaters are diverse in composition ranging from pharmaceutical products, polymers, petrochemicals, intermediates, and fertilizers. The wastewaters from these industries contain both organic and inorganic materials. They are further characterized by an abundant organics content and they can contain traces of toxic pollutants as well. As such, care must be taken when handling and treating these wastewaters. Additionally, pretreatment techniques are utilized to separate inorganic matter. Common methods used for treating chemical industry wastewater are trickling filters, rotating biological contactor (RBC), activated sludge, or lagoons. Several case studies will be investigated throughout this paper to discuss various methods for treating these types of wastewaters.

Keywords Oxidation · Anaerobic treatment · Aerobic treatment · Pretreatment · Chemical industry wastewater treatment · Biological treatment

1 Environmental Practices of the Early Chemical Processing Industry

Today, harsh chemicals continue to be released into the environment, poisoning both plants and animal species. These chemicals derive from many sources. However, one of the most prominent of them in the chemical industry. Even with EPA regulations in place, the amount of wastewater generated from these industries remains high. One of the main factors for this high amount of wastewater production is the result of a long-lasting industrial production model and of a slowly changing industrial mindset toward environmentalism.

The issue of corporate environmentalism didn't become a major concern until the late 1900s. It was until this time that changes toward more sustainable production models were adopted by the US chemical industry. To understand the mindset of chemical industries towards environmental issues prior to this time period, it is essential to understand the relationship between organizations and institutions evolved. Several federal lawsuits were analyzed to better understand the organizational structure of the U.S. industry. There were four historical stages that outline environmental management within the US chemical industry [1].

The first stage took place between1962 and 1970. During this time, environmental issues were a low priority for booming industries. Approximately five environmental articles appeared in *Chemical Week*. Although there were no federal environmental cases filed, the concern about environmental issues emerged in coming years. The first environmental event that received significant coverage was the publication of Silent Spring by Rachel Carson. Her book identified that there was a persistent presence of DDT in the food chain posing a hazard to all living organisms including humans While Rachel Carson's book was compelling, the journal dismissed her findings and deemed them as unrealistic. The journal ultimately concluded that her data and methods lacked credibility. In 1964, over a million mass deaths of fish washed up on the Mississippi River. During this period of time, it was predicted that a non-polluting auto would be available in 1975, which would use fuel that that extracted from shale. This innovation was ignored because the industry did not want to admit that there was a problem that had an impact on chemical wastewater and its processing methods.

The second stage of environmental management occurred between 1971 and 1982. On April 22, 1970, Earth Day was celebrated for the first time and several chemical companies were identified as being the "the handmaidens of Satan". Because of growing concerns that revolved around environmental issues, President Nixon initiated the second most important event of this decade, which was the establishment of the U.S. Environmental Protection Agency. This time period was marked where nongovernmental organizations (NGOs) and industries fought of legitimate environmental practices. The EPA's guidelines became more of a compliance with government standards and framework and less of an environmental protection agency. Pollution policies became the main focus soon after the initiation of the EPA. These policies were meant to establish monitoring regulations for industries to implement greater levels of environmental controls. However, these changes would come at a cost. The EPA's proactivity on pollutant regulation matters led Congress to implement the Toxic Substances Control Act, a legislation established to ensure the implementation of health and safety regulations from chemical industries.

The third stage occurred between 1983 and 1988. During this time, environmentalism became common belief at the institution level. Throughout this period, enforcement and regulation still gained a significant amount of environmental coverage.

The fourth and final stage occurred between 1998 and 1993. During this time several fatal accidents took place, one of which involved a methyl isocyanate release at Union Carbide's Bhopal India plant killing over 3000 people and injuring more than 300,000 individuals. During this time period, public concern about global warming and the thinning of the ozone layer began to arise. These concerns ultimately led to the establishment of mandates which required companies publicly report all forms of pollution created at their plants beginning in 1987. Other environmental issues that occurred during this time included: the U.N. halting the production of ozone-depleting chemicals and the Exxon Valdez oil spill. The environmental event that potentially made the largest impact on the structure of the chemical industry during this time was the initiation of the Responsible Care Program of the Chemical Manufacturers Association in 1990. This program outlined a set of proactive environmental principles that all members of the trade association would be required to adopt.

By the end of 1993, attention to environmental issues had reached unprecedented levels. What were known as good environmental practices such as recycling and water treatment were now being implemented in the chemical industrial sector. This era saw support and acceptance of corporate environmental responsibilities. These newfound ideals ultimately led companies to change their consumption patterns and minimize the amount of hazardous wastes discharged into the environment.

Political negotiation processes ultimately guide organizational, especially industrial behaviors. Public interest in environmental issues as well as the establishment of key environmental organizations such as the EPA was crucial to pave the path toward cleaner industry practices. These two factors will continue to shift and affect the way that industry develops in the future. Ultimately, a crucial step toward more environmental change is through governmental action. Environmental problems must be solved through changes in the institutional arrangements that govern industry and social actions. As environmental issues evolve, the need to develop new innovations must be considered [1].

One research paper studied the effects of the organizational size of chemical plants on the rate of toxic emissions. The main question is how does human behaviors pollute nature. The environmental consequences of human behavior are tremendous and have been documented in studies that involve global warming, acid rain, loss of animal habitats and species extinctions. Factors that cause pollution, which is related to lifestyle consumption habits, are called econstructuralism [2].

The effects of exploring the environmental factors of econstructuralism, which comprises : urbanization, modernization, class hierarchies, long economic cycles, and the world-system have been considered to be the "most intensive and effective environmental destroyer" of all-organizations and the effects of their structures. New approaches regarding pollution focus on the variations in organizational characteristics focus on the organizational size and toxic emissions of chemical plants. As a result, this study focuses on the emission rates regarding the percent of chemicals used on site by a plant that has released toxins into the environment. The goal is to understand how effectively plants of different sizes manage their chemical waste. This study's focus is also to debunk the notion that suggest that it is not the chemicals used that lead to pollution but how chemicals are distributed across small or large plants that lead to pollution.

Size has been used to predict numerous organizational outcomes. It is the most studied variable regarding organizational structure. Organizational size matters because there are a growing number of people such as lawyers and lobbyists who believe that extra regulatory burdens that have been placed on large organizations are both unjustified and destructive. For example: the SBREFA for small organizations requires that the EPA and other agencies give small businesses special treatment and exemptions.

In 1986, Congress passed the Emergency Right to Know Provision, which authorized the EPA to collect annual data on the amount and type of toxic chemicals emitted by individual manufacturing facilities. Without a doubt, toxic emissions occurred in the process of extracting raw materials and the transportation of finished products. Therefore, it is important to examine the plant size and the toxic emissions. By researching this information, the study design enables stakeholders to determine the relative importance of facility size and how to evaluate its effects based on the corporate structures, with the hope of finding the links among various structures that have caused pollution.

The problem is that organizations grow and their ability or motivation to adopt new environmental technologies diminishes to the point where the largest plants do a similarly poor job of containing toxic releases. Research revealing that large organizations abuse their economic power and are less innovative suggests that positive linear relationships exist between size and emission rates.

In the nation's economy chemical industries is one of the most pollution intensive industries. This study involved chemical plants and an analysis of over 2000 cases from their data files. The toxic emissions were the dependent variable and the data was taken from the EPA's Toxics Release Inventory or TRI.

There were limitations to the data from TRI as over 949 cases filed were incompatible and information was missing. Other problems with the data included: (a) plants were excluded if they had greater than 10 full time worker, (b) the data was self-reported, (c) chemical waste of toxicities were weighed in pounds instead of being weighed by pounds of chemical waste emitted. Finally, the EPA was not responsible to collect data on quality control on toxic emissions. However, TRI has become the core database for many industrial pollution research studies in the future.

Based on the data, the results show that large chemical plants emit toxins at a significantly higher rate than do small plants, especially if they are embedded in a wider corporate structure. However, the effect of plant size fails to achieve statistical significance. Unfortunately the type of pollution that was examined, which was toxic emissions by manufacturers, is largely unregulated by the EPA.

The environmental groups should continue to insist that the toxic emissions of large chemical plants be closely monitored and that selective incentives be put in place that encourage more regularity constrains. Also, organizational characteristics or conditions on how effective chemical plants manage their toxins in poor or minority neighborhoods should be included. Overall, organizational size has proven to be a strong predictor of industrial organizations that link pollution as contributors to organizational and environmental systems.

It was suggested that in the future researchers study the impact of organization structures on the adaptation of green production designs and technology [2].

2 Overview of the Chemical Processing Industry

The chemical industry describes industries that produce industrial chemicals [3]. The chemical industry is one of the largest industries in the world, producing over 50,000 compounds [4]. The industry constitutes 7% of global income and 9% of international trade. It also produces 11% of the total manufacturing value added to the United States.

Within the chemical industry there are three major subsectors: petroleum, coal, and basic chemicals; resin, rubber, artificial fibers, agricultural and pharmaceutical manufacturing; and paint, adhesive cleaning, and other chemicals. Resource consumption within these sub industries can provide useful insight for identifying limiting resources. From the petroleum refining sector, crude oil and natural gas are consumed in the highest quantities. Furthermore, the majority of the power generated from chemical processing industries is from renewable energy sources such as hydro potential, geothermal, and wind. However, large amounts of fossil fuels such as coal, crude oil and natural gas were used to generate energy, while SO_2, NO_2, and CO_2 were identified as the most widely produced emissions [5].

2.1 Energy Consumption

The US chemical industry utilizes a very energy-intensive process to generate chemical products.

Furthermore, the chemical industry consumes some of the largest amounts of energy in the industrial sector in the United States. The industry produces 11% of products and consumes 20% of energy from the industrial sector. Three of the most energy-intensive products from the chemical sector are ethylene, nitrogenous fertilizer, and chloride and caustic soda. Ethylene is mainly produced from the petrochemical industry and uses a total of 520 PJ (LVH) of fuel excluding feedstock and 26 GJ/tonne ethylene (LVH). Nitrogenous fertilizer production uses a total of 268 PJ of fuel without feedstock and 368 PJ (LVH) of fuel with feedstock. This fertilizer production uses 14 PJ of electricity and uses 16 GJ/tonne (LVH). Chlorine is produced from electrolysis reactions in a salt solution. Chlorine production requires 173 PJ of electricity and 38 PJ of fuel. The primary energy consumption of chlorine was reported to be 47.8 GJ/tonnes [4].

CO_2 emission consists of 20% of the total energy use from the chemical industry in 1994. Overall, emissions grew at an annual rate of 2.9% and value added grew at an annual rate of 4.6%.

Several subsections within the chemical industry can be very intensive processes. Sections of the chemical industry that produced that largest amount of energy in the chemical industry were: unspecified industrial organic chemicals, unspecified industrial inorganic chemicals, plastic materials and resins, nitrogenous fertilizers, industrial gases, and alkalis and chlorine. Overall, unspecified organic chemical production required the largest amount of energy in 1994.

Ethylene and steam cracking derivatives consist of products within this category. These chemicals are used to create plastic, resins, and fibers and detergents. Ethylene is of particular concern. In 1994, ethylene was known as the fourth most produced chemical. Ethylene production has continued to grow annually. Today, the United States produces 28% of ethylene around the world. Additionally, unspecified inorganic chemical production was listed as the second largest energy-intensive process in 1994. Chemicals which fall within this range include: sulfuric and hydrochloric acid, potassium fertilizers, alumina, and aluminum oxide. Among these chemicals, hydrochloric acid and potassium fertilizers were produced in highest quantities, being identified on the top 40 chemicals produced in the United States in 1994.

Plastic and resin subsection produced lower energy requirements. However, this section was responsible for the highest carbon dioxide emissions. Chemicals falling within this category include polyethylene, polypropylene, polystyrene, and polyvinyl chloride (PVC). Industrial gases accounted for 6% of CO_2 emission from the chemical industry. Within the industrial gas section, nitrogen and oxygen are chemicals which are produced in the greatest quantity. Both chemicals accounted for 85% of energy consumption within the industrial gas sector. Oxygen requires 2 GJ/tonne of energy. Ammonia from the nitrogenous fertilizer subsection produces the most energy from this subsection. Ammonia production alone accounts for 85% of energy consumption from this sector. Ammonia production continues to grow annually [4].

3 Characteristics of Chemical Industry Wastewaters

Chemicals comprise pharmaceuticals, polymers, bulk petrochemicals and intermediates, derivatives of basic industrials, inorganic and organics, and fertilizers. The concentration of organics and inorganics present in chemical wastewaters varies and depends on type of industry. Chemical wastewaters can also contain toxics, mutagens, carcinogens, and other nonbiodegradable substances. These characteristics result in a high-strength wastewater. Certain chemicals such as surfactant, emulsifiers, and petroleum hydrocarbons present a challenge, as they reduce the performance efficiency of many treatment systems [3, 6].

Many of the chemicals from the chemical industry are toxic and consist of heavy metals. Certain chemicals such as chromium, mercury, lead, and arsenic appear in chemical wastewaters in high concentrations. Operations such as electroplating, metal or surface finishing, and solid state water processing are used to treat wastewater from the chemical industry with high concentrations of toxics [3].

Oil and grease are frequently found as pollutants in wastewaters. Oil and grease rich wastewaters are typically classified as containing animal and vegetable oils, fatty acids, petroleum hydrocarbons, surfactants, phenolic compounds, and naphthenic acids. Wastewaters can contain free, dispersed, and emulsified oils and greases. Free oils have droplet sizes greater than 150 mm, whereas dispersed oils have a size of 20–150 mm and emulsified oils have a size of less than 20 mm. The amount of oils and grease in wastewater can be determined by extracting them using a solvent, typically freon or hexane. Large quantities (up to 200,000 mg/L) of oil and grease are commonly found in chemical industry wastewaters. However, discharge limits for oil and grease effluent are listed as 48 mg/L for old facilities and 29 mg/L for new facilities.

Because of these characteristics, strict standards have been placed on wastewater. Treatment of chemical processing industry wastewaters must be extremely efficient in order to meet the required EPA effluent standards [3].

4 Pretreatment (Physicochemical Methods)

Physicochemical treatment methods have been proven to be effective for reducing oil concentrations in wastewater. These methods include: gravity separation and skimming, dissolved air flotation, de-emulsification, coagulation, and flocculation.

Gravity separation is an effective, low-cost oil-water separation technique. This method is primarily used to remove free oils from wastewaters, and is ineffective at removing smaller oil particles. American Petroleum Institute oil-water separators are common separators.

Dissolved air flotation (DAF) is another oil-separation method that can be used to improve separation for smaller particles such as emulsified oils. DAF units utilize chemicals and or thermal energy to reduce smaller particles into larger particles. Before the DAF process can be implemented, oils must be chemically pretreated and settled. In addition, the wastewater must be heated to reduce viscosity, improve density differences and weaken oil films. Acidification, cationic polymer/ alum addition, and pH raising are primary chemical processes which are used to produce floc during the DAF process. Lastly, the floc is separated from water, thickened, and dewatered.

Coagulation and flocculation can also be used to remove oils from wastewaters. Coagulation describes the process of adding inorganic and organic compounds such as aluminum sulfate, aluminum hydroxide chloride, or high molecular weight cationic polymers to wastewater in order to accelerate the sedimentation process. The implementation of coagulation allows for settled solids to be removed as sludge and floating solids to be removed as scam. The goal objective is to remove 90% of organic compounds. These processes are typically used in a reservoir, sedimentation tank, or clarifier, and are implemented as the first stage of treatment. The main design parameters for this process are retention time, temperature, tank size, and equipment used [3].

4.1 Adsorption

Adsorption describes the process when molecules of dissolved compounds collect on and adhere to the surface of an adsorbent solid. Furthermore, it occurs when attractive forces at a carbon surface overcome the attractive forces of the liquid. While processes such as precipitation, coagulations, and sequestration can be used to remove toxics in high concentrations, adsorption is a useful process for removing low concentrations of toxic heavy metals. Three adsorption techniques which are readily used for wastewater treatment are granular activated carbon (GAC), fixed biofilm reactors, and electrosorption [3].

4.2 GAC

GAC methods are efficient adsorbents due to their high surface area to volume ratio. One gram of activated carbon typically requires a surface area equivalent of 1000 m^2. Materials that can be used for adsorption include peat, wool, silk, water hyacinth, and agricultural and industrial solid wastes [3].

4.3 Fixed Biofilm Reactor

Fixed biofilm reactors are trickling filters or attached growth reactors. It is the most effective during the secondary treatment process. To prevent clogging biofilms primarily implement media and microbes to treat wastewater. In this type of reactor, microorganisms such as bacteria and protozoa grow on the media as a slime layer when wastewater is passed through the filter. This layer becomes thicker with time, as more wastewater is filtered through the filter. As this layer thickens, oxygen is prevented from reaching the total depth of the slime layer, creating anaerobic conditions deeper in the layer. Slough is generated from anaerobic products and is carried off in effluent. In order to ensure the best effluent quality and remove slough, fixed biofilm reactors should be followed by secondary sedimentation tanks. This method may be beneficial compared to a conventional activated sludge system due to its low process control requirements. Challenges that arise from using this system include excess organic loading, implementation of incorrectly sized media, clogging, non-uniform media, and breaking media [3].

4.4 Electrosorption

Electrosorption is defined as potential polarization-induced adsorption on the surface of electrodes. After polarization, polar molecules can be removed from the solution and adsorbed onto an electrode surface. Common electrodes used during this process include activated carbon fiber cloth with high specific surface area and high conductivity. When these types of electrodes are used, consideration to the surface chemistry must be made. Additionally, electrosorption can be enhanced by increasing their adsorption capacity. This can be done by implementing modification processes which boost the feasible removal rates and adsorption capacities. One such example entails the immobilization of a chelating agent on the adsorbent surface. Electrosorption's low energy requirements make it a variable and efficient alternative to other treatment methods. However, this system can be largely limited by the type and performance of the electrode material [3].

4.5 Membranes

Membrane technology is commonly implemented for wastewater treatment methods. Several types of membranes exist today, including MF (microfiltration), UF (ultrafiltration), NF (nanofiltration), and RO (reverse osmosis). Polymeric UF and MF technologies have an average shelf life of 3–5 years. However, their use is widely dependent on the application and frequency of use. Membranes are most effective for treating stable emulsions, specifically for water-soluble oily wastewater. The operation for membrane technology utilizes a semi-batch recycle where wastewater feed is added to the tank at the same rate at which the permeate is withdrawn, thus keeping a constant water level throughout the system. Any oil and grease collected are recycled to the process tank. The system operates in cycles. In the first stage, the wastewater is treated in the membrane until the concentration of oils, greases, and suspended solids reaches a set value, usually this occurs when the concentration volume reaches 3–5% of its initial feed volume. Once this concentration is reached, the feed is stopped and the system is cleaned.

The main advantages of using a membrane system include its wide range of applications, its ability to treat wastewater uniformly, small number of chemicals needed for treatment, reuse of waste streams in the plant, lower energy costs than thermal treatment methods, and the system's low operation requirements. Overall, these systems are appealing to operators due to their efficiency in treating wastewater to appropriate discharge standards. However, several limitations with using membranes include: scale-up, high capital costs for large effluent volumes, some membranes, polymeric membranes, can become easily degraded or fouled during use. In these cases, membranes need to be replaced more frequently, which will increase operating costs of treatment of wastewater [3].

5 Biological Treatment Methods

Biological treatment is a necessary step in wastewater treatment that mainly deals with organic removal. Typically, biological treatment utilizes microbes to feed on organics in the wastewater, and thus reduce the organic concentration significantly. Biological treatment processes can be aerobic, anaerobic, or anoxic. Furthermore, biological treatment can occur using suspended growth reactors or attached growth reactors. Chemical industrial wastewater can be treated by biological oxidation methods such as trickling filters, rotating biological contactors (RBCs), activated sludge, or lagoons [6].

5.1 Aerobic Treatment

Aerobic treatment utilizes microbes under oxygenated conditions to destroy biodegradable organics. Biodegradable organics are sources of biodegradable oxygen demand (BOD). Aerobic treatment is the primary treatment method for removing BOD from domestic wastewater. Additionally, aerobic treatment can be used on industrial wastewaters. This treatment method is simple, inexpensive, and efficient. Several factors can affect the efficiency of treatment. The factors include temperature, moisture, pH, nutrient rate, and aeration rate. Aeration takes place ten times faster than anaerobic reactions, and as a result, they are designed with small volume and open. One of the major disadvantages of using aerobic treatment processes is the large quantity of sludge produced as the result of a high biomass yield (amount of cells produced per unit mass of biodegradable organic matter).

There are a number of reactions which microorganisms use to degrade organic pollutants. One such pathway involves the attack of xenobiotics by organic acids produced by microorganisms. Another reaction involves the production of noxious compounds (H_2S) and chelating agents which increase solubility of xenobiotics, and further allow them to be degraded.

Chemical industry wastewater can induce toxic effects on microorganisms. The chemicals from these wastewaters can inhibit growth of the microorganisms and affect the degradation process. Two aeration methods – a membrane bioreactor and a phase partitioning system – are viable biotreatment methods that can be used to treat highly toxic, high-strength chemical industry wastewaters [3].

5.1.1 Membrane Bioreactors

Membranes are more commonly used for small-scale activated sludge operations. Membrane systems can be beneficial systems than activated sludge systems due to their reduced footprint and efficient treatment. There are two main configurations for these types of reactors: a submerged membrane and an external membrane.

A study was conducted in which a membrane bioreactor was used to treat 3-chloronitrobenzene [1]. The wastewater was pumped into the system at a flow rate of 64 mL/h. The results found that the membrane was able to remove 99% of pollutants found in the wastewater. Further, the carbon from the wastewater was completely degraded to CO_2. An important consideration to ensure proper functioning of these systems, is their operating conditions. Membrane reactors, if not operated correctly, can become subject to fouling. Fouling is a common problem with membrane technology. Coating can occur in hydrophobic membranes, when free oils accumulate. This coating results in a poor flux. In order to overcome these effects, these types of membranes must be constructed in a tubular manner, which allows for better mixing conditions. Membranes are also sensitive to pressure, temperature and pH changes. As a result, these systems need to be monitored and maintained frequently.

5.1.2 Two Phase Partitioning System

Two phase partitioning systems are aerated systems which use nonbiodegradable, non-volatile solvents to treat. These systems are self-regulating. Xenobiotics are produced from this system at the same rate as the consumption rate of microorganisms. These systems operate under conditions which limit the exposure of microorganisms to organic pollutants, which ultimately reduces the toxic effects on the microbes and increases the rates of xenobiotics. However, care must be taken when using this system, as the interaction of microflora from the system and metal ions from the wastewater can increase the number of reactions needed before effluent discharge.

The degradation of xenobiotics was observed in the following case study. In the study, benzene was to be treated in a two phase partitioning system using Alcaligenes xylosoxidans Y234. It was found that 63.8% of benzene was degraded within a day while 36.2% was stripped using aeration processes. However, benzene is known to be toxic and hard to degrade at high concentrations. To combat these conditions, the stripping effect was adjusted to allow for 99.7% degradation of benzene. The results from this case study emphasize the effectiveness of two-phase systems for treating toxics and, therefore, emphasize the usefulness of these systems for treating chemical industry wastewaters [3].

5.1.3 Sequencing Batch Reactors

A sequencing batch reactor describes a process in which a reactor conducts each stage (aeration, oxidation, sludge settling, and recycling) of an activated sludge process. Batch reactors are operated in a periodic, discontinuous process and can be used to treat low-to–medium-strength wastewaters or specific organic pollutants. They have many applications ranging from landfill leachate treatment to domestic and industrial treatment and contaminated soil treatment. Before a new stage can begin, the reactor is emptied of all continents except a layer of activated sludge on the bottom. Then the reactor is filled with wastewater where it is mixed and aerated. The mixing is stopped only once the satisfied level of degradation of the pollutant is achieved. Sludge is allowed to settle. The top layer is discharged as effluent. One major advantage of SBRs is that they can adapt to changing wastewater flow rates. Additionally, the settling times for sequencing batch reactors can also easily be adjusted to better allow for complete settling before discharging. However, each step in the process requires a separate reactor [3].

5.2 Anaerobic Treatment

Anaerobic digestion is a sequential process which involves the complete breakdown of organics to carbon and methane. Methanogenic microbes are used to degrade BOD in anaerobic systems. Anaerobic digester or stabilizers are capable of degrading many toxic organics under methanogenic conditions. They can be applied to a variety of applications including automobile industry wastewater as well as sulfate bearing and hypersaline chemical wastewater. Unlike aerobic systems, anaerobic systems are closed off to the environment to induce an oxygen-free environment. Anaerobic systems are more advantageous to use compared to aerobic treatment for treating hazardous, high-strength wastes. They produce better removal of color, halogens, and heavy metals than aerobic systems. These systems pose numerous benefits, including the ability to lower sludge production rate, operate at higher influent BOD and toxic levels, and produce useful by-products such as methane gas.

These systems are designed to have a vent in order to filter gaseous methane and carbon dioxide produced from the system. Conversely, the capital and operating costs of these systems are higher than those of conventional aerobic systems. Anaerobic systems are limited by low flow rates.

Anaerobic reactors typically operate under a 10 to 20-day hydraulic and solids retention time and at a temperature of 35 °C. There are four main steps which occur during an anaerobic process: hydrolysis/liquefaction, acidogenesis, acetogenesis, and methanogenesis. Coupling is a necessary design consideration to prevent accumulation of intermediates and ensure a balanced digestion process. Anaerobic reactors can be numerous configurations ranging from Upflow Anaerobic sludge blankets (USAB), and Anaerobic Sequencing Batch Reactor (ASBR) which both have applications in industrial treatment. These two processes will be discussed further [3].

5.2.1 Upflow Anaerobic Sludge Blankets (USAB)

This type of reactor has been used to treat many types of industrial waste including chemical industry wastewaters. There are four main criteria for designing a USAB: sludge bed, sludge blanket, gas-sludge-liquid separator, and a settlement compartment. Mixing occurs in the reactor from upflow forces caused from influent wastewater flow [3].

5.2.2 Anaerobic Sequencing Batch Reactor (ASBR)

ASBRs are high-rate reactors which generate granular biomass as a result of treatment. One major advantage of using this system is that it can maintain a higher biomass within the reactor. These reactors have also proven to be simple, efficient, and applicable for a wide range of effluents. Treatment in these reactors occurs in five separate stages: filling, reaction, settling, decanting, and idling [3].

5.3 Combined Treatment

Combined or integrated treatment systems use both aerobic and anaerobic procedures microorganisms to treat wastewater. Combined systems are commonly implemented for high-strength wastewaters and in cases where the incoming wastewater has a BOD of above 1000 mg/L. Combined systems can take place in a single or multiple steps. Single-stage processes occur when bacteria are stationed in fixed film bioreactors. These combined systems are especially good for treating saline wastewater for nutrient COD, N and P removal [3].

6 Chemical Treatment Methods

Chemical oxidation is defined as the process by which electrons are transferred from one substance to another [1]. COD is used as a key parameter to indicate oxidation efficiency. Usually oxidation processes are implemented on wastewaters with a COD less than 5000 mg/L. Wet oxidation or incineration can be applied in cases where COD contents are higher than 20,000 mg/L. There are two main types of chemical oxidation processes: classical oxidations and advanced oxidation [3].

6.1 Classical Oxidation

Classical oxidation describes the process by which an oxidant is added to an oxidant, wastewater and oxidation occurs. Five commonly used oxidants are chlorine, potassium permanganate, oxygen, hydrogen peroxide and ozone. Chlorine can be used in cases where water evaporation is needed. While inexpensive and easy to use, large amounts of chlorine are needed for effective treatment. Carcinogenic byproducts are also produced from chlorine; therefore, care must be taken during the application process. Potassium permanganate is an expensive oxidant that can be used for a wide range of pHs. However, by-products produced from this oxidant require additional clarification or filtration. Like potassium permanganate, the use of oxygen as an oxidant requires large installation costs.

Oxygen is typically the most effective under high temperature and pressure conditions. Hydrogen peroxide has a wide range of applications. It is usually applied either directly or with a ferrous sulfate, iron salt, or a metal catalyst for reactions. In addition to hydrogen peroxide being easy to apply and having a high oxidizing power, it is also the least expensive oxidant option. Unlike many of the other oxidants, hydrogen peroxide does not produce toxic by-products that require additional treatment. Hydrogen peroxide oxidation efficiency is largely dependent on the production of hydroxyl radicals. Ozone is the last major oxidant. Ozone is primarily used during tertiary treatment to treat organic pollutants from industrial and agricultural wastewaters. Insoluble under standard conditions. Large quantities of it are needed for treatment. A disadvantage of using ozone as an oxidant is that it must be produced at the site of treatment. Further, systems must be put in place to capture and trap the ozone after it is used for treatment. As a result of these conditions, the use of ozone is very expensive [3].

6.2 Advanced Oxidation

Advanced oxidation describes oxidation processes which take place near ambient temperatures and produce highly reactive radicals, which are utilized during the treatment process. This process is applicable to groundwater, surface water and wastewater which contain nonbiodegradable organic pollutants. AOP (advanced oxidation process) processes are mainly applied as a pretreatment technique for industrial wastewaters. The most common types of reagents for advanced oxidation include: UV/O_3, UV/H_2O_2, O_3/H_2O_2, Fe^{3+}/UV, UV/TiO_2, and H_2O_2/Fe^{2+} with the Fenton reagent (H_2O_2/Fe^{2+}) being the most effective.

The Fenton reaction can be described by the following equation.

$$\mathrm{M}^{n+} + \mathrm{H_2O_2} \rightarrow \mathrm{M}^{(n+1)+} + \mathrm{HO}^{-} + \mathrm{HO}\cdot$$

where M is described by a transition metal such as Fe or Cu.

The Fenton reaction has seen numerous applications in textile and chemical industrial treatment. Because it does not require energy input to activate the reagent, this method is simpler to use and more cost-effective than other reagents. However, many problematic by-products such as iron III oxide hydroxide and iron salts are produced from the reaction. To combat this, iron sources are added as catalysts.

Overall, API-oil separators are useful treatment methods for wastewater with high oil contents. Combined, aerobic and anaerobic systems are the most efficient at removing both toxic and nontoxic organics from wastewater [3].

7 Natural Treatment Methods

Constructed wetlands are types of natural treatment system that have been used to treat chemical industry wastewater in the past. Constructed wetlands utilize natural processes such as wetland vegetation, soils, and microbes to treat wastewaters. These systems are modeled after natural wetlands. However, unlike their natural counterparts, constructed wetlands take place in a controlled environment. The systems have been used to treat landfill leachate, runoff, food processing wastewaters, industrial wastewaters, agricultural farm wastewater, and mine drainage wastewater. Constructed wetlands can be classified according to their macrophytic growth, which may be emergent, submerged, free floating, or rooted with floating leaves. They could also be classified by the water flow type such as surface flow, subsurface vertical or horizontal flow. Combined wetlands have been used to improve nitrogen removal performance during treatment.

Plants have an essential role in a constructed wetland environment. Plants roots provide a stable and safe habitat for microorganism growth within the wetland. Plant uptake further enhances the treatment process. Uptake describes a chemical process that occurs in constructed wetlands in which nutrients such as nitrogen and phosphorus are absorbed by plant roots. Plant uptake increases the nutrient removal efficiency of the system, as a whole. Water hyacinth is a plant species that is commonly implemented in constructed wetlands due to its highly efficient uptake ability. However, constructed wetlands that use this plant must be built in tropic, subtropic, or environments that promote yearlong growth, as these climates are the most suitable environments for water hyacinth to thrive in. In order to maintain efficiency, plants must be maintained regularly within the system [3].

8 Case Studies

The effects of treatment of chemical industry wastewaters were investigated in the following case study. Wastewater originating from building and construction chemical factories and plastic shoes manufacturing factories was analyzed. This wastewater was directly discharged into the public sewage system for both observed factories. Hu developed a process for how to select the appropriate treatment process for chemical industrial wastewater based on molecular size and biodegradability of the pollutants. Bury developed a dynamic simulation to chemical-industry wastewater treatment to manage and control the treatment plant. Two methods were utilized for treatment: chemical treatment using coagulation precipitation for the chemical factory and biological treatment using an activated sludge reactor and a rotating biological reactor (RBC) for the manufacturing factories [6].

8.1 Case Study 1: Treatment from Plastic Shoes Manufacturing Factory

The chemical factory produced concrete mixtures, painting and coating materials and bitumen products. The flow effluent coming from this factory ranged between 11 and 15 m^3/day.

Chemical coagulation was performed using lime aided with ferric chloride or aided with aluminum sulfate. A continuous treatment system was operated at optimum pH and coagulant dose, both of which we determined using a jar test. For lime aided with ferric chloride, a dosage of 700 mg of lime and 600 mg of ferric chloride. For lime aided with aluminum sulfate, a dosage of 300 mg of lime and 1000 mg of aluminum sulfate was used. The construction cost of the treatment system was $3,71,017 and operating costs were $12,315 [6].

Samples from effluent water were collected and physicochemical analyses were conducted. It was found that the building and construction chemical factory wastewater contained high levels of organics. Average values of COD and BOD were given as 2912 and 150 mg/L. The BOD/COD ratio was 6%. Phenol up to 0.3 mg/L was also detected. The oil and grease concentration ranged between 149 and 600 mg/L. The average oil and grease concentration was 371 mg/L. The average total suspended solids (TSS) concentration was 200 mg/L. Using the batch chemical process, an 94% removal efficiency of COD, an 81% removal efficiency of TSS, and an 91% removal efficiency of oil and grease were achieved.

The plastic shoes manufacturing factory melted raw materials and used forming, molding, and painting processes to produce a finished product. Biological treatment was utilized to treat this type of wastewater. A majority of pollution from this industry originated from the painting department. Furthermore, the wastewater from the paint department contained high levels of organics. The construction chemical factory contained an average COD concentration of 15,441 mg/L and a BOD of

7776 mg/L. The average phenol concentration was 0.93 mg/L. Domestic wastewater was mixed with this chemical industry wastewater at a ratio of 1:3. The domestic wastewater allowed for the addition of nutrients such as nitrogen and phosphorus. After mixing, the effluent from the factory had an average COD and BOD of 5239 and 2615 mg/L respectively. Due to the high BOD/COD ratio, biological treatment was chosen as the appropriate treatment method for this kind of waste.

Activated sludge processes were conducted in a batch reactor in a laboratory. Two-liter plexiglass columns were used to conduct the reaction. The aeration was conducted by filling the columns with inoculated (with activated domestic sludge) wastewater from the chemical processing industry. The columns were aerated daily. At the end of each cycle, the sludge was allowed to settle in the columns. The column was then drained and refilled. This process was repeated until a large amount of sludge was produced from the system. The aeration time was determined by conducting an experiment in another column. For this experiment, sludge and pretreated wastewater were allowed to settle for a detention time ranging between 1 and 24 h and an MLSS of 3 g/L. The minimum dissolved oxygen (DO) concentration was given as 2 mg/L. Samples were taken an hour after settlement. The rotating biological reactor operated under continuous flow conditions where the effluent was filtered into the reactor with an organic load of 7.8 kg BOD/m^3 for 4 months. The construction cost of the activated sludge system was $54,912 and the operation cost was $19,912. The construction cost of the rotating biological reactor was $54,035 and the operation cost was $10,614.

From this study, it was found that the highest BOD removal occurred at a retention time of 24 hrs. After activated sludge treatment, the average COD, BOD, TSS, and oil and grease concentration values were 376, 131, 12, and 26 mg/L, all of which were compatible with effluent limits. An RBC treatment process was also used. After RBC treatment, the average wastewater COD and BOD concentration values were 474 and 277 mg/L. The average suspended solids residual value was 76 mg/L. The oil and grease residual value was 16 mg/L. The average removal rate of suspended solids and oil and grease was 88% and 93% respectively. The wastewater treated from this reactor was also within discharge limits.

While both biological treatment systems were effective for treating wastewater and reducing pollutant concentration to acceptable limits, the RBC system was recommended due to its easy operating requirements and lower cost [6].

8.2 Case Study 2: Treatment of PVCs

Another case study from Zhejiang province, China examined the treatment of wastewater rich in polychlorinated biphenyls (PCBs). PCBs are toxic organic pollutants which are highly resistant to biodegradation, biological accumulation, and long-range transport. As a result of these characteristics, PCBs present numerous environmental challenges and health risks ranging from neurological disorders, reproductive toxicity, endocrine disruption, cancer, deformity. Additionally, PCBs can be harmful in both high and low concentrations. While PCB production has been banned since the late 1900s, these pollutants still remain in the environment. Many PCBs originated from the waste incineration process, from the chemical processes, or from dyeing processes. Wastewater treatment plants can also act as another source of PCB. While the PCB concentration is expected to decrease during treatment, as it was reduced from 1000 to 250 ng/L in Greece, PCB concentration can sometimes increase during the treatment processes as it did in Sweden (0.3–1 ng/L) and Lithuania (9–34 ng/L). Furthermore, the number and variety of pollutants can impact the characteristics of PCBS in wastewater [7].

For this particular case study, the treatment of PCBs from wastewaters consisting of 70% industrial wastewater from the chemical industry and 30% of domestic wastewater was investigated. The chemical industry wastewater consisted of 13.6% of wastewater from the dyeing sector. This industry was responsible for producing pharmaceuticals and intermediates, pigments and dyes, textile dyeing and finishing, biochemical, inorganic chemicals, and other specialty chemicals. Specifically, indicator PCBs, dioxin-like PCB congeners and three lightly chlorinated biphenyls and total PCBs were analyzed. The treatment plant used was fed an average daily load of 90,000–120,000 m^3. The wastewater was first pretreated using grit and grease chambers and mixing regulation tank. The treatment system consists of primary sedimentation, anaerobic/aerobic biochemical treatment secondary sedimentation, and a high-density clarifier.

Samples were taken after each stage of the treatment process in October and November of 2010. After collection, wastewater samples were filtered through 1 L glass fiber filters and spiked with 200 ng of 13 carbon surrogate standards and extracted three times under ultrasonic conditions using a liquid-liquid extraction method. PCBs were analyzed by isotope dilution methods. Quantification of the PCBS was determined by using an Agilent 6890A gas chromatograph with a 5795X inert mass spectrometer with an electron impact ion source [6]. One microliter of extract solution was injected into a DB-5MS capillary column with a 0.25 μm film thickness. The injector temperature was 280 °C and the source temperature was 250 °C.

PCB concentrations from each stage of the treatment process were analyzed. PCB-11 was the most abundant, accounting for more than 66.1% of polychlorinated biphenols, found in the wastewater. The concentration of PCB-11 found in the raw wastewater was 10321.6 pg/L. Other PCBs present in this wastewater included PCB-15 (241.6 pg/L), PCB-52 (249.6 pg/L), PCB-28 (173.5 pg/L), and PCB-77 (114.4 pg/L), PCB-126, PCB-169, PCB-189. The PCB concentrations of PCB-28, PCB-52, and PCB-77 increased after the anaerobic hydrolysis unit by 270%, 35.7%, and 52.3%, respectively. This effect may be caused by the release of PCBs from solid to liquid phase. These dissolved PCBs pose less of a risk than nondissolved PCBS. The distribution of PCBs within the system varied from stage to stage. Distribution was affected by factors such as solute concentration, the amount of solids available for sorption, and the competition between pollutants for sorption sites of particles.

Two methods utilized for reducing the PCB concentration from this wastewater were adsorbing PCBs onto a solid surface and dissolving the PCBs into the wastewater. The adsorption of other hydrophobic chemicals was strongly dependent on the sorptive behavior. Adsorption is typically affected by the octanol water coefficients (Kow). There was a low correlation between the log Kow value and the removal efficiency percentage for primary sedimentation, anaerobic hydrolysis, aerobic bioprocess, and the high-density clarifier. It was also found that other processes such as advection, volatilization, biotransformation, oxidation and coagulation are useful for removing less hydrophobic compounds.

Mean removals of PCBs were calculated by using the equation.

$$R(\%) = \frac{\left(C_{\text{in}} - C_{\text{out}}\right)}{C_{\text{in}}} * 100$$

where C_{in}describes the amount of influent PCBs from a treatment stage and C_{out} describes the amount of effluent PCBS from a treatment stage. The removal efficiencies were the highest in the aerobic bio-process and the high-density clarifier. Mono-Cbs, and Hexa-CB removal efficiency was greater than 90%. The removal of Penta-CB and Hepta-CB was greater than 80%. The lowest removal occurred during anaerobic hydrolysis. This low efficiency may have been the result of selective adsorption of PAC flocculants and anaerobic sludge. Specifically, Di-Cb and Nona-CB were isomers that had the lowest removal. The treatment system removed a total of 23.2% of PCBs. Additionally, the removal of Octa-Cb, Nona-Cb during primary sedimentation and of TRi0Cb and Tetra-CB during anaerobic hydrolysis was less than zero (indicating the increase of PCBs). Overall, the removal of most PCBs isomers during treatment was above 40% and the removal efficiency was 23.2%. However, the removal of Di-CB, Nona-CB, and Deca-CB in the aerobic stage and the removal of Di-CB, and Tetra-CB in the high-density clarifier was below 40%.

PCB levels from the sludge were much higher than effluent limits. Partitioning between the dissolved and adsorbed phases indicated that Di-PB were the most dominant isomers in the wastewater, accounting for 70% of the PCBS present. 89.8–97.4% of Di-CBs were absorbed on the particles and sludge in the influent and effluent of each treatment stage [7].

8.3 Case Study 2: Treatment Organics Using Activated Sludge

Currently, there are at least 114 organic pollutants that pose a threat to the environment. It is important to better understand the physical, biological, and chemical characteristics of these compounds in order to better treat them. To best determine the removability of a specific compound, it is essential to obtain more data during the treatment process. Existing design treatment models are derived from substrate mass balance of substrate removal from biological consumption. However, these models do not account for natural chemical reactions such as stripping and adsorption. More accurate models that consider these chemical reactions need to be developed [8].

In this case study, the performance of the activated sludge process was investigated. The main objective of this study was to gain insight into the behavior of specific organic compounds found in industrial wastewaters. Biochemical oxygen demand (BOD5), chemical oxygen demand (COD), and total organic carbon TOC concentrations were used as primary parameters to characterize the wastewaters from this case study. These parameters are used to compare treatment to effluent limits. A continuous flow activated sludge system was used to treat a mixture of synthetic wastewater from chemical, plastic, petrochemical, and petroleum industries. The wastewater contained ethylene glycol, ethyl alcohol, glucose, glutamic acid, acetic acid, phenol, ammonium, sulfate, phosphoric acid, and salts. The CSTR reactors were constructed as stainless steel with a 3.0-1 activated sludge volume and a 3.23-1 settling volume. Each compartment of the reactors was fitted with air-tight stainless steel covers. Air flow meters were also used to control influent air and off gas.

System operation consisted of a pumped influent wastewater feed stream and an exit stream that transferred the effluent stream to collection tanks. The feed was filtered into the activated sludge tanks from a feed tank. The hydraulic retention time within the activated sludge system was 8 h. Effluent then flowed by gravity from the settling compartment to the collection tanks.

Two types of studies were conducted. The first was a nonbiological study designed to determine stripping characteristics of a specific chemical in the absence of biological activity. The second study used biological treatment to determine the treatability and fate determination of the same organic compounds during biological activated sludge treatment [8].

In the first study, the reactors were filled with distilled water before feed wastewater was pumped into the tanks. Total organic carbon levels and pollutant concentration levels of each organic compound were observed as a function of time. Samples were then collected and analyzed for each specific organic compound under investigation. The percentage of each compound stripped from wastewater was determined. Overall, stripping had a high effect on three compounds, a moderate effect on four compounds, and no effect on five compounds. BOD_5, TOC, COD, and concentrations. A total of 15% of benzene was stripped, 17% of ethyl acetate, and 24% of 1,2-dichlorobenzene.

In the second study, activated sludge was collected from local municipal sludge treatment plants to be used for seeding. The sludge was then acclimated to wastewater containing pollutants. Three activated sludge systems were used. Each system was operated at a different mean cell residence time: 2, 4, and 6 days. The hydraulic retention time of all reactors was 8 h. Samples were taken over a 60-day period and analyzed. The BOD_5, TOC, COD, and concentrations of specific compounds were studied. TOC analysis was performed using a TOC analyzer and procedures were in compliance with the Federal Register. All other parameters were analyzed according to US EPA procedures. Other parameters such as pH, dissolved oxygen, oxygen uptake rates, effluent solids sludge settling characteristics, and population dynamics were also monitored [8].

Gaudy, Lawrence, and McCarty biokinetic models were used to determine the treatability and fate of specific organic compounds. Constants used for these models were determined in terms of BOD_5, TOC, and COD for control, a base mix with the addition of one specific compound, and for the base mix for the addition of three specific compounds. These constants were also corrected for the stripping of the specific organic compound from the biological system. Each system was operated to control the solids retention time by wasting sludge daily according to the following equation.

$$F_{\mathrm{w}} = \frac{\frac{VX}{\theta_{\mathrm{c}}} - FX_{\mathrm{e}}}{X - X_{\mathrm{e}}}$$

where F_{w} is the sludge waste flow rate (d^{-1}), θ_{c} is the mean cell residence time (d), V is the reactor volume (L), F is the influent flow rate (L/day), X_{e} is the suspended solids effluent (mg/L), and X is the mixed liquor or volatile suspended solids (mg/L).

The performance efficiency of one particular compound, benzene, was determined over a two-week operation period. Observation of this data indicates that the effluent level remained stable after 2 weeks. Additionally, the effluent benzene concentration remained below 50 µg/L and the effluent soluble BOD5 was 1.0 mg/L.

The influent, effluent, and treated efficiency values for the BOD_5, TOC, and COD of 12 specific organic compounds were also determined. These values were also determined for combined compounds including volatile organic compounds, base-neutral extractable organic compounds, and acid extractable organic compounds. Overall, removal efficiencies for both types of systems (specific and combined) were high. Among individual compounds, the effluent concentration varied [8].

8.4 Case Study 4: Treatment Coal Chemistry Wastewater

Coal chemical industry wastewater can also pose a variety of environmental challenges. Coal is a readily used material to produce oil and natural gases. In order to produce these products, combustion, gasification and cooling and washing must be used. These processing techniques are highly energy-intensive and they produce large amounts of wastewater. Coal chemistry wastewater is characterized by high concentrations of COD and toxics. Toxic organic compounds which are commonly found in these wastewater include phenol, cyanogens, oils and ammonia nitrogen. Organics such as polycyclic aromatic hydrocarbons and heterocyclic compounds containing nitrogen and sulfur are also common. For this study, influent COD concentrations were found to be between 300 and 5000 mg/L and influent ammonia nitrogen concentrations were found to be between 150 and 400 mg/L [9].

Characterization of these types of wastewaters is also influenced by coal quality and the gasification process. Low-temperature gasification wastewaters contained polycyclic aromatic compounds such as benzene, phenol, and polyhydric phenols, heterocyclic compounds, and refractory organics. These wastewaters are highly saline and alkaline. Furthermore, treatment efficiency of these waters is determined by the phenol ammonia recovery method utilized, the selection of extractant, and the pretreatment method used. However, wastewater can also change based on coal quality, which can range from long flame coal to lignitous coal.

Treatment was conducted using biochemical treatment in several stages including pretreatment, treatment and polishing. Pretreatment needs to be conducted to remove oils from the wastewater. Systems that can be used to pretreat coal wastewater include regulation tanks, oil-water separators, and air flotation devices. Conventional biochemical treatment uses the activated sludge process which consists of an oxidation ditch, SBR, A/O common activated sludge reactor, and an MBR. Using hydrolysis or anaerobic treatment before biological treatment may further enhance treatment. Secondary biological treatment is needed to treat small amounts of ammonia nitrogen and organic substances that pass through primary treatment. Lastly, tertiary treatment implements a biological aerated filter (BAF), contact oxidation, filtration, ozonation, biological/ activated carbon, disinfection, membrane treatment, a biological oxidation pond, and other combined processes. Ozone and hydrogen peroxide are needed during this stage of treatment to improve biodegradability.

Phenol and ammonia was recovered from the wastewater. Slow degradation of coal chemical wastewater is a common challenge during treatment. The sludge produced by the sewage treatment biochemical system is mainly flocculation sludge and biological excess sludge, which is dehydrated by a belt-type pressure filter. The sludge produced by life softening is inorganic sludge, which contains inorganic particles that are more abrasive to the equipment. The screw-type dehydrator and centrifugal dehydrator are widely used along with the use of most imported products.

The pretreatment, and the sludge treatment units of sewage biochemical treatment produce harmful waste gases [8]. The main treatment methods are activated carbon adsorption that puts the gas into the adsorber with activated carbon, liquid absorption, absorption oxidation, and biological deodorization which is a method of deodorizing artificially by natural microorganism that control the biota within a facility. The advantages of activated carbon adsorption are that they have a: quick reaction, short contact time, and a high treatment capacity.

Biochemical wastewater reclamation and desalting process can be softened by petrochemical softening plus walnut shell filter, plus gas water backwash filter, plus ultrafiltration, plus primary reverse osmosis treatment process. Gradual maturity of fouling membrane products and RO membrane desalination are the most widely used treatment processes in the field of water reuse. Ultrafiltration is used to remove residual contaminants in water. The effects of pretreatment facilities are based on the effects of the membrane treatment process. Air flotation was used to remove oil and small-suspended matter that may contain water and the filters were used to reduce suspended solids. When the wastewater has a certain degree of hardness, lime-softening method is adopted to reduce the hardness of water inflow, and to protect reverse osmosis membrane. The purpose of these processes is to minimize the pollution load of RO membrane and improve the high-efficiency cycle of the equipment. The desalination process is required to meet the needs of industrial reuse of the recirculating of the water system [9].

8.4.1 Standard Treatment of Concentration Treatment of Concentrated Brine

After the enrichment by the membrane method, the amount of concentrated brine is still large and concentrated brine contains a certain amount of organic pollutants. Without treatment, emissions can cause heavy pollution to the local environment. When zero emission requirements exist, it is very uneconomical to evaporate the concentrated brine from the double membrane process, because of its: large size, high equipment investment, and large amount of energy. The concentrated brine process in foreign countries, includes a highly effective reverse osmosis process. It is important that the brine concentration is stable which is beneficial to the safe and long-term operation.

8.4.2 Evaporation Crystallization Process

The concentration of brine is high based on the biochemical treatment process, which is difficult to be recycled. Therefore, the evaporation and crystallization treatments are needed in order to realize the zero discharge of wastewater. Forced circulation technology is used in a crystallizer. The concentrated waste brine passes through a crystallizer or a dryer to crystallize various salts dissolved in the sewage and become solid.

Coal chemical wastewater characteristics involve complex water quality characteristics, large amounts of water, and the inability to deal with this type of wastewater. Because the technology that exists today cannot meet the national environmental protection requirements, it is necessary to develop an integrated and complete process with stable systems that: are shock resistant, have a low treatment cost, and have a good effluent effect in order to achieve near-zero emissions of coal chemical wastewater.

Overall, the biodegradability of coal chemical wastewater is poor. Therefore it is necessary to strengthen the pretreatment technology to improve the biodegradability of the sewage and reduce biological toxicity. Secondly, it is key to select the biological treatment process with strong toxicity resistance and to cultivate and adapt activated sludge for treating coal chemical wastewater. Finally, post-processing techniques are needed to meet the requirements for water reuse by treating coal chemical wastewater.

By having a zero discharge of the real coal chemical wastewater along with advanced oxidation and membrane assembly process may address the problem of chemical wastewater of coal, but the cost of providing these treatments is still too high. Therefore, further research is needed to reduce the treatment cost and control the membrane fouling assembly process.

8.5 *Case Study 5: Treatment Mixed Chemical Wastewater by a Two-Stage A/O Process*

Aerobic biological oxidation tank resulted in excellent toxic matter removal. The acute toxicity of the whole system dropped from 0.165 to 0.042 mg $HgCl_2$/L. The two stage AO system with sludge return system can be used for treating wastewater containing COD, nitrogen and toxic substances.

The mixed wastewater generated from industrial plants which produce chemicals such as flurochemicals, petrochemicals, coal-chemicals chloro-alkali chemicals and pharmaceuticals, may contain high concentration of COD, nitrogen and toxic substances. By removing the COD nitrogen and toxic matter before discharge, the sewage will not pollute the receiving water bodies that seriously poison the aquicolous and terricolous creatures.

Therefore, treatment of wastewater discharge from a single chemical factory was the basis of this study. Although many wastewater treatments were studied where the processes obtained good COD and nitrogen removal outcomes, the main problems identified were the strict operating requirements and the high running costs. In comparison, bio-treating processes like anaerobic and anoxic/oxic process membrane bioreactor (MBR), biofilm reactor [3, 5] and anaerobic baffled reactor (ABR) [11] are easier to manage, are lower in cost, and are more popular in lab and full-scale experiments and applications. Unfortunately, a high COD and toxic matters on microorganisms are a problem for mixed chemical wastewater treatment systems because the information needed is rarely studied [10]. COD oxidation and nitrification carry out two kinds of microorganism that can inhibit each other under two opposite COD/N ratio conditions. Because of this information, an independent COD oxidation and nitrification system is necessary.

This study focuses on a two-stage A/O process with an independent sludge system, which has a separate COD oxidizer and nitrifiers in two subsystems. Mixed wastewater produced by a chemical group containing high concentrations of COD, nitrogen and toxic matters was treated. The removal efficiency of COD and nitrogen was examined, the acute toxicity of the wastewater from different treating units was appraised (bioassayed), and the system was evaluated [10].

The two-stage A/O system consists of two subsystems. Subsystem one is for COD removal and subsystem two is for nitrogen removal. Each system consists of a whole A/O system with an anoxic tank, an oxic tank, and a settling tank that finish its removal work independently. The influent flux was maintained at 10 L h and the HRT's had different units. The mixed liquid return was not settled and the sludge return ratios were set at 100–200% to maintain a high usable sludge concentration. The temperature of 25 + 2 and 30 + 2 °C was maintained for both subsystems. The two oxic tanks were aerated continuously with rubber diffusers to keep the DO concentration levels at 3–5 mg/L. and the mixing velocity was kept at 60 rpm.

The mixed chemical wastewater used was from the equalizing tank of Juhua wastewater treatment plan (WWTP) Zhejiang province, China. The organic nitrogen in the wastewater was from PVN production. And the $C_6H_{11}NO$ (raw material of PVN) was added to the wastewater to enhance loading rates of NH4-N. The Org-N/NH_4N ratio was kept at approximately 1:1. The seed sludge was the condensed sludge of the Juhua water treatment plant. The seed sludge inoculation for both subsystems was at 10,025 and 10,828 mg/L. Sixty-seven days of run passed before the mixed chemical wastewater was adapted. No excess sludge was discharged. DO was determined by an oxygen meter. The pH and temperatures were determined by the pH meter and the concentration of alkalinity was measured by the standard methods.

Marine luminescent bacterium was used to estimate acute toxicity. The bioassays were carried out by adding 2 mL wastewater and 10 mL bacterial suspension to a low-background vitreous tube. After 15 min of exposure, the relatively light units of wastewater were recorded by the luminator. The temperature was constant at 15 °C.

Overall, the two-stage A/C system showed excellent performance in COD removal. Average influent COD concentration of subsystem one of days 1–9, 10–19, and 20–52 were around 943.5. With different $C_6H_{11}NO$ additions the COD increases did not make any influence on COD removal efficiency. Subsystem two had a further removal of COD and average removal efficiency was 50.1% based on subsystem one effluent. The average removal efficiency of the whole system was 93.3%. COD was mostly removed by subsystem one with little nitrification. Overall, it was presumed that autotrophic nitrifiers were more sensitive than heterotrophic COD oxidizers and the inhibition of toxic matters was stronger for nitrifiers than COD oxidizers. Therefore, most of the COD was removed, but very little ammonium was oxidized.

The average removal efficiency of subsystem one of KN was only 6.8% and the KN removal loading rate was 0–0.014 kg KN (kg MLVSS day). On the other hand, subsystem two had a further removal of ORG-N at a low influent ORG-N concentration to the organic matter. Average 86.0%. Additional treatment is required to reduce effluent KN to a concentration of 13.6 mg/L KN, 9.9 mg/L NH_4-N and 3.7 mg/L Org-N.

It was suggested that the coagulation process could remove a part of toxic matters. After coagulation, the acute toxicity was dropped to 0.100 mg $HgCl_2$ L. Overall, coagulation just transferred toxic matters from wastewater to deposits while the aerobic biological oxidation changed toxic matters to nontoxic matters like CO_2 N_2 and H_2O.Therefore, the two-stage A/O process was sufficient. Coagulation made little impact on the acute toxicity of subsystem two effluent.

The two-stage A/O system, which could remove 87.63% COD, 92.1% KN, and eliminate 75% acute toxicity, performed excellently. After comparing the four biological systems, the sludge system was the main difference and each subsystem had an independent sludge system. Organic carbons were removed and the toxic matters were eliminated in subsystem One. As a result, it guaranteed high nitrifying activity in subsystem 2.

The two-stage A/O system removed COD and KN efficiently from the mixed chemical wastewater with two completely independent microorganism subsystems that performed different functions under their own optimal COD/KN ratio. Subsystem One obtained high COD and OR-N removal capability while nitrification was totally inhibited with only 7.6% KN assimilated by microorganism. Subsystem Two had high nitrification capacity because of the low influent COD/KN ratio and the low nitrification toxicity of 92.1%KN removal efficiency was achieved. Subsystem Two also had a further removal of COD and Org-N. Aerobic biological oxidation of oxic tank one showed excellent toxic matter eliminating ability and the two-stage A/O system can eliminate most of the toxic matters effectively. This study used independent functional activated sludge systems, and established the discharge of mixed wastewater treatments by comprehensive chemical groups, which contained high concentrations of COD and toxic matter [10].

8.6 Case Study 6:Treatment of Chemical Wastewater Using Adsorption

Adsorption is a useful method for treating chemical industry wastewater for the removal of heavy metals and dissolved organic compounds and the reduction of BOD, COD, and color. Adsorption has proven to be an effective treatment method for treating wastewater which varies in composition and concentration of pollutants. There are a variety of adsorbents (materials which absorb pollutants on their surface) including granulated or powdered activated carbon, clay bentonite, fly ash, alumina, magnesium oxide, ferric oxide, silica, saw dust, zeolites, anthracite, and volcano ash soils. For this particular case study, adsorption using activated carbon, and other inorganic adsorbents was studied. The wastewater studied originated from a petrochemical industry. The given wastewater was biologically treated before adsorption was applied. Activated and powdered carbon were adsorbents used. Activated carbon was efficient from removing color from the original amber-colored influent. COD and color were parameters which were used to quantify the amount of organic solutes. The system used a three stage adsorption tank with activated carbon implemented in each stage [12].

Eleven different wastewater samples were analyzed in the laboratory. It was found that they contained dye intermediates (H-acid, dihydroxydibenzanthrone, dibenzyl oxybezaldehyde, dibenzanthronyl), benzanthrone crude, ethanol, drug intermediates (diethyl malonate), complex manufacturing vat dyes and their intermediates. The samples were directly taken from processing plant wastewater streams. Each sample was analyzed for pH, color, and COD. The experiments were all conducted at room temperature. 500 mL of the sample was placed in a cylindrical flask where it was mixed with 2.5 g of activated carbon. Every 15 min, 5–10 mL was extracted from the sample and analyzed for pH, color, and COD. After 2 h, mixing was stopped and the experiment was repeated several times using other adsorbents: once using 5 g of bentonite and another time using 5 g of lignite. The performance of each adsorbent was measured to be effective if percent reduction of COD and color was above 40%, moderately effective if the percent reduction of COD and color was between 20 and 40%, and ineffective if the percent reduction of COD and color was below 20%.

Phenols and cyanides were also removed using activated carbon. Phenol concentrations were reduced to less than 0.5 mg/L. Phenols were more easily adsorbed than pyridines. More than 80% of COD was removed from wastewater containing benzene derivatives, carboxylic acids, pesticides, and phenols. The COD was removed by using an activated anthracite adsorbent. Heavy metals were removed using fly ash. The process was maintained at a pH above 8. Organic impurities such as sodium chloride (NaCl), sodium carbonate (Na_2CO_3), sodium nitrate, monochlorobenzene, polyamines, diaminodiphenylmethane, and toluenediamine were also removed. The concentrations of these impurities were 5–15 mg/L for NaCl, 1.5 mg/L for Na_2CO_3, and 2 mg/L for toluene diamine.

Overall, activated carbon was highly efficient at removing H-acid, dihydroxydibenzanthrone, ethanol, and diethyl malonate and moderately efficient at removing dibenzanthronyl, benzanthrone crude, and vat dyes and their intermediates. Bentonite was ineffective at removing H-acid while lignite was ineffective at removing H-acid and dibenzyl oxybenzaldehyde. While all three adsorbents were effective for removing COD and color from wastewater, activated carbon had better performance than the other adsorbents. One drawback of using activated carbon is that it was ten times more expensive than the other adsorbents used. However, activated carbon as well as lignite provides easy and safe disposal.

COD values at different durations were predicted using the following models.

Weber and Morri's equation

$$C_{\mathrm{i}} - C) = m_1 t^{0.5} + c_1$$

Lagergren equation

$$\log\left(C - C_{\mathrm{eq}}\right) = m_2 + c_2$$

Rathi Puranik equation

$$\log\left(\mathrm{CODRT}\right) = m_1 + c$$

The predicted values were plotted along with the data obtained from wastewater analysis. The Rathi Puranik equation was found to predict the COD with the least amount of error [12].

8.7 Case Study 7: Treatment of Chemical Coking Wastewater Using Combined Anaerobic–Aerobic Treatment

Anaerobic–aerobic systems are efficient systems for reducing high-strength wastewater. Their efficiency was examined in a case study lasting 300 days. During the study, a combined system was analyzed for treating wastewater from the coking industry. Contaminant removal was also studied using a two-dimensional gas chromatography with time-of-flight mass spectrometry with SCN^- and CN^- under stable operation. Microbial communities were assessed by using a Roche 454 pyrosequencing and real-time quantitative polymerase chain reaction (qPCR) [11].

The combined system that was used during this study was a bench-scale sequential anaerobic and aerobic system. The system consisted of an upflow anaerobic sludge blanket reactor (USAB) and a conventional aerobic bioreactor. The hydraulic retention time was 42 h for the USAB and 72 h for the aerobic reactors [10]. Operating temperature ranged between 20 and 25 °C. Dissolved oxygen was kept 2–4 mg/L in the aerobic reactor during the entirety of the study period (300 days). The concentration of suspended solids in the aerobic reactor was maintained between 3000 and 4000 mg/L.

Coking wastewater is produced from the coke industry. This wastewater is characterized by a mixture of organic contaminants such as phenols and toxic compounds such as cyanides that are hazardous to ecosystems and human health. Methods such as ammonia stripping or solvent extraction are commonly used for pretreatment of coking wastewaters while aerobic activated sludge systems are typically implemented to treat these wastewaters. However, anaerobic systems can also be used in tandem with aerobic systems to better help treat high-strength industrial wastewater and reduce toxic compound concentrations.

Choking wastewater was obtained from an equalization tank of a coking facility in Tangshan City, Hebei Province, China. Ammonia and phenol were recovered from the wastewater, giving it a COD ranging between 2500 and 3500 mg/L. Prior to treatment, the raw wastewater was supplemented with 0.2 g/L of potassium phosphate mono-basic (KH_2PO_4) and 1 mg/L of a micronutrient solution [10]. The pH of the influent wastewater was adjusted to 7.5 ± 0.5 using a concentrated hydrochloric acid solution [10]. Seed sludge originated from a full-scale sewage plant in Beijing, China.

Samples used were using grab samples and were taken at influent and effluent locations every 5–7 days. For the determination of organic and inorganic compounds, wastewater samples were collected in triplicate before the termination of bioreactor operation [11]. Aerobic and anaerobic sludge samples were collected on days 125, 194, 228, 276, and 325, whereas anaerobic sludge samples were collected on days 154 and 261 of the study period. Sludge composite samples were obtained from a mixture of three samples. From these composites, 1 mL was used as anaerobic sludge and 1.5 mL was used as aerobic sludge. The sludge samples were separately placed into 2 mL tubes and placed into a centrifuge at 10,000 rpm for 10 min at 4 °C. After the centrifuge process was completed, the samples were filtered through a filter 0.45 μm in size. COD was measured using the open reflux method. Total, phenol, total nitrogen, ammonia-nitrogen, thiocyanate, and free cyanide were measured using spectrophotometry. The TOC was measured using a TOC analyzer. Sulfate was measured, using ion chromatography. Lastly, DO and ph were measured using a meter.

Overall, the removal efficiency of the anaerobic treatment system ranged between 0 and 84.6%. It was found that anaerobic treatment removed one third of organics consisting of 32.7% of COD and 34.2% of TOC and more than half of the total phenols (54%) from the wastewater.

The hydraulic retention time of the anaerobic system was 42 h. Anaerobic treatment removed an average of 58% of NHCs and 58.6% of phenolic derivatives. The combined system was able to remove 81.8% of COD, 85.6% of total organic carbon (TOC), 99.9% of total phenols, and 85.4% of thiocyanate and cyanide. The COD concentration was reduced to an effluent concentration of 520.1 ± 73.1 mg/L and a TOC concentration of 112.1 ± 21.8 mg/L. These values are fairly high. Additionally, the system removed 98.2% of SCN^- and 85.4% of CN^-. However, the system had minimal effect on nutrients, as the total nitrogen concentration was constant throughout the treatment process. The ammonia-nitrogen concentration and sulfate concentration increased to 149.5 ± 27.1 and 1512.5 ± 320.7 mg/L after treatment.

Microbes within the system were also examined. It was found that *Proteobacteria*, specifically *Betaproteobacteria* (34.4–70.1%), *Alphaproteobacteria* (10.9–31.7%), were present in the combined system (10–11%). Bacteria such as *Betaproteobacteria* (64.2–76%), *Ottowia, Soehngenia,* and *Corynebacterium* were the most abundant in the anaerobic stage. Other bacteria with high populations in the anaerobic reactor include *Actinobacteria*, which had an abundance ranging between 3.1 and 14.1% of the total bacteria present in the reactor; *Firmicutes*, which had an abundance ranging between 11.9 and 13.5% of the total bacteria present in the reactor; bacteroids, which had an abundance ranging between 3.3 and 4.7% of the total bacteria present in the reactor. Bacteria such as *Thiobacillus, Diaphorobacter, Trichosporon,* and *Comamonas* were the most abundant in the aerobic stage.

The archaea and fungi population was low in both the aerobic and anaerobic systems. However, the following archaea appeared in the highest numbers: *Methanosarcina* (41.7–44.3%), *Methanobacterium* (19.8–20.9%), *Methanomethylovorans*, and *Euryarchaeota* (96.2–98.3%), which can further be classified by two subcategories, *Methanomicrobia* (73.0–75.7%) and *Methanobacteria* (20.2–20.9%).Out of the fungi present, phylum *Basidiomycota* was the most abundant fungi in the system. *Trichosporon* was the most abundant yeast present in the aerobic reactor, having an abundance between 62.9–88.3 and 10.2–34.5% of fungi were listed as unclassified.

Ultimately, these results are in agreement with the presented material about combined systems described earlier. Combined systems provide a simple, less energy-intensive alternative for treatment. These systems can be useful for removing pollutants such as phenolics, NHCs, SCN^-, and CN^- in coking wastewater [11].

8.8 Case Study 8: Treatment of Chemical Industry Wastewater Using an MBBR System

This study examined the use of an moving bed biofilm reactor (MBBR) for pretreating complex chemical industry wastewater. Wastewater from the study originated from the Exxon Chemical Baton Rouge Chemical Plant in Louisiana. The plant implemented physical pretreatment, trickling filters and activated sludge to treat the wastewaters. However, the existing treatment system was unable to meet stringent effluent guidelines specified and therefore need to be either replaced or upgraded. Recommendations were made to replace the existing trickling filter unit with an MBBR system to enhance efficiency [13].

MBBR systems have proven to be efficient for treating wastewaters from the food industry, pulp and paper industry, and municipal wastewaters. However, this was one of the first applications of using an MBBR on chemical industry wastewaters. Therefore, a pilot system was developed to establish criteria for full-scale MBBR system design. The biofilm was constructed as a small, 10 mm diameter, 7 mm tall cylinder made of polyethylene with a density of 0.96 g/cm^3. The cylinder was designed with a cross shape on the interior and longitudinal fins on the exterior surface. Perforated plates sized 5 mm × 25 mm were used to support the biofilm. The maximum specific growth area was specified as 350 m^2/m^3. The system was designed with no sludge return to the biofilm reactors. The system was designed with two MBBR units in parallel, with one operating at a medium organic load and a high organics load. The conventional aerated activated sludge plant was then fed effluent from one MBBR at a time. Air flow was controlled manually by using values.

For the study, wastewater from three streams was collected and analyzed. Phosphoric acid was added to the wastewater to provide ample nutrients for treatment. Daily composite samples were taken from the three points and stored in a refrigerator. Samples were also taken from the activated sludge stage (point 4), the mixed liquor (point 5), and the RAS (point 6). Samples were analyzed for total and filtered BOD_5, total and filter COD, total Kjeldahl nitrogen (TKN), NH_4-N, NO_3-N, PO_4-P, total suspended solids (TSS), and volatile suspended solids (VSS). Mixed liquor and RAs were analyzed for TSS and VSS.

The organic load of typical MBBR systems is 53 g BOD_5/m^2/day and the BOD fraction ranges between 60 and 80%. Lower organic loads between 10 and 20 g BOD_5/m^2/day have been observed to metabolize organic matter. For this system, MBBR 1 was loaded with a high load and MBBR 2 was loaded with medium loaded wastewater. In previous studies, when MBBR were combined with activated sludge, chemical wastewater effluent was found to have BOD_5 as low as 3.4 mg/L. The operating average conditions for the systems are as follows. Both MBBR systems were operated at the same pH, 7.9 ± 0.1.

MBBR 1 operated with a flow of 7.8 ± 0.4 m^3/day, an empty bed HRT of 1.9 ± 0.2 h, a DO of 4.3 ± 0.8 mg/L, an ammonia nitrogen concentration of 4.1 ± 3.7 mg/L, and a phosphate phosphorus concentration of 1.1 ± 0.8 mg/L. MBBR 2 operated with a flow of 3.8 ± 0.1 m^3/day, an empty bed HRT of 3.8 ± 0.1 h a DO of 4.0 ± 0.5 mg/L, an ammonia nitrogen concentration of 3.1 ± 2.9 mg/L, and a phosphate phosphorus concentration of 1.1 ± 0.9 mg/L. The MBBRs were operated at nearly the same temperature with the temperature of 34.1 ± 1.1 °C for MBBR 1 and 34.2 ± 1.0 °C for MBBR 2.

The average flow into the activated sludge system ranged between 1.4 and 2.8 m^3/day between the study period that took place between June 3 and August 15. The activated sludge system was also operated with an average MLSS ranging between 4.9 ± 1.6 and 5.8 ± 2.5 g/L, an average MLVSS ranging between 3.8 ± 1.2 and 4.4 ± 1.8 g/L, an average ammonia nitrogen concentration ranging between 3.0 ± 2.5 and 4.3 ± 0.1 mg/L, and an average phosphate phosphorus concentration ranging between 3.0 ± 0.5 and 4.5 ± 0.7 mg/L.

From analysis, it was found that MBBR 2 has a 10–15% higher removal efficiency of organic matter and a lower sludge production than MBBR 1. Both MBBRs had a BOD removal efficiency 6–8% higher than the COD removal efficiency. A change in influent concentration did not affect the removal efficiency. Of the BOD analyzed, it was found that 60–80% of the BOD was easily removed. Organic loads above 25 g $TBOD_5/m^2$day were observed to have no change on the removal efficiency. The removal efficiency of high loaded wastewater ranged between 70 and 80% BOD removal. For low loads between 10 and 20 g $TBOD_5/m^2$day, 95% of total and filtered BOD_5 was removed. The highest removal rates observed were 40 g $TBOD_5/m^2$day and 35 g $FBOD_5/m^2$day.

From this study it can be concluded that MBBRs can offer a compact alternative for treating chemical industry wastewaters [13].

9 Waste Minimization

While the wastewater treatment process removes harmful chemicals from water after chemical production, other steps can be taken within the chemical industry to reduce the amount of wastewater and the concentrations of pollutants within the wastewater during the manufacturing. Waste minimization during the production process is an important step to avoid waste formation during production [6].

Resource efficiency is an important consideration for sustainability in the chemical industry. Resource efficiency is defined as the use of natural resources in a way that minimizes the amount of resources needed to produce a particular product. Resource efficiency is especially concerned with material use efficiency as well as energy and water efficiency. Proper design and management are essential for the development of efficient systems. One particular method to reduce waste within the chemical industry is to implement green chemistry practices. Implementation of green practices allows for the design of chemical products all the while minimizing the harmful effects of these products on humans and the environment. Furthermore, green engineering methods can be utilized for better design practices, which can aid in waste reduction [14].

A few key steps for waste minimization in the chemical industry include: (1) determining the cost of the waste, (2) understanding the products and processes utilized, (3) analyzing the performance efficiency and identifying areas where reduction can be made, (4) narrowing options and prioritizing improvement ideas, (5) implementing reuse and recycling methods when possible, and (6) monitor and maintain practices. Ultimately, the best waste management practices account for environmental, economic, and social concerns [14]. In order to produce efficient, sustainable products which account for all of these factors, engineers and other stakeholders must come together to prioritize and implement the best waste management practices. Good communication is essential during this process.

The resource efficiency from the chemical industry was measured in a case study from Finland. The chemical industries from the study consisted of pharmaceutical, oil refining, plastic, and rubber manufacturing industries as well as other chemical product industries. Most of these industrial facilities were located within 200 km of Oula. Hazardous waste generated from the chemical industry totaled 111,000 tonnes. To determine the efficiency, questionnaires were sent to several chemical plants in Northern Ostrobothnia in 2004 and 2005. Questions asked respondents about actions that were taken to prevent waste, benefits of said actions, future actions that could be implemented, and key parameters that were used to reduce waste. The questionnaire had a total of 14 questions.

Results show that companies mainly implement waste reduction during the manufacturing process. Ninety-two percent of respondents identified improved machine maintenance as the favored management techniques opposed to others. Eighty-five percent of respondents identified the importance of training for waste management procedures. Furthermore, 85% of respondents reported waste reduction by using a smaller amount of raw materials and 77% of respondents reported waste reduction by using more efficient processes. Water and energy considerations are typically important considerations in industrial processes. From the survey, 77% of respondents indicated the importance of energy reduction while only 44% of companies indicated the importance of water reduction. Other actions that were taken indicated that 23% use cheaper electricity, 31% adjust temperature, 31% use reusable packages, and 31% use less water for flushing. Additionally, 54% of respondents bought raw materials in bulk, 61% used recycled solvents and plastics, 31% used energy recovery methods, and 23% used off site recycling [14].

10 Summary

There is need for better and more frequent monitoring waste practices from the chemical industry. Furthermore, water reduction practices were rarely used from chemical industries. Company culture largely affected the way in which company addressed waste management. In order to implement the most efficient and optimized process, employees should be knowledgeable about the processes utilized at their chemical company as well as any restrictive regulations and resources available. With proper education and training, chemical industries can properly reduce the amount of waste produced [14, 15].

Glossary

Aerobic treatment A biological process that uses oxygen to break down organic contaminants and other pollutants like nitrogen and phosphorous.

Anaerobic treatment A biological process where microorganisms degrade organic contaminants in the absence of oxygen.

Biological treatment *Biological treatment* (or biotreatment) processes are those which remove dissolved and suspended organic chemical constituents through biodegradation, as well as suspended matter through physical separation.

Chemical industry The *chemical industry* comprises the companies that produce *industrial chemicals.*

Oxidation Any chemical reaction that involves the moving of electrons.

Pharmaceutical products Fundamental component of both modern and traditional medicine.

Pretreatment Any treatment received before some other process.

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Chapter 4
Agricultural Waste as a Low-Cost Adsorbent

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Contents

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Abstract The use of low-cost adsorbents from agricultural wastes was reviewed for industrial applications. Agricultural Waste is needed for sustainable agricultural practices but could also be considered essential in wastewater treatment operations. Adsorption will be reviewed heavily in this chapter. Chemical and physical characteristics that aid its role as an adsorbent and the suitable industrial applications will be explored.

Keywords Adsorption · Low cost · Adsorbent · Dye removal · Agricultural waste · Heavy metals · Kinetic models

Abbreviations

AC	Activated carbon
CRS	Carbonized rice straw
DO	Dissolved oxygen
EDTA	Ethylenediaminetetraacetic acid
PCB	Polychlorinated biphenyls
VOC	Volatile organic compounds

1 Introduction

Adsorption is heavily relied upon for the removal of pollutants. Activated Carbon is the primary adsorbent in water and wastewater treatment, but production is inefficient and energy intensive. The result is that activated carbon remains an expensive and largely unavailable product. Investigation into alternatives is necessary, and this chapter analyzes low-cost adsorbents produced from agricultural waste without the removal of pollutants.

Adsorption is adhesion at the molecular level. It is a physiochemical reaction, where interactions determine the behavior of the adsorbed phase. This process is dependent upon the mutual participation of the adsorbent and adsorbate, and because interactions determine adsorbance, this study becomes one of thermodynamics. Physical adsorption and chemical adsorption are the means for energy and pollutant transfer, and in this chapter, liquid to solid phase adsorption will be the focus, but applications exist in all phases.

2 Adsorption

2.1 Physical Adsorption

Van der Waals forces of physical attraction are responsible for physical adsorption. Van der Walls forces are a result of a transient shift in electron density, and electrons may temporarily shift to one side of the nucleus, which generates a temporary charge and subsequent attraction of nearby atoms. Adsorption is an exothermic reaction where the adsorbate penetrates the sorbent in search for a position of minimum energy. The sorbate continues to move among low energy sites within the sorbent, and thus, highly porous activated carbons are effective for adsorption. The atoms of a solid surface enhance Van der Waals forces by being in high concentration and naturally attract sorbate molecules to themselves. Since adsorption is dependent on the behavior of molecules, study on the cause of adhesion becomes a study of behavior at the atomic level. This field is quantum mechanics, but adequate knowledge of intermolecular binding is enough to possess a strong understanding of adsorption dynamics.

Intermolecular forces are composed of a repulsive component that prevents the collapse of molecules (Pauli exclusion principle and electrostatic interactions). Electrostatic interactions are interactions caused by molecular charge, shifting of electrons is known as induction or polarization, and the reactions formed are known as dispersion (London dispersion interactions). London's dispersion forces are responsible for Van der Waals's forces of physical attraction, and when the electrons of an atom all go to the same place, a dipole moment is formed momentarily. A dipole moment is when opposite charges are separated in a molecule at two ends. The presence of a negatively charged end causes the surrounding molecules to have a momentarily dipole moment as well, and oppositely charged ends of adjacent molecules will bind temporarily. Significance to absorbance is the necessary physical attraction between sorbent and sorbate for the binding and subsequent removal of sorbent pollutants.

2.2 Chemical Adsorption

Physical adsorption is caused by intermolecular forces, while chemical adsorption is caused by intramolecular forces. The difference is that instead of the dipole attraction between molecules, we are now dealing with attraction that exists within a molecule. Intramolecular forces of attraction are composed of ionic, covalent, and metallic bonds.

2.2.1 Ionic Bonds

Ionic bonds are formed by a complete transfer of valence electrons between atoms and generate two oppositely charge ions. An electron is essentially donated between two molecules that differ greatly in their electronegativity. In ionic bonds, metals lose electrons to become a positively charged cation and require a nonmetal electron acceptor. The net charge of the produced compound must be zero. This results in a cation and anion bonded by an ionic bond [1].

2.2.2 Covalent Bonds

Covalent bonds are much more common than ionic and involve the sharing of electron pairs. Electrons are covalently bonded to gain stability with the formation of a full electron shell. Nonmetals readily form covalent bonds with other nonmetals, but the sharing of electrons is often unequal.

Polar Covalent Bonds

In a covalent bond where the two atoms are the same element, the sharing of electrons is equal. Among atoms of different elements, the electrons will be drawn more toward the atom of higher electronegativity and create a polar covalent bond. Polar covalent bonds are usually weaker than ionic bonds, having lower melting points and a less tendency to dissolve in water [2].

2.3 Bonds in Water

Water is a polar molecule. Ionic compounds are more likely to dissolve than covalent compounds: the cation by negatively charged ends of water molecules and the anions by the positively charged ends of the water molecule. The surrounding of water molecules is known as hydration, this process releases energy, and if it exceeds the energy of the lattice structure of the compound, dissociation will occur [3].

Familiarity with chemical and physical reactions inspires an understanding of the physical and chemical nature of the sorbent and sorbate.

3 Pollutants

Ghangrekar and Chatterjee (2018) classify water pollutants by (1) Organic pollutants, (2) Pathogens, (3) Nutrients and agriculture runoff, (4) Suspended solids and sediments, (5) Inorganic pollutants (salts and metals), (6) Thermal pollution, (7) Radioactive pollutants, and (8) Nanopollutants [4].

3.1 Organic Pollutants

Organic pollutants are composed of oxygen demanding wastes, synthetic organic compounds, and oils. Oxygen demanding wastes can be treated by biological waste treatment. Oxygen demanding waste is generated from sewage, food processing industries, canning industries, dairies, slaughterhouses, paper and pulp mills, tanneries, breweries, distilleries, and other industries. Depletion of dissolved oxygen (DO) in water is of serious concern and can be lethal to aquatic life if DO is reduced past 5–6 mg/L [4]. Synthetic organic compounds include synthetic dyes, polyaromatic hydrocarbons, pharmaceutical active compounds, endocrine disruptors [5], halogenated organics, aliphatic and aromatic hydrocarbons, synthetic pesticides, synthetic detergents, food additives, pharmaceuticals, insecticides, paints, synthetic fibers, plastics, solvents, and volatile organic compounds (VOCs) [6]. Some synthetic organic compounds are recalcitrant and are named BioRefractory Organic Compounds (BioROCs). Refraction is due to toxicity to microbial populations that either completely or partially inhibit microbial metabolism (antibiotics, antiseptics, and hydrophobic solvents) and particular physical properties such as weak solubility and limited adsorption due to complexity of molecular structure (e.g., carbamazepine and naproxen). Common BioROCs include benzene, chloroform, methyl chloride, styrene, tetrachloroethylene, trichloroethane, and toluene [6]. Synthetic Organic compounds include the commonly used polychlorinated biphenyls (PCBs), which are fat soluble, move through tissues and cells, and often become chlorinated, resulting in the formation of chlorinated hydrocarbons suspected to be carcinogenic. Oils are a harmful water pollutant, reducing photosynthetic activity, coating aquatic organisms, and reducing DO concentrations. The removal of oil from water can be achieved through lower-cost methods than adsorption given the natural separation.

3.2 Inorganic Pollutants

Inorganic pollutants are nonbiodegradable and persistent environmental pollutants; examples are Mineral acids, inorganic salts, trace elements, metals, metallic compounds, metal/organic compound complexes, cyanides, sulfates, etc. Heavy metals may cause health concerns for metals in high concentrations can be toxic (Hg, Cu, Cd, Pb, As, and Se). Copper in quantities greater than 0.1 mg/L is toxic to microorganisms. Cadmium may cause kidney and skeletal damage. Mercury exposure may cause lung damage, and metallic mercury may cause kidney damage. Lead poisoning symptoms include headache, irritability, abdominal pain, and various symptoms related to the nervous system. Inorganic arsenic can cause severe disturbances to gastrointestinal, cardiovascular, and central nervous systems and eventually death (also bone marrow depression, hemolysis, hepatomegaly, melanosis, polyneuropathy, and encephalopathy) [4].

3.3 Radioactive Pollutants

Radioactive contamination is hazardous for the radioactive decay of the contaminants. Radioactive decay emits ionizing radiation such as alpha or beta particles, gamma rays, or neutrons. Severity of contamination is determined by the concentration of the contaminants, the energy of emitted radiation, the type of radiation, and the proximity of the contamination to organs of the body. Radioactive materials originate from mining and processing of ores, use in research, agriculture, medical, and industrial activities using isotopes such as I-131, P-32, Co-60, Ca-45, S-35, and C-14, radioactive discharge from nuclear power plants and nuclear reactors, e.g., Sr-90, Cesium, Cs-137, Plutonium Pu-248, Uranium-238, and Uranium-235, and use and testing of nuclear weapons [4]. Sources of production include the nuclear fuel industry, where the production of nuclear weapons and power generates hazardous waste at every stage of production. The mining of uranium produces highly radioactive tailing, which can be blown into the air, contaminate soils, and leach into bodies of water. Nuclear waste is harmful primarily due to radiation; these isotopes are toxic and cause serious disorders, and the safe concentration for lifetime consumption is 1×10^{-7} μCi/mL [6].

3.4 Nanoparticle Pollution

Nanotechnology is growing at unprecedented rates. Nanoscale materials are becoming popular in most industries for their unique physical and chemical properties. Nanoparticles can enhance catalytic, antimicrobial, and oxidative properties and subsequently have experienced worldwide research and development. Materials that are inert at the millimeter or micron scale may exhibit different properties at nanoscale, e.g., chemical reactivity, thermal and electrical conductivities, and tensile strength. Nanoparticle pollution may cause serious damage and disease and is considered the most difficult pollution to manage and control [4].

4 Pesticides

U.S. pesticide expenditures at the producer level totaled nearly $9 billion in 2012. Between 2008 and 2012, U.S. expenditures accounted for 18–16% of total world pesticide expenditures. U.S expenditures at the user level for conventional pesticides totaled nearly $14 billion dollars in 2012 [7].

Glyphosate is the most used herbicide and was considered nontoxic, but excessive application has resulted in severe acute and chronic toxicological effects. Post World War II, starvation was ever present and demanded maximum agricultural production. The need of hour persuaded widespread use of synthetic chemicals in agriculture and has ever since been a dependency. In 2014, the annual consumption of Glyphosate had increased to 240 million pounds. Glyphosate kills the plant by hampering the biosynthesis of essential aromatic amino acids required for growth [8]. It hinders the production of enzyme, 5-enolpyruvylshikimate-3-phosphate synthase of shikimate pathway, and scarcity creates a deficiency of aromatic amino acids, which affects various metabolic functions. Sorption of glyphosate into soils is very large, and it is a polyprotic molecule with three polar functional groups (amino, phosphate, and carboxyl group) [8]. Desorption is considerably low, and glyphosate is fairly immobile in soils. Biological degradation is the in situ treatment, microbial communities are capable of many degradation pathways, cleavage of glyphosate to glyoxylate and aminomethylphosphonic acid by the enzyme glyphosate oxidoreductase, conversion to aminomethylphosphonic acid and glyoxylate in the presence of glycine oxidase [9], and cleavage of glyphosate to inorganic phosphate and sarcosine by enzyme C-P lyase.

Mutations on commercial crops allow glyphosate resistance, but weed species are also growing immunity to this herbicide. Overuse brings glyphosphate residue in food crops, and with growing weed tolerance, this is only expected to rise. Toxicity to life of all orders has been noted, and it is to be expected from a chemical that is meant to disrupt enzyme production and amino acid formation. Glyphosate reduces the growth of fungal microorganisms and causes significant effects to community structure. Rhizospheric communities have undergone dynamic changes in the presence of glyphosate with increases in the abundance of proteobacteria and decreases in the abundance of acidobacteria. Poultry gut microbia see reduction populations of beneficial bacteria. Algae witness a reduction in photosynthetic capabilities. Earthworm populations in contaminated soils lack the presence of cocoons and juveniles but do show the presence of morphological abnormalities and steady decrease in mean body weight [10]. Many similar exist with decreases in cocoon viability, biomass, and feeding activity. Glyphosate was found to act as an uncoupler of oxidative phosphorylation in the mitochondria of earthworms. Glyphosate due to the presence of several binding sites often combines with metal ions and forms metal complexes, which reduce toxicity of Cu ions for earthworms.

Zaller et al. analyzed the effects of glyphosate effects on earthworm and symbiotic mycorrhizal fungi and noticed a decrease in earthworm activity in mesocosms containing arbuscular mycorrhizal fungi, mycorrhizal fungi spore biomass, and reduced root mycorrhization. Overall, with a decrease in fungi, earthworm interactions were recorded, which marks a serious threat to natural systems [11]. Honeybees suffer from the extermination of beneficial bacteria found in their gut [12], diminished short-term memory, decreased elemental learning, and increased time to return to their hive, all revealing that glyphosate impairs the intellective capabilities of bees [13]. Frogs and toads endure neurotoxicity, oxidative stress, and immunological depression [14]. This next detail is of great importance, and tadpoles treated with different concentrations of the herbicide exhibited a consequential decrease in the activity of main enzyme used in the catalysis of neurotransmitters.

Mammals are also harmed by the use of glyphosate. The long-term toxic impacts on rats were determined by histopathological changes that occur in the stomach, kidneys, liver, brain, spleen, and pancreas [15]. Toxic effects on swine cardiovascular systems were found in Ref. [16].

The UK Food Standard Agency conducted residue testing of glyphosate in bread and found 0.2 mg/kg of glyphosate in 27 out of 109 samples [17]. The USDA divulges the presence of glyphosate in 90.3% of 300 soybean samples at the concentration of 1.9 ppm [18]. Inhalation of glyphosate damages epithelial cell membranes, impairs mitochondrial functions, and damages DNA [19]. Toxicity tests on human hepatic, embryonic, and placental cells witnessed induced necrosis of cells and endocrine disruption only after entering the cell, and the addition of surfactants was found to increase toxicity [20]. Gasnier et al. investigated effects on human liver cells. Concentration of Grands Travaux (the most active formulation of glyphosate) above 2 mg/L inhibited transcriptional activities in estrogen and hepatic cells and above 10 mg/L caused severe cytotoxic effects with DNA damage at concentration of 5 mg/L [21].

4.1 Glyphosate

The Virtual Museum of Molecules and Minerals from the University of Wisconsin-Madison provided information on the glyphosate molecule [22]. Acid dissociation constants are pK_a1 0.8 (first phosphonic), pK_a2 2.3 (carboxylate), pK_a3 6.0 (second phosphonic), and pK_a4 11.0 (amine). The pK_a value is directly proportional to the standard Gibbs free energy. Just as with pH, K_a can be expressed with negative logarithms,

$$pK_a = -\log_{10} K_a$$

It was stated that the molecule tends to dissociate one proton from the most acidic group and associate that proton with the most basic group, forming a dipolar-molecule [23].

Additional protons can be dissociated to form inorganic and organic salts of glyphosate. Roundup is the molecule's most common use and is used as an isopropyl ammonium salt. The molecular formula is $C_6H_{17}N_2O_5P$.

4.1.1 Adsorption of Glyphosate

Sen et al. (2016) analyzed the use of forest soils for glyphosate removal from aqueous solutions [24]. Several binding mechanisms for glyphospate have been suggested for sorption of this herbicide (extremely acid media [25], hydrogen bonds with humic substances [26], and especially covalent bonds with Fe and Al oxides) [26, 27]. The physicochemical characterization of the sample forest soil is provided in reference [24].

To determine removal percentages, a dry soil sample was added to 100 mL of solution with 5–30 mg/L of glyphosphate and stirred for 30 min. The zero-point charge is the pH of the sorbent when the surface has no charge. The soil surface will be protonated by the competition of H^+ ions only if pH of the surface is lower than that of the solution deprotonation of the soil by OH^- ions that will occur.

Sen et al. (2016) studied the effect of pH, adsorbent dose, initial concentration, contact time, and temperature on adsorption. Using a dimensionless equilibrium parameter R, the favorability of adsorption was determined,

$$R = 1/\left(1 + KC_{\text{O}}\right)$$

The above equation solves for this dimensionless parameter, where C and K are the initial concentrations of the adsorbate and the Langmuir isotherm constant, respectively. R was found to be between 0.0022 and 0.013, significantly less than one, indicating favorable adsorption. Freundlich and Dubinin-Radushkevich isotherms were also modeled but found to fit the data only moderately. An optimization study was performed to analyze the effects of dependent variables using ANOVA software [24].

For the optimization, 87.8% glyphosphate removal was obtained at initial pH 12, initial glyphosphate concentration of 25.74 mg/L, adsorbent dose 0.005/50 mL, and contact time of 119.19 min.

4.1.2 Glyphosate Behavior

Organic matter, clays, and inorganic particles with polyvalent cations such as iron and aluminum oxides are important in glyphosate adsorption [28]. Phosphorus present in fertilizers may favor desorption and transport of glyphosate, but Lupin found 88.1% of the applied glyphosate that was retained as opposed to runoff or leaching. An experimentation with undisturbed soil columns and the application of recommended glyphosate rates for weed control were conducted by Lupi et al. (2018). Runoff samples were obtained from a nearby riparian zone and leaching samples from subsurface soil samples [28].

Results concluded that the presence of earthworm casts was linked to reduced runoff and enhanced infiltration. Runoff concentrations exceeded national (SRHRA 2003: 240 mg/L) and internationals' maximum limits (CCME, 2012: 800 mg/L; USEPA, 2017: 700 mg/L) for surface water protection and runoff, being similar to the levels reported by Yang et al. (2015) in a short-term transport glyphosate runoff experiment [28]. There were trace amounts detected in subsurface soil samples, and it was concluded that there is low risk of leaching. Lupi et al. detected concentrations of glyphosate in rainwater from riparian zones adjacent to rural areas and recommended the use of biological degradation and sorption for the consumption of harvested rainwater.

4.2 Conclusion

The application of organic matter in agricultural fields would increase adsorption and infiltration and improve biological degradation of applied glyphosate. Mature compost is evaluated as an adsorbent later in this review. Increased time between the application of pesticides and fertilizers may reduce desorption and transport of glyphosate. No till compared to a conventionally tilled plot of land under previous no till management resulted in higher runoff quantities of glyphosate with no till. This is unfortunate, for no till is highly recommended to reduce erosion, application of pesticide amount was not investigated, and I hypothesize that reduced quantities are needed for untilled soils. The use of buffer zones is strongly supported to decrease surface runoff pollution.

Cheah et al. studied the degradation of f 2,4-D, lindane, paraquat, and glyphosate in sandy loam and muck soils [29]. Degradation of glyphosate was observed to be slow in aerobic and anaerobic muck soils; Cheah hypothesizes that the high adsorptive capacity of the herbicide to muck [30] renders it inaccessible to microbial metabolism. The half-life of glyphosate in sandy loam soils was found to be 19.2 days, but others have reported half-lives of 11.2–22.7 years in soils with strong sorption k [30, 31], rendering it inaccessible to microbial metabolism. The table below provides first order rate constants, half-lives with 95% confidence intervals, and determination coefficients for the four pesticides and three soil conditions [29].

Schappert et al. compared the ability of cover crop mixtures with repeated stubble tillage and glyphosate treatments [32]. Seven weed management treatments are flat soil tillage, deep soil tillage, plowing, single glyphosate application, dual glyphosate application, and a cover crop mixture sown in a mulch till and no-till system. Results showed the worst weed suppression under deep soil tillage (including plowing) and thus is not recommended for it is a labor-intensive and costly practice that hinders weed control and soil conservation. Both cover crop mixtures were successful in weed suppression including the suppression of A. *myosuroides*, which was found to be one of the most challenging weeds. The dual glyphosate application achieved the highest weed control, but a single application was not sufficient to control A. *myosuroides* weeds. It was concluded that cover crops are the best management practice for weed suppression but under years with unfavorable growing conditions for cover crops, stubble tillage, and glyphosate applications may be more efficient methods [32]. Below is a table providing the mean number of weed species with all eight treatments.

5 Heavy Metals in Wastewater

Arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc are common heavy metal pollutants and arise from many anthropogenic sources. Agriculture (fertilizers, animal manures, and pesticides), metallurgy (mining, smelting, and metal finishing), energy production (leaded gasoline, battery manufacture, and power plants), microelectronics, sewage sludge, and scrap disposal can be included in the anthropogenic sources [33]. The main sources of contamination include mining waste, landfill leaches, municipal wastewater, urban runoff, and industrial wastewater. Heavy metals are among the most common wastewater pollutants [33].

Remediation technologies are summarized by precipitation, coagulation, ion exchange, membrane filtration, bioremediation, heterogeneous photocatalysts, and adsorption. During the past few years, microbe-assisted bioremediation and phytoremediation of heavy metals have been investigated as cost-effective technologies in the treatment of wastewater. Constructed wetlands have been actively used to treat heavy metal wastewater from agricultural runoff, mine drainage, and municipal wastes. Aquatic macrophytes, viz. Typha, Phragmites, Eichhornia, Azolla, and Lemnaare, have been successful wetland plants for the removal of heavy metals and metalloids due to their morphological change. Plant uptake is caused by phytostabilization, phytoextraction, phytofiltration, or rhizoremediation. Different plants have different affinities for uptake of heavy metals, some plants even possess barriers to prevent metal uptake, but in high concentrations, uptake is inevitable. This is very worrisome for a large source of heavy metal pollution stems from agricultural practices. To compensate for low metal accumulation, synthetic chelators or ligands such as ethylenediaminetetraacetic acid (EDTA), *S*,*S*-thylenediamine disuccinic acid (*S*,*S*-EDDS), nitrilotriacetate (NTA), and naturally occurring low molecular weight organic acids are used to enhance the availability of heavy metals and increase phytoextraction efficiency [33]. This presents a possibility for the biological treatment of many inorganic or recalcitrant organic pollutants. The physiochemical treatment of heavy metals is discussed below.

5.1 Physical-Chemical Treatment of Heavy Metals

Ion exchange is the displacement of ions in an insoluble material, and the greatest example is the cat ion exchange capacity of soils, where imbedded nutrients are displaced by hydrogen cations produced by autotrophs. In treatment, resin beds are used to trap heavy metals and are later backwashed for regeneration. Coagulation-Flocculation can treat inorganic effluents with low metal concentrations but has high operational costs due to chemical consumption. Membrane filtration can reduce heavy metals, but membrane fouling is a concern, and this topic is not the focus of this chapter.

5.1.1 Adsorption of Heavy Metals with Rice Straw

Nawar et al. studied the adsorption of Fe^{3+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} by rice straw [34]. Rice straw was washed, filtered, dried at 100 °C, and then dried at 500 °C for 3 h. Absorption wavelengths were used for the identification of metal with hollow cathode lamps. Single element solutions of 100 mg/L concentrations were prepared. 20 mL of each solution and known weights (0.1–2 g) of the carbonized rice straw (CRS) were added to 250 mL beakers for contact times ranging from 5 to 120 min. The effect of pH and sorption competition among metal ions was studied as well [34].

Hundred percent removal efficiency was achieved at 0.6 g of carbonized rice straw per 20 mL of metal solution with 100 mg/L concentration for all metals, excluding Mn^{2+} and Cd^{2+} [34].

The effect of pH was significant, and the pH of the solution determined the surface charge of the sorbent and the degree of ionization and speciation of the sorbate.

The Langmuir and Freundlich constants are provided along with graphs of the linear relation in reference [34].

Nawar [34] concluded that treatment of 1 m^3 of wastewater would cost approximately 31.25 L.E or 1.98 usd, making carbonized rice straw an effective adsorbent for the removal of heavy metals.

6 Adsorption by Rice Straw

6.1 Adsorption of 2-Chlorophenol with Rice Straw

Chlorophenols are a group of chemicals produced by adding chlorines to phenol. Phenol is an aromatic compound derived from benzene. Popular in many industrial wastewaters, specifically paper and textile industries, chlorophenols have poor degradability and possess toxic and carcinogenic characteristics [35–37]. Industrial activities such as pharmaceutical, petrochemical, plastic, wood preserving, pesticide, iron, steel, textile, and paper were all reported as major sources of contribution. The microbial degradation of herbicides, especially 2,4-dichlorophenoxyacetic acid (2,4-D), yields numerous chlorophenols as intermediate metabolites, and usage has been limited in most parts of the world [38].

Chlorophenols generally contain a benzene ring, –OH group, and chlorine atoms. As a family, chlorophenols differ greatly among one another in molecular structure and physical and chemical properties. Chlorophenols have a weak acidity and yield salts that are highly soluble in water when reacted with alkaline metals (Sodium and Potassium) [39].

Chang et al. aimed to clarify the effects of surface functionality of rice straw-derived ash (RSDA) on the sorption of 2-CP from wastewater with commercial activated carbon employed for comparison [40]. Rice straw was collected, dried at 25 °C, and burned at 400 and 700 °C in a supply of air for 1 h. RSDA 400 and RSDA 700 were collected, washed with double deionized water, to remove soluble salts, then air dried, passed through a 100 mesh sieve, and stored in a plastic bottle prior to use. Commercial activated carbon (AC) was obtained from Merck, Darmstadt, Germany, for reference. The C, O, and H contents were analyzed using a Heraeus

Elemental Analyzer, Electron micrographs using from a Jeol JSM 6500F scanning electron microscope, and surface functional on original straws and RSDAs using a Thermo-Nicolet Nexus 470 Fourier transformed infrared spectroscopy. The original straws (ORS) and the rice straw-derived ash (RSDA) were subjected to solid-state nuclear magnetic resonance using a Bruker Dsx400WB NMR (CP/MAS) for determining their aliphaticity and aromaticity, and surface area and pore volume were obtained using a micrometric ASAP 2000 surface area analyzer with nitrogen adsorption at 77 K [40].

The effect of agitation was performed with batch reactions at pH 4 and 10 with ORS, RSDA, and AC samples. 0.05 g of adsorbent and 10 mL of 0.01 M $CaCl_2$ were mixed in a series of centrifuge tubes for 1 h, and pH was monitored and adjusted. Agitation was done at 150 rpm, at given time intervals, the tubes were centrifuged, and the supernatants were filtered using a 0.45 μm (pore size) polyvinylidene fluoride syringe filter. A high-performance liquid chromatograph (HPLC, Varian ProStar), which was equipped with an Ultraviolet-Visible (UV-VIS) detector and a C18 column (Supelco 516), was used to analyze the residual 2-CP in the filtrates.

Adsorption isotherms were studied in batch experiments of 2-CP by RSDA and ACs. 0.05 g of adsorbent and 20 mL of 0.005 $CaCl_2$ were used. Initial 2-CP concentrations ranged from 10 to 200 mg/L, and pH ranged from 4 to 10. Centrifuge tubes were sealed with Teflon lined caps, shaken for 24 h, and then centrifuged at 5000 rpm for 30 min, supernatants were filtered using 45 μm (pore size) polyvinylidene fluoride syringe filter, and final concentrations of 2-CP were determined by HPLC.

Adsorption data were fitted with Freundlich and Langmuir models.

Results concluded that H/C and O/C decreased with higher burning temperatures, indicating a more unsaturated and aromatic structure. The FT-IR spectra of the ORS, RSDA, and ACs are presented in reference [40].

The wave numbers of 3500–3200 cm^{-1} of IR broad absorption bands of water molecules are assigned to OH stretching, and those of 3000–2840 and 720–1450 cm^{-1} are assigned to C–H stretching. The wavenumber of 1800–1600 cm^{-1} of IR vibration bend denotes C C of aromaticity and C O/C–O of oxygen-containing functional group stretching, and 1262 cm^{-1} is C–O of aromatic and O–H of phenolic functional groups. On the other hand, 1100–1000 and 790–805 cm^{-1} of IR vibration modes are assigned to the major Si-containing functional groups, such as Si–O, Si–C, and Si O [40]. The ratios of aliphaticity and aromaticity of ORS and RSDA's are given in reference [40].

There was a significant increase in the amount of aromatic C (110–160 ppm) after carbonization especially in samples dried at 700 °C. There existed oxygen content for both ashes, indicating the presence of oxygen containing functional groups on the surface of the ashes, which therefore determined their surface charge properties [41]. Below are the curves obtained from the pH-drift method that gave rise to the PZC of the ashes; the PZC of RSDA 400 was 6.7, and that of RSDA 700 was 9.1. The PZC ratio is correlated with the O/C ratio of the ashes and 700 is higher than 400, which is attributed to the lower O/C ratio. This indicates low oxygen-containing functional groups on the surface. Surface acidity is linked to these oxygen-containing functional groups that have hydrogen bonds, and burning at higher temperatures decreases surface acidity and increases PZC of the ashes. PZC is the point of zero charge or the pH at which the net charge of the surface is equal to zero. The surface charge of the adsorbent is characterized by the ions that lie on the surface of the particle. At a pH lower than the PZC value, the surface charge of the adsorbent would be positive, and anions would be adsorbed. At a pH higher than the PZC value, the surface charge would be negative, and cations would be adsorbed. RSDA 700 had a higher PZC value and therefore greater potential for adsorbance of cations [40].

Surface area and por volume of the RSDA-400 were 7.6 m^2/g and 0.010 cm^3, respectively. RSDA-700 had a surface area of 173.6 m^2/g. An increase in surface area is a result of improved porosity and increased microporosity. The surface area of micropores accounted for 80% of the total surface area, and even the number of large pores increased in RSDA700 (35.2 m^2/g) compared to RSDA-400 (7.6 m^2/g) [40].

The adsorption reaction required a retention time of at least 12 h to reach equilibrium. The RSDA-700 at pH ten adsorbed a greater quantity of chlorophenol than RSDA-400 at pH 4. The effects of pH on adsorption were studied. Adsorption by RSDA-400 decreased from 6.2 to 5.5 m^2/g from pH 4 to pH 7. 2-Chlorophenol is a weak acid with a pK_a of 8.44 and in neutral form is at $pH < 6$. If the pH is increased beyond the pK_a value, electrostatic repulsion dominates between negative charges of the sorbate and sorbent, resulting in a dramatic decrease in 2-CP adsorption at $pH > 7$.

Pure carbon surfaces are considered hydrophobic and desirable for the adsorption of 2-CP. Silica is highly hydrophilic and not considered to contribute to adsorption, nor is the presence of surface oxygen-containing functioning groups, which renders the surface polar or hydrophilic. Previous studies proposed that the adsorption of phenolic compounds on carbon surfaces is mainly determined by dispersive hydrogen bonding and electrostatic interactions between sorbates and sorbents. Functional oxygen groups would be responsible for electrostatic attraction, but is insignificant in the adsorption of 2-CP. RSDA-700 had the greatest surface area, enhanced aromaticity, and the lowest surface acidity causing the greatest adsorption of 2-CP. Water has a higher H-bonding strength than the OH groups of 2-CP, and therefore, oxygen functioning groups caused no increase of adsorption. The maximum adsorption of RSDA-700 was 52 mg/g at pH 4. 2-CP was adsorbed mainly on surface pores, and it is hypothesized that some portions of the surface are not accessible due to steric hindrances and blocking by water molecules. Steric hindrances are the inhibition on molecular binding due to molecular shape.

Comparison to activated carbon indicated that activated carbons had better adsorption than RSDA-700. If the data are normalized to 2-CP adsorption per unit C, comparable results were obtained at pH 4, but at pH 10, AC had significantly greater adsorption. In conclusion, higher burning temperatures increase 2-CP adsorption capabilities and provide argument for rice straw-derived ash as a replacement of activated carbon.

6.2 Adsorption of MG Oxalate by Carbonized Rice Straw

Adsorbents are commonly used to prevent air and water pollution with activated carbon being the most important engineered adsorbent for water treatment. Activated carbon is the most successful and widely used adsorbent. Carbon has a high surface area to molecular weight and has many bonding locations. The physical structure of activated carbon is porous, pore size ranges from less than a nanometer to several thousand nanometers, pore shapes include ink bottle, cylindrical, and V shaped, and capillaries open at both ends. Micropores have effective radii less than 2 nm and contribute to approximately 95% of the total surface of the carbon, mesopores have effective radii from 2 to 50 nm and contribute to about 5% of the surface area, and macropores have effective radii larger than 200 nm and contribute very little to the total surface area. Physical pores contribute to treatment for micro- and mesopore fill with pollutants and increase surface areas for chemical bonding.

There exist chemical and biological methods of water treatment, filtration, coagulation, oxidation, and ion exchange, but to manage the great variety and high concentrations of pollutants, the use of activated carbon adsorption is essential.

Adsorption on activated carbon is highly efficient for the removal of pollutants; however, the production cost and regenerability inhibit large-scale application [42]. Low cost-activated carbons are needed for the removal of various pollutants, including heavy metals, dyes, pesticides, and other organic pollutants.

Rice husk possesses a granular structure, is insoluble in water, and has a high chemical stability and high mechanical strength, making it a good absorbent material [42]. Rice Husk may facilitate the adsorption of heavy metals and other pollutants because of irregular morphology and heterogenous chemical nature [42].

Rice husk was dried and then carbonized at 900 °C under N_2 flow for 5 h. Inert gas and heating rate were fixed at 100 mL/min and 10 °C/min, respectively. Then, the sample was kept at 400 °C for 10 min followed by several washings with distilled water.

Physical Properties were measured using the nitrogen gas adsorption technique using a surface area analyzer with liquid nitrogen at 77 K, and they were specific surface area and pore volume distribution, among others. Prior to experiment, the samples were outgassed at 523 K for 3 h. Adsorption tests of 100 mL of dye solution with NRH/PRH adsorbents were carried out at a temperature of 300 K. Initial MG concentrations (10–30 mg/L) and adsorbent dose (100–200 mg) effects on pollutant removal were investigated. 250 mL samples of 10–30 mg/L malachite green solutions were mixed with 200 mg of NRH/PRH and stirred at 303 K with constant speed of rotation up to 90 min. Temperature effects and pH effects were also measured.

PRH had the capacity to remove up to 90% even for concentrated solution of 30 ppm, 75% with NRH. Rapid uptake occurred for concentrations of 10 mg/L, where 85% of dye can be removed with PRH and 70% of dye removed with NRH after only 45 min. For concentrations of 20 and 30 mg/L, a relatively slow dye uptake can be observed and took 75 min to reach 85% removal with PRH and 70% removal with NRH.

Increases in pH improved the amount of MG absorbed and the percentage removal efficiency. MG is a cationic basic dye as denoted by the presence of the positive nitrogen ions in its structure. In carbon aqueous systems, the potential of the surface is determined by the activity of the H+ ions, which react with the carbon surface [42]. For the carbon surface, the potential determining ions are H^+ and OH^- ions, and complex ions are formed by bonding with H^+ and OH^-. The broken bonds along the surface of the carbon result in hydrolysis [42],

$$\text{Carbon} - \text{OH} + \text{H}^+ \rightarrow \text{Carbon} - \text{OH}_2^{\,+}$$

$$\text{At high pH} : \text{Carbon-OH} + \text{OH}^- \rightarrow \text{Carbon-O}^- + \text{H}_2\text{O}$$

Increased pH causes increased negative charge on the carbon surface and will exhibit cation exchange capacity.

7 Activation

7.1 Activation Agents

The production of activated carbons often entails activation by the application of a certain compound.

Liou (2009) looked to achieve a mesoporous structure in activated carbons produced from sugar cane bagasse and sunflower seed hull [43]. Sugar cane bagasse has a low content and sunflower seed has a high proportion of ash content, and so much information can be obtained from this study. Traditional production of mesoporous activated carbon consists of carbon precursors (lignocellulosic materials, coals, and phenolic resins) in the presence of transition metals, followed by the carbonization and physical activation with steam or carbon dioxide. Recent studies have developed mesoporous activated carbons and have used activation agents of cerium oxide [44], H_3PO_4 and $ZnCl_2$, [45, 46] and simultaneously $ZnCl_2$ and CO_2 [47]; however, Liou states that the mesopore surface area and volume are not high enough and the proposed approaches are complicated and require expensive equipment [43].

Sugar cane bagasse (SCB) and sunflower seed hull (SSH) were first washed with distilled water and dried at 100 °C and then crushed and sieved to obtain uniform grain size of approximately 10 mm × 2 mm. Weight percentages of ash content for SCB and SSH were 3.82 and 11.79 wt%, respectively.

Preparation can be divided into three stages, base leaching, activation, and acid washing. First, SCB and SSM were leached into a 0.5 M NaOH solution and boiled in a glass round flask at 100 °C for 1 h. The solution was drained with distilled water, and the resultant pH was about 7. The material was dried at 105 °C for 24 h. Second, H_3PO_4 and $ZnCl_2$ were mixed with distilled water, and SCB and SSH were impregnated in the acidic solution in the mass ratio of 1–4 (activation agent to dried solid). A weighted amount of impregnated samples was placed in a fixed bed reactor made of quartz and purged with high-purity (99.95%) nitrogen gas at a high flow rate to avoid oxidation. The reactor was inserted into an electric furnace at temperatures ranging from 400 to 800 °C, and the reaction was allowed to continue for 1 h. After activation and cooling to room temperature, 3 M hydrochloric acid was used to remove the phosphorus and zinc compounds. Activating agents and carbon mixtures were refluxed with hot acidic solutions for 1 h. The remaining solid was washed with distilled water and dried at 105 °C for 24 h [43].

Sugar cane bagasse or sunflower seed hull is only base leached with NaOH, without activation, which is labeled SB. Bagasse or hull that is base leached, activated with H_3PO_4 and $ZnCl_2$, and then washed with HCl solution is labeled as SBAH. When acid washing is replaced with water washing, the samples are labeled as SBAW. Raw bagasse or hull washed with distilled water, activated with H_3PO_4 and $ZnCl_2$, and then washed with HCl solution is labeled as SWAH. When acid washing is replaced by water washing, the samples are labeled as SWAW.

Measurement of physical and chemical properties was performed using an inductively coupled plasma-mass spectrometer, a Heraeus elemental analyzer, an X-ray diffractor, a spectrometer, and a scanning electron microscope. Samples were characterized by specific surface area, pore volume, and pore diameter. The specific surface area of each specimen was calculated using the BET method. In the BET method, an assumption of the cross-sectional area of a nitrogen molecule is.162 nm^2. The total pore volume was determined from the amount of adsorbed nitrogen in liquid form at a relative pressure of approximately 0.95. Adsorption tests were conducted with iodine, and titration of the filtrate with $Na_2S_2O_3$ was used to determine quantity of iodine adsorption [43].

The above table shows the purity of the samples. Raw materials had the greatest concentration of metallic ingredients, besides P and Zn elements. Metal elements are clearly reduced in samples that experienced activation. P and Zn quantities decrease when treated with an HCl solution for the improved removal of activation agents. The HCl rinse also greatly reduces the concentration of other metals, and metal concentrations are lower in $ZnCl_2$ than H_3PO_4 activated samples. Explanation is due to the incorporation of phosphate species into the carbon mixture and subsequent difficult removal. When raw materials are base leached, ash content decreases due to the removal of silica in the sample [43].

Results show that base leaching and acid washing increase surface area in all samples. The surface areas for raw bagasse and seed hull were 0.6 and 0.06 m^2/g, respectively. The surface areas of base leached samples were 1.56 and 0.59 m^2/g, respectively. Base leached samples removed ash and increased the quantity of micropores. Base leaching is found to have a greater effect on increased surface area than acid washing, for base leaching is effective in the removal of ash and prevents blocked pores during adsorption. Maximum adsorption is obtained by both base leaching and acid washing.

Base leaching is proposed to have reduced the ash content, which aided activation agents to enter the interior of the carbon tissue, and to have decomposed or softened the organic matter, which facilitated the pyrolysis during the activation reaction [43].

Presented above are graphs that show the BET surface area and iodine adsorption capacity of H_3PO_4 activated samples with different activation temperatures and impregnation ratios. Graphs (a) and (b) show the effect of impregnation ratio on surface characteristics of SCB and SSH samples; when impregnation ratio is increased from 1 to 2, adsorption capabilities are enhanced but decrease with greater impregnation ratios. Graphs (c) and (d) highlight that the greatest adsorption occurs at 500 °C, and exceeding this temperature results in decreased surface area. Contraction and collapse of pores are proposed as the cause for decrease in surface area at high temperatures. Results also displayed greater adsorbent capabilities from SCB as opposed to SSH, warranting the use of lignocellulosic carbonaceous material to produce activated carbons by base leaching and acid washing. If base leaching softens the carbonaceous materials, maybe less recalcitrant forms suffer from base leaching and thermal decomposition [43].

The nitrogen adsorption-desorption isotherm of H_3PO_4 activation samples at impregnation ratios of 2 for SCB-based carbon (a) and SSH-based carbon (b) was described by Liou [43].

The curves are Type 1 isotherms without an apparent desorption hysteresis loop, which indicates a highly microporous structure. At a relative pressure of 0.4, a hysteresis loop was exhibited and indicates a type IV isotherm as a characteristic of a mesoporous structure. Base leaching decreases ash content and leaves several tiny pores, activation agents permeate the new voids and promote the release of volatiles converting micropores to mesopores, and acid washing removes the activation agent enlarging the micropores and increasing mesoporosity. Optimum temperature was carbonization at 500 °C [43].

The above table presents pore volume, BET surface area, mesopore surface area, and % yield. Due to the intensive measures of this study, the wide array of variables tested in production, the high surface areas achieved, and values from this study will be used for comparison of other low-cost adsorbents. $ZnCl_2$ activation produced a higher mesopore volume and mesopore surface area than H_3PO_4 and is due to the inability for acid washing to completely remove $H_3PO_{4.}$ The proportion of SCB and SSH mesopore volume at 500 °C approached 77% and 72.2%, respectively, exceeding the values of conventional activated carbon. An analysis of physical properties with XRD patterns of raw and activated materials displayed a broad peak at $2\theta = 22.5°$ for raw materials. This peak is a typical silica characteristic, and its removal in activated samples suggests ash removal. Kennedy et al. reported Peaks at $2\theta = 45°$, which represent the creation of pores along the direction of the graphic structure [46]. If it is true, a more well-organized aromatic carbon would be produced as opposed to amorphous-like carbons.

Liou also conducted a thermogravimetric analysis to observe the change in mass over the period of thermal decomposition [43].

The thermogravimetric analysis (TGA) displayed mass losses in three temperature zones, 200, 200–450, and 450–800 °C. Researchers do not fully understand the pyrolysis paths of activation due to its complex series of reactions. The TGA of this study shows a small initial mass loss of both H_3PO_4 and $ZnCl_2$ activation, indicating chemical reactions with organic matter and subsequent depolymerization of celluloses and lignin into intermediates with smaller molecular mass. Gaseous volatiles of H_2O, CO, CO_2, CH_4, and aldehydes occur simultaneously. This initial mass loss was proposed by Jagtoyen and Derbyshire [48] to be the loss of aliphatic character, which brings an increase in aromaticity by rearranging the atomic structure. The mass loss in the second stage is likely the gradual expansion of the volumetric structure, which reduces the release of volatiles. Olivares-Marin et al. [49] show that the mass loss deceleration at 250–500 °C with H_3PO_4 may be the result of cellulose phosphorylation simultaneous cross-linking reactions among carbon, oxygen, and hydrogen, which may also control the activation of samples rather than decomposition. As reaction temperature increases, so does the formation of a mesoporous structure. The third mass loss is caused by the boiling and melting points of the activation agents. This mass loss can be attributed to the loss of activation agents and a few volatiles [43].

7.2 Physical Activation

Activated carbon can be prepared by physical or chemical activation. Physical activation is composed of two steps: carbonization at temperatures (500–1000 °C) in an inert environment to eliminate oxygen and hydrogen elements and thermal activation at the same or higher temperature in the presence of an oxidizing agent (H_2O, CO_2, or both). With chemical activation, dehydrating agents (e.g. $ZnCl_2$, H_2SO_4, and KCl) allow simultaneous pyrolysis and activation.

Bouchelta et al. state that organic material with high carbon contents like wood, coal, lignite, and coconut shells has been the common precursor for activated carbon, but in recent years, agricultural by-products have been used as sources [50]. Byproducts include cherry stones, olive stones, oil palm stones, apricot stones, almond shells, sugar cane bagasse, walnut shells, cotton stalks, and date stones.

Date stones were used in this study to produce activated carbon. Composition is 42% cellulose, 18% hemicellulose, 25% sugar, and other compounds, 11% lignin and 4% ash. Pyrolysis was conducted under nitrogen flow and activation under water vapor. Pyrolysis of the raw material was carried out with a horizontal tubular furnace within a quartz tube [50].

Twenty grams of date stones were placed in the reactor and at different pyrolysis temperatures of 500, 600, 650, 700, and 800 °C. Nitrogen flow rate was 100 cm^3/min, and heating rate was 10 °C/min for all samples. Once pyrolysis temperature had been reached, it was maintained for 1 h. The chars were then physically activated at 500, 600, 650, 700, or 800 °C for 0.5, 1, 2, 3, or 6 h under nitrogen flow of 100 cm^3/min saturated in steam. CO, CO_2, H_2, and H_2O were evacuated by an extractor hood, and the samples were left to cool at room temperature under N_2 flow rate. Granular and powdered activated carbons were produced [50]. The yield of pyrolyzed date stones is the mass of the final product over the mass of the raw material.

The yield decreased with increasing temperature, and Bouchelta stated that the optimum temperature is 700 °C for a significantly lower yield, which was not obtained with increasing temperatures past this point. Decreases in yield from 500–650 °C are attributed to the removal of volatile matter during decomposition of major compounds such as cellulose (long polymers of glucose without branches) and hemicellulose (w/various branched saccharides). Above 700 °C, there is little decrease in yield for the hemicellulose and cellulose are already decomposed. What remains is lignin, which decomposes slowly up to 900 °C. Bouchelta et al. stated that the degradation of cellulose and hemicellulose creates porosity, which aids degradation of lignin by improving contact with oxidizing agent.

At constant temperature, yield dramatically decreases with hold times from 0.5 h to 0.6 h, 24.51–13.62%. At 700 °C, the endothermic reaction of carbon and water to produce carbon dioxide and hydrogen is thermodynamically more favorable and faster.

N_2 adsorption isotherms are shown above and are type 1 isotherms according to the IUPAC classification, representing a microporous structure with rather narrow pore size. The BET surface area and micropore volume increase with the hold time, and at 700 °C, the stones undergo partial graphitization with the formation of graphene structures. Graphene structures are porous and possess a high surface area. Fourier transformed Infrared analysis showed that raw material possessed functional groups of alkene, ester, aromatic, ketone, alcohol, hydroxyl, ether, and carboxyl. Bands at 3400, 2926, 2870, and 1640 cm^{-1} disappeared, indicating the removal of water and aliphatic compounds. A new band appeared at 1540 cm^{-1}, and this band is assigned to the C=C skeletal stretch and indicates an increase of aromaticity.

This research supports the production of activated carbon without chemical activation, but research comparing the two processes' effect on adsorption is needed for further evaluation [50].

7.3 Physical vs. Chemical Activation

A well-cited article by Reinoso and Sabio prepared lignocellulosic materials (almond shells and olive and peach stones) by either physical or chemical activation [51]. Physical activation was via gasification (uncatalyzed and iron catalyzed) in CO_2 or in a water nitrogen mixture. Chemical activation with $ZnCl_2$ was used for comparison.

Physical activation is carbonization in an inert atmosphere. An inert atmosphere is necessary to avoid the volatilization of carbon and to produce a char as opposed to ash. The resultant char from physical activation is subjected to controlled gasification at high temperatures with steam, CO_2, air, or a mixture. Gasification eliminates the more reactive carbon and increases porosity.

After carbonization, hydrogen, oxygen, and nitrogen are removed in the form of gases and tars, and a carbon skeleton remains. Weight losses compared to carbonization temperature agreed with earlier studies and states losses from 300 to 470 °C).

8 Compost as an Adsorbent

Agricultural waste is not a waste product, and its fate is never landfill disposal. If left on fields, agricultural waste can be used to repress weeds, reduce pesticide application, reduce erosion, provide organic matter, replenish nutrients loss to crops, and feed the soil ecosystem. Although there are immense benefits to leaving crop residue on feeds, there exist few operations that follow this practice. This is because crop residue is valuable for many other industries, i.e., sileage, livestock bedding, ground cover, and biogas production. Best management practice would be to use agricultural waste that has already been removed and produced through material processing.

Sustainability in agriculture is a dire concern, but an equivalent one exists in the treatment of polluted water. The need for agricultural waste far exceeds its production, and the best solution is the usage of food waste and manure/sludge. Manure and food waste, unlike agricultural residue, are treated as waste. Food waste and sludge are disposed of in landfills, and manure waste management is often a major contributor to greenhouse gas emissions. It is well known that composting is the best management practice for the treatment of manure, reducing volatilization and nutrient losses, dependency on landfills, and producing a nutrient-rich humic substance.

Increasing the number of products from composting will aid its adoption; since any carbon source can be used to produce activated carbon, I will explore the use of compost as a carbon source. Compost is dependent on a rich carbon feedstock (crop residue, leaves, and saw dust) to maintain a high C/N ratio, reduce nitrogen losses, and aid porosity and subsequent tortuosity. Food waste and manure are rich carbon sources as well, but manure and sludge contain high amounts of nitrogen, heavy metals, and other impurities. Activation and carbonization will remove these impurities but produce pollutant gases and wastewater. The incorporation of manure will also increase the dosage of activation agents, bases, and acids, for activated carbon production without significance of a carbon production. I hypothesize that the composting reaction will aid the production of activated carbons for the rich quantity of humic substances and the biological degradation of the initial feedstock, which may increase carbon density.

Keshtkar et al. stated that there are abundant cellulose, hemicellulose, and lignin present in compost, which are only degraded to a limited degree [52]. Bilitewski et al. tried to prepare activated carbon from poultry dropping but concluded high ash content made for a low-grade carbon [53]. Lima and Marshall produced granular activated carbons from poultry litter and cake using steam activation and argued that the adsorptive properties are dependent on activation conditions [54].

Qian et al. presented a study to prepare a high-surface area activated carbon from cattle-manure residue (CMC) from anaerobic digestion [55]. Manure residue was washed, dried at 105 °C for 12 h, milled and sieved, and activated with zinc chloride and phenol prior to carbonization. Five to 40 g of $ZnCl_2$ were dissolved in 200 mL of distilled water, and then 20 g or dried manure residue was mixed at 85 °C for 2 h. The mixtures were dried at 110 °C for about 24 h. The $ZnCl_2$ impregnated dried manure residue was pyrolyzed in a horizontal tubular furnace under nitrogen flow of 300 mL/min, temperatures varied from 400–900 °C, and different retention times were conducted. The activated carbon (AC) was washed with 3 M HCl, filtered, and rinsed until the washed solution was free of zinc ions. The AC was then dried at 105° in an oven for about 12 h and weighed to calculate yield. CZ 14405 represents a $ZnCl_2$/CMC ratio of 1–4 (first two numbers), a pyrolysis temperature of 400 °C (third number), and a carbonization of 0.5 h (last two numbers).

N_2 adsorption-desorption isotherms were measured on a surface area analyzer at a liquid nitrogen temperature of 77 K, thermogravimetric analysis was used to determine pyrolysis behavior, and phenol was used as an adsorbate to inspect the capability of the activated carbon.

The yield of activated carbon ranged from 35.3 to 47.5% of the initial mass of CMC. The yield increased at low $ZnCl_2$/CMC ratios up to 0.5 but gradually decreased from 0.5 to 2. Oxygen and Hydrogen atoms had to be removed as H_2O, CO, CO_2, CH_4, and aldehydes or by distillation of tar. Yield depends upon the amount of carbon removed by binding with O and H atoms. Low yields were experienced without $ZnCl_2$ impregnation because a large amount of carbon was removed as CO, CO_2, and CH_4 and by tar coupling with O and H atoms. Carbonization with low $ZnCl_2$ impregnation ratio resulted in higher yields (47.5%) since $ZnCl_2$ removed O and H from the CMC as H_2O and H_2 instead of hydrocarbons. Low yields with higher $ZnCl_2$/CMC ratios are hypothesized to be a result of enhanced carbon burn off from enlarged pore size [55].

According to the IUPAC classification, the carbon prepared without activation exhibited a type II isotherm, which means a nonmicroporous development. Carbon prepared from 0.25 to 1.5 exhibited steep type I isotherms with a small hysteresis loop of type H_4. The adsorption curve rose at relative pressure less than 0.1 and then plateaued with increasing relative pressure; the adsorption and desorption branches were parallel, indicating highly narrow microporous materials with slit-like pores. At $ZnCl_2$/CMC ratios exceeding 2, the increment of adsorption was significant between every pressure range, and the isotherms became a combination of type I and II with a hysteresis loop of type H_2, indicating a large amount of mesopores.

The maximum BET surface area (S_{BET}) and maximum micropore surface area (S_{MI}) were around 2170 and 1580 m^2/g, respectively. Both S_{BET} and S_{MI} increased with increased $ZnCl_2$/CMC to a ratio of 1.5. Beyond 1.5, S_{MI} decreased sharply from 1800 m^2/g to zero and is due to the behavior of mesopore surface area (S_{ME}). At ratios less than 1, S_{ME} was constant or only slightly increased, at ratios of 1–1.5, S_{ME} increased gradually, and at ratios above 1.5, S_{ME} increased sharply to a maximum value of 2040 m^2/g. Total pore volume was found to be directly proportional to the $ZnCl_2$/CMC ratio, but the micropore volume (V_{mi}) and the mesopore volume (V_{me}) behaved similar to S_{MI} and S_{ME}. Results concluded that $ZnCl_2$ created new pores and enlarged existing ones. A temperature of 400 °C and a holding time of about 0.5 h were found to be optimum.

Thermogravimetric analysis revealed a small amount of weight loss at 30–120 °C corresponding to a release of moisture, and a significant weight loss from 200 to 500 °C accompanied by a large peak at the temperature of 360 °C was assigned to the degradation of CMC and distillation of tar. Weight loss occurred in a broad manner above 500 °C, indicating that the basic structure of carbon was already readily formed [56]. The presence of $ZnCl_2$ had a significant effect on decomposition due to its dehydration effect and restriction of tar formation [57]. Qian found that the impregnated CMC basic structure was readily formed at 400 °C, whereas temperatures from 450 to 600 °C were considered preferable in literature [55].

Phenol adsorption plots are provided above. The results suggested that there was favorable adsorption of phenols by the activated carbons. Results demonstrated that heterogeneity of carbon decreased with increased temperature and $ZnCl_2$ quantity from 400 to 900 °C and from a 32 to 52 ratio. Adsorption capacity was found to decrease with increased heterogeneity.

Qian concluded that cattle manure compost could yield high quantities of activated carbon (47.5%) by activation with zinc chloride. That activation could be carried out at 400 °C for 0.5 h, and that acid washing could develop porosity by the removal of impregnated $ZnCl_2$ and volatilization of $ZnCl_2$ at 728 °C. The maximum BET surface and total pore volume of the carbons were 2170 mg^2/g and 1.7 cm^3/g, respectively, and it was concluded that pore size could be adjusted by $ZnCl_2$ ratio, activation temperature, and retention time. In conclusion, cattle manure compost was demonstrated to be an excellent candidate for the manufacturing of activated carbons.

8.1 Compost Biosorption

Compost is a porous medium capable of adsorbing various organic and inorganic compounds [58]. Compost has a high amount of organic carbon, and Pushpa et al. investigated the use of compost as a low-cost adsorbent of malachite green. Compost was prepared by layering cow dung, kitchen waste, and saw dust and then inoculating with an effective microorganism spray and adding water and jaggery (cane sugar) [59]. After 30 days, the compost was air dried at 70 °C for 2 h.

Batch mode adsorption of MG was conducted, and the effects of pH, contact time, adsorbate concentration, adsorbent particle size, and adsorbent dose were determined. Hundred milliliter of dye solutions were taken into 250 mL Erlenmeyer flasks of different initial concentrations (50–1000 mg/L) at pH 8 by adding fixed amount of sorbent. Five equilibrium isotherm models were used to fit the experimental data,

$$\text{Freundlich model}: Q = K_{\mathrm{f}} C_{\mathrm{f}}^{1/n}$$

where K_f is the Freundlich constant (mg/g), and n is the Freundlich exponent;

$$\text{Langmuir model}: Q = \frac{Q_{\max} b C_{\mathrm{f}}}{1 + b C_{\mathrm{f}}}$$

where $Q_{\max}$ is the maximum dye uptake (mg/g) and b is the Langmuir equilibrium constant (L/mg).

$$\text{Redlich-Peterson Model}: Q = \frac{K_{\mathrm{RP}} C_{\mathrm{f}}}{1 + a_{\mathrm{RP}} C_{\mathrm{f}}^{\beta_{\mathrm{RP}}}}$$

where K_{RP} is the Redlich-Peterson isotherm constant (L/mg), a_{RP} is the Redlich-Peterson isotherm constant, and β_{RP} is the Redlich-Peterson model exponent.

$$\text{Sips model}: Q = \frac{K_{\mathrm{S}} C_{\mathrm{f}}^{\beta_{\mathrm{S}}}}{1 + a_{\mathrm{S}} C_{\mathrm{f}}^{\beta_{\mathrm{S}}}}$$

where K_{S} is the Sips model isotherm coefficient (1/g) β_{S}, a_{S} is the Sips model coefficient (1/mg), and β_{S} is the Sips model exponent.

$$\text{Toth model}: Q = \frac{Q_{\max} b_{\mathrm{T}} C_{\mathrm{f}}}{(1 + \left(b_{\mathrm{T}} C_{\mathrm{f}}^{1/n_{\mathrm{T}}}\right)^{n_{\mathrm{T}}}}$$

where $Q_{\max}$ is the maximum dye uptake (mg/g), b_{T} is the Toth model coefficient, and n_{T} is the Toth model exponent.

Adsorption is dependent on the pH of the solution. Pushpa et al. investigated pH effects by agitating 100 mg/100 mL of MG in solutions with various amounts of adsorbents at pH from 2 to 9. Maximum adsorption capacity was observed at pH 8, and recorded uptake was 23.8 mg/g. Dye removal efficiencies increased from 49 to 95.1% from pH 2–8. This relationship may be explained by the solution containing excess H^+ ions in the solution that protonates the surface of the adsorbent and causes a smaller concentration gradient and weakened electrostatic attraction among dye and adsorbent. This decreases the quantity of dye adsorbed and rate of adsorption.

The effect of dye concentrations was investigated with malachite green dosage from 50 to 1000 mg/L and a fixed amount of adsorbent at pH 8. MG removal efficiency decreased (96.8–66.3%), but the amount sorbed increased (12.11−136.6 mg/L). Higher concentrations cause greater driving force for transporting cations but decrease the number of binding sites. Effects of adsorbent particle size were analyzed with 0.6, 1.18, and 2.36 mm particles of compost. Decreasing particle size increases surface area and enhances dye uptake capacity. Although an inverse relationship between particle size and sorption performance was observed, only a 0.6% increase was found between 0.6 and 1.18 mm compared to 1.18 and 2.36 mm. The smaller differences in biosorption performance among small particle sizes may help reduce the use of energy intensive practices for the production of small adsorbents. Large particles were also found to be desirable in sorption for they can tolerate extreme operating conditions [60]. Absorbent dosage was the last experiment conducted [59]. Adsorbent dosage varied from 2 to 12 mg/L at pH 8, a dye concentration of 100 mg/L, and a particle size of 1.18 mm. Removal efficiencies increased with adsorbent dosage. Biosorption percentage increased from 76.22% (2 g/L) to 95.67% (4 g/L), but increased dosage past (4 g/L) had no influence on percent removal. MG uptake capacity was found to be reduced from 23.9 mg/g at (4 g/L) to 8.25 mg/g at (12 g/L). Increasing biosorbent concentration increased the number of binding sites but decreased dye uptake; this phenomenon may be a result of complex interactions of several factors. Responsible factors include the inability of dye molecules to cover all the binding sites decreasing dye uptake. Freundlich isotherm was determined to be 0.33 (<1), indicating favorable adsorption.

The textile industry uses a gross amount of dyes in producing textile products, and fibers absorb around 50% of applied dyes, which produces a highly concentrated wastewater [61]. As an environmental pollutant, dyes cause chronic effects on organisms and diminish photosynthetic activity, and disassociation causes the release of carcinogens.

Dyes used in textile industries can be both anionic and cationic. Congo Red is a common anionic dye, which easily dissolves and is commonly found in the form of red crystal [62]. Congo red is very adhesive to cellulose fiber but as a constitute of wastewater causes increased BOD and water-borne diseases [63].

Conventional wastewater treatment removes coloration through filtration, coagulation, flotation, etc. but is inadequate treatment for many color variations [64, 65]. Kristanto et al. (2017) conducted a study to assess compost as a sorbent for the treatment of Congo Red dye, analyzing optimum compost dosage, particle size, and column height vs. dye percentage removal and adsorption capacity data [62].

Compost was obtained from a municipal solid waste composting processing unit with pH 7.6, a C/N ratio of 17, and a water content of 42%. Maturity was determined from these parameters in accordance with the Indonesian National Standard of SNI: 19-7030-2004 for matured compost quality (National Standardization Agency of Indonesia, 2004). The compost was then sieved through 0.85–1, 1–2, and 2–2.36 mm mesh and then oven dried at 70 °C for 2 h. The adsorbate was artificial and contained a Congo Red dye concentration of 200 mg/L. The pH of the Congo Red dye and distilled water solution was lowered to 3–3.5 by adding 1 N hydrochloric acid. Acidic conditions were created for compost has a carboxyl matrix and under alkaline conditions is anionic and unable to bind to anionic dyes.

Congo Red dye was contacted with dosages of compost (1–12 mg/L) of various particle sizes (0.85–1, 1–2, and 2–2.36 mm) in 100 mL glass bottles to simulate a batch reactor. The mixtures were shaken at 150 rpm for 2 h followed by centrifugation for 5 min [62]. After determining optimum dosage and particle size of adsorbent, an experiment testing of compost sorbance was conducted in packed towers.

Adsorption capacity was determined by dividing the difference in dye concentration (mg/L) by the mass of sorbent (g) and multiplying by the volume of solution (mL),

$$q_{\mathrm{e}} = \frac{\left(C_0 - C_{\mathrm{E}}\right)}{m} V$$

Langmuir and Freundlich isotherm models were common in wastewater engineering and were used for data analysis.

The batch experimental results concluded that sorbate percent removal increased until it reached around 20% removal at 8 and 11 g/L. Adsorption capacity displayed a similar trend but peaked at 5.33 mg/g with an 8 g/L dose and then decreased. Dosage exceeding 8 g/L had no effect on percentage removal, and it decreased adsorption capacity [62]. The column experiment showed percent removal increase with increase in column height due to increased surface area and sorbate/sorbent contact. Repeated trials caused decreases in adsorption for dye accumulation prevented the binding of future sorbates. In the first sample, 27.06% removal was observed from the 20 to 40 cm outlet and 20.27% between 60 and 80 cm outlet. Later trial experienced higher percentage removals in the 60–80 cm outlet as opposed to the 20–40 cm outlet, indicating that sorbent replacement is required.

The table below shows the adsorption capacity of the adsorbent in the column experiment.

Unlike Pushpa, Kristanto witnessed a greater R^2 value with the Langmuir model as opposed to Freundlich, indicating a monolayer homogeneous adsorption. I believe this to be a result of experimental methods, and in a packed tower, sorption into multiple layers seems less likely than in a batch reactor due to decreased retention time. It was concluded that optimum dosage to treat 200 ppm Congo Red dye was 8 g/L and optimum particle size was 1–2 mm [62]. The most efficient column height was 60 cm, but after saturation has occurred, replacement of sorbent is required.

9 Adsorption of Malachite Green by Fig Leaves

The textile industry is not unique in its excessive use of dyes. Manufacturing of paper, pharmaceuticals, leather, rubber, plastics, cosmetics, printing, and foods uses dyes for synthetic colors. Malachite green is a common used dye and is popular for dyeing cotton, leather, wool, silk, paper, distilleries, jute, and more, with usage also as a fungicide, antiseptic, and antiparasitic agent. Oral consumption by animals has been found to be toxic, carcinogenic, mutagenic, and teratogenic [66–68]. This dye is prohibited in several countries, usage in food production is banned in the United States, and testing is conducted in fish for remnants of the dye. Many dyes are stable to heat, light, and oxidizing agents, which hinders conventional wastewater treatment. The usage of many low-cost adsorbents has been investigated for the high cost of activated carbon. Extensive research has been conducted in [69], and studies using bagasse fly ash [70], Pithophora sp. [71], bottom ash [72], Arundo donax [73], oil palm trunk fiber [74], Sugarcane bagasse [75], neem leaves [76], Prosopis cineraria [77], Pleurotus ostreatus [78], Limonia acidissima [79], Rice husk [80], sawdust [81], etc. have been reported for the removal of MG from aqueous solution.

Gebreslassie (2019) investigated the use of chemically activated *Ficus Cartia* leave powder (AFLP) as an adsorbent for the removal of malachite green, and effects of dye concentration, adsorbent dosage, solution pH, temperature, and contact time were studied. Adsorption isotherm, kinetics, and thermodynamics of adsorption of MG were also investigated [69].

Fig leaves were collected, rinsed, dried, and activated with 0.1 N phosphoric acids in a weight ratio of 1:2 (w/w) and heated in a muffle furnace at 200 °C for 24 h. The carbonized material was washed again and then soaked in $NAHCO_3$ solution for 24 h to remove the remaining acid. After that, the product was dried in an oven at 105 °C for 24 h, ground, and then sieved through a 200 mesh (>75 μm) sieve.

The influence of contact time on percentage removal was investigated at dye concentrations varying from 50 to 500 mg/L. Absorbent dose and pH were held constant at 400 mg and 10, respectively. Batch adsorption reactions were used to evaluate dependent variables on adsorption.

The influence of contact time on percentage dye removal was investigated with different initial dye concentrations (50–500 mg/L) whilst keeping adsorbent dose (400 mg), solution pH [10] constant, and temperature (298 K) constant [50].

The rate of adsorption decreases with concentration time as a result of electrostatic repulsion between adsorbed MG cations and the dye solution. Equilibrium in adsorbate concentration was attained at 200 min when the maximum MG adsorption onto adsorbent was reached.

Increasing initial dye concentration decreased dye removal percentage (97.96 to 40.34%) with increased MG concentration from 50 to 500 mg/L but increased the amount of dye adsorbed per unit mass adsorbent from 12.25 to 50.43 mg/L [70].

The effect of adsorbent dosage (50–500 mg) was evaluated, and the removal percentage increased was found to increase from 36.12 to 96.96%. The consequence is that the amount of dye adsorbed on each particle surface decreased from 72.24 to 19.39 mg/g.

The pH of solution has a strong effect on the adsorption of Malachite Green. Percentage of dye removed increased from 24.12 to 94%, and the amount of dye adsorbed increased from 7.03 to 23.41 mg/g when pH was increased from 2 to 12. Increasing solution pH decreases the amount of bound hydrogen molecules and subsequently the amount of positively charged surface particles. The greater number of negatively charged surface particles present in the solution increases adsorption of the positively charged adsorbent. Adsorption was found best represented by the Langmuir Isotherm; this assumes monolayer adsorption of adsorbate with a finite number of binding sites on the surface. Gebreslassie studied intraparticle diffusion rates, and the below equation represents time-dependent adsorption capacity [69],

$$q_t = k_{\mathrm{id}} t^{1/2} + C$$

where q_t is the adsorption capacity at time t, C is the intercept, and k_{id} is the intraparticle diffusion rate constant. Over means of transport will affect adsorption capacity given that there is convective flow as in a packed tower. The larger the intercept value, the greater contribution of surficial adsorption.

The values of R^2 for intraparticle diffusion parameters were found to be in the range of 0.814 and 0.944, indicating that the adsorption followed intraparticle diffusion. Below is a graph of adsorption capacity per unit time vs. $t^{1/2}$. Gebreslassie states that because the graph exhibits two slopes, there exist two stages of adsorption, an initial bulk diffusion followed by an intraparticle diffusion. The y intercept is nonzero, indicating a significant contribution of boundary layer diffusion on adsorption capacity per unit time. C values increased with increased initial dye concentrations, showing increased initial surficial adsorption.

Temperature was found to be very influential [69], and varying temperature from 298 to 328 K resulted in increased adsorption capacity and rate of adsorbance. Thermodynamic parameters such as Gibbs energy (ΔG), enthalpy of adsorption (ΔH), and entropy of adsorption (ΔS) were examined using the relations given below,

$$\Delta G^0 = -RT \ln K_{\mathrm{C}}$$

$$K_{\mathrm{C}} = \frac{C_{\mathrm{ad}}}{C_{\mathrm{e}}}$$

$$\ln K_{\mathrm{C}} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

where R is the gas constant (8.314 J/K mol), T is the temperature (K), K_{c} is the equilibrium constant, and C_{ad} and C_{e} are equilibrium concentrations on the adsorbent and the solution, respectively.

10 Adsorption by Grasses

Even passive treatment methods, such as constructed wetlands and compost bioreactors, possess a large initial cost, and the potential utilization of indigenous South African grasses for acid mine drainage remediation was investigated [82]. Greben et al. (2009) studied the adsorption of acid mine drainage on fermented grass cuttings. Fermented grass cuttings were found to remove up to 86% of sulfates [83]. Ramla and Sheridan prepared the following beakers: Beaker 1: Hyparrhenia hirta and AMD solution (HH), Beaker 2: AMD solution control (Control), Beaker 3: Hyparrhenia hirta and Zantedeschia aethiopica growing in the AMD solution (HHZ), Beaker 4: Hyparrhenia hirta with attached soil from a Zantedeschia aethiopica root and AMD solution (HHM), and Beaker 5: Setaria sphacelata and AMD solution (SS). Samples were taken frequently over a 70-day period.

Bioreactor four (HHM) and bioreactor three (HHZ) achieved a 98 and 97% iron removal by 70 days. The best sulfate reduction occurred in bioreactor 4 (HHM), with 80% sulfate removal. Consistent with other research [84], it was shown that it is advantageous to include a soil or sludge inoculum from an anaerobic environment.

11 Acid Mine Drainage Adsorption

Acid mine drainage (AMD) results in gross amounts of pollutants from the metal and coal mining industries. Heavy metals unlike organic pollutants are not biodegradable. Treatment including chemical precipitation, ion exchange, membrane filtration, reverse osmosis, and activated carbon adsorption is associated with high cost and labor-intensive practices, which led Zhang to study the adsorption of PB(II), CU(II), and ZN(II) using dairy manure compost (DMC) [85]. It is hypothesized that ion exchange is responsible for the biosorption of heavy metals, and so under batch experimentation, the release of Ca^{2+}, Mg^{2+}, K^+, Na^+, and H^+ was determined while adsorbing Pb, Cu, and Zn in a single metal system.

The dairy manure compost was oven dried at 105 °C for 24 h, ground, and passed through a 1 mm sieve. Standard stock solutions of Pb, Cu, and Zn (1000 mg/L) were used to prepare appropriate concentrations of each heavy metal in single, binary, and ternary adsorption studies. In single metal ion adsorption experiments, 0.3 g of DMC and 20 mL of Pb, Cu, or Zn solution (adsorbent does, 15 g/L) were put into centrifuge tubes. The effect of pH on Pb, Cu, and Zn adsorption on DMC was studied with experimentation of solution pH from 1 to 8 by the addition of HNO_3 or NaOH. Sodium nitrate was used to study the effects of ionic strength on heavy metal adsorption.

Results concluded in binary and tertiary studies; metals competed with one another for adsorption. Competitive ability followed the order of Pb > Cu > Zn. The optimum pH of Pb, Cu, and Zn ion adsorption occurred at 3.5, 4.5, and 5.5, respectively. There was a significant release of Ca^{2+}, Mg^{2+}, K^+, Na^+, and H^+ after interaction showed heavy metal adsorption from predominantly cation exchange. Repeated cycles were tested to investigate the regeneration and reutilization of the adsorbent, HCl was used as a desorbing agent, and little variation in adsorption capacity existed until the third cycle, where a nonsignificant decrease occurred [86].

12 Mycoremediation of Congo Red Dye by Filamentous Fungi

Congo red, a diazo dye (containing N_2), is considered xenobiotic (synthetic) and recalcitrant to biodegradation. Several fungi have demonstrated the capability of transferring azo dyes to nontoxic products using laccases [86]. A successful dye is stable during washing, and in light, these factors help promote the use of recalcitrant compounds. Azo dyes are the largest class of dyes with the greatest variety of colors

[87–89]. They are typically not degraded under aerobic/conventional treatment, but the azo linkage can be reduced to form aromatic amines, which are colorless but toxic and carcinogenic. Congo red is a common diazo dye that is recalcitrant and carcinogenic for the aromatic amine group [90–92]. Several ascomycetes and basidiomycetes fungi have been reported to produce lignin degrading enzymes, and lignin is a recalcitrant natural organic compound. Enzymes include laccase, Lignin Peroxidases (LiP), and Manganese Peroxidases (MnP) [93]. Bhattacharya et al. demonstrated the aerobic biodegradation abilities of six fungal species, Aspergillus niger, Aspergillus flavus, Aspergillus oryzae, Penicillium chrysogenum, Cladosporium rubrum, and Pleurotus ostreatus for the azo dye Congo red and the factors influencing the degradation [86].

13 Natural Sorption Processes

Sorption occurs commonly in natural systems where there are fluid solid boundaries [29].

The extraction of drinking water from wells rather than surface water is for the removal of pollutants via biological, chemical, and physical treatment with emphasis on cat-ion exchange. Organic materials in soils are important for the binding of organic compounds, while clay minerals or oxidic surfaces are important for the binding of ionic species.

13.1 Adsorbents

Natural adsorbents include clay minerals, natural zeolites, oxides, or biopolymers. Engineered adsorbents include carbonaceous adsorbents, polymeric adsorbents, oxidic adsorbents, and zeolite molecular sleeves. Adsorbents from agricultural waste are carbonaceous engineered adsorbents.

Activated Carbon is produced from organic carbons subjected to dehydration and carbonization. Raw materials are first heated at 400–500 °C to remove volatile matter, and then partial gasification at 800–1000 °C with high temperature steam, air, or CO_2 produces a porous nature. Chemical activation is where the materials are impregnated with strong acids, bases, or salts prior to carbonization. Activated carbons are the most widely used adsorbents in water treatment.

Stringent demands for water quality and specific absorbance capacities limit the application of low-cost adsorbents in water treatment, but in wastewater treatment, adoption should be strongly supported.

13.2 Surface Area

Solid surfaces containing active, energy-rich sites able to interact with solutes in an adjacent aqueous phase allow the adsorption and removal of pollutants from fluid phase. The solid surface is considered the adsorbent and the species that will be adsorbed, the adsorbate. Changes in environmental conditions and in fluid properties have great consequences on adsorption. Species concentration, temperature, pH, are well-known variables that affect adsorption. Adsorbed materials commonly revert back to the fluid phase, and this action is referred to as desorption.

Adsorption is a surface phenomenon and is strongly dependent on the surface area of the adsorbent. Gibbs free energy, *G,* is a fundamental equation used to describe thermodynamic potentials. Thermodynamics is used to describe energy transfers, and Gibb's free energy is a function of temperature (T), pressure (p), and composition of the system (number of moles, n_i) and of the surface, A. The fundamental equation is provided below,

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \sum_i \mu_i \mathrm{d}n_i + \sigma \mathrm{d}A$$

where S is the entropy, V is the volume, μ is the chemical potential, and σ is the surface free energy or surface tension,

$$\sigma = \left(\frac{\partial G}{\partial A} \right)_{T,p,n}$$

Adsorption causes a decrease in surface free energy that is dependent on the quantity of adsorbed material. The difference between initial and final surface tension is referred to as spreading pressure (π),

$$\sigma_{\mathrm{ws}} - \sigma_{\mathrm{as}} = \pi > 0$$

Gibbs free energy and the relationship between spreading pressure and adsorbent loading provide the basis for the frequently applied ideal adsorbed solution theory. The change in entropy during adsorption is negative for the decreased randomness after interaction between adsorbent and adsorbate and thus makes adsorption an exothermic process.

Adsorption enthalpy consists of physical adsorption (physisorption) and chemical adsorption (chemisorption). Physical adsorption is caused by van der Waals forces (dipole-dipole interactions, dispersion forces, and induction forces). Physical adsorption has considerably low enthalpy (<50 kJ/mol). Chemical adsorption has considerably higher enthalpies and is based on chemical reactions between adsorbate and surficial sites.

Adsorbent uptake due to surface concentration (T) is equal to the quotient of adsorbed amount (n_{a}), and the adsorbent surface area (A). Since the surface area is difficult to determine, a mass related adsorbance (q) is common practice, where m_a is the adsorbent mass and

$$q = \frac{n_a}{m_a}$$

Adsorbents are commonly used to prevent air and water pollution with activated carbon being the most important engineered adsorbent for water treatment. Water treatment removes organic micropollutants including phenols, chlorinated hydrocarbons, pesticides, pharmaceuticals, etc. by adsorption. Activated carbon is not selective with organic pollutants, and so competition among adsorbates is not of great concern.

Wastewater treatment has a great concern for effluent phosphate, and adsorption onto ferric hydroxide or aluminum oxide is an alternative to biological and precipitation processes for smaller treatment facilities. Micropollutants are also a concern for wastewater treatment and adsorption by activated carbon is a promising treatment, but competition with organic pollutants and micropollutants for adsorption will exist. In industrial wastewater, adsorption by activated carbon is common practice. If desorption of valuable chemicals is desired, alternative adsorbents could be used where the use of solvents will cause desorption. Powdered activated carbon (PAC) can also be used as an additive to activated sludge to increase efficiency by adsorbing nonbiodegradable or inhibiting substances. The activated carbon will be constantly regenerated by biological degradation, but never to the adsorption capacity of virgin material. Activated carbon is commonly used as a buffer in industrial wastes, and landfill leachates where high toxicity is common. Use in membrane filtration is also common to improve filtration and reduce membrane fouling.

Gibbs free energy is dependent on sorbent surface area in which engineered adsorbents are considerably higher than natural ones. High porosity and large amounts of internal surface are desirable and greatest with small pores, but a fraction of large pores is necessary for sorbate transport.

13.3 Activated Carbon Production

The most common raw materials for the production of activated carbons are wood, wood charcoal, peat, lignite, lignite coke, hard coal and coke, bituminous coal, petrol coke, and residual materials. Organic raw material like wood, sawdust, peat, coconut shells, and agriculture waste must undergo a preliminary carbonization phase to transform cellulose structures into carbonaceous material. Cellulose structures contain oxygen and hydrogen containing functional groups that must be removed by dehydrating chemicals. Carbons must be dehydrated, which is carried out at elevated temperatures under pyrolytic conditions that lead to the destruction of cellulose structures and results in a carbon skeleton. Dehydration involves the application of dehydrating chemicals including zinc chloride and phosphoric acid, these agents must be removed after cooling from pyrolytic conditions, but remnants pose concern for leaching during water treatment. Recycling of these chemicals is expensive, their use is in the production of powdered activated carbon with low quantities of micropores, and therefore, activated carbon for water treatment is typically produced by physical, thermal, or gas activation.

Gas activation uses coals or cokes for raw material. The raw material is contacted with an activation gas (steam, carbon dioxide, and air) at temperatures from 800 to 1000 °C. The activation gas and carbon material form gaseous products, and pores open and enlarge. This process normally produces granular activated carbon (GAC) typically used in fixed bed reactors.

Activated carbon structure consists of crystallites with a strongly disturbed graphite structure [94]. In graphite, carbon atoms are located in layers and connected by covalent bonds (sp^2 hybridization). Graphite possesses a delocalized π-electron system that is able to interact with aromatic structures in the adsorbate molecules. Graphite crystallites are randomly oriented and interconnected by carbon cross-links, and micropores are formed by the voids between these crystallites and are typically slit-like pores. Activated carbons adsorb mainly by van der Waals forces and in particular dispersion. Attractions can be superimposed by π-π interactions.

General trends in activated carbon are that adsorption is enhanced with increased internal surface area of adsorbent and increased molecular size of adsorbate, but decreased with increased temperatures (adsorption is exothermic). Absorbability of organic substances onto activated carbon increases with decreasing polarity (solubility and hydrophilicity) of adsorbate, aromatic compounds are better adsorbed than aliphatic compounds, organic ions are not as strongly adsorbed as neutral compounds, competitive adsorption is a common problem for the removal of particular pollutants, and inorganic ions can be adsorbed by interactions with the functional groups of the adsorbent at a much lower extent than organic substances, which are adsorbed by dispersion and hydrophobic interactions [94].

14 Adsorption Equations

Solid surfaces containing active, energy-rich sites able to interact with solutes in an adjacent aqueous phase allow the adsorption and removal of pollutants from fluid phase. Changes in environmental conditions and in fluid properties have great consequences on adsorption. Species concentration, temperature, and pH are well-known variables that effect adsorption. Adsorbed materials commonly revert back to the fluid phase, and this action is referred to as desorption.

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$$q = \frac{n_{\mathrm{a}}}{m_{\mathrm{a}}}$$

The Langmuir adsorption isotherm is used to quantify the performance of adsorbents. The above equation represents the linear form, where C_{e} (mg/L) is the equilibrium concentration of the MG, q_{e} (mg/g) is the amount of MG adsorbed per unit mass of adsorbent, and Q_{m} (mg/g) and K_{L} (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The equation is given below,

$$\frac{C_{\mathrm{e}}}{q_{\mathrm{e}}} = \frac{1}{Q_{\mathrm{m}} K_{\mathrm{L}}} + \frac{C_{\mathrm{e}}}{Q_{\mathrm{m}}}$$

15 Summary

Various methods of preparation were evaluated to determine the effectiveness of agricultural waste sorbates. The raw material, activation process, and the characteristics of the reaction were found to be significant variables in liquid solid adsorption of pollutants.

Adsorption is adhesion at the molecular level. There exists intramolecular and intermolecular binding that represents physical and chemical adsorption, respectively. Van der Waals forces of physical attraction are responsible for physical adsorption. Van der Waals forces are a result of a transient shift in electron density, and electrons may temporarily shift to one side of the nucleus, which generates a temporary charge and subsequent attraction of nearby atoms. Adsorption is an exothermic reaction where the adsorbate penetrates the sorbent in search for a position of minimum energy. The sorbate continues to move among low energy sites within the sorbent, and thus, highly porous activated carbons are effective for adsorption. Chemical adsorption is the attraction that exists between molecules and is composed of ionic, covalent, and metallic bonds. Ionic bonds are formed by a complete transfer of valence electrons between atoms and generate two oppositely charge ions. An electron is essentially donated between two molecules that differ greatly in their electronegativity. In ionic bonds, metals lose electrons to become a positively charged cation and require a nonmetal electron acceptor. The net charge of the produced compound must be zero. This results in a cation and anion bonded by an ionic bond. Covalent bonds are much more common than ionic and involve the sharing of electron pairs. Electrons are covalently bonded to gain stability with the formation of a full electron shell. Nonmetals readily form covalent bonds with other nonmetals, but the sharing of electrons is often unequal.

The physical and chemical nature of the sorbent and sorbate has a great effect on adsorption. An investigation into water pollutants was completed to further understand the varieties and behavior of various pollutants. Water pollutants can be classified by (1) Organic pollutants, (2) Pathogens, (3) Nutrients and agriculture runoff, (4) Suspended solids and sediments, (5) Inorganic pollutants (salts and metals), (6) Thermal pollution, (7) Radioactive pollutants, and (8) Nanopollutants [4]. Organic pollutants are composed of oxygen demanding wastes, synthetic organic compounds, and oils. Oxygen demanding wastes can be treated by biological waste treatment. Inorganic pollutants are nonbiodegradable and persistent environmental pollutants, and examples are Mineral acids, inorganic salts, trace elements, metals, metallic compounds, metal/organic compound complexes, cyanides, sulfates, etc. Heavy metals may cause health concerns for metals in high concentrations can be toxic (Hg, Cu, Cd, Pb, As, and Se). Radioactive contamination is hazardous for the radioactive decay of the contaminants. Radioactive decay emits ionizing radiation such as alpha or beta particles, gamma rays, or neutrons.

Pesticides were investigated at the greatest depth for their relationship to agriculture. Glyphosate is the most used herbicide and was considered nontoxic, but excessive application has resulted in severe acute and chronic toxicological effects. Desorption is considerably low, it is fairly immobile in soils, and biological degradation is the in situ treatment. Mutations on commercial crops allow glyphosate resistance, but weed species are also growing an immunity to this herbicide. Overuse brings glyphosphate residue in food crops, and with growing weed tolerance, this is only expected to rise. Biodiversity of agricultural fields suffers greatly, and there is great concern for health risks posed to higher organisms. The application of organic matter on agricultural fields would increase adsorption and infiltration and improve biological degradation of applied glyphosate. The use of buffer zones is strongly supported to decrease surface runoff pollution.

Schappert et al. [32] compared the ability of cover crop mixtures with repeated stubble tillage and glyphosate treatments. Seven weed management treatments are flat soil tillage, deep soil tillage, plowing, single glyphosate application, dual glyphosate application, and a cover crop mixture sown in a mulch till and no-till system. Results showed the worst weed suppression under deep soil tillage (including plowing) and thus is not recommended for it is a labor-intensive and costly practice that hinders weed control and soil conservation. Both cover crop mixtures were successful in weed suppression including the suppression of A. *myosuroides*, which has been found to be one of the most challenging weeds. The dual glyphosate application achieved the highest weed control, but a single application was not sufficient to control A. *myosuroides* weeds. It was concluded that cover crops are the best management practice for weed suppression, but under years with unfavorable growing conditions for cover crops, stubble tillage, and glyphosate applications may be more efficient methods.

The adsorption of heavy metals by rice straw was reviewed. Nawar et al. studied the adsorption of Fe^{3+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} by rice straw. Rice straw was washed, filtered, dried at 100 °C, and then dried at 500 °C for 3 h. It was concluded that treatment of 1 m^3 of wastewater would cost approximately 31.25 L.E or 1.98 usd, making carbonized rice straw an effective adsorbent for the removal of heavy metals [34].

The adsorption of chlorophenol with rice straw was reviewed. In a study conducted by Chang, rice straw-derived ashes from 400 to 700 °C were compared for their potential adsorption of chlorophenols. It was concluded that a 700 °C carbonization greatly increased the pore size and surface area of the activated carbon, improving adsorption. This study provided argument for rice straw-derived ash as a replacement of activated carbon [40].

Different activation agents were compared in a study completed by Liou (2009) [43]. Both sugar cane bagasse and sunflower seed hull were used as raw materials to evaluate the effect of ash content on adsorption. Traditional production of mesoporous activated carbon consists of carbon precursors (lignocellulosic materials, coals, and phenolic resins) in the presence of transition metals, followed by the carbonization and physical activation with steam or carbon dioxide. Base leaching, activation with H_3PO_4 and $ZnCl_2$, and washing with acid or water were completed and compared. Results showed that base leaching and acid washing increased surface area in all samples. The surface areas for raw bagasse and seed hull were 0.6 and 0.06 m^2/g, respectively. The surface areas of base leached samples were 1.56 and 0.59 m^2/g, respectively. Base leaching is proposed to have reduced the ash content, which aided activation agents to enter the interior of the carbon tissue, and to have decomposed or softened the organic matter, which facilitated the pyrolysis during the activation reaction. Optimum temperature was found to be 500 °C, and $ZnCl_2$ activation produced a higher mesopore volume and surface area than H_3PO_4. X ray diffraction analysis reported peaks at $2\theta = 45°$, which represent the creation of pores along the direction of the graphic structure. If it is true, a more well-organized aromatic carbon would be produced as opposed to amorphous-like carbons.

Physical activation is an alternative to the use of chemical activation agents. Physical activation is composed of two steps: carbonization at temperatures (500–1000 °C) in an inert environment to eliminate oxygen and hydrogen elements and thermal activation at the same or higher temperature in the presence of an oxidizing agent (H_2O, CO_2, or both). Oxygen-free environments are used to minimize the volatilization of carbon. Bouchelta et al. produced activated carbons from date stones with pyrolysis temperatures ranging 500–800 °C under nitrogen flow of 100 cm^3/min [50]. The chars were then physically activated at 500, 600, 650, 700, or 800 °C for 0.5, 1, 2, 3, or 6 h under nitrogen flow of 100 cm^3/min saturated in steam. Bouchelta stated that the optimum temperature is 700 °C for a significantly lower yield was not produced with increasing temperatures past this point [50]. Decreases in yield from 500 to 650 °C are attributed to the removal of volatile matter during decomposition of major compounds such as cellulose (long polymers of glucose without branches) and hemicellulose (w/various branched saccharides). Above 700 °C, there is little decrease in yield for hemicellulose and cellulose are already decomposed. What remains is lignin, which decomposes slowly up to 900 °C. It was stated that the degradation of cellulose and hemicellulose creates porosity, which aids degradation of lignin by improving contact with oxidizing agent [50].

Agricultural waste is valuable to numerous industries, and the use of compost as an adsorbent was investigated. Qian et al. presented a study to prepare a high-surface area activated carbon from cattle-manure residue (CMC) from anaerobic digestion. The maximum BET surface area (S_{BET}) and maximum micropore surface area (S_{MI}) were around 2170 and 1580 m^2/g, respectively. Both S_{BET} and S_{MI} increased with increased $ZnCl_2$/CMC to a ratio of 1.5. Qian concluded that cattle manure compost could be yield high quantities of activated carbon (47.5%) by activation with zinc chloride [55]. That activation could be carried out at 400 °C for 0.5 h, and that acid washing could develop porosity by the removal of impregnated $ZnCl_2$ and volatilization of $ZnCl_2$ at 728 °C. The maximum BET surface and total pore volume of the carbons were 2170 mg^2/g and 1.7 cm^3/g, respectively, and it was concluded that pore size could be adjusted by $ZnCl_2$ ratio, activation temperature, and retention time. In conclusion, cattle manure compost was demonstrated to be an excellent candidate for the manufacturing of activated carbons. Many studies were performed on the adsorption of dyes by raw compost. It was reported that a removal rate above 90% was achieved with 100 mg/L concentrations of dye. Pushpa obtained an experimental uptake of 159.22 mg/g and a maximum dye removal of 895.755 [59]. Compared to activated carbons, adsorption capabilities of raw materials are much lower and less consistent, but potential uses exist in the treatment of polluted runoff.

Acid mine drainage (AMD) results in gross amounts of pollutants from the metal and coal mining industries. Heavy metals unlike organic pollutants are not biodegradable. Treatments including chemical precipitation, ion exchange, membrane filtration, reverse osmosis, and activated carbon adsorption are associated with high-cost and labor-intensive practices, which led Zhang to study the adsorption of

PB(II), CU(II), and ZN(II) using dairy manure compost (DMC). It is hypothesized that ion exchange is responsible for the biosorption of heavy metals, and so under batch experimentation, the release of Ca^{2+}, Mg^{2+}, K^+, Na^+, and H^+ was determined while adsorbing Pb, Cu, and Zn in a single metal system. Results concluded in binary and tertiary studies; metals competed with one another for adsorption. Competitive ability followed the order of Pb > Cu > Zn. The optimum pH of Pb, Cu, and Zn ions adsorption occurred at 3.5, 4.5, and 5.5, respectively. There was a significant release of Ca^{2+}, Mg^{2+}, K^+, Na^+, and H^+ after interaction, showing heavy metal adsorption from predominantly cation exchange. Repeated cycles were tested to investigate the regeneration and reutilization of the adsorbent, HCl was used as a desorbing agent, and little variation in adsorption capacity existed until the third cycle, where a nonsignificant decrease occurred. This study brings further merit to the use of compost as an adsorbent.

Ramla and Sheridan (2015) stated that even passive treatment methods, such as constructed wetlands and compost bioreactors, possess a large initial cost, and they investigated the potential utilization of indigenous South African grasses for acid mine drainage remediation [82].

The most common raw materials for the production of activated carbons are wood, wood charcoal, peat, lignite, lignite coke, hard coal and coke, bituminous coal, petrol coke, and residual materials. Organic raw material like wood, sawdust, peat, coconut shells, and agriculture waste must undergo a preliminary carbonization phase to transform cellulose structures into carbonaceous material. Cellulose structures contain oxygen- and hydrogen-containing functional groups that must be removed by dehydrating chemicals. Carbons must be dehydrated, which is carried out at elevated temperatures under pyrolytic conditions that lead to the destruction of cellulose structures and results in a carbon skeleton. Dehydration involves the application of dehydrating chemicals including zinc chloride and phosphoric acid, these agents must be removed after cooling from pyrolytic conditions, but remnants pose concern for leaching during water treatment. Recycling of these chemicals is expensive, their use is in the production of powdered activated carbon with low quantities of micropores, and therefore, activated carbon for water treatment is typically produced by physical, thermal, or gas activation. °.

Gas activation uses coals or cokes for raw material. The raw material is contacted with an activation gas (steam, carbon dioxide, and air) at temperatures from 800 to 1000 °C. The activation gas and carbon material form gaseous products, and pores open and enlarge. This process normally produces granular activated carbon (GAC) typically used in fixed bed reactors [94].

General trends in activated carbon are that adsorption is enhanced with increased internal surface area of adsorbent and increased molecular size of adsorbate, but decreased with increased temperatures (adsorption is exothermic). Absorbability of organic substances onto activated carbon increases with decreasing polarity (solubility and hydrophilicity) of adsorbate, aromatic compounds are better adsorbed than aliphatic compounds, organic ions are not as strongly adsorbed as neutral compounds, competitive adsorption is a common problem for the removal of particular pollutants, and inorganic ions can be adsorbed by interactions with the functional groups of the adsorbent at a much lower extent than organic substances that are adsorbed by dispersion and hydrophobic interactions [94].

In conclusion, carbon-based adsorbents can be generated from most carbonaceous material. Lignocellulosic materials have high amounts of carbon and after activation produce a highly adsorbent carbon skeleton. Materials with greater ash content such as rice straw and compost have also proven to produce effective adsorbents.

Activation and Carbonization have a great impact on the quality of sorbents. Chemical activation produces a greater surface area than physical activation, but leaching of chemicals is a concern. Chemical activation is primarily used in the production of powdered activated carbons, while physical activation is used for granular activated carbons and potable water treatment. Temperature for carbonization varied among studies, with the ideal value ranging from 400 to 700 °C. Multiple studies using thermogravimetric analyses state the 500–700 °C range is critical for the production of a porous carbon-based material. Both activation and carbonization must occur in inert environments to prevent the volatilization of carbon.

Raw materials can be used for adsorption, but pollutant uptake is considerably less than manufactured carbons. Raw compost has been found to be an effective adsorbent in lab experiments, but no research was found on large scale application. Acid mine drainage and untreated industrial wastewater are of great concern in developing areas. The use of adsorbents produced from agricultural waste may be critical in water treatment for small-scale production of potable water.

Glossary

Adsorbent A substance that adsorbs another.

Adsorption The process by which a solid holds molecules of a gas or liquid or solute as a thin film.

Agricultural waste Agricultural waste is defined as unwanted waste produced as a result of agricultural activities (i.e., manure, oil, silage plastics, fertilizer, pesticides, and herbicides).

Dye removal The dye removal techniques are physical, chemical, and biological methods.

Heavy metals Any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations.

Kinetic models Kinetic models are a simplification of the physiological processes in the tissue, and so not every aspect of the kinetic process can be considered.

Low-cost adsorbent Low-cost adsorbents can be viable alternatives to activated carbon for the treatment of metal-contaminated wastewater.

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Chapter 5
Waste Vegetable Oils, Fats, and Cooking Oils in Biodiesel Production

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Contents

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Abstract This chapter provides a critical overview of the methods of biodiesel production from waste oily by-products from edible oil refinery, waste fats, and waste cooking oils with emphasis on factors that impact the synthesis of fatty acids alkyl esters. The aim is to show exploitation possibilities of the mentioned waste materials for making biodiesel. Various technologies such as chemical (homogeneous and heterogeneous) and enzyme catalysis as well as non-catalytic processes have been applied in biodiesel production from waste oils, fats, and cooking oils. The future commercial process of biodiesel production will be a choice among solid catalysts, lipases, and non-catalytic processes.

Keywords Biodiesel · Esterification · Transesterification · Waste cooking oils · Waste fats · Waste vegetable oils

Nomenclature

AG	Acylglycerols
DAG	Diacylglycerols
DD	Deodorizer distillate
FAAE	Fatty acid alkyl esters
FAEE	Ethyl esters
FAME	Fatty acid methyl esters
FFA	Free fatty acids
MAG	Monoacylglycerols
SBE	Spent bleaching earth
SSR	Soap-splitting route
TAG	Triacylglycerols
WAF	Waste animal fats
WCO	Waste cooking oils

1 Introduction

Technological development, global warming, and increasing environmental pollution have directed scientific research toward alternative and ecologically acceptable energy resources. In a group of alternative fuels, which are substitutes for the conventional ones, the most perspective are biofuels among which biodiesel has great significance. Biodiesel is defined as a mixture of long-chain fatty acid alkyl esters (FAAEs) that satisfy specified standards. It is mainly produced by transesterification (alcoholysis) of triacylglycerols (TAGs) from different natural resources, in excess of alcohol, and most commonly in the presence of a catalyst. Annual world biodiesel production is growing rapidly in the last decade, reaching a level of approximately 35–45 million tonnes in 2019 [1]. The world's largest biodiesel producers in 2019 were the EU and the USA with annual productions of over 14 million tonnes and 5.6 million tonnes, respectively.

There are many advantages in the appliance of biodiesel, such as:

- It can be used “as is” or in mixture with diesel D-2, without or with minimal engine modifications;
- It is biodegradable;
- It can be derived from biologically renewable recourses (vegetable oils and animal fat);
- During the combustion of biodiesel emission of carbon and sulfur oxides, soot particles and non-combusted hydrocarbons are reduced.

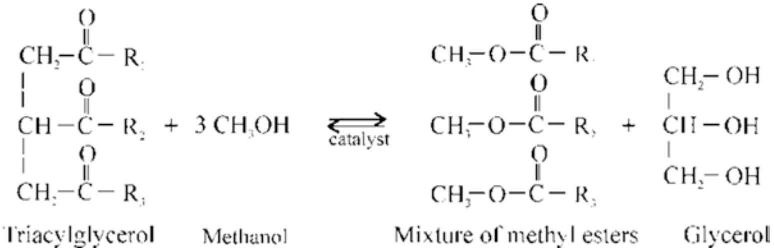
Despite many advantages of biodiesel compared to fossil diesel, high manufacture price is the primary barrier in commercial usage of biodiesel. The manufacture price is determined by feedstock type, production capacity, and applied technology [2, 3]. Research shows that edible vegetable oils, included in current industrial processes, participate with 70–95% in the total price of biodiesel production [4]. Also, the use of edible oils in the biodiesel production process is restricted by their usage in the human diet and food industry. Furthermore, even if the whole amount of available edible vegetable oils were used for biodiesel production, the gained amount of fuel would not satisfy current diesel requirements [5]. As a consequence, attention of the researchers is significantly turned to examining possibilities of new and cheaper oily feedstocks for biodiesel production, such as waste oily by-products from edible oil refinery (called here waste vegetable oils), waste animal fats (WAFs), waste cooking oils (WCOs), and nonedible oils.

Methods of biodiesel production from waste vegetable oils, WAFs, and WCOs with an overview of factors that impact the synthesis of FAAEs are critically reviewed. The aim is to show exploitation possibilities of the mentioned waste materials for making an economically sustainable and ecologically acceptable product such as biodiesel.

2 Biodiesel Production from Conventional Oily Feedstocks

According to its chemical composition, biodiesel is most commonly a mixture of fatty acid methyl esters (FAMEs) or ethyl esters (FAEEs), obtained from TAGs via transesterification or from free fatty acids (FFAs) via esterification:

- Transesterification reaction:



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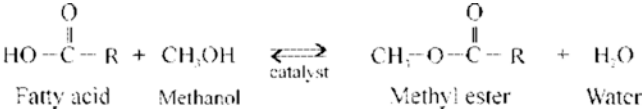
- Esterification reaction:



$$HO-\overset{O}{\overset{\|}{C}}-R + CH_3OH \xrightleftharpoons[\text{catalyst}]{} CH_3-O-\overset{O}{\overset{\|}{C}}-R + H_2O$$

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- The basic feedstocks for biodiesel production are vegetable oils or animal fats consisting mainly of TAGs. Therefore, transesterification is the main reaction for biodiesel production, whereas esterification is needed for feedstocks having a higher content of FFAs. Transesterification is a sequence of three reversible reactions in which TAGs are gradually converted into diacylglycerols (DAGs), monoacylglycerols (MAGs), and glycerol. Esterification is also an equilibrium reaction. In both reactions, to shift the equilibrium to the right, methanol is added in an excess relative to the stoichiometric amount, or an end product is removed out of the reaction system. For instance, because of their immiscibility, FAMEs and glycerol separate easily, and the latter is removed from the reaction mixture enabling a high conversion degree. The rate of both reactions is usually enhanced using a catalyst, which can be an acid, a base, or an enzyme, although the reactions can be conducted in the absence of any catalyst but at higher temperatures and pressures.

According to the type of catalyst employed, the reactions for biodiesel production can be classified into four groups: (a) homogeneously catalyzed, (b) heterogeneously catalyzed, (c) enzymatically catalyzed, and (d) non-catalyzed.

2.1 Homogeneously Catalyzed Reactions

Due to the short reaction time, low demands concerning the quality of equipment, and small investments, transesterification is usually performed in the presence of a homogeneous base catalyst: hydroxides or alkoxides of sodium or potassium. The reason for the massive usage of alkali hydroxides is good catalytic activity, low cost, and simple transport and storage manage. Alkali methoxides are more catalytically active, but more expensive and highly hygroscopic, which makes them much harder to handle [7]. The main limitation of using these catalysts is the quality of oily feedstock, which refers to the contents of FFAs (<1%) [8] and water (<0.1%) [9]. As the transesterification reaction is reversible, the maximal conversion of TAGs is reached with an initial molar ratio alcohol-to-oil higher than the stoichiometrical one. When methanol is used, the optimal ratio, according to most researchers, is 6:1. Acid-catalyzed transesterification is significantly slower but more suitable for oils with a higher content of FFAs. To keep the alcohol liquid, temperatures of up to 100 °C and pressures of up to 5 bars are typically employed in homogeneously acid-catalyzed methanolysis. Therefore, acid catalysts are usually used for esterification reactions. Concentrated sulfuric acid is the best and cheapest acid catalyst for esterification reactions. The major disadvantage of homogenous catalysts is the fact that they cannot be reused. Figure 5.1 shows the process scheme of homogeneously catalyzed biodiesel production process, depending on FFA content [6]. The process includes pre-esterification of a feedstock with high FFA content under acidic conditions, followed by base-catalyzed transesterification.

One of the best-known industrial methods of synthesizing biodiesel using a homogeneous base catalyst is the Lurgi process [10]. Refined vegetable oils are mainly used as feedstock. A two-stage mixer-settler unit is used to running the process continuously (Fig. 5.2a). The reaction takes place in the mixing section at 60 °C and atmospheric pressure, using sodium methoxide. The FAME light phase is separated from the glycerol-water heavy phase in the settling section. The FAME product was washed by water in a countercurrent washing column and then dried. Methanol contained in the glycerol water is recovered in a rectification column and used again in the process. Glycerol can be recovered from the glycerol water and further purified. Biodiesel plants have an annual capacity in the range between 40,000 and 250,000 tonnes of biodiesel according to EN14214.

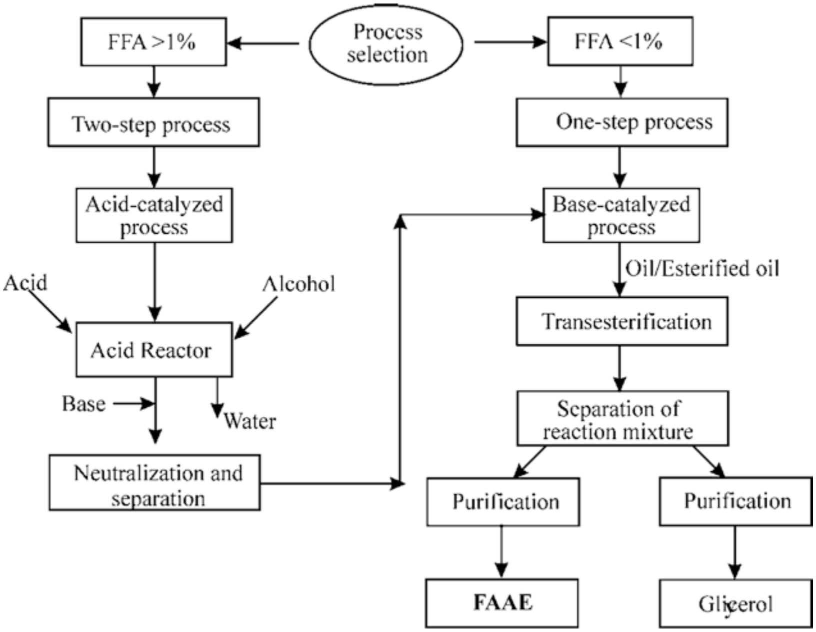

Fig. 5.1 Process selection and steps for biodiesel production. (Adapted from [6])

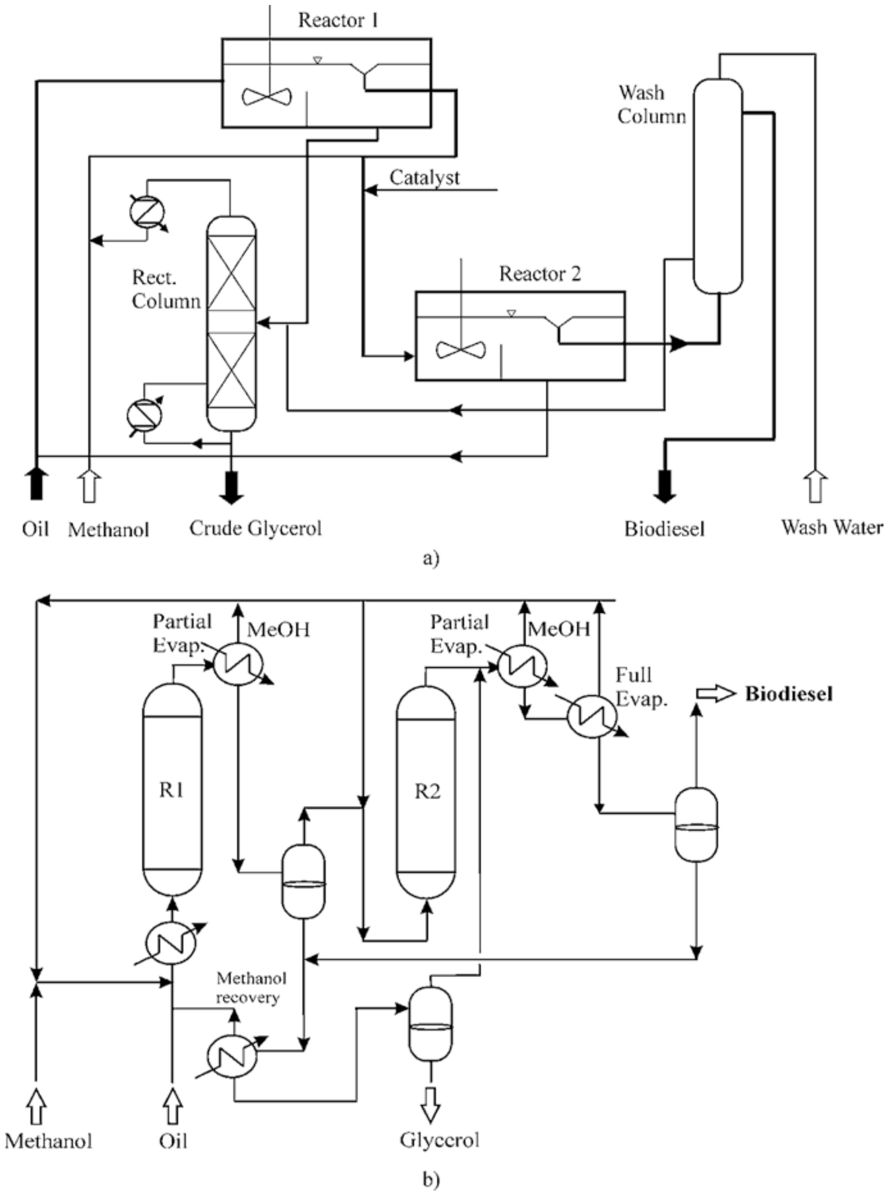

Fig. 5.2 Simplified (**a**) Lurgi and (**b**) Esterfip-H biodiesel production process flow sheets. (Adapted from [10] and [11], respectively)

2.2 Heterogeneously Catalyzed Reactions

The use of heterogeneous catalysts, both acidic and basic, simplifies the product purification step. Namely, solid catalysts can be recovered by filtration or decantation or be used in fixed-bed reactors, so there are no wastewaters. They can be reused with or without regeneration. Their major drawbacks are mass-transfer limitations in the three-phase reaction system, higher initial methanol-to-oil molar ratios, and the complex catalyst preparation in some cases. The most frequently used heterogeneous base catalysts are alkali metal- and alkaline earth metal oxides and carbonates. The application of calcium oxide seems to be promising because it is an easily available and cheap substance [12]. The other tested solid catalysts are zeolites, ion-exchange resins, Mg-Al hydrotalcites, etc. The future attention of researchers will be focused on discovering bifunctional and superacid solid catalysts that catalyze both esterification of FFAs and transesterification of TAGs.

The only commercial continuous process of biodiesel production based on the use of a non-noble metal solid catalyst is the Esterfip-H process realized by Axens (France) [11]. Suitable feedstocks are virgin and semi-refined vegetable oils. The plant includes two fixed-bad reactors with the catalyst (Fig. 5.2b). Excess methanol is removed after each reactor by partial flash evaporation, while FAMEs and glycerol are separated in a settler. Biodiesel is produced after the final removal of methanol by evaporation under vacuum, and the yield is close to the theoretical one. Salt-free glycerol of high purity (>98%) is also produced. The annual plant capacity is up to 200,000 tonnes of biodiesel.

2.3 Enzyme-Catalyzed Reactions

Lipases from different microorganisms have been tested in biodiesel production in the last decade. These enzymes catalyze both esterification of FFAs and transesterification of TAGs under mild reaction conditions at low initial methanol-to-oil molar ratios. Therefore, feedstocks having high FFAs content can be used without any pretreatment. The separation and purification of the end products are simple, and a minimal amount of wastewater is generated. The basic barriers to performing enzyme-catalyzed processes industrially are the high price of the enzyme, low enzyme activity, and stability in the presence of polar alcohols and the necessity of careful control of process variables. Being better from the ecological point of view, compared to other catalyst types, the enzyme-catalyzed biodiesel production will become more important in the future. A promising strategy is to use lipases immobilized on a carrier, enabling easy enzyme removal and reuse.

2.4 Non-catalyzed Reactions

Transesterification of TAGs with lower alcohols can occur in the absence of a catalyst at high temperatures and pressures (above the critical point for methanol 239 °C and 8.1 MPa). Under supercritical conditions, the reaction takes place in a single phase without mass-transfer limitation. Also, high-purity esters and soap-free glycerol are produced. During this process, esterification, hydrolysis, and methanolysis occur at the same time, which is suitable to produce biodiesel from used and waste materials [13]. However, supercritical processes still have no industrial application due to the high capital investment and high energy consumption, which indicates the necessity of a good design of the process in terms of energy recovery [14]. Because of a high initial methanol-to-oil molar ratio (up to 50:1), most of the energy is spent on the recovery of methanol. A two-step non-catalyzed process, which includes hydrolysis of TAGs into FFAs with an excess of water and subsequent esterification, requires lower amounts of methanol [15].

3 Biodiesel Production from By-products of Edible Oil Refinery Process

Edible oils are primarily obtained from various oilseeds. The first step in producing edible oils is the separation of so-called crude (unrefined) oil by pressing followed by solvent extraction. The major component of the crude oil is TAGs, while the other minor components are MAGs, DAGs, FFAs, phosphatides, sterols, tocopherols, squalene, pigments, glycerol, hydrocarbons, vitamins, glycolipids, metals, etc. The crude oil is refined by employing specific processes in several steps to remove the minor components contributing to undesirable appearance, odor, and flavor. The refinery process results in edible oil as the main product and several by-products (waste vegetable oils) containing primarily TAGs and/or FFAs, which can be used as raw materials for biodiesel production. At first, phospholipids (gums) are removed by the degumming process, the obtained so-called oil sediments. If the chemical refinery is applied, FFAs are neutralized by a weak alkaline solution, and the by-product obtained is soapstock. Soapstock is usually acidulated by adding mineral acid to liberate FFAs, generating so-called acid oil or acidulated soapstock. Physical refinery processes include vacuum steam distillation to remove FFAs, producing acid oils. In the bleaching step, pigments, residual phosphatides, soaps, and metals are removed by using bleaching earth, producing another solid waste called spent bleaching earth (SBE). Finally, FFAs and odoriferous components are removed in the deodorization step by vacuum steam distillation, producing a by-product called deodorizer distillate (DD). Details on the chemical composition and utilization of the main by-products from edible oil refining processes can be found elsewhere [16, 17].

3.1 Biodiesel from Soapstocks, Oil Sediments, and Acid Oils

When designing processes for biodiesel production from soapstock, one should consider the presence of both acylglycerols (AG) and FFAs, as well as its high-water content and semisolid nature under ambient conditions. Generally, two-step processes are needed, consisting of acid-catalyzed esterification of FFAs followed by a base-catalyzed transesterification of AGs, because the latter reaction is ineffective at esterifying FFAs. Also, water inhibits both transesterification and acid-catalyzed esterification and favors ester hydrolysis, which is unfavorable for biodiesel production. The biodiesel production from acid oils involves less difficulty than that from soapstocks because the former raw material has lower water content. Both raw materials, however, contain other impurities such as phospholipids that, as surfactants, lead to the difficulty in separating methyl esters from glycerol after the washing step. Based on the annual world's production of the selected edible oils (soybean, rapeseed, sunflower, and palm kernel: 533.7 million metric tonnes) [18] and the estimates suggested by Echim and coworkers [17], the world's generation of soapstock and acid oils in 2019 can be estimated to be 14.7–19.4 million metric tonnes and 6.7–11.4 million metric tonnes, respectively.

There are two main routes to produce biodiesel from soapstocks (Fig. 5.3), namely direct conversion and pretreatment of soapstocks before conversion either by acidulation to produce acid oils (so-called WCO SSR) or by hydrolysis of neutral oil (hydrolysis route). Another route is the esterification of FFAs with glycerol to

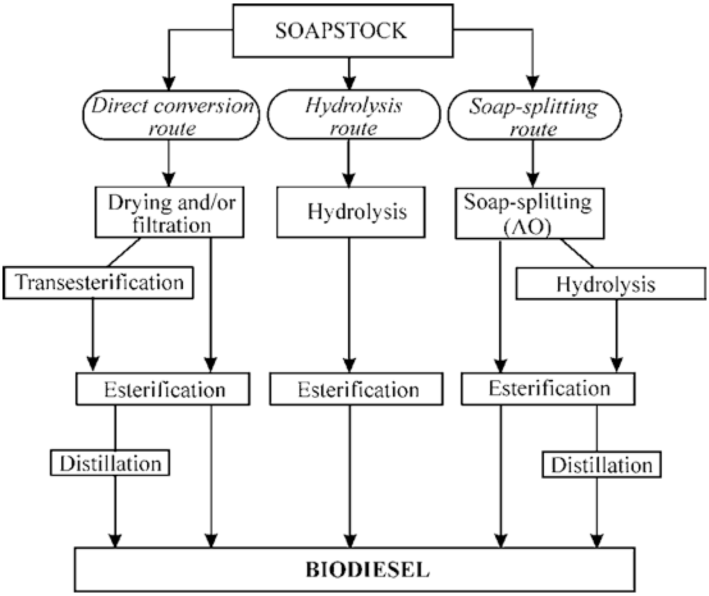

Fig. 5.3 Schematic representation of different routes used to convert soapstock to biodiesel. (Adapted from [17])

AGs (termed glycerolysis) prior to transesterification. The process of direct soapstock conversion into biodiesel is on the laboratory scale, while the only industrial process is undertaken via SSR [17]. Table 5.1 reviews the selected literature related to the use of soapstocks, oil sediments, and acid oils in biodiesel production. Soapstocks originate mainly from the refinery of soybean oil, and methanol is only used as an esterification agent. Processes are usually conducted in batch stirred reactors, although packed-bed and tubular reactors are also applied. Direct esterification of FFAs from soapstocks was catalyzed by either sulfuric acid or lipases after appropriate pretreatment. Different soap-splitting procedures are employed to produce acid oils which are further esterified using sulfuric acid, solid acid catalysts, and lipases. Non-catalyzed esterification and glycerolysis processes have been rarely studied. The final product yield depends on the origin of soapstock or acid oil and the employed process conditions.

3.1.1 Direct Conversion of Soapstock

Direct conversion of soapstock “as is” has been seldom studied. Acid-catalyzed [19] and enzyme-catalyzed [20] esterification is employed to convert cotton oil soapstock and soybean oil soapstock to biodiesel, respectively. In the former process, the splitting of the soaps and esterification was performed in the presence of sulfuric acid as a catalyst at 75 °C in 2 h [19]. The latter process employs sequentially a base-catalyzed transesterification and enzyme-catalyzed esterification to convert AGs and FFAs of soapstock to the esters of monohydric alcohols [20]. Water from the soapstock was removed by freeze-drying prior to the transesterification, and the pH of the final reaction mixture was adjusted to pH 6.0 prior to esterification to obtain a significant activity of *C. antarctica* SP-435 lipase. Only 63% conversion of FFAs was achieved at the ethanol-to-FFA ratio of 20:1 in the presence of water (0.70%) within 39 h. The process combining transesterification and esterification reached the overall conversion of only 81%. Therefore, the enzymatic process was judged as insufficient for achieving complete esterification.

3.1.2 SPR (via Acid Oil as an Intermediate)

Chemically Catalyzed Processes

Eaveas et al. [29] converted acidulated soapstock (acid oil) to methyl esters using HCl and Twitchell reagent in a packed column reactor. The optimum conditions for the highest conversion of up to 86% are as follows: the temperature of 110–120 °C, the pressure of 11.34 bar, the methanol-to-FFA ratio of 5:1, the acid catalyst of 3–5% (based on the FFA mass), and the reaction time of 15 min. Passing the acid oil pretreated by hydrolysis twice through the reactor the conversion degree was increased up to 97%.

Table 5.1 A review of the use of soapstocks, oil sediments, and acid oils in biodiesel production

Raw material	Production method	Reactor	Alcohol	Catalyst (based on oil mass)	Alcohol/ FFA ratio	Temperature, °C	Yield/time (reaction conditions)	Reference
Cotton oil soapstock	Direct acid esterification after filtration and drying	Batch, stirred magnetically	Methanol	H_2SO_4, 4%	1:5 g/g	75	NA/2 h	[19]
Soybean oil soapstock	Direct enzyme esterification after transesterification	Batch, stirred	Ethanol (in the presence of water 0.70%, pH 6.0)	Immobilized lipase from *C. antarctica* (Lipozyme SP-435), 1.1%	20:1 mol/ mol	42	63%/39 h	[20]
Soybean soapstock	SPR[a] (acid esterification after alkali hydrolysis)	Batch, shaken	Methanol	H_2SO_4, 9.7 mol%	15:1 mol/ mol	65	NA/26 h (acid oil)	[21]
				H_2SO_4, 5.7 mol%	1.8:1 mol/ mol		89%/14 h (high acid acid oil)	
Soybean soapstock	SPR (acid esterification after acidification)	Batch, stirred (250 rpm), under pressure (3.9 bar)	Methanol (in the presence of water, 0.8% and 3.15%)	H_2SO_4, 10%	1.5:1 g/g	80 for 1 h, then 95 for 4 h	>90%/3–5 h	[22]
Soybean oil sediments and soapstock	SPR (extraction, acidulation, acid esterification, and base-catalyzed transesterification)	Batch, stirred	Methanol	H_2SO_4, 1.0–5.0%	2:1–9:1 mol/mol	20–90	92.1% (5:1 mol/ mol, 3% catalyst, 80–90 °C)/5 h	[23]
Rapeseed soapstock	SPR including acidification short-path distillation (acid esterification)	Batch, stirred	Methanol	H_2SO_4, 0.8–2.4 vol%	0.2:1–0.4:1 v/v	60	96.45%/1.42 h (0.33:1 v/v, 1.44 vol%)	[24]

(continued)

Table 5.1 (continued)

Raw material	Production method	Reactor	Alcohol	Catalyst (based on oil mass)	Alcohol/ FFA ratio	Temperature, °C	Yield/time (reaction conditions)	Reference
Soybean soapstock	SPR (acidulation followed by acid esterification)	Batch	Methanol	Amberlyst-15, 30%	3:1–9:1 mol/mol	80	91.7%/6 h (9:1 mol/mol)	[25]
Soybean soapstock	SPR (acid esterification after acidification and transesterification)		Methanol	Amberlyst-15	3:1 mol/mol	80	85.16%/6 h	[26]
				H_2SO_4			85.55%/6 h	
Soapstock	SPR (acidification, molecular distillation, esterification, and transesterification)	Batch, stirred magnetically	Methanol	Solid superacid catalyst $SO_4^{2-}/ZrO_2–TiO_2/La^{3+}$, 5%	15:1 mol/mol	60	98%/4 h	[27]
Soybean soapstock	SPR (extraction, acidification, esterification)	Batch, stirred	Methanol	Solid acid lignin-derived carbonaceous catalyst, 1–7%	3:1–9:1 mol/mol	50–80	97%/5 h (9:1 mol/mol, 7%, 70 °C)	[28]
Buriti oil soapstock	SPR (acidulation followed by acid esterification)							[29]
Acid oil	Acid esterification	Packed column reactor	Methanol	HCl, 3%	5–1 mol/mol	70	73.4–80.1%/10–60 min	[30]
						110	80%/10 min	
				Twitchell reagent with H_2SO_4 in excess, 3%[b]		120	82%/13 min	
Acid oil	Simultaneous esterification and transesterification	Batch, under pressure (up-34.5 bar)	Methanol	H_2SO_4, 0.125%, 0.25%	0.35:1 g/g	150	92.5%/4.5 h	[31]
						180	90.6%/1 h	

Raw material	Production method	Reactor	Alcohol	Catalyst (based on oil mass)	Alcohol/ FFA ratio	Temperature, °C	Yield/time (reaction conditions)	Reference
Acid oil	Acid esterification followed by adsorption	Continuous packed-bed reactor (186–250 bar)	Methanol	Base modified titania	32.7:1 mol/mol	339–348	90.2%	[32]
Acid oil	Simultaneous esterification and transesterification	Batch, stirred, under pressure (up to 34.5 bar)	Methanol	Vanadyl phosphate catalyst, 5%	0.55:1 g/g	125	87% and 94%/6 h	[33]
Acid oil	Two-step process: enzyme-catalyzed esterification followed by enzyme-catalyzed transesterification	Batch, shaken	Methanol	Immobilized lipase from *C. antarctica*, 1%	1:1 mol/mol	30	91%/24 h	[34]
Rapeseed soapstock	Enzyme-catalyzed esterification preceded by saponification, acidification	Batch, stirred	Methanol, water 2–10%	Immobilized lipase from *C. rugosa*, 1%	2:1–6:1 mol/mol	35–55	63.6% (4:1 mol/mol, enzyme 8%, water 6%, 45 °C)	[35]
Acid oil	Simultaneous enzyme-catalyzed esterification and transesterification	Batch, stirred (324–1275 rpm)	Methanol, stepwise addition (1/8 of the total amount after each hour), water 10%	Soluble lipases NS81020/NS81006 from genetically modified *A. oryzae*/*A. niger* microorganism	0.13:1–0.37:1 mL/g	28–52	88.7%/8 h (NS81020: 40.5 U/g, NS81006: 20.1 U/g, 2.4:1 mol/mol, 600 rpm, 28.11 °C),	[36]

(continued)

Table 5.1 (continued)

Raw material	Production method	Reactor	Alcohol	Catalyst (based on oil mass)	Alcohol/FFA ratio	Temperature, °C	Yield/time (reaction conditions)	Reference
Acid oil	Enzyme-catalyzed reaction preceded by filtration, acidification, and adsorption	Three packed-bed reactors in series with removal of glycerol at each step (mass flow rate 0.4–1.6 g/min)	Methanol (*n*-hexane 0–15%, water 0–15%)	Immobilized lipase from *Candida* sp. 99–125, 5–20%	1:1 mol/mol	35–55	90.2% (lipase 15%, *n*-hexane 10%, water 10%, 45 °C, 0.8 g/min)	[37]
Corn and sunflower acid oils	Enzyme-catalyzed esterification in *n*-hexane	Batch, stirred magnetically	Methanol (*n*-hexane, 5 mL/g of oil)	Immobilized lipase from *C. antarctica* (Novozym 435), 5–20%	0.5:1–2:1 mol/mol	30–60	63.6%/1.5 h (sunflower acid oil, lipase 15%, 1:1 mol/mol, 40 °C)	[38]
Olive acid oil	Non-catalytic esterification in supercritical conditions	Continuous tubular reactor (200–280 bar, flow rate 0.4–1.2 mL/min)	Methanol	–	0.7:1–1.5:1 mol/mol	300–380	92.3% (380 °C, 240 bar, 1.12:1, 0.4 mL/min)	[39]
Soybean soapstock	Acid-catalyzed esterification preceded by alkali saponification	Batch, shaken	Methanol	Sulfuric acid	0.83:1–3.3:1 g/g	35	>99%/10 min (methanol/fatty acids/sulfuric acid 30:1:5 mol/mol)	[40]

Raw material	Production method	Reactor	Alcohol	Catalyst (based on oil mass)	Alcohol/ FFA ratio	Temperature, °C	Yield/time (reaction conditions)	Reference
Acid oil	Enzyme-catalyzed esterification preceded by enzyme-catalyzed hydrolysis	Batch, stirred	Methanol	Immobilized lipase from *C. antarctica*, 1%	0.52:1 g/g	30	96%/24 h	[41]
Acid oil	Enzyme-catalyzed esterification preceded by enzyme-catalyzed hydrolysis	Batch, shaken (200 rpm)	Methanol	Lipase from *T. lanuginosus*, 2%	2:1 mol/mol	35	94/7 h	[42]
Soybean soapstock acid oil hydrolyzed in subcritical water	Enzyme-catalyzed esterification	Packed-bed bioreactor with a closed-loop for recirculation (5 mL/min) and a magnetically stirred tank (200 rpm)	Ethanol	Fermented solid produced (92 U/g and 5.8 U/g of hydrolytic and esterification activity, respectively) using *B. cepacia* grown on a mixture of sugarcane bagasse and sunflower seed meal (1:1 w/w)	3:1 mol/mol	45	88%/48 h	[43, 44]
Soybean soapstock acid oil hydrolyzed in subcritical water	Enzyme-catalyzed esterification	Batch, shaken (200 rpm)	Ethanol	Fermented solid produced (15 U/g) using *R. microsporus* grown on enriched sugarcane bagasse (20% of FFA)	10:1 mol/ mol	40	86%/48 h	[45]

(continued)

Table 5.1 (continued)

Raw material	Production method	Reactor	Alcohol	Catalyst (based on oil mass)	Alcohol/ FFA ratio	Temperature, °C	Yield/time (reaction conditions)	Reference
Acidulated rice bran soapstock	Enzyme-catalyzed transesterification	Continuous packed-bed reactor	Ethanol	Immobilized lipase from *T. lanuginosus*	4:1	20	92%/4 h	[46]
Acidulated soybean soapstock	Glycerolysis	Batch, stirred (350–500 rpm)	Glycerol, excess of 4–65%	Zinc Zinc acetate dihydrate (0.1–0.4% Zn)	NA	180–230	94.7%/2 h (0.1% catalyst, 200 °C, 350 rpm)	[47]

[a] *SPR* soap-splitting route

[b] 1 mol of naphthalene, 1 mol of distilled cottonseed fatty acids and 6 mol of 100% H_2SO_4 (a mixture of naphthalenstearosulfonic acid and H_2SO_4)

Haas et al. [21] optimized soybean acid oil esterification with methanol and catalyzed by sulfuric acid at 65 °C using statistical experimental design. Since greater than 15% of the FFAs remaining in the final reaction mixture as free or glycerol-linked, the reaction was inefficient within 26 h and therefore unacceptable for industrial use. In an alternative method, a high acid acid oil was prepared by the complete hydrolysis of AGs from the soapstock. The high acid acid oil was then esterified by sulfuric acid catalysis. The conversion of 89% was reached within 14 h at a methanol/FFAs/catalyst molar ratio of 1.8:1:0.17 at 65 °C. The uncompleted esterification was the result of the action of water formed. The new reaction step following removal of the formed water by centrifugation reduced the content of FFAs to 0.2%. Park et al. [25] esterified a high acid acid oil, obtained by the same procedure as in the previous study, using methanol and Amberlyst-15 and reached a maximum final ester content of 91.7% at the methanol-to-FFAs of 9:1 after double water evaporation during the process. Biodiesel yields reached with Amberlyst-15 and sulfuric acid were similar [26].

Luxem and Troy [30] patented a method where esterification of FFAs and transesterification of AGs occurred simultaneously under pressure (34.5 bar) with methanol in the presence of sulfuric acid at 130 and 150 °C without removing the by-products (glycerol and water). An 82% conversion was achieved within 60 min and 15 min, respectively. At longer reaction times and at higher temperatures, conversion degrees higher than 90% were achieved.

Wang et al. [22] studied biodiesel production from soybean acid oil in a pressurized stirred reactor using methanol and sulfuric acid as a methylation agent and as a catalyst, respectively, at 80 °C for the first 1 h and at 95 °C for the following 4 h. Under the optimal mass ratio of methanol/acid oil/catalyst (1.5:1:0.1), a conversion of 92% was reached within 3–5 h depending on the initial water content and the methanol-to-acid oil ratio. After distillation, the purity of the final biodiesel product was 97.6%, corresponding to a yield of 94% based on total FFA content in the initial raw material.

McNeff et al. [31] used microspheres of metal oxides (Zr, Ti, and Al) as catalysts to convert continuously different raw materials (acid oil among them) to methyl esters in a packed-bed reactor under high pressure and temperatures (300–450 °C). A good conversion of acid oils (90.2%) was achieved without loss of catalytic activity overextended applications.

Jin et al. [23] utilized a mixture of oil sediments and soapstock for producing FAMEs in a three-step process. The mixture of oil sediments and soapstock was first extracted with ethyl ether and, after the addition of saturated sodium chloride solution, it was centrifuged to obtain three phases. Sulfuric acid was added to the soap phase to get FFAs. This high acid acid oil was esterified (conversion degree 92.1% of theoretical) using methanol (5 mol per a mole of FFAs) and sulfuric acid (3%) at 85 °C within 5 h. In the third step, TAGs and phosphatides were extracted from the organic phase with acetone and then transesterified by methanol and sodium hydroxide at 65 °C within 1 h, producing a maximum FAME yield of 94%.

Shao et al. [24] optimized biodiesel production from rapeseed soapstock employing soap-splitting and short-path distillation. A biodiesel yield of 96.45% was achieved from the acid oil within 1.42 h with a methanol-to-acid oil ratio of 0.33:1 v/v and sulfuric acid of 1.44 vol% at 60 °C.

Li et al. [27] employed acidification of a soapstock, molecular distillation to separate FFAs and AGs, followed by acid-catalyzed esterification and base-catalyzed methanolysis, respectively. A solid superacid catalyst, $SO_4^{2-}/ZrO_2–TiO^2/La^{3+}$ (5%), was used in the esterification reaction undertaken at a methanol-to-oil molar ratio of 15:1 at 60 °C; the conversion of 98% was reached in 4 h. Base-catalyzed methanolysis reached a conversion of 97.25% within 30 min at the catalyst (sodium methoxide) loading of 0.6%, the methanol-to-oil molar ratio of 5:1, and 55 °C.

Guo et al. [28] prepared acid oil from a soybean oil soapstock by a process involving the removal of phospholipids and acidification of the soap phase. The acid oil was esterified with methanol in the presence of a solid acid lignin-derived carbonaceous catalyst. This catalyst had 3.5 times higher catalytic activity than sulfuric acid. The best conversion of above 97% was achieved within 5 h with a catalyst loading of 7% at a methanol-to acid oil molar ratio of 9:1 at 70 °C.

Pantoja et al. [29] optimized the FAME production from the buriti (*Mauritia flexuosa*) oil soapstock via acidulation and esterification using H_2SO_4 as a catalyst. The best acidulation conditions were the 0.8 molar ratio and the reaction time of 60 min whereas the best esterification conditions were the molar ratio of 18:1, catalyst loading of 4%, and reaction time of 14 h, which provided a yield of 92% and a conversion of 99.9%.

Domingues et al. [33] reported the use of a solid vanadyl phosphate catalyst in the simultaneous esterification of FFAs and transesterification of AGs from rapeseed acid oil with methanol. A mixture contacting 87% of methyl esters and 7.2% of FFAs was obtained within 6 h at 125 °C. The increase in the reaction temperature at 150 °C led to the biodiesel product containing 93.5% of methyl esters and 3.3% of FFAs. Spent catalyst can be regenerated by reoxidation of the reduced vanadium with air.

The production cost of biodiesel obtained from soybean soapstock was shown by an economic analysis to be for 25% less than that estimated for biodiesel produced from refined soybean oil, whereas engine emissions and performance during operation on the former biodiesel were comparable to those on the latter one [48].

Enzyme-Catalyzed Processes

Watanabe et al. [34] applied a two-step process including enzyme-catalyzed esterification of FFAs from acid oil and enzyme-catalyzed methanolysis of AGs using immobilized lipase from *C. antarctica*. In the first step, the esterification degree of 91% was achieved within 24 h at the methanol-to-acid oil molar ratio of 1:1. In the repeated batches, the biodiesel content at 24 h decreased by 24% after the tenth cycle, indicating that the lipase was unstable. At higher methanol-to-acid oil molar ratios (5–7.5:1), the lipase inactivation was avoided, and the esterification of FFAs within 24 h was increased (>96%). The second step included the dehydrated first-step product, refined rapeseed oil, methanol, and glycerol to convert AGs into methyl esters using immobilized lipase. The final product contained 91.1% of methyl esters. The enzyme was successfully employed in 100 cycles.

Shao et al. [35] optimized the biodiesel production from rapeseed soapstock by immobilized enzyme-catalyzed esterification after its saponification and acidification. All four employed parameters (enzyme amount, methanol-to-acid oil molar ratio, water content, and temperature) were found to be statistically important. The best conversion of 63.6% was reached under the optimal conditions. After molecular distillation, the methyl ester yield was increased above 95%.

Chen et al. [36] studied biodiesel production from acid oil using soluble lipases from genetically modified *Aspergillus oryzae*/*Aspergillus niger* microorganism. A central composite design showed that the influences of enzyme concentration, methanol-to-acid oil molar ratio, temperature, and agitation speed on the methyl esters yield were statistically significant. Under the optimal conditions, the biodiesel yield was 88.7%.

Chen et al. [37] catalyzed the reaction between a pretreated acid oil and methanol by immobilized *Candida* lipase in a series of three packed-bed reactors. The influences of lipase, *n*-hexane and water contents, temperature, and mass flow rate were analyzed. Under the optimum reaction conditions, the best methyl esters yield of 90.2% was obtained. The immobilized enzyme can be recycled with a relatively stable activity after removing glycerol adsorbed.

Tüter et al. [38] performed esterification of corn and sunflower acid oils with several alcohols using lipase Novozym 435 in *n*-hexane. The highest methyl ester content (6.6%) was obtained within 1.5 h at the methanol-to-acid oil molar ratio of 1:1 and 40 °C using a 15% enzyme. However, higher ester yields (about 70%) were obtained with other primer alcohols (*n*-propanol, *n*- and *i*-butanol, *n*- and *i*-amyl alcohol, and *n*-octanol).

Non-catalyzed Process

Akgün et al. [39] optimized the production of biodiesel from olive acid oil using non-catalyzed esterification with methanol under supercritical conditions in a continuous tubular reactor. The most effective factors were reaction temperature and flow rate of the reactants. The methyl ester yield of 92.3% was obtained under the optimum conditions (pressure of 240 bar, temperature of 380 °C, methanol-to-acid oil molar ratio of 1.12:1 and flow rate of 0.4 mL/min). After treating with bleaching earth and calcium hydroxide at 80 °C and filtering, the resulted product contained 96.6% methyl esters.

3.1.3 Hydrolysis Route

This route consists of hydrolysis (saponification) of all AGs to FFAs, followed by esterification of the obtained product containing primarily FFAs (Fig. 5.3). Alkali- and enzyme-catalyzed saponification was performed to achieve the complete hydrolysis. Acid and enzymatic esterifications were conducted to convert FFAs to methyl esters of fatty acids.

Chemically Catalyzed Processes

Haas et al. [40] described a two-step process involving alkaline hydrolysis of AGs and acid-catalyzed esterification of the obtained sodium salts of fatty acids. Although soapstock is already alkaline, sodium hydroxide has to be added to a final total concentration of 4.2% followed by incubation at 100 °C to complete hydrolysis within 2–4 h. Under these conditions, both AGs and phosphoacylglycerols were completely hydrolyzed. Before esterification, water was removed from the product of saponification by freeze-drying. The resulting dried product was converted to methyl esters by reaction with methanol in the presence of sulfuric acid. At the minimum molar ratio of methanol/fatty acids/sulfuric acid of 30:1:5, the resulting product containing more than 99% methyl esters was obtained at 35 °C within 10 min. The process produced biodiesel of high quality, but the product yield was only 60% of the theoretical yield.

Enzyme-Catalyzed Processes

A two-step enzymatic process for conversion of acid oil to biodiesel consisting of hydrolysis of AGs by lipase followed by esterification of FFAs with methanol by another lipase has been used [41, 42]. Watanabe et al. [41] used *Candida rugosa* lipase and immobilized *C. antarctica* lipases for hydrolysis of acid oil and esterification of FFAs with methanol to biodiesel, respectively. In the first esterification, where the hydrolyzed acid oil and methanol (molar ratio of 1:5) reacted in the presence of the enzyme (1%) at 30 °C, the conversion of 96% was reached within 24 h. The resulting reaction mixture was dehydrated and subjected to the second esterification to reach the total conversion of 99% for 24 h. Over 98% of total conversion was maintained for 40 cycles. Cruz et al. [42] obtained a FAME yield of 94% using the hydrolysis of an acid oil from soapstock of vegetable oil refining (a mixture of seeds) at 35 °C (shaking rate of 200 rpm, 1:0.5 water:oil mass ratio, 24 h) by *Thermomyces lanuginosus* lipase (3%) and then the esterification of the obtained FFAs with methanol (2:1 mol/mol, 35 °C, 200 rpm, 7 h) by the same lipase (2%).

A research group has been investigating a strategy for reducing the biodiesel production costs by a fermented solid with lipase activity in a solvent-free system in both batch reactor systems [43–45]. Lipases are produced by solid-state cultivation of a pathogenic (*Burkholderia cepaciaon*) [43, 44] or non-pathogenic (*Rhizopus microsporus*) microorganism [45] on a mixture of sugarcane bagasse and sunflower seed meal or sugarcane bagasse enriched with urea, soybean oil, and a mineral solution, respectively, and the dried fermented solid is directly used as the catalyst in the esterification of fatty acids with ethanol in a solvent-free system. When used in a packed-bed bioreactor in a closed-loop batch system, up to 30% of the reaction medium is sorbed onto the dried fermented solid, and the sorbed medium has a different composition compared to the bulk phase [43]. In further work, this research group develops a combined sorption-kinetic model describing the reaction kinetics for multiphasic ethyl esterification of fatty acids from soybean soapstock acid oil

[44]. Botton et al. [45] have improved this reaction system by using the non-pathogenic *R. microspores* to produce the fermented solid catalyst. The conversion of 86% of the soybean soapstock acid oil hydrolyzed in subcritical water was reached by the esterification reaction with ethanol (10:1 molar ratio, 40 °C, 48 h). The use of a fermented solid produced by a non-pathogenic microorganism and the possibility of using hydrolyzed low-quality fatty raw materials could render the scale-up of the enzymatic biodiesel production via hydro-esterification more feasible and more competitive with the chemically catalyzed processes. These results foster further studies on the scaling-up of the environmentally friendly biodiesel production process.

Choi et al. [46] synthesized FAEEs from acidulated rice bran soapstock via the *T. lanuginosus* lipase-catalyzed transesterification of acid oil with ethanol in a continuous packed-bed reactor. The water content of the substrate, temperature, and lanuginosus affected considerably the FAEE yield, and the optimum conditions were 4%, 20 °C, and 1:4, respectively, ensuring the maximum yield of 92%. The corresponding composition of the final product was 92% FAEEs, 3% FFAs, and 5% AGs. When glycerol was removed from the reaction mixture by intermittent washing with ethanol, the relative lipase activity was maintained over 82% for 27 cycles.

3.1.4 AG Route

The AG route is conducted by esterification of FFAs with glycerol (termed glycerolysis) to form AGs, which is then transesterified conventionally. High reaction temperatures (up to 250 °C) are required to complete the reaction. For the purpose of decreasing the reaction temperature in the AG route, Luxem and Mirous [49] screened various acid, base, and transition metal catalysts. The glycerolysis reactions between acid oil and crude neutralized glycerol were carried out at 180 °C for 4 h. The amount of catalyst was normalized based on equal equivalents of metal content per mole of acid oil. The most efficient catalysts were organo-metal catalysts, tetrabutyl titanate, dibutyl tin oxide, and tin oxalate. The best conversion of FFAs of 93% was achieved using tin oxalate (1%), whereas dibutyl tin oxide (2%) reached the conversion of 81%. The process was scaled-up using the latter catalyst, and the nearly complete acid conversion was achieved, resulting in the product with a low acid value (0.5 mg KOH/g). The final product of esterification was converted by base-catalyzed transesterification into biodiesel with the overall yield of 95%, which was reduced to 92% after distillation. Felizardo et al. [47] studied the glycerolysis reaction of FFAs from acidulated soybean soapstock using metallic zinc and zinc acetate dihydrate as a catalyst. The best methyl ester yield of 94.7% was obtained with a 0.1% catalyst at 200 °C for 2 h.

The produced methyl esters do not satisfy the specific biodiesel standards and can be used as a biofuel for steam or power generation [17].

3.2 Biodiesel from SBE

Acid-activated bleaching earth is an adsorbent of high capacity that is commonly used in the crude vegetable oil refining process (so-called bleaching process) to remove coloring pigments, residual phosphatides, soaps, etc. The produced solid waste material is known as SBE. Besides almost all impurities, this material adsorbs crude vegetable oil by up to 20–40% by mass [50]. A large amount of SBE is discarded from edible oil production. Based on 1.2–1.6 kg of the SBE per tonnes of edible oil produced [51] and the world edible oil production of 150.8 million tonnes in 2011 [18], the world generation of SBE is estimated to be about 180,000–240,000 tonnes/year. Most SBE is disposed of by inclusion in animal feeds, incineration, landfilling, or concrete manufacturing [17], and only its small amount is recovered and reused [51]. Disposal at landfills is unacceptable due to the potential environmental hazards and the cost of disposal.

More convenient ways to manage SBE are to utilize it as an alternative raw material and to convert it into valuable products. The adsorbed oil can be recovered from SBE by solvent [50, 52–55], supercritical carbon dioxide [56, 57], and lye [58] extractions. The extracted vegetable oil can be either recycled to the vegetable oil refining process or sold as a raw material to lubricant and biodiesel industries [51, 59–61]. The SBE reactivated by heating treatment (500 °C) and a combination of heating and acid treatment (0.1 M HCl) improves palm oil biodiesel filterability [62]. By physical, chemical, or biochemical treatment, the amount of organics contained by SBE are reduced to nearly zero, and the remaining deoiled solid material (up to 60%) can be freely disposed on landfills, recycled to the oil refining process, or used as a soil conditioner [63].

The conversion of the waste vegetable oil from SBE into biodiesel has already been investigated. A review of the selected literature related to the use of SBE in biodiesel production is presented in Table 5.2. SBE originates from the refinery of palm, soybean, or rapeseed oils. Two possible ways of biodiesel production processes are employed. The first group includes the extraction of waste vegetable oil that is followed by transesterification of the extracted oil, and the second group involves in situ extraction and transesterification of waste oil.

3.2.1 Extraction Followed by Transesterification

The waste vegetable oil absorbed on SBE is usually recovered by solvent (conventional maceration and Soxhlet extraction) and supercritical CO_2 extraction. *n*-Hexane is mainly used as an extracting solvent, although some other solvents are also employed, such as methanol, ethanol, and petroleum ether. The biodiesel production method is performed as a one-step (methanolysis) or two-step (esterification followed by methanolysis) process in agitated batch reactors.

Table 5.2 A review of the use of SBE in biodiesel production

Vegetable oil	Extraction method/ solvent	Biodiesel production method	Reactor	Alcohol	Catalyst[a]	Alcohol/oil ratio	Temperature, °C	FAME yield/ time	Reference
NA	Soxhlet apparatus/*n*-hexane	Homogeneously catalyzed	Batch, stirred 800 rpm	Methanol	NaOH 1.5–2.5%	5:1–7:1 mol/ mol	50–60	26.0–93.2%/30 min	[64]
Palm	Soxhlet apparatus/ methanol, ethanol, petroleum ether, *n*-hexane	Heterogeneously catalyzed	Batch, stirred	Methanol	CaO 6.0%	0.5:1 g/g	65	98.6%/2.5 h	[65]
		Homogeneously catalyzed			NaOH, KOH 1.0%	0.25:1 g/g		99%/1 h	
Palm	Cold extraction/*n*-hexane	Heterogeneously catalyzed	Batch, stirred	Methanol	Cocoa pod ash 2.2%	5.62:1 mol/ mol	100	86%/2 h	[66]
		Homogeneously catalyzed			KOH 1%			81.2%/2 h	
Palm	Double maceration/*n*-hexane	Lipase-catalyzed; water, 75%	Batch, reciprocally shaken 175 spm	Methanol	*R. oryzae* lipase, 200 IU/mL	1:1–6:1 mol/ mol	37	10–55%/96 h	[67]
Soybean									
Rapeseed									
Palm (from acid-activated and neutral SBE)	Soxhlet apparatus; maceration/*n*-hexane	Two-step process: esterification followed by alcoholysis	Batch	Methanol	Sulfonated ion-exchange resin, 10%	1:2 g/mL	80	84%/30 min (from acid-activated SBE)	[61]
	Supercritical CO_2 extraction				NaOH, 0.031 M (acid-activated SBE) or 0.026 M (neutral SBE)			82%/10 min (from neutral SBE)	

(continued)

Table 5.2 (continued)

Vegetable oil	Extraction method/ solvent	Biodiesel production method	Reactor	Alcohol	Catalyst[a]	Alcohol/oil ratio	Temperature, °C	FAME yield/ time	Reference
Soybean	Soxhlet apparatus/*n*-hexane	Two-step process: esterification followed by alcoholysis	Batch, stirred	Methanol	NaOH 1.0%	0.29:1 g/g; 6:1–12:1 mol/mol	60–80	85–90%/30–90 min	[51]
Palm	In situ extraction	In situ homogeneously acid or base catalyzed	Batch, stirred	Methanol	KOH H_2SO_4		65	Up-16%/5 h	[68]
Palm	In situ extraction	In situ two-step process (acid-catalyzed esterification followed by base-catalyzed transesterification)	Batch, stirred	Methanol	NaOH 2.39%	6:1 mol/mol	64.3	21.5% (biodiesel/SBE)/2.3 h	[69]
Palm	In situ extraction	In situ two-step process (acid-catalyzed esterification followed by base-catalyzed transesterification)	Batch, stirred (730 min)	Methanol	NaOH 1.5% of SBE	10:1 L/kg SBE	65	84.5%/90 min	[70]
Palm	In situ extraction	In situ; lipase-catalyzed; *n*-hexane, kerosene, diesel oil, 10% of SBE	Batch, stirred 250 rpm	Methanol	*C. cylindracea* lipase, 10% of SBE	4:1 mol/mol	37	100%/2–3 h	[71]

Vegetable oil	Extraction method/ solvent	Biodiesel production method	Reactor	Alcohol	Catalyst[a]	Alcohol/oil ratio	Temperature, °C	FAME yield/ time	Reference
Palm	In situ extraction	In situ; lipase-catalyzed; *n*-hexane, 0.33–0.82 g/g of SBE	Batch, reciprocally shaken 120 spm	Methanol, ethanol, 1-propanol, 1-butanol, *iso*-butanol, *iso*-amyl alcohol, *n*-octanol	*P. pancreas* Type II, *C. rugosa*, *C. cylindracea*, *R. oryzae*, *A. niger*, *R. japonicas* lipases, 5 IU/g of SBE	3:1–6:1 mol/mol	37	96%/8 h (*C. cylindracea*, 1-butanol, *n*-hexane)	[63]
Rapeseed	In situ extraction	In situ; lipase-catalyzed; kerosene, diesel oil, 1.0:2.5 kg/kg of SBE	Batch, pilot, 30 rpm	Methanol	*C. cylindracea* lipase, 10% of SBE	3.5:1 mol/mol	15–55	97%/12 h (25 °C)	[72]

[a] Percentages are based on oil mass

One-Step Processes

In this case, base- or enzyme-catalyzed methanolysis is undertaken. Alkali hydroxides (KOH, NaOH), calcium oxide, and *Rhizopus oryzae* lipase are employed as catalysts. Gűl et al. [64] optimized NaOH-catalyzed methanolysis of the waste vegetable oil extracted from SBE by response surface methodology. Lim et al. [65] compared the effects of CaO and alkali hydroxides as catalysts for methanolysis of the waste vegetable oil. In the CaO-catalyzed reaction, the highest FAME yield of 98.6% was achieved within 2.5 h at the following reaction conditions: the methanol-to-oil mass ratio of 0.5:1, CaO loading of 6%, and reaction temperature of 65 °C. Alkali hydroxides achieved 99% conversion in 1 h at the following optimal reaction conditions: methanol-to-oil mass ratio of 0.25:1, catalyst loading of 1%, and reaction temperature of 65 °C. The use of CaO as a catalyst has several advantages over homogeneous catalysts. CaO can be easily separated from the reaction mixture and reused for several runs without significant deactivation [73]. Aladetuyi et al. [66] used cocoa pod ash as a solid catalyst to produce biodiesel from palm kernel oil recovered from SBE. The biodiesel yield provided by cocoa pod ash was 86% and higher than that achieved by potassium hydroxide (81.2%), respectively. Therefore, this work suggests that agricultural residues could replace alkali catalysts for biodiesel production. Lara Pizarro and Park [67] used *R. oryzae* lipase to catalyze the methanolysis of extracted waste vegetable oils in a water-containing system. Optimum reaction conditions were the methanol-to-oil molar ratio of 4:1, the water content of 75%, the enzyme amount of 67 IU/g, and the reaction temperature of 35 °C. The highest FAME yield of 55% was reached with palm oil within 96 h of reaction.

Two-Step Processes

These processes are used for producing FAMEs from waste vegetable oils having a high content of FFAs, such as waste palm and rapeseed oils. The presence of FFAs strongly affects process performance and economics. If a homogeneous base catalyst is employed, soaps will be produced in the reaction between the base catalyst and FFAs, which inhibits FAME synthesis. If a homogeneous acid catalyst is used, saponification is avoided but the transesterification rate is slow. By applying a two-step process consisting of acid-catalyzed esterification followed by base-catalyzed transesterification, the mentioned disadvantages of homogeneous base and acid catalysts are overcome.

Kheang et al. [61] employed a sulfonated ion-exchange resin and sodium hydroxide as a catalyst to obtain FAMEs from the waste vegetable oil extracted from SBE, which contains more than 11% of FFAs. The esterification step using the resin catalyst (oil-to-resin ratio 10:1) converts most of the FFAs to FAMEs. The conversion of TAGs to FAMEs in the transesterification step using sodium hydroxide was more than 98%. If the content of FFAs is extremely higher, such as in SBE exposed to air for a couple of months, the amount of resin catalyst and the reaction time should be increased. The obtained methyl esters have comparable fuel characteristics as petroleum diesel.

Huang and Chang [51] esterified FFAs from waste oil by methanol in the presence of sodium hydroxide until its content was reduced below 2%, and then, the esterified oil was subjected to methanolysis using again sodium hydroxide when the conversion gave a FAME yield between 85% and 90%. They also performed a financial analysis showing that the production cost of biodiesel from the waste oil was lower than those of diesel or biodiesels obtained from refined oil or WCO.

3.2.2 In Situ Extraction and Transesterification

In situ biodiesel production is a novel method for producing biodiesel from oil-bearing materials in which extraction and transesterification take place simultaneously. It integrates the oil extraction from SBE and the extracted oil conversion into biodiesel in one continuous process so that the process can reduce the time and the cost of biodiesel production [69]. The biodiesel production from SBE containing waste oil can be performed through two consecutive or simultaneous oil extraction and reaction processes; commonly transesterification stage is proceeded by the pre-esterification stage due to a high FFA content of the SBE oil. Extracting solvent may be either alcohol used as esterification/transesterification reagent or an organic solvent. The esterification is usually catalyzed using an acid (sulfuric acid). Only homogeneously and enzyme-catalyzed methanolysis has been investigated so far.

Mat et al. [68] have compared the activity of homogeneous base (potassium hydroxide) and acid (sulfuric acid) catalysts for in situ methanolysis of SBE containing waste palm oil in the presence of *n*-hexane as an extracting solvent. The use of base catalyst produced a higher FAME yield in a shorter time than the use of acid catalyst, as expected. However, reported FAME yields are too low (below 20%) to be interesting for developing an industrial biodiesel production process.

In situ homogeneous biodiesel production from SBE containing waste palm oil can be carried out through a two-stage process that includes in situ esterification and transesterification [69, 70]. The first esterification stage is catalyzed by an acid (sulfuric acid) whereas the second transesterification is base-catalyzed using an alkali (sodium hydroxide). Sugiharto et al. [69] optimized the in situ transesterification of the pre-esterified SBE palm oil using sodium hydroxide regarding reaction temperature, catalyst concentration, and time. The optimum conditions (64.33 °C, 2.39% NaOH, and 2.32 h) provided a biodiesel yield of 21.45% (biodiesel/SBE). Under the optimum agitation speed (730 rpm), Suryani et al. [70] obtained the biodiesel yield and purity of 84.5% and 99.3%, respectively, for 90 min.

Park and coworkers [63, 71, 72] have investigated in situ transesterification of waste oils catalyzed by lipases of different origin in the presence of different organic solvents. Various primary alcohols were used for transesterification. Of several tested lipases, the most active originates from *Candida cylindracea*, displaying a conversion of 78% within 4 h of methanolysis reaction in the presence of *n*-hexane. However, this lipase reached the conversion of 96% in 8 h of reaction in the presence of 1-butanol and *n*-hexane. Kojima et al. [71] investigated fossil fuels (diesel oil and kerosene) as a solvent for the transesterification of TAGs embedded in

SBE. The lipase showed the highest stability in diesel oil. A nearly 100% conversion within 3 h was obtained from SBE using diesel oil as a solvent in the presence of 10% lipase. Kerosene was shown to be as good solvent as *n*-hexane. These results were utilized to perform lipase-catalyzed biodiesel production from SBE in a 50-L pilot plant [72]. With 1% lipase added to SBE, the conversion reached 97% within 12 h at 25 °C. A mixture of biodiesel and diesel oil at the ratio of 45:55 meets the standard EN 14214.

Schematic presentation of in situ FAME production from SBE based on the use of lipase in the presence of an appropriate solvent is shown in Fig. 5.4. The production process using diesel oil is much simpler than that using *n*-hexane [71]. When diesel oil is used, a mixture of FAMEs and diesel oil is produced directly the following filtration after the extraction/esterification, while when *n*-hexane is employed, an additional separation step is needed. The filtration cake consists of oil-free waste solid material, FAMEs, glycerol, solvent, and enzyme. The main product, FAMEs, can be recovered from the filtration cake by extraction with *n*-hexane. The solvent can be recuperated and reused in the process. However, it is impossible to isolate lipase from the FAME-free waste solid material. This final by-product can be regarded as immobilized lipase that can be recycled to the process so long as the lipase is active, which will decrease the catalyst cost. The repeated production of FAMEs with SBE was demonstrated in solvent-free systems [74]. The repeated batch and fed-batch processes were conducted for nine and six cycles without a significant enzyme inactivation, but the FAME yield was twice higher in the former process.

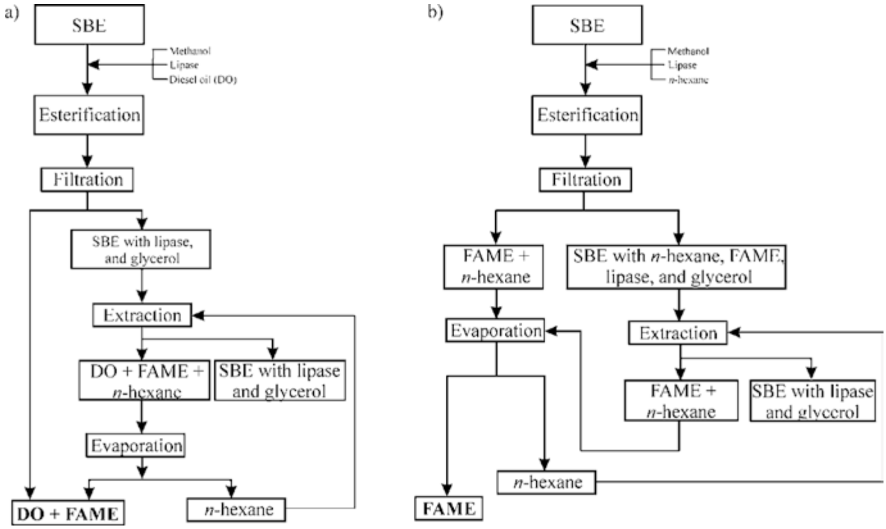

Fig. 5.4 Schematic diagram of the FAME production from spent bleaching earth using diesel oil (**a**) and *n*-hexane (**b**) as the solvent. (Adapted from [61])

3.3 Biodiesel from DD

DDs are a valuable by-product in the last step of vegetable oil refinery, called deodorization, where odoriferous components and FFAs are removed from the refined oil by vacuum steam distillation. The amount of DD is typically about 0.2–0.5% of the raw material. Based on the annual world's production of edible oils [18] and the assumptions suggested by Echim and coworkers [17], the world's generation of DD in 2019 is estimated to be 4.7–8.1 million metric tonnes, respectively. The composition of DD depends on the vegetable oil origin, the refining procedure, and the operating conditions of the distillation plant [17]. Generally, it is rich in FFAs (33–81%), the unsaponifiable matter containing tocopherols (vitamin E), sterols and squalene (6.6–41.2%), and AGs (0.72–13.6%).

DDs are a good source of bioactive compounds (sterols, tocopherols, and squalene). These compounds can be extracted and further used in the pharmaceutical industry, cosmetics, and as food additives. Furthermore, FFAs from DDs are mostly used as additives for animal food, fluidizing agents for lecithin, or as medium-grade soaps. DD have also nonfood applications, such as a biofuel in the mixture with the fuel oil to fire the steam boilers [17].

There are two possible routes to produce biodiesel from DD, namely by direct esterification of FFAs or by conversion of FFAs to AGs by glycerolysis prior to transesterification, as shown in Fig. 5.5. Direct FFA esterification is performed not only for the biodiesel production but also as a preliminary step in the purification of the tocopherols and sterols. Reviews of the literature on biodiesel production from

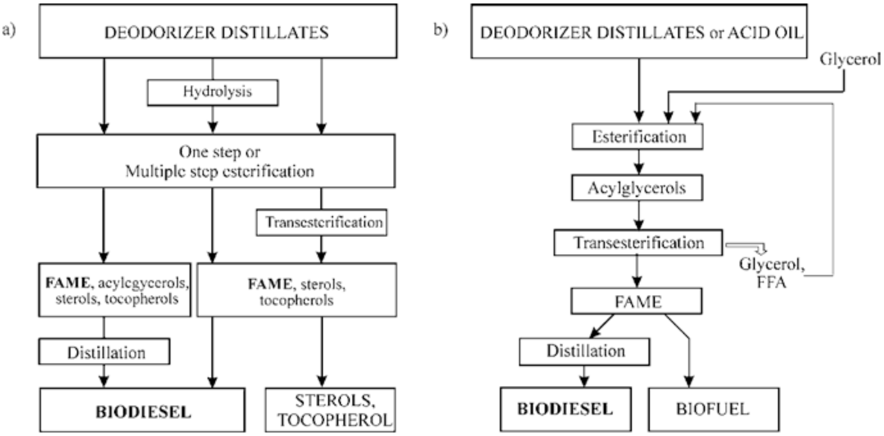

Fig. 5.5 Production of biodiesel, sterols, and tocopherols from deodorizer distillates by direct esterification (**a**) and production of biodiesel/biofuel via acylglycerols route from deodorizer acid oils or distillates (**b**). (Adapted from [17])

DD via the two routes are given in Table 5.3. DD originates from the refinery of palm, soybean, rapeseed, corn, and canola oils. Direct esterification of FFAs catalyzed by sulfuric acid, ion-exchange resins, or lipases has been much more studied than glycerolysis of FFAs which has been catalyzed either by lipases or was conducted in the absence of any catalyst. Usually batch stirred reactors are employed, although a packed-bed reactor and a continuous stirred tank reactor are also applied. Methanol is mainly used as an esterification agent, whereas other alcohols (ethanol, butanol) are rarely employed. The yield of final reaction products depends on the origin of DD and the reaction conditions applied.

3.3.1 Direct Esterification

Chemically Catalyzed Esterification

Facioli and Arellano [75] described an esterification process catalyzed by concentrated sulfuric acid to obtain FAEEs from soybean DD. The process was statistically optimized, and a conversion degree of 94% was achieved under the optimum conditions: ethanol-to-FFAs molar ratio of 6.4:1 to 11.2:1, H_2SO_4 amount of 0.9–1.5% and reaction time from 1.3 to 2.6 h. The esterification of FFAs with ethanol was the predominant reaction, while the loss of tocopherols was lower than 5.5%. An excess of ethanol was necessary for obtaining the best conversion.

Verhé et al. [76] reported a process of converting the DD to biodiesel by methanolysis catalyzed by sulfuric acid at 75 °C for 5 h. The methanol-to-FFA weight ratio of 1:1 and 5% sulfuric acid were employed. The crude biodiesel was washed with water, dried, and distilled to increase the quality of the FAMEs. The distillation pitch was processed for obtaining sterols and tocopherols.

Chongkhong et al. [77, 78] studied batch and continuous esterification of palm fatty acid distillate (93% FFAs) with methanol in the presence of sulfuric acid as a catalyst. The conversion higher than 95% was achieved in the batch process with the methanol-to-distillate molar ratio of 4.3:1 with 1.834% of H_2SO_4 at 90 °C within 2 h, while the optimum conditions for the continuous process were methanol-to-distillate molar ratio of 8:1, 1.834% of H_2SO_4, 70 °C and retention time of 60 min. The batch esterification yield (99%) was higher than the continuous yield (97%). A further treatment of the obtained product, consisting of FFA neutralization and AG transesterification, was required to obtain biodiesel, which complies with the specifications. The flow diagram for the proposed continuous process operated under mild reaction conditions is shown in Fig. 5.6.

Villardi et al. [79] compared the conversion of FFAs present in soybean DD into FAEEs through the batch esterification reaction using methanol with and without catalyst (sulfuric acid) and free catalyst in a batch reactor. In the presence of the catalyst (3%), the maximum conversion was 99.7% at the ethanol-to-oil molar ratio of 10:1 and 100 °C in 180 min whereas in the absence of the catalyst, the maximum conversion was lower (89.0%) at the same ethanol-to-oil molar ratio at a higher temperature (280 °C) but a shorter reaction time (105 min). These results indicate

Table 5.3 A review of the use of deodorizer distillates in biodiesel production

Vegetable oil	Biodiesel production method	Reactor	Alcohol	Catalyst[a]	Alcohol/FFA ratio	Temperature, °C	Yield/time	Reference
Soybean	Direct acid esterification	Batch, stirred magnetically	Ethanol	H_2SO_4, 0.4–1.6%	2:1–12:1 mol/mol	80	45.6–94.2%/0.2–2.8 h	[74]
	Direct acid esterification	Batch	Methanol	H_2SO_4, 5%	1:1 g/g	75	NA/5 h	[75]
Palm	Direct acid esterification	Batch	Methanol	H_2SO_4, 0–5.5%	0.4:1–12:1 mol/mol	70–100	96% (4.3:1 mol/mol, 1.83% H_2SO_4, 90 °C)/2 h	[76]
		Continuous stirred tank reactor		H_2SO_4, 1.834%	6.5:1–9.5:1	70 and 75	/60 min	
Palm	Direct acid esterification followed by neutralization	Batch, stirred magnetically, 300 rpm	Methanol	H_2SO_4, 0.92–2.75%	5.7:1–8.8:1 mol/mol	65–75	99% (8.8:1 mol/mol, 75 °C)/60 min	[77]
		Continuous stirred tank reactor		H_2SO_4, 1.83%	8.8:1 mol/mol	75	97%/60 min	
Soybean	Direct acid esterification followed by neutralization	Batch, stirred magnetically	Ethanol	SBV-780, SAPO-34, niobia, niobic acid, 3%	2:1 mol/mol	100	30%/2.5 h	[78]
Soybean	Direct acid esterification, supercritical conditions	Batch	Ethanol	H_2SO_4, 3%	10:1 mol/mol	100	99.7%/180 min	[79]
				Catalyst-free		280	89.0%/105 min	
Palm	Direct acid esterification	Packed-bed column reactor	Methanol	Cation-exchange resins D001	8:1–22:1	52–60	81.66% (17.25:1, 60 °C)/56.28 min	[80]

(continued)

Table 5.3 (continued)

Vegetable oil	Biodiesel production method	Reactor	Alcohol	Catalyst[a]	Alcohol/ FFA ratio	Temperature, °C	Yield/time	Reference
Rapeseed	Direct acid esterification	Packed-bed column reactor	Methanol	Cation-exchange resins D002	3:1–15:1 mol/mol	40–80	97% (9:1 mol/mol, 60 °C, catalyst 18%, 4 h)	[81]
		Batch, stirred 200 rpm		H_2SO_4, 5%	12:1 mol/mol	60	97%/4 h	
Rapeseed	Direct acid esterification followed by transesterification	Packed-bed column reactor	Methanol	Cation-exchange resins D002	8:1 mol/mol	60	93.7% (substrate flow rate 1 mL/min)	[82, 83]
				KOH, 0.8%	4:1 mol/mol	60	97.4%	
Soybean	Esterification of pre-esterified DD	Batch	Methanol	Duck eggshell (CaO), calcined (900 °C), 10%	10:1	60	94.6%/80 min	[84]
Corn	Direct esterification	Batch, under reflux	Methanol	Tin-alginate bead, 4%	12:1 mol/mol	65	96.8%/2 h	[85]
Soybean	Ultrasound-assisted esterification of pre-esterified DD	Static probe sonication	Methanol	NaOH, 1.8%	10:1	25 (initial)	72.6%/40 min (on/off-time 2 s/2 s)	[86]
		Countercurrent probe sonication (200 mL/min)					96.1%/50 min (on/off-time 4 s/2 s)	
Soybean	Dual-frequency countercurrent (150 mL/min) ultrasound-assisted (20/28 kHz, 400 W of each probe) esterification of pre-esterified DD (<0.4% water, <2 mg KOH/g)	Simultaneous mode	Methanol	NaOH, 1.8%	8:1	25 (initial)	96.3%/40 min (on/off-time 4 s/2 s)	[87]
		Sequential mode		NaOH, 1%			90%/30 min (on/off-time 4 s/4 s)	

Vegetable oil	Biodiesel production method	Reactor	Alcohol	Catalyst[a]	Alcohol/FFA ratio	Temperature, °C	Yield/time	Reference
Canola	Enzyme-catalyzed esterification	Batch, stirred magnetically	Methanol	Immobilized lipase Randozyme SP-382 (2.7–4.3%)	1:3:1–1.9:1 mol/mol	51.6–68.4	>95% (1.8–2.0 mol/mol, 50 °C)	[83]
Soybean	Enzyme-catalyzed esterification, solvent-free	Batch, stirred magnetically	Ethanol	Immobilized lipase *M. miehei* (Lipozyme$^{\text{IM}}$)	0.3:1–3.7:1 mol/mol	30–70	>88% (1.7:1–2.3:1 mol/mol, catalyst 13.6–16.5%, 46.4–53.6 °C)	[88]
Soybean	Enzyme-catalyzed esterification; *n*-hexane	SC-CO$_2$ reactor	Butanol	Immobilized lipase *M. miehei*, 15%	1.2 M	36	95%/3 h	[89]
		Shake flask					88%/7 h	
Soybean	Simultaneous enzyme-catalyzed esterification and transesterification; *tert*-butanol, 80%	Shake flask, 150 rpm	Methanol	Immobilized lipases *T. lanuginosa* (Lipozyme TL-IM, 3%) and *C. antarctica* (Novozym 435, 2%)	3.9:1 mol/mol	40	>90%/24 h	[90]
Soybean	Enzyme-catalyzed methanolysis, solvent-free	Shake flask, 150 rpm	Methanol	Immobilized lipase *C. antarctica* (Novozym 435, 2%)	3.0:1–3.9:1 mol/mol	40	>60%	[91]
Palm	Enzyme-catalyzed esterification, solvent-free	Batch, stirred magnetically	Methanol Ethanol (stepwise addition)	Immobilized lipases from *R. miehei* (Lipozyme RM-IM), *T. lanuginosus* (Lipozyme TL-IM), and *C. antarctica* (Novozym 435); up-9%	1:8–4:1 g/g	60	93% (1% Novozym 435, ethanol)/2.5 h	[92]

(continued)

Table 5.3 (continued)

Vegetable oil	Biodiesel production method	Reactor	Alcohol	Catalyst[a]	Alcohol/ FFA ratio	Temperature, °C	Yield/time	Reference
Rapeseed	Enzyme-catalyzed esterification	Batch, shaken (200 rpm)	Methanol	*Candida rugosa* lipase (750 U/g, content 50% water)	167 mL/2 g oil	35	92.63%/30 h	[93]
				Rhizopus oryzae lipase (200 U/g, content 37.5% water)		40	94.36%/9 h	
				Synergetic effect of the two lipases (0.84 oil/ lipase ratio; 46% water)		34	98.16%/6 h	
Palm	Enzyme-catalyzed esterification, solvent-free, various solvents	Batch	Methanol	Immobilized lipase *C. antarctica* (Novozym 435, 13%)	0.5–6% of the distillate	50–60	95%/1 h	[94]
	Direct acid esterification			Ion-exchange resin (Amberlyst 15, 20%)	10–60% of the distillated		97%/6–8 h	
Corn	Enzyme-catalyzed glycerolysis	Batch, stirred magnetically, 800 rpm	Glycerol	Immobilized lipases from *R. miehei* (Lipozyme RM-IM), *T. lanuginosus* (Lipozyme TL-IM); *A. niger* (Lipase A6), *M. javanicus* (Lipase M10), *R. oryzae* (Lipase F-AP15), *P. fluorescens* (Lipase AK), and *R. niveus* (Newlase F), 10%	1:1–3:1 mol/mol	50–70	70%/5 h	[95–97]
Palm							52%/6 h	
Soybean							69.9%/4 h	

Vegetable oil	Biodiesel production method	Reactor	Alcohol	Catalyst[a]	Alcohol/ FFA ratio	Temperature, °C	Yield/time	Reference
Mixed oils	Enzyme-catalyzed glycerolysis	Batch, stirred, 900 rpm	Glycerol	Immobilized lipase from *C. antarctica* (Novozym 435), *R. miehei* (Lipozyme RM-IM), and *T. lanuginosus* (Lipozyme TL-IM), 1.9%	0.11:1–5.15:1 mol/mol	60	46% (Novozyme 435, 2.5:1 mol/mol)/3 h	[98]
Fatty acid distillate	Non-catalyzed glycerolysis	Batch reactor, stirred, 60 rpm (90 mbar)	Glycerol	–	1:1	200	85.3%/345 min	[99]

[a] Percentages are based on oil mass

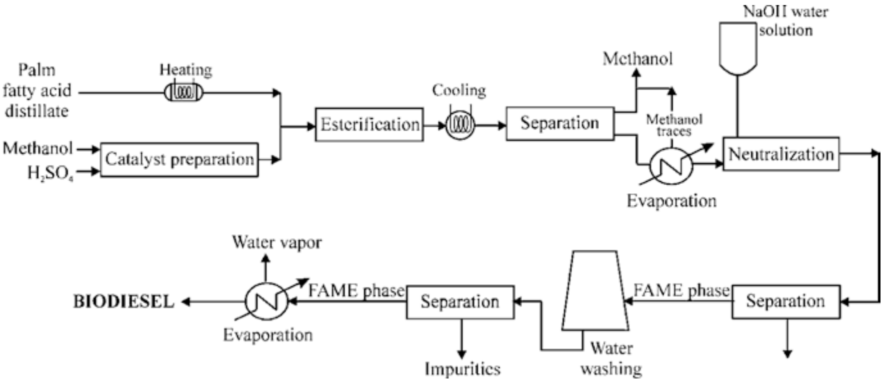

Fig. 5.6 A schematic diagram of a continuous unit for biodiesel production from palm fat acid distillate. (Adapted from [68])

that the supercritical medium reduces the oil conversion to FAEEs due to the parallel reactions occurring and to the degradation of acids and esters at the required high temperature and pressure. The developed kinetic model based on the one-step reversible second-order reactions agrees well with the experimental data.

Souza et al. [80] tested several solid acid catalysts for the esterification of soybean oil DD with ethanol. The highest conversion (49%) was achieved with 9% of a commercial zeolite type (CBV-780) at 100 °C within 2.5 h. Xi and Cao [81] esterified a palm oil DD using a cation-exchange resin as a catalyst and achieve the conversion of about 82% under the optimum reaction conditions (methanol-to-DD molar ratio of 17.25:1 and 60 °C).

Liu and Wang [82] performed esterification of FFAs from rapeseed oil DD catalyzed by a cation-exchange resin in a packed column reactor. The conversion of over 96% was achieved under the following optimal conditions: the resin catalyst dosage of 18% (based on oil mass), the methanol-to-oil molar ratio of 9:1, the reaction temperature of 60 °C, and the reaction time of 4 h. The catalyst can be regenerated and reused. In ten repeated batch cycles (40 h), biodiesel yield was over 88%. This process was as effective as the process catalyzed by sulfuric acid, but it had no washing step. The process was further improved by including alkali-catalyzed transesterification after the pre-esterification step [83]. The biodiesel yield by KOH-catalyzed transesterification was 97.4% using a methanol-to-oil molar ratio of 4:1 at 60 °C within 1.5 h. Furthermore, biodiesel and tocopherols were co-produced from soybean oil DD combining a pretreatment with supercritical carbon dioxide extraction. The pretreatment included cation-exchange resin-catalyzed esterification, cold recrystallization to removing sterols, and then alkali-catalyzed transesterification.

Yin et al. [84] produced biodiesel from a pre-esterified soybean oil DD using calcined duck eggshell (DES) as an inexpensive and environment-friendly catalyst after calcination (900 °C). The DD pre-esterification with methanol (12:1) was catalyzed by sulfuric acid (1.5%) at 60 °C for 2 h. The process of biodiesel production from pre-esterified DD using the obtained CaO as catalyst was carried out under the optimal conditions (catalyst amount of 10 wt%, methanol-to-oil ratio of 10:1, 60 °C, 80 min) provided the biodiesel yield of 94.6%. The derived catalyst can be reused five times with the biodiesel yield above 80%. The obtained results indicate that catalysts prepared from carbonate-rich waste or natural products are suitable for catalyzing biodiesel production.

Naz et al. [85] prepared a novel solid tin-alginate catalyst was prepared from sodium alginate polymer, which was used for the esterification of corn DD with methanol. High recovery of 97.6% of FAMEs was obtained after eight cycles using the reprocessed catalyst under the optimized reaction conditions. Hence, by replacing the homogeneous acid and base catalysts and ease of catalyst separation, the tin-alginate catalyst has a great potential for green biodiesel production from DD with a high free fatty acid content.

Although the ultrasonic-assisted biodiesel production from a variety of feedstock has been frequently studied, a few studies have focused on DD as feedstock [86, 87]. Biodiesel production from soybean oil DD was enhanced by countercurrent pulsed ultrasound [86], compared to the transesterification under static probe sonication; the values of the rate constant were 0.68 L/mol/min and 0.56 L/mol/min, respectively. Under the optimal conditions (initial temperature 25 °C, methanol-to-oil molar ratio 10:1, flow rate 200 mL/min, catalyst content 1.8%, ultrasound working on/off-time 4 s/2 s and total operating time 50 min), determined using a single-factor experiment design, the biodiesel conversion was 96.1%. The same research group intensified the transesterification of the pre-esterified soybean oil DD by dual-frequency countercurrent pulsed ultrasound, compared to a single-frequency ultrasound-assisted reaction [87]. The highest biodiesel conversion was achieved by the combination of 20/28 kHz. Under the optimum conditions (methanol-to-oil molar ratio 8:1, catalyst content 1.8%, the water content less than 0.4%, the acid value less than 2 mg KOH/g), the biodiesel conversion was 96.3%. The transesterification reactions assisted by single-frequency static and dual-frequency countercurrent (simultaneous mode) pulsed ultrasound are pseudo-second-order with the energy activation of 26.034 kJ/mol and 18.122 kJ/mol, respectively, indicating that the latter is easier to occur than the former.

Enzyme-Catalyzed Esterification

Ramamurthi et al. [88] obtained up to 96.5% conversion by methyl esterification of FFAs from canola oil DD (CODD) using immobilized lipase *Randozyme* SP-382 as a biocatalyst at temperatures around 50 °C and at a methanol-to-FFA molar ratio between 1.8 and 2.0 with no use of vacuum or water-removing agent. The inhibitory effect of methanol on the lipase activity was reduced by working at the lower temperature (around 50 °C). The esterification was considered to be a preliminary step preceding the recovery of sterols and tocopherols.

Facioli and Barrera-Arellano [89] reported the enzymatic esterification of the FFAs from soybean DD with ethanol using immobilized fungal lipase (Lipozyme IM) as a catalyst. The best conversion (above 88%) was obtained within 2 h with the lipase concentration of 10.7–23.0%, ethanol-to-FFA molar ratio of 1.7–3.2:1, and temperature of 46.4–53.6 °C. During the process, no losses of tocopherols were noticed.

Nagesha et al. [90] showed that supercritical carbon dioxide was a potential medium for esterification of FFAs from hydrolyzed soybean DD with butanol using an immobilized *Mucor miehei* lipase. Process conditions were optimized by conducting a statistical design method. A pressure of 122 bar, butanol concentration 1.2 M, enzyme concentration 15% (w/w), temperature 36 °C, and incubation time of 3 h were the optimal conditions ensuring 95.2% conversion of FFAs into butyl esters. This esterification process of FFAs is faster than the shake-flask method, where it takes 7 h to reach 88% conversion.

Wang et al. [91] described a process of simultaneous esterification of FFAs (28%) and transesterification of AGs (60%) from soybean DD to alkyl esters. A mixture of two enzymes (3% Lipozyme TL-IM and 2% Novozym 435) was employed in the presence of *tert*-butanol as cosolvent, which eliminated the negative effects of the methanol excess and glycerol on the enzyme stability. The activity of lipase was stable after 120 cycles. The maximum FAME yield of 84% was achieved with increasing *tert*-butanol content up to 80% (based on the oil mass). An adsorbent, silica gel or molecular sieve, was added to the reaction mixture (ten times maximum water mass) to control by-product water concentration, ensuring the biodiesel yield of 93% and 97%, respectively.

Du et al. [92] studied the enzymatic esterification of soybean oil DD. The reaction was Novozym 435-catalyzed methanolysis at 40 °C in a solvent-free medium. The lipase could maintain its stability and high activity even with more than 3 M of methanol existing in the reaction system, which was attributed to the presence of FFAs. Lipase tolerance to methanol had an almost linear relationship to free fatty acid content. There was almost no loss in lipase activity after being reused for ten cycles, each cycle of 24 h. The highest conversion of 95% was achieved by adding the molecular sieve to the reaction system.

Zeng et al. [93] produced biodiesel yields of 92.63% for 30 h and 94.36% for 9 h from rapeseed oil DD using liquid forms of *Candida rugosa* lipase and *Rhizopus oryzae* lipase, respectively, whereas the synergetic effect between the two lipases enhanced biodiesel yield to 98.16% in 6 h under the optimized conditions (DD-to-lipase ratio 0.84, water content 46%, 34 °C).

Dos Santos Corrêa et al. [94] investigated esterification of FFAs from palm oil DD with short-chain alcohols (methanol and ethanol) using immobilized commercial lipases (Lipozyme RM-IM, Lipozyme TL-IM, and Novozym 435). Among the enzymes studied, Novozym 435 showed the highest conversion using methanol (95%) and ethanol (91%). In the case of this enzyme, stepwise addition had a minor effect on the conversion. No significant increase in the conversion and the initial rate was observed when the amount of Novozym 435 was increased from 0.5% to 9%. A conversion of 86.7% was obtained using only 0.5% of Novozym 435. This enzyme was reused ten times with conversion reaching 88% and 65% after the eleventh batch with ethanol and methanol, respectively.

Rahman Talukder et al. [95] applied an immobilized *C. antarctica* lipase (Novozym 435) and an acidic styrene-divinylbenzene sulfonated ion-exchange resin (Amberlyst 15) as catalysts for biodiesel production from palm oil acid distillate in the presence and absence of organic solvents. Both catalysts were shown as effective catalysts for the mentioned process, but Amberlyst 15 was more methanol tolerant than Novozym 435. However, Novozym 435 acted fast, its optimal specific activity was 50-fold higher than that of Amberlyst 15, but its maximum biodiesel yield (95%) was somewhat smaller than that of Amberlyst (97%). Also, the minimum amount of Novozym 435 (1% of distillate) required for obtaining maximum biodiesel yield was much lower than that of Amberlyst 15 (30% of distillate). Novozym 435 activities at both 50 and 60 °C were the same and the biodiesel yield reached 90% within 2 h, while Amberlyst 15 was more active at a higher temperature and the biodiesel yield reached a maximum (97%) within 6–8 h. Water inhibited the activity of Amberlyst 15 more considerably than that of Novozym 435. Nonpolar solvent (isooctane, hexane) improved biodiesel yield in the enzymatic system from 90% to 95%, while their impact on the biodiesel yield in the Amberlyst 15 catalytic system was negligible.

3.3.2 Biodiesel Production via AG Route

Esterification of FFAs from DD with glycerol to form AGs as an intermediate step is another approach in the production of biodiesel or biofuels (Fig. 5.5b). This reaction leads to a mixture of MAGs, DAGs, and TAGs as well as unreacted reactants. The composition of the mixture depends on the reaction conditions such as the presence and type of catalyst, temperature, and the FFA-to-glycerol molar ratio.

Pure AGs can be prepared by the direct esterification of glycerol with the use of homogeneous basic (NaOH, KOH) and acidic (*p*-toluene sulfonic acid) catalysts, although the use of different heterogeneous catalysts has been reported. Enzymes have also an enormous catalytic potential in the processes requiring high regioselectivity [80], but these are not yet competitive at the commercial scale because of the high cost of the enzyme [17]. However, most of the research has been done on the synthetic samples and less on the sidestream refining products. The existing studies of the synthesis of AGs as an intermediate step in the biodiesel/biofuels production include enzymatically or non-catalyzed processes.

Enzymatically Catalyzed Process

Lo et al. [96–98] reported the synthesis of AGs (mainly DAG)s by lipase-catalyzed esterification of glycerol with FFAs from corn oil, palm oil, and soybean oil DD. Impact of reaction conditions, such as enzyme type and load, substrate-to-glycerol molar ratio, reaction time, temperature, and water content, as well as the effect of a water adsorbent, was studied. Lipozyme RM-IM was the most effective lipase among the lipases screened. Under the optimum reaction conditions (10%

catalyst, 2.5:1 FFA-to-glycerol molar ratio, 65 °C and 30% molecular sieves), the AG yields of 70.0%, 52.0%, and 69.9% were achieved from corn oil, palm oil, and soybean oil DD in 5 h, 6 h, and 4 h, respectively.

Tangkam et al. [99] studied the enzymatic preparation of DAGs from DD resulting from the refining of various vegetable oils. A direct glycerolysis of a mixed distillate with Novozym 435 led to moderate proportions (52%) of DAGs. The application of a two-stage reaction involving hydrolysis of DD followed by glycerolysis led to a higher synthesis (62–72%) of DAGs. Furthermore, the high initial concentration of FFAs in the distillate had a positive effect on the concentration of DAGs in the final product (>71%). Short-path vacuum distillation of the esterified product led to a concentrate containing 94% of DAGs, up to 3.9% of TAGs below 1% of FFAs. Reaction temperature strongly increased the esterification rate, whereas the effect of pressure was moderate.

Non-catalyzed Process

Smet [100] described the esterification of a fatty acid distillate (93% FFA) with glycerol in a stirred batch reactor at 200 °C and 90 mbar. The novelty of the process is in synthesizing AGs in less than 6 h with no catalyst present in the reaction system. The total AG content of 85.3% was obtained using a glycerol-to-FFA molar ratio of 1:1 in 345 min reaction time. A similar yield of total AGs (86.2%) was obtained at a reduced molar ratio of 1:2. However, at an increased molar ratio of 2:1, the reaction was slowed down and the total AG content was reduced to 64.9%. Because of the high content of FFAs, a distillation step was necessary to increase the purity of the synthesized AGs. The by-products of distillation were further used as reaction products in the synthesis of AGs.

4 Biodiesel Production from WAFs

Animal fats, like vegetable oils, are biological materials (lipids), having similar chemical structures, but a different distribution of fatty acids. Both materials are water-insoluble, hydrophobic, soluble in nonpolar organic solvents, and made up mainly of TAGs, although DAGs, MAGs, and FFAs are also present. Their fatty acids content can be very high [6]. While vegetable oils are generally liquid at ambient temperature, many animal fats and greases tend to be predominantly solid due to their high content of saturated fatty acids (SFAs) [101]. For example, the SFA content in beef tallow is 45.6%, mutton tallow 61.1%, lard 39.3%, and chicken fat 32% [102]. As a result, the synthesis of FAMEs from WAFs can be realized at higher temperatures unlike the processes of WCO conversion [103]. WAFs have not been studied as extensively as sources for biodiesel production as vegetable oils, although their methyl esters have some advantages such as high cetane number and non-corrosivity [104]. The use of WAFs as a feedstock for biodiesel production eliminates the possibility of their disposition and contributes to the biodiesel supply. However, the available amount of WAFs is limited, meaning that these feedstocks will never meet the world's fuel needs. The main sources of WAFs are meat animal processing facilities, large food processing, service facilities, and the collection and processing of animal mortalities by rendering companies [9]. About 1 million tonnes of biodiesel was produced from inedible rendering by-products in 2018 in the EU with a stable use of category 1 and 2 fats and a slight decrease in category 3 fat [105]. The first biodiesel plants in the world using not only trap grease and WAFs but also, the plants based on WCOs and palm fatty acid distillate were built in the Netherlands and Hong Kong in 2010 and 2011, respectively, both with capacities 100,000 tonnes/year [106].

Different WAFs such as pork lard (rendered pork fat), tallow (beef tallow from domestic cattle and mutton tallow from sheep), chicken fat, and grease are used as feedstocks for biodiesel production [106]. Tallow is a waste final product generated in slaughter, processing facilities, or by rendering operations. Its use is declined in time due to changing feeding habits of people and the soap industry cannot take up all produced excess WAFs. Recycled grease products are referred to as waste grease, which is generally classified based on the FFA level in two categories, yellow grease, and brown grease. Yellow grease is produced from animal fat and vegetable oil that is heated, used for cooking, and collected from commercial or industrial cooking businesses. It should have an FFA content of less than 15%. If the amount of FFAs exceeds 15%, then the grease is classified as brown grease. It sometimes referred as trap grease, a material that is collected in special traps in restaurants to prevent the grease from entering the sanitary sewer system. They are inexpensive material compared to food-grade vegetable oil and hence often cited as a potential feedstock for biodiesel production. One kilogram of most WAFs can be converted to a kilogram of biodiesel. If all the 5300 million tonnes/year of WAFs were converted to biodiesel, it would replace about 5.7 million L of diesel fuel [9].

The problem with the processing of WAFs in biodiesel production is their generally high content of FFAs, which determines the viability of the transesterification process. WAFs can be often converted to biodiesel using a base catalyst, but the great problem is the formation of soaps, which leads to loss of catalyst and ester, prevents separation of two fractions: biodiesel and glycerol and increases production processing costs [107]. An alternative method is to use acid catalysts, which are capable of catalyzing FFA esterification and TAG transesterification at the same time. Although the water content of WAFs is relatively low, it can affect the conversion [108]. For the base-catalyzed process, the conversion is slightly reduced when more water was added, but when the acid catalyst was used, the addition of only 0.1% of water leads to some reduction of the yield of esters. The presence of water has a more negative effect on transesterification than the presence of FFAs. To achieve the best results, the water content of beef tallow should be kept not beyond 0.06% [109].

To exclude the disadvantages of both base and acid catalysts, two-step (acid/base) processes for biodiesel production from WAFs with a high FFA content are developed. They consist of the acid-catalyzed FFA esterification (pretreatment, first step) for reducing the FFAs below 0.5% [109], or to less than 2 mg KOH/g [110, 111] and the base-catalyzed TAG transesterification (second step). In this way, compared to one-step processes, it is possible to achieve high biodiesel yield in short reaction time at mild reaction conditions. The only disadvantage of the two-step process, compared to the one-step process, is the higher production cost.

4.1 One-Step Processes

Different alternative procedures, such as homogeneous and heterogeneous catalysis, enzymatic production, and non-catalytic transesterification, have been studied with the goal of achieving higher conversion and shorter reaction time in the one-step processing of WAFs. The studies on one-step transesterification of different WAFs are reviewed in Table 5.4. Acids, bases, and enzymes are used as catalysts in these processes, although non-catalytic processes are also employed. Therefore, the processes for biodiesel production from WAFs are classified as follows: (a) acid-catalyzed, (b) base-catalyzed, (c) enzyme-catalyzed, and (d) non-catalyzed processes.

4.1.1 Acid-Catalyzed Processes

The use of acid catalysts in transesterification reactions has not only advantages such as the tolerance and less sensitivity toward the high FFA presence in the low-cost feedstocks (>6%) but also disadvantages such as the slower reaction rate, the requirement for higher alcohol-to-oil molar ratio, lower catalyst activity, and higher reaction temperature [151]. Biodiesel yield in homogeneous acid-catalyzed transesterifications is in the range 80–99%, and the reaction time is longer, compared to the base-catalyzed process [112, 113]. Catalyst loading, alcohol quantity, reaction temperature, and time are the factors that influence ester yield [112–114]. Ethanol is found to be better than methanol for converting WAFs from restaurants into esters since the former gives lower viscosity and maximum conversion of 78% [114]. The transesterification rate is usually greater at higher alcohol concentrations [113]. Also, with increasing catalyst quantity ester yield firstly increases up to the maximum value and then decreases, independently of WAF type and reaction temperature [112, 113]. This can be explained by the reversible nature of the transesterification reaction [112]. Also, esters produced from WAFs using acid catalysis results in a higher yield, compared to base catalysis [112].

Trap greases can be efficiently used for biodiesel production [115]. Two acid catalysts were employed to optimize the reaction conditions for the esterification of trap grease prior to the conventional base-catalyzed transesterification. Sulfuric acid is a more efficient catalyst than $Fe_2(SO_4)_3$ in reducing the FFA content of trap grease under identical reaction conditions. Therefore, Montefrio et al. [115] recommended H_2SO_4 as a catalyst, although $Fe_2(SO_4)_3$ has some advantages such as insolubility in

Table 5.4 A review of one-step WAF transesterification processes

Type of animal fat	Type, volume of reactor, mL/type of agitator, agitation intensity, rpm	Type of alcohol	Alcohol:fat molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
Acid-catalyzed processes								
Homogeneous catalysis								
Chicken fat	Flask, 250/magnetic, 130	Methanol	30:1	conc. H_2SO_4, 25–100%	30–60	50 °C, 25%	99/24	[112]
Mutton fat						60 °C, 50%	93.2/24	
WAF (10.7% FFA)	Glass reactor, 1000/mechanical	Methanol	6:1–18:1	H_2SO_4, 5–9%	35–65	6:1, 9%, 60 °C	89/48	[113]
WAF (10–15% FFA)	–	Ethanol	–[b]	H_2SO_4, 10%	50–90	50 °C, 100%	(78)/2	[114]
Fats, oil, and grease	Bottle, 250/shaking, 200	Methanol	10:1–26:1	H_2SO_4, 1–10%	30	20:1, 10%	93.8[c]/24	[115]
		Methanol	10:1–26:1	$Fe_2(SO_4)_3$, 1–10%	30	26:1, 10%	45[c]/24	
Heterogeneous catalysis								
Brown grease	Vial with sealed cup, 4/–	Methanol	15:1	Mesoporous silica diphenylammonium triflate, 15 molar ratio	95		(98)/2	[116]
Brown grease	Batch reactor, 45/–	Methanol	10.5:15[d]	ZnO/ZrO_2, 0.8 g	200	Autogenous pressure	78/2	[117]
Lard	Batch reactor, 250/magnetic, 300	Methanol	4:1	Amberlyst 70, 1.25–10%	65	10%	(≈95)/6	[118]
Beef tallow	Flask, 100/magnetic, –	Ethanol	100:1	Sulfonated polystyrene, 20 mol%	64		(75)/18	[119]

(continued)

Table 5.4 (continued)

Type of animal fat	Type, volume of reactor, mL/type of agitator, agitation intensity, rpm	Type of alcohol	Alcohol:fat molar ratio, mol/mol	Catalyst^{a}	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
Fat	Autoclave, 25/ mechanical, –	Methanol	45.8:1	Zr-SBA-15, 12.45%	209		90/6	[120]
Lard							95/6	
Mixture of fats							92/6	
Base-catalyzed processes								
Homogeneous catalysis								
Bovine fat	Tubular^{e}	Methanol		KOH, 2%	65		(95)/1.5	[121]
Beef tallow	Pilot plant^{e} Mechanical, 400	Methanol	6:1	KOH, 1.5%	65		(96.4)/3	[122]
Beef tallow	Vessel, 2000/ Mechanical, 600	Methanol	6:1	KOH, 0.5%	60		(91)/1	[123]
							(92)^{f}/0.02	
Beef tallow	Flask, –/–, 150	Methanol	3:1–12:1	KOH, 0.75–1.75%	55–65	6:1, 1.25%, 65 °C	87.4/2	[124]
Chicken fat							89.2/2	
Beef tallow	Flask, –/Magnetic, –	Methanol	9:1	NaOH, 0.6%	20		(96.3)^{g}/0.083	[125]
Tallow	Flask, 1000/ Magnetic, –	Methanol	6:1	NaOH, 0.5%	60		–/3	[101]
Tallow	Flask, –/Magnetic, –	Methanol	6:1	KOH, 1.5%	50–55		55.6/1	[126]
Duck tallow	Flask, 500/ Mechanic, 600	Methanol	3:1–18:1	KOH, 0.5–3%	55–85	6:1, 1%, 65 °C	97.1/3	[127]
Beef tallow	Flask, 1000/ Shaking, 60	Methanol	6:1	KOH, 0.8%	60		90.8/2	[128, 129]
Pork lard							91.4/2	
Chicken fat							76.8/2	

Chicken fat	Flask, 250/ Magnetic, 130	Methanol	33.5 cm^3:120 g	KOH, 1.5%	30		88.4/1	[112]
Mutton fat							78.3/1	
Lard	Four-necked reactor, 1000/propeller	Methanol	3.48:1–8.52:1	KOH, 0.16–1.84%	24.8–75.2	7.5:1, 1.26%, 65 °C	97.8/0.33	[130]
Chicken fat	Ultrasound reactor	Methanol	4:1–8:1	KOH, 0.75–1.25%		7:1, 1%	(94.8)/0.15	[131]
Lard	Flask, 250/ Magnetic, 400	Methanol	6:1	KOH, 1%	40–60	60 °C	97/0.05	[132]
Heated lard							97/0.05	
Waste pig lard							97/0.05	
Blend of chicken fat and chicken oil	Flask, 1000/ Mechanic, 600	Ethanol	3:1–10:1	KOH, NaOH, CH_3ONa, CH_3CH_2ONa, 0.25–1.5%	40–78	8:1, KOH, 0.75%, 60 °C	96.94/1	[133]
Pig lard	Reciprocating plate reactor, 1000/ reciprocating, 60	Methanol	4.5:1–7.5:1	KOH, 0.5–1.0%	60	4.5:1, 0.9%	96.2/0.167^h	[134]
Soybean oil and pork lard (1:4 w/w)	Flask, 1000/ Magnetic, –	Methanol	6:1	NaOH, 0.8%	60		88.6/1	[135]
Catfish fat		Methanol	6:1	KOH, 0.8%	50		92.7/0.75	[136]
			12:1		47		92.7^i/0.33	
Heterogeneous catalysis								

(continued)

Table 5.4 (continued)

Type of animal fat	Type, volume of reactor, mL/type of agitator, agitation intensity, rpm	Type of alcohol	Alcohol:fat molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
Catfish fat		Methanol	10:1–14:1	KOH/γ-Al_2O_3, 5–8%	60	8:1, 6%	92.6/1.5	[136]
					51	12:1, 6%	92.3[i]/0.33	
Pork lard	Flask, 250/ Magnetic, –	Methanol	6:1–24:1	$CaMnO_x$, CaO, 0.6–4%	60–70	18:1 $CaMnO_x$, 3%, 60 °C	92.4/4	[137]
Lard	Flask, 250/ Magnetic, 900	Methanol	6:1	Quicklime, CaO, 5%	40–60	60 °C	95–98	[138]
Heated lard							>98	
Waste pig lard							>98	
Waste pig lard	Packed-bed tubular reactor, 353, –	Methanol	6:1	Quicklime, 5%	40–60	60 °C	97.6/1	
Mutton fat		Methanol	11:1–22:1	MgO-KOH-*X* (*X* = 5–20)[j], 1.5–4%	45–65	22:1, MgO-KOH-20, 4%, 65 °C	98/0.33	[139]
Poultry fat		Methanol	10 cm^3:3 g	Nanocrystalline CaO, 1 mmol	23–25		(100)/6	[140]
Poultry fat	Batch, –/–, 1417	Methanol	6:1–60:1	$Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$, 10–20%	60–120	30:1, 10%, 120 °C, 6.8 atm	(93)/8	[141]
		Methanol	6:1–60:1	$Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$, 4 g/$cm^3$		30:1, 120 °C, 6.8 atm	(70)[k]/8	
Enzyme-catalyzed processes								

Lard	Screw-cap vial, –/Magnetic, 200	Methanol	1:1	*C. antarctica* lipase (Chirazyme L-2), 10%	30		(74)/72	[142]
Lard	Flask, –/Reciprocal, 180	Methanol	3:1	*Candida* sp. 99–125 lipase, 20%	40–60	40 °C, 20%	87.4^k/30	[143]
Lard	Flask, –/Reciprocal shaking	Methanol	3:1–7:1	*C. antarctica* (Novozym 435) with *T. lanuginosus* (Lipozyme TL-IM) lipases, 2–6%	50	5.12:1, 4	97.2^l/20	[144]
Beef tallow	Reactor, 25/Magnetic, 150	Ethanol	12:1	*Burkholderia cepacia* lipase (Lipase PS), 20%	50		89.7/48	[145]
							40.2/48	
Rendered animal fat	Vial, 30/Shaking, 60	Ethanol	1:1–6:1	*M. meihei* lipase (Lipozyme IM), 21.7 U	25–65	4:1, 35 °C	27/120	[146]
Lamb fat	Tubular	Methanol	3:1–6:1	*C. antarctica* lipase (Novozyme 435) in SC CO_2, 30–50	35–60	4:1, 50%, 50 °C, 20 MPa	(49.2)/1500^h	[147]
Lamb fat	Packed bed, 10/–	Methanol	5:1–20:1	*C. antarctica* lipase (Novozyme 435) in SC CO_2, 3.27 g	50	10:1, 20 MPa	53.5/60^h	[148]
Non-catalyzed processes								
Chicken fat	Batch, 6.2/–	Methanol	3:1–6:1	–	300–400	6:1, 400 °C, 41.1 MPa	88/6	[149]
Chicken fat	Tubular, 2/–	Methanol	3:1–12:1	–	350–400	9:1, 400 °C, 30 MPa	(≈100)/6^h	

(continued)

Table 5.4 (continued)

Type of animal fat	Type, volume of reactor, mL/type of agitator, agitation intensity, rpm	Type of alcohol	Alcohol:fat molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
Lard	Autoclave, 25/ Magnetic, 500	Methanol	30:1–60:1	–	320–350	45:1, 335 °C, 20 MPa	89.9/15	[150]

[a] Percentages are based on oil mass
[b] Excess of alcohol 100–200%
[c] Reduction of FFA content (%)
[d] mL/mL
[e] Capacity, 800 kg/day
[f] Ultrasonic heating (400 W, 24 kHz)
[g] Radio-frequency heating (0.7 kW, 27.12 MHz)
[h] Residence time
[i] Ultrasonic heating (20 kHz)
[j] X: wt% of KOH impregnated over MgO
[k] In the presence of hexane as cosolvent
[l] In the presence of *t*-butanol as cosolvent

methanol and grease, easily use and recovery, as well as the possibility of reduction for equipment corrosion. Mixing intensity is a significant parameter in the efficient pretreatment because of the heterogeneous nature of the reaction mixture. The efficiency of esterification increases with mixing intensity much higher in the presence of H_2SO_4 than in the presence of $Fe_2(SO_4)_3$ [115].

The type of a heterogeneous catalyst for biodiesel production from WAFs depends on the FFA content in the feedstock. Base solid catalysts are preferable in the case of WAFs with a lower FFA content [137, 139], while acid solid catalysts are used for FAME synthesis from WAFs with high FFA content (>5%) [116–118, 120]. Different heterogeneous catalysts (basic, acidic, or mixed materials) can be used for biodiesel production. Most of them, as metal hydroxides, metal complexes, metal oxides such as calcium, magnesium or zirconium oxide, zeolites, hydrotalcites, and supported catalysts, can overcome some of the drawbacks on the use of homogeneous catalysts [152]. Kim et al. [117] showed that ZrO_2 supported catalyst was highly active for esterification of brown grease, while Bianchi et al. [118] recommended strongly acidic cation-exchange resin Amberlyst for pretreatment of lard. Zirconium-containing SBA-15 silica (Zr-SBA-15) displayed good catalytic activity in FAME production by methanolysis of low-grade WAFs, accompanied by high stability and reusability after calcination [120]. Also, diarylammonium salts supported onto silica SBA 15 were very effective for the esterification of FFAs in greases [116].

In order to obtain biodiesel from brown greases with high FFA content (40% and 87%, respectively), Ngo et al. [116] and Kim et al. [117] developed new catalyst technologies using different solid catalysts. Silica-supported diarylammonium and ZrO_2 supported metaloxide catalysts were very effective in the conversion of waste greases. The long-term activity of the ZnO/ZrO_2 catalyst has been also confirmed in a packed-bed continuous flow reactor system for esterification of 90% technical grade oleic acid as a model compound for brown grease with methanol [117]. The FAME yield remained over 97% for 60 days.

Melero et al. [120] showed that for low-grade WAsF, independently of their acid value or unsaponifiable matter content, Zr-SBA-15 catalyst is highly active in the simultaneous esterification of FFAs and transesterification of TAGs with methanol.

4.1.2 Base-Catalyzed Processes

Homo- and heterogeneously base-catalyzed transesterification reactions are often used for biodiesel production from WAFs (Table 5.4). The most important factors which influence the reaction rate and biodiesel yield are the presence of water and FFAs in raw material, type and concentration of catalyst, alcohol-to-fat molar ratio, reaction time, and temperature.

The high biodiesel yield (about or above 90%) was achieved in most of the studies, independently of the type of animal raw material and type of catalyst. For the homogeneously catalyzed methanolysis of lard, the highest ester yield of about 98% was achieved for only 20 min and at the alcohol-to-fat molar ratio 7.5:1 [130]. Also, in the methanolysis reaction of duck tallow (molar ratio 6:1), a high ester yield of 97% was obtained within 3 h [127]. Bhatti et al. [112] showed that the higher FAME yield could be achieved using rather chicken than mutton fats at the same operating conditions. Results of Mata et al. [128] showed that it was viable to produce biodiesel from three different feedstocks (tallow, lard, and poultry fat) at the same operating conditions, whereby the highest yield was obtained using lard (91.4%). Biodiesel B100 (100% biodiesel) from these feedstocks cannot be used in vehicle engines without further additives introduction. Also, the high biodiesel yield was obtained in the presence of solid catalysts using mutton fat [139] and poultry fat [140].

The ester yield can be negatively affected by water and FFAs, so a pretreatment is needed to reduce or eliminate FFAs from WAFs. To reduce water content, the WAFs must be heated over 100 °C. The high acidity can be reduced in many ways, namely by applying acid-catalyzed esterification of FFA, acid-catalyzed transesterification, or heterogeneous catalyst [129]. The water content in the reaction mixture should be kept below 0.06%, while the FFA content should be kept below 0.5%. Beef tallow with 0.3–0.9% FFAs [122, 123], duck tallow with 0.28% FFAs, and lard with 0.33% FFAs [130] were successfully treated by homogeneously base-catalyzed methanolysis, and high biodiesel yields (above 90%) were achieved. On the contrary, Araújo et al. [153] successfully performed transesterification of beef tallow with high acidity (above 3.6%) after heating and preliminary formation of a microemulsion. However, Mutreja et al. [139] reported that catalyst MgO-KOH-20 was effective and tolerant to water or palmitic/oleic acids as FFAs.

The most used base catalysts in homogeneous transesterification are KOH and NaOH. The initial catalyst concentration is a very important factor having an influence on the ester yield. The optimal amount of the base catalyst is in the range 0.5–1% (based on oil weight), which depends on type of WAFs, although some researchers have reported slightly higher catalyst concentrations such as 2% [121]. An increase in catalyst amount increases the ester yield at a constant reaction temperature [112, 124, 127, 130]. However, beyond a certain catalyst concentration, a decrease in the FAME yield was observed due to soap formation [112, 124]. The soap prevents separation of biodiesel from glycerol fraction, increases the biodiesel viscosity, and decreases yield [124]. Comparing the type of catalyst under the same operating conditions, Chung et al. [127] found that the lower ester yield was obtained from duck tallow using CH_3ONa (83.6%) and NaOH (81.3%) than KOH (97%). The KOH-catalyzed methanolysis of waste lard from piglet roasting takes part in a pseudo-homogeneous regime, obeying to the irreversible pseudo-first-order reaction law [132]. The reaction rate constant increases with raising the fatty acid unsaturation degree. A higher conversion degree (>97%) was achieved with waste lard within shorter reaction time (3 min) than with palm, sunflower, and waste cooking oils. In the presence of *n*-hexane as a cosolvent, the FAEE yield in the KOH-catalyzed ethanolysis of a blend of chicken fat and waste chicken oil is enhanced up to about 97% and the biodiesel properties were improved compared to the product of the non-solvent process [133]. This reaction follows also the first-order kinetics. Miladinović et al. [134] have recently shown that the continuous

KOH-catalyzed transesterification of waste lard with methanol in a reciprocating plate reactor follows either the irreversible pseudo-first-order reactions or the reactions involving the changing mechanism and TGA mass transfer. The positive characteristics of continuous reciprocating plate reactor, such as frequent renewal of the interfacial contact area, plug flow, and effective mixing between immiscible reactants, shorten residence time (only 10 min) and make this novel reactor promising for upgrading biodiesel production processes using homogeneously catalyzed transesterification reactions.

For the heterogeneously catalyzed reaction, the preparation of basic catalysts is particularly important. It could be carried out by a wet impregnation method with the addition of an aqueous solution of KOH over MgO [139] or Al_2O_3 [136], followed by calcination of impregnated catalyst at a high temperature. Crystal nanonization is an efficient technique for preparing catalysts for biodiesel production even at room temperature because of reactivity and increased surface area of nanosized oxides [140]. The calcination of hydrotalcite yields mixed oxides, which show high surface areas and pore volumes, affecting positively their catalytic performance [120]. The decrease in the amount of MgO catalyst impregnated with KOH showed an increase in time for completion of the reaction [139]. An increase in catalyst amount increases the ester yield [136, 139], but after a certain limitation in the catalyst concentration, there is a decrease in the ester yield [136]. Mg-Al mixed oxide was found to be thermally and mechanically stable, and no significant difference was observed in particle size and morphology of the used catalyst. The similar Mg-Al ratio of the fresh and used catalyst also confirmed that the catalyst did not leach in the reaction mixture of poultry fat and methanol [141]. To catalyze the transesterification of waste lard from piglet roasting with methanol, Stojković et al. [138] used powdered quicklime (<15 µm, basically CaO) and pure CaO in a batch stirred reactor and quicklime bits (2.0–3.15 mm) in a continuous packed-bed tubular reactor. The kinetic models involving the changing- and first-order reaction rate laws with respect to TAGs and FAMEs, respectively, were verified for both reactors. At the methanol-to-lard molar ratio of 6:1, the catalyst amount of 5% (based on the lard weight) and the reaction temperature of 60 °C, a high FAME concentration in the produced biodiesel (97.5%) for 1 h, were obtained with quicklime in two consecutive batches. Under the same reaction conditions and the residence time of 1 h, the biodiesel yield in the continuous reactor was 97.6% while the FAME concentration in the biodiesel product was 96.5%.

The alcohol-to-fat molar ratio usually used in homogeneously catalyzed transesterification of WAFs is 6:1 [101, 122, 123, 126, 128, 129, 154], although some researchers suggest a higher molar ratio such as 7.5:1 [130] and 9:1 [125]. Some authors [124, 127] showed that the ester yield did not increase when the alcohol-to-fat molar ratio increased above 6:1. The authors generally agreed that the increase in the initial alcohol-to-fat molar ratio up to a certain limit increased the ester yield for both homogeneous [124, 125, 127] and heterogeneous [136, 137, 139, 141] processes. The alcohol-to-fat molar ratios in heterogeneously catalyzed transesterification are higher, for example, 18:1 [137] and 30:1 [141].

Homogeneous base-catalyzed transesterification of WAFs requires about 1–3 h. It was observed that most of the methanolysis process occurred during the second hour [124]. This could be associated with the molecular structure of the feedstock that contains SFAs [124]. The exceptions area much lower reaction time in the case of the lard methanolysis (0.33 h) [130] as well as the beef tallow methanolysis in the presence of ultrasound (0.02 h) [123] and radio-frequency heating (0.083 h) [125]. It was shown that the conversion increased with the reaction time [124, 125, 127]. The required time for heterogeneously base-catalyzed processes is usually longer, up to 8 h [141].

The WAF methanolysis has not been investigated in the wide range of reaction temperature, and the optimal temperature is about 60–65 °C, independently of the type of catalyst. Some researchers recommended lower temperature such as 30 °C for the homogeneously catalyzed methanolysis of chicken and mutton fat [112], but the lower ester yield was achieved. Also, the temperature of 20 °C was suggested for the beef tallow methanolysis using radio-frequency heating [125]. The increase in reaction temperature increases the biodiesel yield so that the average yield could be increased roughly by 5% for every 5 °C for homogeneously catalyzed processes [124]. The proportional increase in ester yield was also observed by the other investigators [127, 130]. The increase in reaction temperature improves the miscibility of poultry fat and methanol in the presence of a heterogeneous catalyst [137, 139, 141].

Da Cunha et al. [122] performed the methanolysis of WAFs using KOH as the catalyst in a continuous pilot plant aiming at the construction of an industrial-scale plant (120,000 kg/day capacity) for biodiesel production from beef tallow. However, it was necessary to introduce two additional steps: a methanol recovery from glycerol and biodiesel and biodiesel separation using a centrifuge.

The solid catalyst could be reused without significant loss of activity [137, 140]. Catalyst nanocrystalline CaO can be successfully recycled three times, but it failed in the fourth cycle [140].

Addition of cosolvent (hexane, toluene, or tetrahydrofuran) could not enhance the conversion of poultry fat using Mg-Al hydrotalcite derived catalyst [141].

The application of ultrasonic irradiation for biodiesel production from waste animal fats has received little attention until recently. This method may be a promising and effective alternative to the conventional method for the production of quality biodiesel from WAFs [123, 131, 136]. The ultrasound-assisted KOH-catalyzed transesterification of chicken fat with methanol provided a similar conversion degree (94.8%) as the conventional method while the reaction time was significantly reduced, making the former method superior to the latter method [131]. A high FAME yield (about 92%) can be achieved in the shorter time, compared to the conventional procedure (1 h), due to a collapse of the cavitation bubbles and ultrasonic jets that impinge methanol to TAGs and cause emulsification. Ultrasonic heating also reduces the reaction time of the solid catalyzed process [136]. Therefore, the TAG methanolysis using ultrasound is feasible, time-saving, and economical method for producing biodiesel. However, ultrasound reduces the activity of a solid catalyst. After the completion of transesterification, the collected solid catalyst could be refreshed by loading an additional catalyst amount and then reused [136].

Beside microwave heating, radio frequency is another dielectric heating technology with a similar mechanism, but simpler, considering the system configuration, and with deeper energy penetration into the material [125]. It is more economical and more suitable to apply in large-scale reactors than microwave heating. A conversion of 96.3% was obtained in the transesterification of beef tallow with NaOH under radio-frequency heating for only 5 min at 20 °C [125].

4.1.3 Enzyme-Catalyzed Processes

Enzymatic catalysts, lipases, are also used in the transesterification reaction of WAFs via a one-step process. They can simultaneously catalyze TAG transesterification and FFA esterification. Lipases are preferred to be used in immobilized form, which allows easy reuse and control of the process. The review of the reaction conditions of the lipase-catalyzed transesterification of WAFs providing a significant ester yields is given in Table 5.4.

Inactivation of the enzyme that leads to the decrease in ester yields mostly depends on the methanol concentration. This problem can be resolved by the stepwise addition of alcohol. Three-step methanolysis is sufficient to convert TAGs from lard to high ester yields [142, 143]. In the first and second steps of alcohol addition, the conversions are low, but methanol is completely soluble in the obtained ester in the third step, making the enzyme-substrate contact more sufficient. Also, Lee et al. [142] applied porous materials, such as silica gel, to keep the lipase active during the reaction when excess methanol was used.

Temperature is an important factor in the enzymatic processes of biodiesel synthesis. Generally, the enzymatic reaction is performed at temperatures between 30 and 50 °C [136, 142, 143, 145, 146]. Higher temperatures denature the enzyme, lead to the loss of solvents through volatilization [143], and decline the product amount [146].

Water content is one of the key parameters in the enzyme-catalyzed process, because it affects the catalytic activity of lipase. According to Lu et al. [143], the FAME yield decreases when the water content is more than 30% due to reduced homogeneity of substrate mixtures. Several organic solvents are indicated for their suitability in the enzymatic production of biodiesel [143]. In the lard methanolysis catalyzed with *Candida* lipase, the ester yield increases by the addition of *n*-hexane in the reaction mixture [143], although the immobilized *Candida* lipase can convert lard effectively to esters in a solvent-free system [142]. Generally, enzyme-catalyzed transesterification is performed with a high lipase amount (about 4–20%). The FAME yield increased rapidly with increasing the amount of lipase up to 20% but slowly above this limit [143].

The main drawback of the enzyme-catalyzed process, the high cost of the lipase, can be reduced by enzyme immobilization, which enables the reuse and easy recovery of the enzyme. Immobilized lipase is operationally stable over seven repeated cycles of the lard methanolysis with no evident decrease in the lipase activity [143]. Also, two immobilized lipases (non-specific Novozym 435 and 1,3 specific

Lipozyme TL-IM) were successfully reused for 20 cycles [136]. The combined use of these two lipases is a potential way to reduce the cost of enzyme-catalyzed biodiesel production from lard using methanol as acyl acceptor and *tert*-butanol as the solvent [136].

The enzymatic approach in the presence of supercritical carbon dioxide (SC-CO_2) has been also applied [147, 148]. When WAFs, which have a high melting point close to the denaturation temperature of lipase, are used for biodiesel production, they must be dissolved in a solvent. SC-CO_2 can be proposed as an alternative to organic solvents which have a harmful effect on human health. The enzymatic process of WAF transesterification using SC-CO_2 has many advantages [148]. Beside low temperature, there is no need for feedstock purification, and lipase is capable of transesterification of TAGs and esterification of FFAs present in the feedstock. However, the optimum ester yields obtained in the presence of lipase Novozym 435 are low (about 50%). By investigating the effects of enzyme loading, reaction temperature, and methanol-to-fat molar ratio on ester yield, Taher et al. [147] showed that FAME yield increased with both enzyme loading and time. The increase in reaction temperature resulted at first in an increase in ester yield because of the increase in rate constants and the reduction in mass-transfer limitations. Further, an increase in temperature resulted in a drop in ester yield because of the denaturation of the enzyme. The critical temperature at which the enzyme starts to deactivate was different, depending on the type of lipase and immobilized surface. As expected, the increase in methanol-to-fat molar ratio from the stoichiometric one resulted in the increased FAME yield to an optimum value, but after that the yield dropped due to inhibition of lipase by methanol [147]. A combined continuous process of extracting fat from meat and ester synthesis using SC-CO_2 in an integrated system seems to be economically feasible [148]. The drop in enzyme activity was observed in the third meat replacement cycle of the continuous experiment, compared to that of the first one. The inhibition effect of methanol is clearly seen from the higher drop in enzyme activity with the increase in methanol-to-fat molar ratio.

4.1.4 Non-catalyzed Processes

Recently, the transesterification of WAFs using supercritical methanol has been suggested to overcome the drawbacks of homogeneous catalytic processes. This non-catalytic process is simpler, environmentally friendly, and does not require any pretreatment of inexpensive unrefined WAFs [147, 150]. Furthermore, the presence of water and FFAs do not affect the ester yield because TAG transesterification and FFA esterification occur simultaneously. For example, different waste lard samples containing various FFAs and water contents were treated successfully using a supercritical process [150]. Obtained FAMEs from waste lard with no pretreatment were found to be comparable with those from refined lard. A review of the operating conditions applied in supercritical one-step processes in batch and continuous reactors is given in Table 5.4.

Marulanda et al. [149, 155] investigated the effect of temperature, pressure, alcohol-to-fat molar ratio, and residence time on the chicken fat conversion and the product quality in batch and continuous reactors under supercritical conditions. A preheating of the feedstock at high temperature (350 °C) was used without a significant thermal fat decomposition. Furthermore, it was concluded that the transesterification was not a reverse reaction at 300–400 °C, but by-product (glycerol) was thermally decomposed. Thus, a continuous process with a moderate excess of methanol and in situ glycerol decomposition could be used as very promising for processing WAFs and increasing biodiesel profitability [155].

The reaction pressure does not significantly affect the efficiency of the TAG conversion at high temperature, but slightly changes the composition of product [155]. Usually, a high biodiesel yield can be achieved at a pressure of 20–40 MPa [149, 155]. When the methanol-to-fat molar ratio was increased, the complete conversion was achieved, but excess methanol was also consumed in other thermal reactions [155].

The ester yield in a tubular reactor initially increased as the residence time increased to a maximum value and then decreased at longer residence times, which was attributed to the thermal decomposition of initially formed FAMEs under supercritical conditions [155].

4.2 Two-Step Processes

A review of two-step homo- and heterogeneous transesterification processes employing different WAFs is presented in Table 5.5. Most studies were related to the use of homogeneous catalysts. The important factors affecting the acid value in the first and the ester yield in the second step are the type of feedstock, type and concentration of catalyst, alcohol-to-fat molar ratio, reaction temperature, and time.

The most important property of acid catalysts used in the two-step processing of WAFs is the possibility of simultaneous accomplishment of esterification and transesterification. Independently of the type of WAFs, sulfuric acid is mainly used as an acid catalyst (the required amount varied from 0.5% to 20%) in the first stage of the process. The most used base catalysts in the second stage of the process are KOH, NaOH, or CH_3ONa (the required amount varied from 0.4% to 1%). The catalyst amount is the most important factor affecting product quality.

After the addition of a mixture of acid catalyst and methanol into heated WAFs, the initial acid value decreases and then intends to stabilize [113, 156–158]. This behavior is attributed to the migration of the catalyst into the accumulated water, so becoming unavailable for the reaction [113]. The increase in base catalyst amount in the second step to the optimal value enhances the ester yield considerably, after which a slight decrease is observed because of soap formation [104, 113, 156, 157]. Actually, there is a desired level of acid or base catalyst amount bellow which the acid value or the ester yield is not reduced.

Table 5.5 A review of two-step (acid/base catalyzed) WAF transesterification processes

Type of animal fat	Type, volume of reactor, mL/type of agitator, agitation intensity, rpm	Step[a]	Type of alcohol	Alcohol:fat molar ratio, mol/mol	Catalyst[b]	Temperature, °C	Optimal reaction conditions		Reference
							Reaction conditions	FFA conversion, %/yield (conversion), %/time, h	
Homogeneous catalysis									
Tallow	Flask, 250/–, 900	I	Methanol	3:1–7:1	H_2SO_4, 1%	60	6:1	–/1	[156]
		II	Methanol	3:1–7:1	KOH, 0.35–0.4%	60	5:1, 0.39%	94/1.5	
WAF	Vessel, 1000/Magnetic, 700	I	Methanol	20:1	H_2SO_4, 6–10%	40	8%	–/1	[104]
		II	Methanol	25:1–40:1	NaOH, 0.5–1.5%	50–70	35:1, 1%, 62 °C	89/1	
WAF (10.7% FFA)	Flask, 1000/Mechanical, –	I	Methanol	3:1–18:1	H_2SO_4, 0.1–1%	35–65	6:1, 0.5%, 65 °C	94.9/4	[113]
		II	Methanol	3:1–12:1	KOH, 0.1–1.5%	65	6:1, 0.5%	97.3/2	
WAF (12.1% FFA)	Flask, –/Magnetic, –	I	Methanol	20:1–30:1	H_2SO_4, 1–15%	60	30:1, 10%	93.7/1	[157]
		II	Methanol	4.5:1–7.5:1	KOH, 0.5–1%	60	7.5:1, 1%	92.6/1	
Chicken fat	Flask, –/Magnetic, –	I	Methanol	10:1–40:1	H_2SO_4, 3–35%	60	40:1, 20%	89.6/1.33	[158]
		II	Methanol	6:1	KOH, 1%	60		87.4/4	
Chicken fat	Flask, –/Magnetic, –	I	Methanol	40:1	H_2SO_4, 20%	60		95/1.33	[159]
		II	Methanol	6:1	KOH, 1%	25 and 60	60 °C	87.5/4	
Chicken fat oil	Flask, –/Mechanical, –	I	Methanol	6:1	H_2SO_4, 0.9%	60			[160]
		II	Methanol	4:1–11:1	KOH, 0.4–1.4%	45–90	8:1, 0.8%, 60 °C	89 (97.68)/1	
Broiler rendering fat	Flask, –/Magnetic, –	I	Methanol	8:1–11:1	H_2SO_4, 2–8%	63	11:1, 4%		[161]
		II	Methanol	6:1	KOH, 1%	63		87/1	

Type of animal fat	Type, volume of reactor, mL/type of agitator, agitation intensity, rpm	Step[a]	Type of alcohol	Alcohol:fat molar ratio, mol/mol	Catalyst[b]	Temperature, °C	Optimal reaction conditions		Reference
							Reaction conditions	FFA conversion, %/yield (conversion), %/ time, h	
Pork fat	Flask, 1000/Magnetic, –	I	Methanol	6:1	H_2SO_4, 1–4%	4–65	2%, 65 °C	56.5/5	[162]
		II	Methanol	6:1	NaOH, 1%	65		66.2/–	
Waste lard	Flask, 500/Magnetic, –	I	Methanol	15:1–23:1	H_2SO_4, 20–40% wt of FFAs	50			[163]
		II	Methanol	6:1–9:1	KOH, 1–2%	50	2%, 9:1	99.4/1	
Swine fat	Ultrasound reactor/15,000	I	Methanol	4:1–8:1	H_2SO_4, 0.6–1.4%	50–70			[164]
	Flask, 150	II	Methanol	4:1–12:1	KOH, 0.4–2%	30–70	7.42:1, 1.11%, 62.3 °C	98/2.94	
Tallow	Flask, –/Magnetic, –	I	Methanol	6:1	KOH, 1.5%	50–55		98.9/1	[126]
		II	Methanol	70:1	HCl, 1 mL/g	60–65		98.3/0.5	
				72:1	BF_3, 1 mL/g	60–65		97/0.5	
				15:1	H_2SO_4, 1 mL/g	60–65		95.3/2	
		I	Methanol	63:1	H_2SO_4, –	60–65		96.9/1	
		II	Methanol		KOH,	50–	1.5%	93.1/1	
		I	Methanol	65:1	1.4–2%	60		98.5/1	
					HCl, –	60–65			
		II	Methanol		$NaOCH_3$, 1.4–2%	50–60	2%	94.3/1	

(continued)

Table 5.5 (continued)

Type of animal fat	Type, volume of reactor, mL/type of agitator, agitation intensity, rpm	Step[a]	Type of alcohol	Alcohol:fat molar ratio, mol/mol	Catalyst[b]	Temperature, °C	Optimal reaction conditions		Reference
							Reaction conditions	FFA conversion, %/yield (conversion), %/ time, h	
Yellow grease	Flask, 1000/–	I	Methanol	7.4:1–40:1	H_2SO_4, 5–10%	60	20:1, 10%, 60 °C,	–/1	[2]
		II	Methanol	6:1–35:1	$NaOCH_3$, 0.35%	Room	6:1, 0.35%	80.5/8	
Brown grease		I	Methanol	7.4:1–40:1	H_2SO_4, 5–10%	60	20:1, 10%, 60 °C,	–/1	
		II	Methanol	6:1–35:1	$NaOCH_3$, 0.21–0.41%	Room	6:1, 0.21%	75.1/8	
Heterogeneous catalysis									
Yellow and brown greases	Flask, 25/Mechanical, – Vial, 4	I	Methanol		Diarylam-monium, 0.68 mmol/g	90		50.6/2	[103]
		II	Methanol		$NaOCH_3$, 0.3%	50		98.1/2	
Lard	Microwave reactor/ Magnetic	I	Methanol	6:1	H_2SO_4, 2%	65			[165]
		II	Methanol	36:1	CaO/zeolite, 10% wt/v	65		90.89/1	

[a] I—first step: acid pretreatment, II—second step: base-catalyzed

[b] Percentages are based on oil mass

Among mineral acids applied so far in the first step, sulfuric acid is the most effective. Sulfamic [158] and phosphoric [113] acid are poor catalysts, as they do not reduce the FFA content of the WAFs significantly.

Methanol is the mainly used alcohol in both steps of the WAF processing. Independently of the type of catalyst, the optimal molar ratio of methanol-to-fat in both steps is varied in the range of 6:1 to 40:1. The increase in methanol-to-fat molar ratio in the first step leads to the reduction of the acid value to the optimal level [113, 157, 158], because the excess of methanol promotes reaction completion keeping the acid in methanol phase [113]. With increasing molar ratio methanol-to-esterified fat in the second step, the ester yield continuously increases to the optimal value and then remains the same or slightly rises [104, 157]. Encinar et al. [113] believed that for ratios higher than the optimal one, the excess of methanol could favor slightly the recombination of esters and glycerol to MAGs.

The reaction temperature for the transesterification of WAFs is a particularly important factor because of the high-fat melting point. The optimal reaction temperatures in both process steps are close to the boiling point of alcohol, i.e., in the range of 60–65 °C, when the maximum ester yield was obtained. The increase in reaction temperature decreases the acid value during the reaction time in the first step [113, 162]. If the temperature in the second step was adjusted at 50 °C, the reaction could not be started [104]. The increase in temperature in the range from 62 to 70 °C caused a decrease in the biodiesel yield because of methanol evaporation [104]. In the temperature range of 25–60 °C, the ester yield increases with increasing the reaction temperature [159]. The reaction temperature and time are interactive parameters in the transesterification reaction. The acid value decreases with time at different reaction temperatures [113, 158]. Decreasing is higher in the initial period of the reaction when the esterification of FFAs is almost complete [113, 162].

Several research groups have optimized the two-step biodiesel production from WAFs by conventional [160, 161, 163] and novel methods involving ultrasonication [164] and microwave heating [165]. Chavan et al. [160] optimized the alkaline transesterification step of biodiesel production from chicken fat oil by methanol whereas Keskin et al. [161] conducted the optimization of the esterification step of biodiesel production from broiler rendering fat with methanol in the presence of sulfuric acid. The overall FAME yields from these feedstocks were 89% [160] and 87.4% [161]. While the biodiesel from chicken fat oil contains 97.7% FAME [160], thus satisfying the standard limit, the final product from broiler rendering fat was 95.5%, i.e., below the limit. However, Sarantopoulos et al. [163] optimized both steps of biodiesel production from waste lard under mild conditions. The esterification step is significantly affected by the methanol:FFA ratio and the reaction time, and the feedstock acidity. On the other side, the transesterification reaction is positively affected by the reaction, time, KOH concentration, and methanol:TAG ratio. Furthermore, two empirical models describing the evolution of the two-step biodiesel production process were developed, which could be useful for scaling-up the two-step process. He et al. [164] enhanced biodiesel production from diseased swine fat by an ultrasound-assisted two-step catalyzed process. The response surface methodology provided the following optimal transesterification reaction conditions: the catalyst concentration of 1.11%, reaction temperature of 62.3 °C, methanol-to-oil molar ratio of 7.42:1, and the reaction time of 116.14 min, which ensured the 98.0% biodiesel purity within 176 min, thus shortening the overall process nearly three times compared with the one-step process. Lawan et al. [165] carried out biodiesel production from waste lard in a microwave reactor using calcium oxide (CaO) loaded on zeolite as a catalyst. Under the optimal reaction conditions, the FAME yield of 90.9% from the pre-esterified feedstock was achieved in a shorter time (135 min).

In order to prevent yield losses caused by the dissolution of FAMEs in the glycerol phase, Fröhlich et al. [126] investigated the possibility of esterifying FFAs either before or after base-catalyzed methanolysis of low-grade tallow (FFA content >8%) into biodiesel-grade esters. Under optimum laboratory conditions, base-catalyzed methanolysis followed by esterification of FFAs in the presence of different acids gave almost theoretical yields (about 98%). Considering the relatively large amounts of reagents required for neutralization in that case, it was concluded that the initial esterification of FFAs from tallow was a more convenient process for large-scale biodiesel production. Also, comparing the two- with the one-step base-catalyzed conversion of the same starting material, a much higher ester yield was obtained in the former case.

Ngo et al. [103] demonstrated that the polymer-immobilized catalysts were equally effective as their homogeneous counterparts in esterifying FFAs to esters and were readily recycled and reused at least three cycles for esterification upon reactivation with triflic acid. The resulting ester-AG mixture was then readily converted to total esters by base-catalyzed transesterification. However, when the reactivated catalyst was used for the fourth time under similar reaction conditions, a significant drop in the esterification activity was observed.

5 Biodiesel Production from WCOs

WCOs are promising feedstocks for biodiesel production because of their lower price than that of pure edible vegetable oils and easy availability. Some WCOs are used for fodder making and soap production, but major quantity is disposed of and thrown into landfills causing environmental pollution, such as water contamination. Since 2002, the European Union has prohibited the use of these oils in animal feeding due to the presence of harmful compounds that are formed during oil frying.

The amount of WCOs depends on the amount of edible oil consumption, and it is different in various world regions. For example, the amount of WCOs per year was estimated to be from 0.3 to 0.4 million tonnes in the United States, 0.135 million tonnes in Canada, 0.14 million tonnes in India, and 0.7–1.0 million tonnes in EU countries [166]. Thus, WCOs can be a potential source for biodiesel production. However, there is a lack of information on the overall WCO quantity used for biodiesel production annually in the world. The reported capacities of commercial plants for biodiesel production from WCO range from small (about 1–19 million L/year) [167–170] to large (16 million tonnes/year) [171].

Biodiesel production from WCOs depends on their physicochemical properties, which differ from "fresh" oils due to thermolytic, oxidative, and hydrolytic reactions occurring during frying. These chemical reactions lead to the formation of undesirable products (oxidized TAGs and DAGs, FFAs, polymers, dimmers), increasing viscosity, density, and tendency to foam, changing in the surface tension and color [172]. Knowing the properties of WCOs, amounts of FFAs and water above all are the first condition for successfully defining the method for its conversion into FAAEs.

The presence of undesirable compounds in WCOs has a negative effect on the course of transesterification reaction and FAAE yield, which makes appropriate pretreatment necessary. Depending on the quality of WCOs, pretreatment includes removal of suspended solid particles by filtration and decrease in moisture and FFA content. To decrease the FFA amount in WCOs, base neutralization [172, 173] and distillation [174] are recommended. Neutralization of FFAs is required especially in the case of base-catalyzed transesterification and can be performed as pretreatment of the oil [173], or simultaneously with transesterification reaction by adding excess catalyst than the amount necessary for catalysis [175]. Decreasing the FFA content prevents soap formation and catalyst consumption. The soap causes gel formation, makes glycerol separation difficult, and reduces ester yield. Water, present in the WCO, hydrolyzes AGs and esters to FFAs which subsequently form soap. Usually, water amount is decreased by heating, adsorption, evaporation, and distillation in vacuum or treatment with magnesium sulfate, silica gel, and calcium chloride [172, 176]. Drying of WCOs in industrial conditions is commonly done by distillation in a vacuum (0.05 bar) and at a temperature from 30 to 40 °C [177]. Simultaneous decrease in FFAs and water amount is achieved by the treatment of WCOs with a mixture of aluminum oxide and magnesium silicate [142] or by steam injection and sedimentation [178].

FAAEs from WCOs are produced in one- and two-step processes, depending mainly on the quality of the oily feedstock. Acid, base, or enzyme catalysts can be used or the transesterification reaction can be performed without catalyst under supercritical alcohol conditions. The application of each type of catalyst has certain advantages and disadvantages, which are influenced mainly by the amounts of FFAs and water in WCOs.

5.1 One-Step Processes

Table 5.6 summarizes the researches on biodiesel production from WCOs in one-step processes, as well as the applied reaction conditions and their optimal values for achieving the highest ester yield.

Table 5.6 A review of one-step WCO transesterification processes

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
Acid-catalyzed processes								
Homogeneous catalysis								
WCO	Round-bottomed three necks flask/ Mechanical	Methanol	4:1–8:1	H_2SO_4, 0.5–2.5%	65	6:1; 1.5%	(95.2)/2	[179]
WCO (palm oil)	–	Ethanol	7.5:1–12:1	HCl, H_2SO_4, 0.5–2.25 M	90	12:1; H_2SO_4; 2.25 M	–/3	[180]
WCO	Stainless steel continuous reactor	Methanol	50:1	H_2SO_4, 15%	80[b]		(97)/4	[181]
WCO	Stainless steel reactor, 5000/ Mechanical, 100–600	Methanol	50:1–250:1	H_2SO_4, 1.5–3.5[c]	70 and 80	400 rpm: 245:1; 1.5 mol%; 80 °C	99.4[c]/4	[182]
WCO	–	Methanol	10:1–24:1	H_2SO_4, 3–6%	95	20:1; 4%	>90/10	[183]
WCO	Three-necked flat-bottomed flask/ Magnetic, 800	Methanol	6:1–12:1	H_2SO_4, 5–15%	50–60	12:1; 5%; 60 °C	94.8/3	[184]
Heterogeneous catalysis								
WCO	Parr reactor, 500/600	Methanol	6:1–18:1	MoO_3/SiO_2, MoO_3/ZrO_2, WO_3/SiO_2, $WO_3/SiO_2–Al_2O_3$, Zinc stearate/ SiO_2, Zinc ethanoate/ SiO_2 and 12-TPA/ZrO_2, 1–5%	200[b]	18:1; Zinc stearate/SiO_2; 3%	98/10	[185]

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
WCO	Stainless steel reactor (Parr 4575 HT/HP)	Methanol	6:1–42:1	ZnO–La_2O_3[d], 2.3%	170–220	36:1; Zn_3La_1; 200 °C	96/3	[186]
WCO	Stainless steel reactor, 300/ Magnetic	Methanol-Ethanol	12:1–18:1	$SO_4^{2-}/SnO_2–SiO_2$, 1–8%	100–200[b]	15:1 (methanol: ethanol molar ratio 9:6); 6%; 150 °C	81.4/1	[187]
WCO	Reactive distillation glass column (pilot plant scale; i.d. 80 mm; flow rate 110–150 mol/h)	Methanol	10:1–70:1	$H_3PW_{12}O_{40} \cdot 6H_2O$		Feed flow rate 116.23 mol/h;	93.9/1	[188]
WCO	Three-neck flask, 500/300	Methanol	30:1–110:1	$H_3PW_{12}O_{40} \cdot 6H_2O$, 5–15%	55–75	70:1; 10%; 65 °C	(88.6)/14	[189]
WCO	Round reactor, 100/ mechanical, 300	Methanol	6:1–90:1	$H_3PW_{12}O_{40} \cdot 6H_2O$, 0.025–0.15 mmol	55–75	70:1; 0.1 mmol; 65 °C	(87)/14	[190]
WCO	50-mL three-necked round-bottomed flask, 50/300	Methanol	20:1	$Zr_{0.7}H_{0.2}PW_{12}O_{40}$, –	65		>96.7/8	[191]
WCO	Parr reactor, 500/400–800	Methanol	9:1–18:1	12-TPA (5–30 wt%)/ Nb_2O_5, 0.005–0.025 g/ mL	150–225	600 rpm; 18:1; 25 wt% TPA/Nb_2O_5; 0.015 g/cm^3 (3%); 200 °C	92/9	[192]

(continued)

Table 5.6 (continued)

						Optimal reaction conditions		
Feedstock	Type, volume of reactor, cm^{3}/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst^{a}	Temperature, °C	Reaction conditions	Yield (conversion), %/time, h	Reference
Acidified WCO	Three-necked batch reactor, 100/ Mechanical, 120–600	Methanol	2.5:1^{c}	Cation ion-exchange resin particle—polyethersulfone (CERP/PES) catalytic membrane, 25%	65	480 rpm;	(94)^{e}/8	[193]
	Three-necked batch reactor under microwave irradiation (120–360 W), 500/ Magnetic		0.5:1–3.5:1^{c}	Cation ion-exchange resin particle—polyethersulfone (CERP/PES) catalytic membrane, 5–25%	35–70	360 W; 2:1^{e}; 15%; 60 °C	(97.4)^{e}/1.5	
Acidified WCO	Three-necked batch reactor, 100/ Mechanical	Methanol	1:1^{c}	Polystyrene sulfonic acid—Polyvinyl alcohol (PSSA/PVA) blend membranes^{f}, –	64	PSSA/PVA = 1:2;	(94)^{e}/8	[194]
Acidified WCO	Three-necked batch reactor, 250/ Mechanical	Methanol	1:1–7:1	Cation-exchange resins (NKC-9, 001 × 7 and D61), 6–24%	60–68	3:1; NKC-9; 18%; 66 °C	(90)^{e}/3	[195]
WCO	–/500	Methanol	5:1–40:1	Carbohydrate (D-glucose, sucrose, cellulose or starch)-derived catalysts, up to 14%	65–100	30:1; starch-derived catalyst; 10%; 80 °C	92/8	[196]
Base-catalyzed processes								
Homogeneous catalysis								

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
WCO (sunflower oil)	Flask/Magnetic	Methanol	4.5:1–9:1	KOH, NaOH, 0.5–1.5%	25	6:1; 1% KOH	≈90/0.5	[197]
WCO (olive oil)	Erlenmeyer flask/ Magnetic, 1100	Methanol	5–18[g]	KOH, 0–1.9%	0–70	12% methanol; 1.26% KOH; 25 °C	94/0.02	[198]
		Ethanol		NaOH, 0–1.9%				
WCO	two necked Would flask/Magnetic	Methanol	3.6:1–5.4:1	NaOH, 0.2–1%	65	4.8:1; 0.6%	≈90/1	[198]
WCO	Three-necked flask, 25/Magnetic	Methanol	3:1–6:1	NaOH, 1% and 2%	55	6:1; 1%	≈100/1	[199]
						5:1; 2%	≈100/2	
						6:1; 2%	≈100/0.5	
WCO (olive and sunflower oil)	Spherical reactor, 500/Mechanical	Methanol	3:1–9:1	NaOH, KOH, CH_3ONa, CH_3OK, 0.1–1.5%	25–65	6:1; KOH; 1%; 65 °C	≈95/2	[200]
WCO	–	Methanol	3:1–9:1	NaOH, KOH, 0.5–1.0%	25 and 65	6:1; KOH; 1%; 65 °C	96.15/1	[201]
WCO (olive and sunflower oil)	Reactor, 2000/ Mechanical, 300 and 600	Methanol	7.5:1	CH_3ONa, 1%	60	600 rpm	>95/1	[202]
WCO	Flat-bottomed two necks flask, 500/ Magnetic	Methanol	3:1–10:1	KOH, 0.5–2.0%	70	6:1; 1%	98.2/1	[203]

(continued)

Table 5.6 (continued)

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
WCO (olive and sunflower oil)	Batch reactor, 1000/Mechanical	Ethanol	6:1–15:1	NaOH, KOH, NaOCH$_3$, KOCH$_3$, 0.1–1.5%	35–78	12:1; 1.0% KOH; 78 °C	72.5/0.5	[204]
WCO (sunflower oil)	Glass reactor[h]/ Magnetic, 1100	Methanol	4:1–6:1	CH$_3$ONa, 0.5–1.5%	55–65	6:1; 1%; 60 °C	(99)/0.08	[205]
WCO (sunflower oil)	–	Methanol	3:1–9:1	KOH, NaOH, 0.5% and 1.0%	25 and 65	6:1; 1% KOH; 65 °C	96/1	[201]
WCO (corn, sunflower and canola oils)							94.5/1	
WCO	Flat-bottomed flask, 1000/ Magnetic	Methanol	6:1	KOH, NaOH, CH$_3$ONa, 0.4–1.2%		NaOH and CH$_3$ONa 0.8%	92/1	[172]
WCO (palm oil)	Teflon tube (0.9 cm ID × 260 cm)[h] (2.45 kHz, 800 W)	Ethanol	12:1	NaOH, 3%			(97)/0.008	[174]
WCO	Round-bottomed flask, 1000[i]/ Magnetic, 600	Methanol	3:1–15:1	NaOH, CH$_3$ONa, 0.5–1.5%		MW 750 W; 6:1; CH$_3$ONa; 0.75%;	98/0.05	[206]
WCO[j]	Erlenmeyer flask, 100/Magnetic	Methanol	3:1–5:1	KOH, 0.1–1.25%	25–50	25% acetone; 4.5:1; 1%; 25 °C	(>98)/0.5	[207]

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
WCO	Reactor, 1000/ Magnetic, 1100 (600)	Methanol	3:1–11:1	KOH, NaOH, CH_3ONa, 0.5–1.6%	30–70	7:1: 1.1% NaOH; 60 °C	88.8/0.25	[208]
WCO (canola oil)	Glass beaker, 500/ Magnetic	Ethanol	0.28:1[k]	NaOH, 0.4–1.2%	60	0.8	94/0.33	[209]
WCO	Three-neck flask, 500/Mechanical	Methanol	5:1–12:1	KOH, 0.5–1.5%	30–70	7:1–8:1; 0.75%, 30–50 °C	88–90/1.3–1.5	[210]
Heterogeneous catalysis								
WCO	Three-neck round-bottomed flask, 100/ Magnetic, 500	Methanol	3:1–60:1	$CaO\text{-}ZrO_2$ (Ca-to-Zr molar ratio 0.1–1), 1–15	65	30:1; Ca-to-Zr molar ratio 0.5; 10%	92.1/2	[211]
WCO	Flask, 200/ Magnetic	Methanol	6:1	K_3PO_4, 1–4	30–60	4%; 60	97.3/2	[212]
WCO	Stainless steel batch reactor (Parr 4842), 300/ Mechanical	Methanol	4:1–20:1	KF/activated C, 3–7	125–175	8.85:1; 3%; 175 °C	80.15/1	[213]
WCO	Round-bottomed flask, 25	Methanol	1.5:1–30:1	Calcined layered double hydroxides—CLDH (M(II)M(III)*x*)[l], 1–8	35–100	5.6:1; $CaAl_2$ 700-CLDH; 5%; 65 °C	>90/5	[214]
WCO	Expanded-bed reactor, ⌀5 cm × 50 cm; ≈0.108–0.110[m]	Methanol	3:1 and 3.5:1	Anion-exchange resin, Diaion PA306S, 603–619 g	50	0.110 mol/h; 3:1, 603 g	93[n]/0.110[m]	[215]

(continued)

Table 5.6 (continued)

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
WCO	Packed-bed reactor (295 cm^3; 25 × 600 mm) with recirculation	Methanol	12:1 and 18:1	Calcined lime stone (CaO), 20–40 cm^3	60	18:1; 20 cm^3 catalyst dispersed with 40 cm^3 of active carbon	>96.5/2	[216]
WCO	Stainless steel batch reactor, 100/ Magnetic, 1500	Methanol	20:1–50:1	TiO_2–MgO mixed oxides, 5–15%	150–170	50:1; Mg/Ti molar ratio 1; 10%; 160 °C	92.3/6	[217]
WCO	Stainless steel stirred reactor (Parr 4575 HT/HP Reactor)/	Methanol	36:1	ZnO-La_2O_3 mixed oxides, 2.3%	170–220	Zn/La molar ratio 3; 200 °C	96/1.5	[186]
WCO	Flat-bottomed two necks flask, 500/ Magnetic	Methanol	3:1–12:1	KOH-alumina (5–20% KOH), 3–9%	70	9:1; 15% KOH loading; 5%	96.8/2	[203]
WCO	Batch system reactor Autoclave Eng., 300/	Methanol	12:1–48:1	Mg-Al hydrotalcite, 3–12%	80–160	24:1; 6%: 120 °C	≈100/6	[218]
WCO	Glass reactor, 250/ Mechanical	Methanol	6:1–24:1	K-pumice, 4–20%	50–60	21:1; 20%; 60 °C	≈94/4	[219]
WCO	Two-neck round-bottomed flask, 250/	Methanol	12:1–21:1	Calcined waste coral fragments (CaO), 70–150%	65	15:1: 100%	98/2	[220]
WCO	Three-necked round-bottomed flask, 500/ Mechanical	Methanol	4.8:1–9.6:1	Calcined snail shell (CaO), 1–4%	50–65	6:1; 2%; 60 °C	(99.6)/8	[221]

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
WCO	Round-bottomed flask/500	Methanol	13:1	Mixed CaO (5%) and boiler ash (BA) from oil palm industrial waste, 1.5–4.5% of BA	65	3% BA	(99)/0.5	[222]
WCO	Glass reactor/1000	Methanol	5:1–20:1	Barium meliorated waste construction marble (Ba/CaO), 2–8%	65	9:1; 3%	(88)/3	[223]
WCO	Erlenmeyer flask, 100/Magnetic	Methanol	3:1–9:1	Copper doped zinc oxide, 2–14%	35–60	8:1; 12%; 55 °C	97.71/0.83	[224]
WCO	Three-neck flask, 250/350	Methanol	2:1–10:1	Bromooctane modified CaO (prepared under conventional and microwave heating), 1–5%	60 and 65	8:1; 4%; 65 °C	(98.2)/1.25[o]	[225]
WCO (palm oil)	Three-necked round-bottomed flask/800–1500	Methanol	3:1–30:1	Calcined chicken manure (CaO), 2.5–20%	50–70	1400 rpm; 15:1; 7.5%; 65 °C	90.8/6	[226]
WCO	Laboratory reactor, 200/Magnetic, 300	Methanol	6:1–12:1	Calcined river snail shell (CaO), 1–3%	65	9:1; 3%	98.2/1	[227]
WCO	Three-necked round-bottomed flask, 250/Mechanical, 500	Methanol	6:1–21:1	Calcined chicken bones (hydroxyapatite, CaO and Ca(OH)$_2$), 2–10%	55–80	15:1; 5%; 65 °C	89.33/4	[228]
WCO	–/Magnetic, 200	Methanol	12:1	Calcined waste quail beaks, 7%	65	–	(91.7)/4	[229]

(continued)

Table 5.6 (continued)

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
WCO	Packed-bed reactor (glass column ⌀2.7 cm and 21 cm high) with recirculation	Methanol	6:1–20:1	CaO/nanocrystal cellulose supported with polyvinyl alcohol (obtained from chicken bone and coconut residue), 0.5–10%	55–65	6:1; 0.5 wt%; 65 °C	98.4/4	[230]
Enzyme-catalyzed processes								
WCO (cottonseed oil)	Cylindrical, flat-bottomed glass reactor, 1000/ Mechanical, 1200	Ethanol	1:1–9:1	*C. antarctica* lipase (Novozym 435), 6.25 g/L	24–75	3:1; 64 °C	230[p]/3	[231]
WCO	Screw-capped vial, 5/900	Methanol	1:1–14:1	*C. antarctica* lipase (Novozym 435), 50 M	40	10:1; 1-octyl-3-methylimidazolium hexafluorophosphate (1:1 mL/mL to the oil); 1 vol% water	2192[q]/48	[232]
WCO (palm oil)	Stoppered flask, 100/Mechanical, 140–220	Methanol	3:1–8:1	*T. lanuginosus* (Lipozyme TL-IM), *R. miehei* (Lipozyme RM-IM), and *C. antarctica* (Novozym 435) lipases, 0.5–15%	40	Novozym 435; 4%; 200 rpm; 4:1; *tert*-butanol	88/12	[233]
WCO	/200	Methanol	4:1	*T. lanuginosus* (Lipozyme TL-IM) free and immobilized lipase, 4%	24	Lipozyme TL-IM free	95/105	[234]

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
WCO	Flask/Magnetic, 220	Methanol[p]	1:1–6:1	*R. oryzae* lipase, 10–45%	30–70	30%; 4:1 (two step addition); 40 °C; 50 wt% water	92/35	[235]
WCO	Stoppered flask, 25/200	Methanol	3:1 (two step addition)	*Penicillium expansum* lipase, 36–108 U/g	25–55	84 U/g; 35 °C;0.2% *tert*-amyl alcohol	92.8[r]/7	[236]
WCO (sunflower oil)	Glass reactor/ Mechanical	Methanol[s]	2:1–4:1	*A. oryzae*, *P. fluorescens*, *P. cepacia*, and *C. rugosa* lipases, 2–6%	25–55	*P. fluorescens*; 5%; 3:1 (two step addition); 45 °C; *n*-hexane	63.8/24	[237]
WCO	Screw-capped vial, 100/Shaker, 125–225	Methanol	1:1–5:1	*P. aeruginosa* lipase/0.25–1.25 g	27–57	170 rpm; 3.05:1; 0.782 g lipase; 44.2 °C	87/24	[238]
Non-catalyzed processes								
WCO	Stainless steel vessel, 100/960	Methyl acetate	25:1–59:1	–	300–345	42:1; 345 °C; 20 MPa	(≈100)/0.83	[239]
WCO	Autoclave, 100/	Methanol	6:1–41:1	–	247–287	41:1; 287 °C	≈100/0.5	[240]
WCO	Batch reactor (Inconel-625), 5/	Methanol	42:1	–	350	43 MPa	96.9/0.067	[108]
WCO (canola oil)	Autoclave, 100/	Methanol	1:1–2:1[t]	–	240–270	2:1; 270 °C; 10 MPa	≈100/0.75	[241]
WCO (palm oil)	Batch-type tube reactor	Methanol	20:1–60:1	–	300–380	40:1; 360 °C	80/0.33	[242]

(continued)

Table 5.6 (continued)

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
						Reaction conditions	Yield (conversion), %/time, h	
WCO	Batch reactor (PARR Micro-reactor)/1000	Methanol	10:1–50:1	–	300	40:1; 10 MPa	80/0.33	[243]

[a] Percentages are based on oil mass

[b] Under pressure

[c] Methanol/acidified oil mass ratio

[d] Ratio of Zn–La: 10:0, 9:1, 3:1, 1:1, 0:10

[e] FFA conversion

[f] PSSA/PVA mass ratio 2:1, 1:1, and 1:2

[g] wt% of the oil

[h] Microwave irradiation

[i] Conventional heating (65 °C) and microwave irradiation (200–750 W)

[j] In the presence of acetone 0–30 wt% of the oil

[k] mL/mL

[l] x—the M(II)/M(III) molar ratio

[m] Flow rate, mol/h

[n] mol%

[o] Catalyst prepared under microwave heating

[p] mmol/L

[q] µmol/(h g)

[r] In the presence of 0.48 wt% of silica gel of the oil

[s] Addition in one to three steps

[t] Mass ratio

5.1.1 Acid-Catalyzed Processes

Acid catalysts are insensitive to the presence of FFAs in the oil and can catalyze esterification and transesterification reactions simultaneously, which makes them suitable for the production of biodiesel from low-cost WCOs with high FFA content [107, 185]. The advantage of the acid-catalyzed process is no soap formation. The FFA esterification reaction is relatively fast, while the TAG transesterification is slow and takes a long time. The main disadvantage of acid-catalyzed reaction is a slower reaction rate, compared to the base-catalyzed reaction. Lotero et al. [107] explained the low activity of homogeneous acid catalysts by different reaction mechanisms of acid- and base-catalyzed transesterification reactions. Another drawback of the acid-catalyzed process is the inhibition of the reaction by the water formed in FFA esterification, which stops the reaction before reaching the completion [166]. Also, the homogeneous catalysts are no reusable and their use causes problems with catalyst separation, acidic effluent, and serious environmental problems as well as the high cost of equipment and corrosion-related problems [183, 185, 244]. As already said, the use of heterogeneous acid catalysts could eliminate these problems, offering several benefits compared to homogeneous acid catalysts such as easy separation from the reaction mixture, simple purification of the products, reusability with or without regeneration, less environmental impact, and less corrosion of equipment [188, 244]. Due to its environmentally and economically advantageous, the heterogeneously catalyzed process is referred to as a green process [176].

Commonly used homogeneous acid catalysts in transesterification of WCOs are inorganic acids (sulfuric acid, hydrochloric acid, and phosphoric acid) and sulfonated organic acids. Among them, the most often used is H_2SO_4 due to its higher catalytic activity [180]. The scheme of biodiesel production from WCOs by H_2SO_4-catalyzed transesterification is shown in Fig. 5.7. The catalyst amount is variable and significantly influences the ester yield. A low catalyst amount is not suitable because the reaction is incomplete, while the high catalyst amount can cause the water formation and decrease in ester yield. Different optimal H_2SO_4 loadings have been reported so far (Table 5.6), which ranges (based on the oil weight) from 1.5% [179] to almost 15% (or H_2SO_4-to-oil molar ratio 1.3:1) [181].

Recent investigations of biodiesel production from WCOs are directed toward the use of heterogeneous acid catalysts which have strong potential to replace homogeneous catalysts [185]. Different heterogeneous acid catalysts have been employed (Table 5.6), such as heteropolyacid, cation-exchange resins, 12-tungstophosphoric acid supported on niobium, MoO_3, WO_3, zinc stearate, zinc ethanoate and 12-tungstophosphoric acid supported on silica or zirconia, cation-exchange resin/polyethersulfone, and polystyrene sulfonic acid/polyvinyl alcohol catalytic membranes. Compared to H_2SO_4-catalyzed methanolysis, high ester yields are achieved in the presence of higher solid catalyst amounts and in longer reaction times. The optimal catalyst amount and reaction time are influenced by the catalytic activity of the heterogeneous catalyst, active site concentration, specific surface area, as well as pore size and volume [245]. In methanolysis catalyzed by zinc stea-

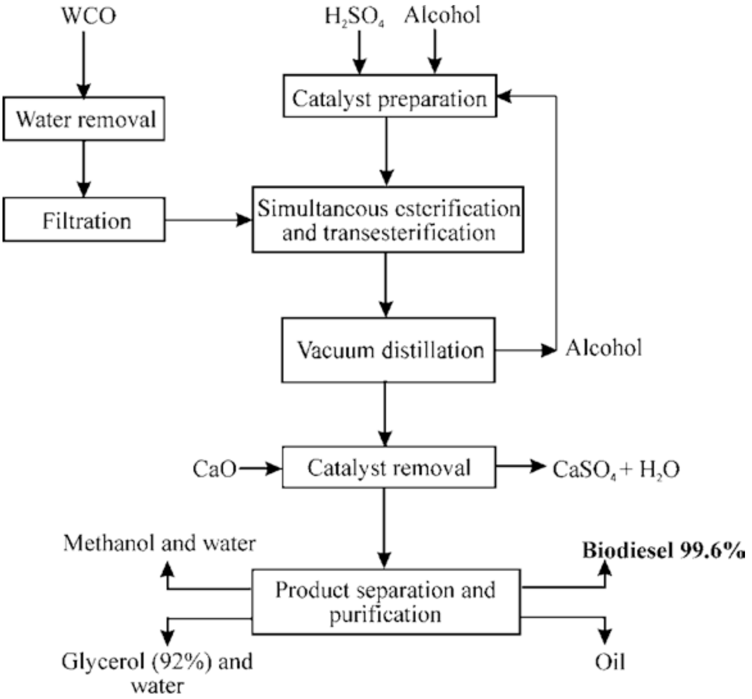

Fig. 5.7 Simplified block flow diagram of the acid-catalyzed process. (Adapted from [91])

rate immobilized on silica, the highest FAME yield of 98% was obtained at the catalyst amount of 3% within 10 h [185], while the optimal catalyst amount and time for a cation-exchange resin (NKC-9) catalyzed methanolysis were 18% and 3 h, respectively [195].

One of the most important variables affecting the ester yield is the methanol-to-oil molar ratio. Wide ranges of the methanol-to-oil molar ratio of 4:1 to 250:1 and 1:1 to 110:1 have been used in homogeneously and heterogeneously catalyzed methanolysis, respectively. Generally, different molar ratios at which the maximum ester yield is reached have been reported. For H_2SO_4-catalyzed methanolysis of WCOs, the optimal methanol-to-oil molar ratio is 6:1 [179] while Zheng et al. [182] suggest a much higher value of 245:1. According to Feng et al. [195], the methanol-to-oil molar ratio of 3:1 provides achieving the highest FFA conversion in WCO methanolysis catalyzed by cation-exchange resin, while Talebian-Kiakalaieh et al. [189] and Cao et al. [190] observe the optimal molar ratio of 70:1 for heteropoly-acid-catalyzed methanolysis. It is obvious that the optimal methanol-to-oil molar ratio depends on the catalyst type and other reaction conditions, and it should be established experimentally.

Reaction temperature has no significant influence on final ester yield but higher temperatures increase the reaction rate and consequently decrease the reaction time [150]. Different values of the optimal reaction temperature for the H_2SO_4-catalyzed methanolysis of WCOs have been reported such as 60 °C [184], 65 °C [179], and 80 °C [182]. The reaction temperature is more crucial in the case of using a solid catalyst because of the existence of a three-phase system which causes mass-transfer limitation, especially in the initial reaction period. High reaction temperature increases rates of both mass transfer and chemical reaction and enables achieving a high ester yield in short reaction time. If the heterogeneous catalyst poses strong acidity, high catalytic activity, and suitable textural properties, such as heteropolyacids [189–191], some cation-exchange resins and catalytic membranes [193, 194], the optimal temperature is around the boiling temperature of methanol, although the long reaction time is required for achieving the highest FAME yield. In the case of $SO_4^{2-}/SnO_2–SiO_2$ [187] and 12-tungstophosphoric acid supported on Nb_2O_5 [192], much higher temperatures are suggested (150 °C and 200 °C, respectively).

Recently, novel carbon-based solid acid catalysts have been developed for biodiesel production from WCOs having high FFA content [196, 246]. They are obtained by sulfonation of incompletely carbonized carbohydrates: D-glucose, sucrose, cellulose, or starch. Incomplete carbonization leads to a rigid carbon material, which after sulfonation becomes a highly stable solid with a high density of active SO_3H sites. These, so-called “sugar catalysts,” are characterized by excellent catalytic performance for the methanolysis of WCOs without leaching of SO_3H groups during the reaction. According to Lou et al. [196], the best catalytic activity for WCO methanolysis has a starch-derived catalyst providing the 92% ester yield at a methanol-to-oil molar ratio of 30:1, catalyst amount of 10%, and 80 °C. The starch-derived catalyst is recyclable, stable, and promising for the development of an eco-friendly process for biodiesel production.

The possibility of reusing heterogeneous catalysts is another of their advantages, which enables the reduction of the process cost. Before reusing, catalysts are regenerated by washing with methanol [190, 191] or hexane and methanol [185, 189] to remove adsorbed compounds, or only filtered without any treatment [196]. Zinc stearate/SiO_2 [185] and $H_3PW_{12}O_{40} \cdot 6H_2O$ [189] were reused up to four times and $Zr_{0.7}H_{0.2}PW_{12}O_{40}$ [191] five times without serious loss in their catalytic activity. The cation-exchange NKC-9 resin exhibited excellent reusability for ten runs, and even an enhancement of catalytic activity was observed, which was attributed to the increase in the surface area due to the breaking of resin particles under agitation [195]. The excellent operational stability was observed for a starch-derived catalyst even after 50 cycles of successive reuse without any treatment of the used catalyst [196].

The reusability and stability of heterogeneous catalysts allow the development of continuous processes, which enable larger biodiesel productivity and reduced production cost, so they are acceptable for industrial biodiesel production. The continuous process for WCO methanolysis catalyzed by a heteropolyacid was developed by Noshadi et al. [188]. The process was conducted in a reactive distillation column, which combines reaction and separation of the products. At a total feed flow rate of 116.23 mol/h and inlet feed temperature of 30 °C, the FAME yield of 93.9% was obtained. Wang et al. [247] proposed a continuous process for biodiesel production from WCO by using the $SO_4^{2-}/TiO_2–SiO_2$ solid acid catalyst. The production process was carried out in a sequence of three reactors with the countercurrent flow of vaporized methanol. Based on this process, an industrial demonstration plant with an annual capacity of 10,000 tonnes of biodiesel was built [247]. Park et al. [248] reported a continuous process for biodiesel production from WCO by using the pellet-typeWO_3/ZrO_2 catalyst. The process was carried out in a packed-bed reactor. However, the steady-state conversion obtained in a 140 h is 70%, and further improvement of the proposed process is needed. The FAME synthesis from acidified WCO was carried out in a packed-bed reactor with cation-exchange resin NKC-9 [249]. At mild optimal reaction conditions, the achieved FFA conversion was over 98% during 500 h of continuous running, indicating high efficiency and operational stability of the process.

5.1.2 Base-Catalyzed Processes

Base-catalyzed transesterification is the most commonly used method for the production of biodiesel from WCOs with low FFA content (less than 2%). However, if FFA content in the WCOs is more than 6%, the base catalyst is not suitable [107]. Generally, base-catalyzed WCO methanolysis occurs at milder reaction conditions, compared to the acid-catalyzed reaction. Apart from the oil properties, the reaction rate and FAME yield depend on the type and amount of the catalyst, methanol-to-oil molar ratio, reaction temperature, and agitation intensity of the reaction mixture. Homogeneous base catalysts are commonly used in biodiesel production because of their high catalytic activity at mild reaction conditions, achieving high ester yield in short reaction time, easy availability, and low cost. The scheme of the homogeneous base-catalyzed biodiesel production process from WCOs with FFA neutralization as pretreatment is shown in Fig. 5.8 [250]. Applying heterogeneous catalysts in biodiesel synthesis from WCOs is the subject of recent researches, and different compounds were investigated as catalysts.

The most commonly used homogeneous base catalysts for WCO transesterification are KOH, NaOH, and CH_3ONa. Dorado et al. [198] compared the catalytic activity of KOH and NaOH in transesterification of WCO with FFA content in the range of 2.76% and 4.33% and concluded that the KOH-catalyzed reaction was faster than the NaOH-catalyzed one. Other researchers also considered that KOH is an optimal catalyst [197, 200, 201]. Exceptionally, Dias et al. [172] reported that KOH was less effective than the sodium-based catalysts. Despite a slower reaction rate, NaOH is often used as a catalyst in WCO transesterification [175, 177, 199, 208]. The amount of base catalyst depends on the type of oil used [210] and ranging from 0.6% [177] to 1.26% [198], based on the oil weight, but according to most investigations, the optimal amount is 1%.

Different solid catalysts were used in the methanolysis of WCOs: metal oxides (pure or as oxides mixture), hydrotalcites, resins, and hydroxides loaded on support. As in the case of acid-catalyzed transesterification, high ester yield in the heterogeneously base-catalyzed reaction is achieved in the presence of higher catalyst amounts. The optimal amount depends on the catalyst type, and it is ranging from

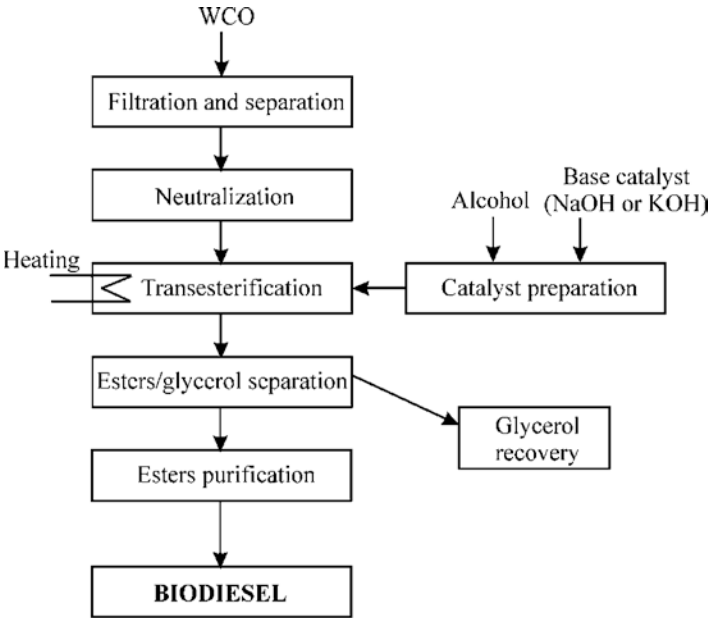

Fig. 5.8 Scheme of biodiesel production from WCOs by base-catalyzed alcoholysis. (Adapted from [215])

3%, based on the oil weight, for activated carbon-supported KF [213] to 100% for calcined waste coral fragments [220].

Ester yield is significantly affected by the used amount of methanol. The homogeneous base-catalyzed methanolysis of WCOs was studied in the range of methanol-to-oil molar ratio from 3:1 to 15:1. Most researchers suggest the methanol-to-oil molar ratio of 6:1 as the optimal one [197, 200, 201, 203, 205, 206, 251], although some researchers suggest somewhat higher mole ratios, such as 7:1 [208], 7:1–8:1 [210], and 12:1 [204]. On the other side, Felizardo et al. [177] found out that the optimal methanol-to-oil molar ratio for NaOH-catalyzed methanolysis of WCO was 4.8:1. For heterogeneously catalyzed reaction, the optimal methanol-to-oil molar ratio is generally higher compared to the homogeneous reaction. According to most researchers, it is higher than 15:1 (Table 5.6), and in some cases, it reaches 30:1 [211] or even 50:1 [217].

Transesterification of WCOs was performed at different temperatures, depending on their properties, catalyst type, and applied reaction conditions. The optimal reaction temperature is in the range from ambient temperature [197, 198, 207] to the boiling temperature of alcohol [177, 200, 201]. The heterogeneously catalyzed methanolysis is performed at a higher temperature, compared to a homogeneously catalyzed reaction. The reaction temperature goes from 60 °C [212] to as high as 200 °C [186] to achieve ester yield more than 96%.

The agitation intensity is of particular importance for the methanolysis rate, especially in the initial reaction period, since the reactants are immiscible and a poor mass transfer between two phases limits the overall process rate. Therefore, intensive mixing is required in order to increase the reaction rate and to short the reaction time [202, 220].

Nowadays, high-efficient catalysts for the methanolysis reaction with CaO as the main component have been obtained from waste materials. Boey et al. [222] used a mixture of CaO from waste mud crab shells and cockleshells and boiler ash from agricultural waste in the methanolysis of WCO and achieved ester yield of 99% under mild reaction conditions. The CaO obtained by calcination of chicken manure was a promising catalyst for WCO methanolysis [226]. Calcined waste coral fragments [220] and calcined snail shell [194, 227] give the FAME yield in WCO methanolysis above 98%. Valuable catalysts for biodiesel synthesis consisting mainly of hydroxyapatite, CaO, and $Ca(OH)_2$ can be derived from waste animal hard tissues using the thermal calcination method. Such catalysts, obtained from waste chicken bones [228] and waste quail beaks [229], were efficient in WCO methanolysis. Effective solid base catalysts for methanolysis reaction were also barium-enhanced waste marble catalyst [223] and potassium-loaded pumice [219].

The catalyst reusing is the subject of many studies in order to obtain high active and stable heterogeneous catalysts which are important for the development of continuous processes. Some catalysts could be reused after the appropriate regeneration method. TiO_2–MgO mixed oxide after washing with methanol [217] and calcined layered double hydroxides $CaAl_{2\ 700}$ after recalcination [214] were reused in four cycles without considerable change in their activity. Borges et al. [219] reported that potassium supported pumice could be reused up to five times after more complex regeneration consisting of washing with ethanol and new ionic exchange of pumice with KOH solution and calcination. The excellent stability was observed for calcined waste coral fragments, which was reused without regeneration up to five cycles reaching FAME yield more than 94%. The natural availability of this catalyst, together with its high stability and possibility to catalyze the methanolysis of WCO, makes it as promising for large-scale biodiesel production.

Shibasaki-Kitakawa et al. [215] developed a continuous process for biodiesel production using anion-exchange resin, Diaion PA306S, in an expanded-bed reactor, where a FAME yield of 93 mol% was achieved under mild reaction conditions. The methanolysis of WCO was also performed in a pilot plant consisting of a packed-bed reactor with recirculation of the reaction mixture [216]. CaO obtained by calcination of crushed limestone was packed into the reactor, and the obtained FAME yield was over 99%. The process was successfully repeated 17 times, and the FAME yield remained over 96.5% for every run. Zik et al. [230] also used the packed-bed reactor with recirculation for biodiesel production from WCO in the presence of a catalyst consisting of CaO and nanocrystal cellulose (obtained from chicken bone and coconut residues, respectively) supported with polyvinyl alcohol. The highest biodiesel yield (98.4%) was obtained under mild conditions (methanol-to-oil molar ratio 6:1 temperature 65 °C, and catalyst loading 0.5%). The catalyst was reused four cycles with maintaining the biodiesel yield above 90% [230].

5.1.3 Enzyme-Catalyzed Processes

Enzyme-catalyzed methanolysis can be successfully used for FAME synthesis from WCOs because of the insensitivity of the enzymatic reactions to FFAs and water amount, easy recovery of product, mild reaction conditions, and catalyst recycling. However, the main disadvantages of enzyme-catalyzed processes are a low reaction rate and a long reaction time needed for achieving high ester yield. Therefore, researches are directed toward the possible improvement of this process, which mainly involves an increase in lipase catalytic activity by techniques of immobilization, optimization of reaction parameters, and application of new reactor systems. High FAME yield from a WCO (about 93%) was achieved by the application of the immobilized *Penicillium expansum* lipase in the presence of an adsorbent (silica gel), which efficiently controlled the amount of water and positively affected the ester yield [236]. Recently, four different lipases from *C. antarctica*, *T. lanuginosus*, *R. miehei*, and *P. fluorescens* are most often used as catalysts for WCO transesterification.

Due to lipase inactivation by methanol, enzyme-catalyzed processes are usually performed at a low methanol-to-oil molar ratio, most often at the stoichiometric amount and with stepwise addition of methanol in accordance with the dynamics of its consumption [237, 252]. In the WCO methanolysis catalyzed by *Candida* sp. 99–125 lipase immobilized on the cotton membrane, the FAME yield increased five times when methanol was added in three steps, compared to single-step methanol addition [252]. Also, the higher methanol amount can be used if the process is carried out in the presence of ionic liquids and solvents which improve mutual solubility of TAGs and methanol and also protect enzymes from denaturation [38, 232, 233, 253]. The FAME yield obtained in the WCO methanolysis in the solvent-free system and in the presence of *n*-hexane (20% to the oil) was increased from 65% to 91%.

The organic solvent can ensure a homogeneous reaction mixture, reduce their viscosity and mass-transfer limitation, accelerate the reaction rate, and stabilize the enzyme. On the other side, the use of solvents increases the cost of the purification steps at the end of the production process [254]. Various organic solvents such as *n*-hexane, *n*-heptane, cyclohexane, acetone, benzene, chloroform, toluene, petroleum ether, *tert*-amyl alcohol, *tert*-butanol, acetonitrile, and isooctane have been used in the enzymatic biodiesel synthesis [233, 237, 252], but *n*-hexane is the most suitable one [237, 252]. Although hydrophilic solvents are much less effective, *tert*-butanol ensured high ester yield due to its moderate polarity and possibility to dissolve glycerol and methanol, resulting in high lipase stability [233]. Recently, ionic liquids [232] and supercritical CO_2 [253] have also been used as solvents in the enzymatic transesterification.

The lipase activity is influenced by the presence of water in the reaction media [38, 252, 255], since it increases the interfacial area between aqueous and organic phases where lipase acting [242]. However, excess water leads to the hydrolysis reaction and the reduced FAME yield. For example, FAME yield increased from 31% to 91% as water content increased from 0% to 10% of the WCO, and then decreased as water content rose from 10% to 20% [37]. The optimal water amount depends on the feedstock, the lipase, the immobilization support, and the organic solvent employed.

Compared to chemically catalyzed reaction, the transesterification of WCOs catalyzed by lipase is performed at the low reaction temperature, and the optimal one is usually up to 45 °C. Exceptionally, Chesterfield et al. [231] and Dizge et al. [255] recommend a higher reaction temperature (65 °C).

In order to improve the lipase catalytic activity and to increase FAME yield, the researchers have investigated the use of different carriers for the enzyme immobilization such as textile materials (338, 252) and microporous polymeric matrix [255], using a lipase mixture [253], recombinant cells [256], or dual lipase modification procedure composed of cross-linking and protein coating with K_2SO_4 [257].

The enzymatic biodiesel production is usually performed in a batch stirred tank reactor. The use of continuously operated reactor contributes to the reduction of operational costs and increases the biodiesel productivity. Packed-bed reactors are suitable and most often applicable to biodiesel production [254]. The main disadvantage of using this type of reactor is that the glycerol remains at the reactor bottom and can be adsorbed on the lipase surface and decreased the process efficiency. Therefore, glycerol must be removed during the production process. Recently, several studies reported the application of a packed-bed reactor for the enzyme-catalyzed methanolysis of WCOs. The reaction setup consisting of two packed-bed reactors was used for WCO methanolysis catalyzed by Novozyme 435, and the reaction conditions were optimized for achieving the highest ester yield [258]. The obtained FAME yield was 80%, and it retained longer than 120 h. Nie et al. [252] conducted the WCO methanolysis catalyzed by *Candida* sp. 99–125 lipase immobilized on the cotton membrane in a series of nine packed-bed reactors with hydrocyclones after each reactor to separate glycerol. The final FAME yield under the optimal condition was 92%, and the lipase operational stability was more than 20 days. This process was recommended for industrial biodiesel production by Nie et al. [252]. The *Candida* sp. 99–125 lipase immobilized on the textile cloth was used for WCO methanolysis in a three-step packed-bed reactor system. The process was conducted for 100 h, with decreasing the FAME yield by 15.7%, which was attributed to lipase inhibition by glycerol or methanol [37]. A packed-bed reactor integrated with a glycerol-separating system was used for WCO methanolysis, yielding a methyl ester content of 94.3% [259]. This reactor system operated for 22 batches achieving the FAME yield over 92%.

The most efficient process for biodiesel production from WCO in a packed-bed reactor followed by downstream separation was developed by Rodrigues et al. [253]. A mixture of two lipases, *C. antarctica* (Novozym 435) and *T. lanuginosus* (Lipozyme TL-IM), in 2:1 mass ratio, was employed, and the reaction was performed in supercritical CO_2. The reaction products were separated into two high-pressure separators. At steady-state and under the optimal reaction conditions, the FAME yield was 99% with the 30 s residence time [253].

Nowadays, a static mixer reactor was employed in the enzyme-catalyzed biodiesel production from WCO catalyzed by *Candida* sp. 99–125 lipase [260]. The main advantages of this reactor are low energy consumption, high mixing efficiency, and better mass transfer, as well as no moving parts. To achieve the highest FAME yield, both the static mixer structure and the process parameters were optimized. The number and length of mixing units, as well as the flow rate of WCO and methanol, were selected based on the pressure drop and methanol volume fraction, which indicated the energy consumption and mixing efficiency, respectively. The lowest pressure drop and the highest methanol volume were observed when six mixing units with a length-diameter ratio of 1.5 and the reactant flow rate of 0.28 m/s were used. Under the optimal reaction conditions, the FAME yield was 82.8% within the reaction time of 12 h, which is twice shorter compared to the reaction time in a batch stirred reactor [260].

Tan et al. [261] have recently reported that a factory in China conducts enzymatic catalysis using WCO as feedstock in a plant with a capacity of 10,000 tonnes. Immobilized lipase *Candida* sp. is used as a catalyst in a stirred tank reactor. The enzyme dosage is 0.4% (based on the oil mass). FAME yields of 90% are achieved under the optimal conditions.

5.1.4 Non-catalyzed Processes

Non-catalyzed transesterification of WCOs is a potential alternative to the above-mentioned catalyzed processes. Although high pressure and temperature are required, this process is attractive due to nearly complete conversion in short reaction time. Since the presence of FFAs and water has a positive effect on the reaction rate due to the faster esterification rate and the water contribution to easier separation [108], non-catalyzed processes are suitable for biodiesel production from WCOs. Because of high capital costs and great energy consumption, the non-catalyzed process is still not employed in industrial biodiesel production. Recently, West et al. [262] have reported that the economics of the non-catalyzed transesterification of WCO was superior to those of chemically catalyzed processes.

Non-catalyzed WCO methanolysis was investigated in wide ranges of reaction conditions (methanol-to-oil molar ratio: 6:1–60:1; temperature: 250–450 °C and pressure: 10–43 MPa). The authors agree that optimal methanol-to-oil molar ratio is from 40:1 to 42:1 [108, 240, 242]. One of the most important variables affecting FAME yield is reaction temperature. Due to the thermal degradation of methyl esters at higher reaction temperatures which lowering the FAME yield [263], recent investigations of non-catalyzed WCO methanolysis are performed at lower temperatures ranging from 240 to 287 °C [240, 241]. The optimal temperature providing FAME yield of almost 100% was reported to be 270 °C [241] and 287 °C [240], despite the longer reaction time (45 min and 30 min, respectively). Contrary, Tan et al. [242] suggested the reaction temperature of 360 °C, but the obtained FAME yield was much lower (80%). The data about the influence of the reaction pressure on the non-catalyzed WCO methanolysis are not available, but it can be expected (as in the case of refined oils) that pressure above 10 MPa does not have a significant influence on the FAME yield [13].

Campanelli et al. [239] used methyl acetate instead of methanol for the non-catalyzed synthesis of FAMEs from WCOs, edible oils, and nonedible oils. Although the reactivity of supercritical methyl acetate was lower than that of methanol, the proposed process produces triacetin, a valuable, active biodiesel component, instead of glycerol. Furthermore, counting the triacetin content, this process led to higher overall biodiesel productivity.

5.2 Two-Step Processes

Two-step processes have been studied during the last years because of their efficiency for achieving higher ester yields from WCOs in shorter reaction times, compared to one-step processes. The most commonly used two-step processes are performed as the acid-catalyzed esterification of FFAs in WCOs (step 1) and the base-catalyzed transesterification of treated oil from the first step (step 2). The use of acid catalysts allows FFA conversion to alkyl esters, thus reducing the FFA content, and the transesterification of the treated oil can then be performed by using a base catalyst. The most commonly used acid catalyst is sulfuric acid, while the KOH is usually used base catalyst, followed by NaOH and CH_3ONa. A review of two-step processes for FAAE synthesis from WCOs is given in Table 5.7.

The homogeneous two-step processes for WCO transesterification were investigated in the presence of different catalysts and methanol amounts as well as reaction temperatures. The optimal acid catalyst amount for the first step depends on the FFA content in the WCO. For the WCO with lower acid value (1.45 mg KOH/g), the optimal H_2SO_4 amount is lower (0.68% based on the oil weight) [264], while in the case of WCO with an acid value of 65 mg KOH/g, optimal H_2SO_4 amount is 15% [264]. Since the first step of the process provides necessary requirements for caring out the second step of the process, the optimal amount of base catalyst is usually around 1%, a typical value for base-catalyzed transesterification.

The most used alcohol in two-step processes is methanol. Excess of methanol is required to drive the reaction toward the formation of products, but the higher methanol amount in the first step can dilute the system results in a reduction of the H_2SO_4 efficiency in the first step [264] and makes the recovery of the glycerol difficult [243]. Therefore, the optimal methanol-to-oil molar ratio should be established experimentally. The base-catalyzed step has been investigated in the range of methanol-to-oil molar ratios from 4.5:1 to 35:1, and different optimal values were reported (Table 5.7). For instance, Charoenchaitrakool et al. [264] and Tanawannapong et al. [269] reported the optimal methanol-to-oil molar ratio of 9:1 at the KOH amount of 1%, while Li et al. [267] observed a higher optimal molar ratio (25:1) and a lower KOH amount (0.15%).

Achieving higher ester yield from WCOs with low acid value and meeting the biodiesel quality standard, two-step base-catalyzed processes were developed with an improved ester yield by 20%, compared to the one-step base transesterification [204]. To reduce the reaction time, Hancsok et al. [265] recommended the addition

Table 5.7 A review of two-step (acid/base catalyzed) WCO transesterification processes

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Step	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst^a	Temperature, °C	Optimal reaction conditions: Reaction conditions	Optimal reaction conditions: Yield (conversion), %/time, h	Reference
Homogeneous catalysis									
WCO	Round-bottomed two necks flask/ Magnetic, 400	I	Methanol	3:1–20.3:1	H_2SO_4, 0.5–1.5%	45–55	6.1:1; 0.68%; 51 °C	–/1	[264]
		II	Methanol	5.2:1–13:1	KOH, 0.5–1.5%	50–60	9:1; 1%; 55 °C	90.6/1	
WCO		I	Methanol	4:1^b	H_2SO_4, 15%	60		/2	[265]
		II	Methanol	4:1^b	CH_3Ona, 3%	60		60/2	
WCO	Round-bottomed reactor/Mechanical, 400	I	Methanol	10–40^c	H_2SO_4, 0.5–3%	20–80	30%vol; 1%; 65 °C	21.5/3	[266]
		II	Methanol	10–40^c	NaOH, 0.5–3%	20–80	30%vol; 1%; 50 °C	90.6/3	
WCO		I	Methanol	30:1	H_2SO_4, 5%	65		–/3	[267]
		II	Methanol	15:1–35:1	KOH, 0.05–0.15%	60–70	25:1; 0.15%; 60 °C	93.2/1	
WCO	Conical flask, 150/ Magnetic, 900^d	I	Methanol	0.5:1–0.8:1	H_2SO_4, 1–3%	60–66	0.8:1; 3%	(97.6)^e/0.13	[268]
		II	Methanol	14.2:1	NaOH, 0.91%		26–60 °C	98.8/0.08	
WCO	Microtube reactor, i.d. 0.508 mm and length 1.2 m length; Batch reactor	I	Methanol	4.5:1–18:1	H_2SO_4, 0.5–2%	55–70	Microtube reactor; 9:1; 1%; 65 °C	(77.5)^e/0.001	[269]
		II	Methanol	4.5:1–12:1	KOH, 1%	65	9:1	91.8/0.001	
WCO (olive and sunflower oil)	Spherical reactor, 1000/Mechanical	I	Ethanol	6:1–12:1	KOH, 0–1%	35–78	12:1; 2%; 78 °C	74.2/2	[204]
		II	Ethanol	3:1–5:1	KOH, 0–1%	78	5:1; 0.75%	94.5/2	

(continued)

Table 5.7 (continued)

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Step	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst^a	Temperature, °C	Optimal reaction conditions		Reference
							Reaction conditions	Yield (conversion), %/time, h	
WCO	Continuous ultrasonic reactor^f, 800/	I	Methanol	2.5:1–4:1	KOH, 0.7%		2.5:1	81/0.009	[270]
		II	Methanol	1:1–2:1	KOH, 0.3%		1.5:1	99/0.007	
WCO	Batch reactor/	I	Methanol	10:1	KOH, 0.094 mol/mol	65		–/0.5	[271]
		II	Methanol	15:1	H_2SO_4, 0.19 mol/mol	65		(>97)/1	
WCO (primarily from soybean oil)	Batch reactor/	I	Ethanol	10:1–33:1	KOH, 0.095–0.35 mol/mol	65–85	20:1; 0.35^f; 65 °C	–/0.5	[272]
		II	Ethanol	15:1–40:1	H_2SO_4, 0.1–3.7 mol/mol	65–85	30:1; 1.4^f; 80 °C	(98)/2.5	
Heterogeneous catalysis									
WCO (different vegetable oils)	Round-bottomed two necks flask, 1000/Magnetic, 600	I	Methanol	30:1	SiO_2(HF) and SiO_2, 2–8%	40–70	SiO_2(HF); 4%; 70 °C	(86)^e/4	[273]
	One neck flask, 250/600	II	Methanol	6:1	NaOH, 1%	60		≈100/	
WCO	Round-bottomed flask, 250/Magnetic	I	Methanol	3:1–12:1	$Fe_2(SO_4)_3$, 0.5–2.5%	100	9:1; 2%	(≈95)^e/2	[243]
		II	Methanol		KOH, –	100		96/1	
WCO	Parr reactor, 300/600	I	Methanol	14:1	25 wt% 12-TPA/Nb_2O_5, 1.65%	65		–/5	[274]
		II	Methanol	3:1–30:1	5–20 wt% ZnO/Na-Y, 5–30%	35–65	24:1; 20 wt% ZnO/Na-Y/20; 65 °C	≈95/9	
WCO	Round-bottomed flask, 250/Magnetic	I	Methanol	3:1–13:1	$Fe_2(SO_4)_3$, 0.4%	42–78	7:1; 60 °C	(97)^e/3	[275]
		II	Methanol	7:1	CaO, –	60		81.3/3	

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Step	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst[a]	Temperature, °C	Optimal reaction conditions		Reference
							Reaction conditions	Yield (conversion), %/time, h	
WCO		I	Methanol	3:1–10:1	$Fe_2(SO_4)_3$, 0.2–4%	95	10:1; 2%	(97.2)[e]/4	[276]
	Round-bottomed one-neck flask, 250/	II	Methanol	6:1	KOH, 1%	65		97/1	
WCO	Spherical reactor, 250/Magnetic, 600	I	Methanol	6:1–15:1	H_2SO_4, 0.35%	60	15:1	(74.2)[g]/3	[277]
		II	Methanol	6:1–15:1	Calcined sea sand (CaO), 5–10%	60	12:1; 7.5%	95.4/6	
WCO	/Magnetic	I	Methanol		H_2SO_4	65		–/1	[278]
		II	Methanol	10:1	Calcined fusion waste chicken and fish bones (hydroxyapatite, CaO, and $Ca(OH)_2$), 0.66–2.34[h]	40–80	1.98% wt/v; 65 °C	89.5/1.54	

[a] Percentages are based on oil mass
[b] Molar ratio of methanol and THF to oil
[c] vol% of methanol to the oil
[d] Assisted by radio-frequency heating
[e] FFA conversion
[f] 20 kHz, 1 kW
[g] FFA conversion
[h] % wt/v

of cosolvent (tetrahydrofuran or dioxane) to the reaction mixture. The main disadvantage of acid/base two-step processes for synthesis is the necessity to remove catalysts in both steps. The removal of acid catalyst from the first step could be done by adding excess base catalyst in the second step [172]. Considering the negative effect of extra-base catalyst (formation of gel, difficulties in product separation), the amount of base catalyst should be carefully chosen. To overcome this problem, Guzatto et al. [271, 272] have recently proposed a base/acid two-step transesterification process (denominated Transesterification Double Step Process—TDSP) for biodiesel production from vegetable oils. The process involves consecutive homogeneous base- and acid-catalyzed reactions without cooling the reaction mixture and the catalyst removal between steps, which significantly reduces the total process time. The proposed TDSP process is characterized by mild reaction conditions, easy separation of phases, high reaction rate, and conversion efficiency [271, 272]. The TDSP process was used for WCO methanolysis [271] and ethanolysis [272], and the achieved oil conversion was 97% and 98%, respectively.

Another, more widely used method for avoiding catalyst removal in the first stage is the use of heterogeneous catalysts. The researchers have suggested the use of ferric sulfate [183, 243, 276], SiO_2 pretreated with HF [273] or 25 wt% 12-tungstophosphoric acid (TPA) supported on Nb_2O_5 [274] as catalysts for the first step. Compared with sulfuric acid, these catalysts are environmentally friendly, high efficiently, reusable, and easily separable from the reaction mixture. For example, the activity of SiO_2(HF) [273] and 25 wt% TPA/Nb_2O_5 [274] remained rather unaffected after 10 runs and 6 runs, respectively.

Nowadays, researches are directed toward the development of two-step heterogeneous catalyzed processes. The FAME yield of 81.3% was achieved in a two-step process involving ferric sulfate in FFA esterification and CaO in methanolysis reaction [275]. The highest FAME yield (95%) was obtained by using 25 wt% TPA/Nb_2O_5 in the first step and 20 wt% ZnO/Na-Y in the second one at almost the same reaction temperatures but at the higher methanol-to-oil molar ratio, higher catalyst loading and longer total reaction time [274].

To reduce the biodiesel production cost, the nonconventional, highly active base catalysts obtained from natural and waste materials were used in the two-step biodiesel production processes. The base-catalyzed transesterification of the pre-esterified WCOs was performed in the presence of calcined sea sand, consisting mainly of CaO [277], and calcined waste chicken and fish bones, a combination of CaO, hydroxyapatite, and $Ca(OH)_2$ [278]. Both catalysts were very active in the methanolysis reaction, providing a high FAME yield under mild reaction conditions.

The improvement of two-step processes includes the novel technologies, such as radio-frequency heating [268], ultrasound [270], and use of microtube reactor [269] which are, up to date, applied in the homogeneous processes. The two-step process of WCO methanolysis with radio-frequency heating was completed (FAME yield of 98.8%) in a reaction time of 13 min [268]. Thanh et al. [270] reported that a continuous ultrasonic reactor with a two-step process was an effective method for the biodiesel production from WCO, ensuring an almost total conversion at the residence time of 0.93 min for the entire process. A continuous microtube reactor exhibits

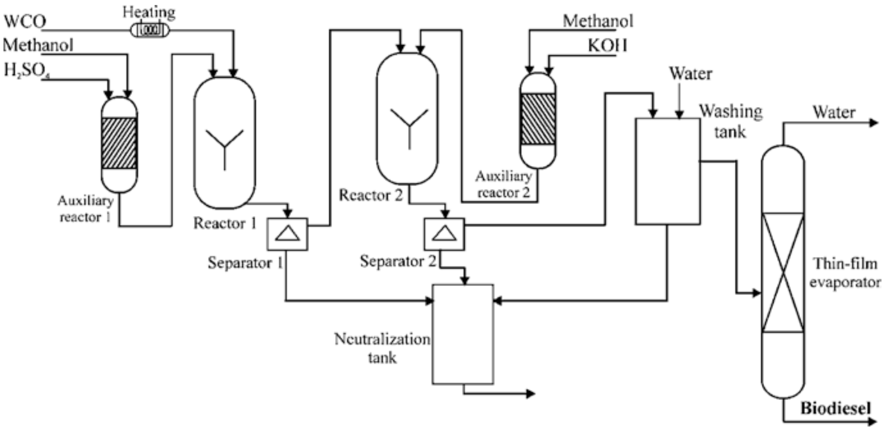

Fig. 5.9 Flow sheet of biodiesel production via two-step process. (Adapted from [241])

excellent performance because of its extremely high mass and heat transfer rates and short molecular diffusion distance [269]. The FAME yield of 91.8% was obtained in this type of reactor for an overall process time of 10 s.

A biodiesel pilot plant production from WCO (acid value from 80 to 120 mg KOH/g) in a two-step process is located in Tianjin, China [279]. A scheme of the process is shown in Fig. 5.9. The capacity of the plant is approximately 3000 kg/day. FFA esterification is performed with methanol (weight ratio to the oil 60%) in the presence of H_2SO_4 (2%, based on the oil weight) and at 70 °C. The methanolysis reaction is catalyzed by KOH (0.8% based on the oil weight) at the methanol weight ratio to the oil of 30% and the reaction temperature of 60 °C. The biodiesel purification includes washing with acidified water, and heating by thin-film evaporator at 120 °C to eliminate water and residual methanol. This project is a first step for the construction of a big plant for biodiesel production with a capacity of 10,000 tonnes/year [279].

6 Fuel Properties of Biodiesel Produced from Waste Oily Feedstocks

Compositional and physical properties of biodiesels produced from conventional vegetable oils, sidestream products of edible oil refining processes, WAFs, and WCOs are presented in Tables 5.8, 5.9, 5.10, and 5.11, respectively. For comparison, the provisional standards for biodiesel according to EN14214 are added. Most of the presented studies were not considered upgrading of crude biodiesel produced from waste oils, WAFs, and WCOs.

Edible-grade vegetable oils are currently the predominant feedstocks for biodiesel production. Based on the predominant oilseeds grown, these are soybean oil

Table 5.8 Properties of biodiesel produced from refined vegetable oils

Feedstock	Soybean oil	Sunflower oil	Rapeseed oil	Palm oil	Corn oil	
Technology[a]	B, BC, HC, Me	B, BC, HC, Me	B, BC, HC, Me	–	B, BC, HC, Me	EN14214 limits min/max
Property, unit						
FAME content, %	97.9	98.7	96	98.5	98.4	96.5 min
Density at 15 °C, kg/m^3		878.9	880[b]	878.3	878.0	860/900
Viscosity at 40 °C, mm^2/s	4.12	4.81	4.15	4.415	4.42	3.50/5.00
Flash point, °C		165	165	182	172	101 min
Sulfur content, mg/kg		0.2	9.5	<10	5.42	10 max
Carbon residue (on 10% distillation residue), %		<0.001		0.02	0.040	0.3 max
Cetane number		67.6		58.3	56	51 min
Sulfated ash content, %		<0.01	0.022	<0.01		0.02 max
Water content, mg/kg		140	100	<500	197	500 max
Total contamination, mg/kg						24 max
Copper strip corrosion (3 h at 50 °C), rating			1a	1a	2.1	Class 1 min
Oxidation stability at 110 °C (h)	5	6.4			1.3	6.0 min
Acid value, mg KOH/g	0.01	0.07	0.37	0.08	0.15	0.50 max
Iodine value, g I_2/100 g	136	72.8		52		120 max
Linolenic acid methyl ester content, %				<0.5		12 max
Polyunsaturated (≥4 double bonds) methyl esters, %				<0.2		1 max
Methanol content, %		<0.01		<0.4		0.20 max
Monoglyceride content, %	0.035	0.08		<0.2		0.80 max
Diglyceride content, %	0.01	<0.01		<0.1		0.20 max
Triglyceride content, %	0.009	<0.01				0.20 max
Free glycerol, %	0.001	0.01		<0.01	0.00	0.02 max
Total glycerol, %	0.055	<0.04		<0.01	0.09	0.25 max
Group I metals (Na + K), mg/kg		0.07			2.2	5.0 max
Group II metals (Ca + Mg), mg/kg						5.0 max
Phosphorus content, mg/kg		<0.1			2	4.0 max
Cloud point, °C	2		−3	15.2		Not specified
Pour point, °C	0		−9	15	−13	Not specified

(continued)

Table 5.8 (continued)

Feedstock	Soybean oil	Sunflower oil	Rapeseed oil	Palm oil	Corn oil	EN14214 limits min/max
Technology[a]	B, BC, HC, Me	B, BC, HC, Me	B, BC, HC, Me	–	B, BC, HC, Me	
Property, unit						
Higher heating value, MJ/kg			44.9			Not specified
Distillation range temperatures, °C					338	Not specified
Reference	[280]	[281]	[282]	[283]	[284]	

[a] *B* batch, *BC* base catalyst, *HC* homogeneous catalysis, *Me* methanol
[b] At 25 °C

in the USA, rapeseed and sunflower oil in Europe, and palm oil in Asia. The oil quality and its fatty acid composition have the most significant influence on the fuel properties of biodiesel. The properties of biodiesel produced from edible oils along with the biodiesel quality standard EN14214 are compared in Table 5.8. Generally, edible oils biodiesel satisfies all standard limits. The exception is iodine value, which is in the case of soybean biodiesel higher than standard limits [280] because of the presence of a large amount of unsaturated fatty acids. Iodine value is dependent on the origin of the vegetable oil, and until recently, it has been believed that it influences the oxidation stability. However, the stability of biodiesel is shown to depend not on content but rather on the position of double bonds in the FAMEs [290]. On the other hand, biodiesel obtained from oils with a high amount of SFAs has a low iodine number, but higher pour and cloud point, as in the case of palm oil biodiesel [283]. This poor cold flow property is one of the most critical obstacles against biodiesel usage in cold climate conditions.

The chemical composition of biodiesel produced from waste vegetable oils can be expected to be essentially identical to that produced from origin vegetable oils as shown for biodiesels from soybean oil and its soapstock [285] and palm oil and SBE from palm oil refining process [61]. The properties of biodiesel produced from waste oily feedstocks are similar to those of biodiesel produced from refined vegetable oils and meet the biodiesel standard quality for all assayed parameters with some exceptions. The density of all biodiesels is within the specified limits, while kinematic viscosity, which is important for the biodiesel quality during the storage, is rarely outside the range specified by the standard. Flash point, carbon residue, cetane number, water content, and acid value are in accordance with the biodiesel standard. However, sulfur and phosphorus contents are not in agreement with the prescribed limits. High sulfur content is undesirable due to the increased emission of sulfur oxides. Most of the biodiesels does not meet the standard value for oxidation stability, which affects the storage of biodiesel. A low iodine value and a high cetane number of the biodiesel produced from an SBE residual oil were explained by a high content of SFAs [51].

Table 5.9 Properties of biodiesel produced from sidestream products of edible oil refining processes

Feedstock	Soybean soapstock	Acidulated soapstock	Acid oil	Olive acid oil	Acid oil	SBE (palm oil)	SBE	SBE	DD (palm oil)	DD (palm oil)	DD (rapeseed oil)	Chicken fat	Broiler rendering fat	EN14214 limits min/max
Technology^{a}	B, BC, HC, Me	C, BC, SC, Me	B, BC, HC, Me	C, NC, AC, Me	C, EC, Me	B, AC, SC, Me	B, BC, HC, Me	B, EC, Me	C, AC, SC, Me	C, AC, HC, Me	B, TS, Me	B, TS, HC, Me	B, TS, HC, Me	
Property, unit														
FAME content, %		90.2		96.6		99.5				99.48	97.1		95.5	96.5 min
Density at 15 °C, kg/m^3	883.6		886	860	891.5	905.1^{b}	890^{b}	870	889	879.3	883	879	882.1	860/900
Viscosity at 40 °C, mm^2/s	4.3	3.4	5.2	4.68	7.47	3.7	5.0	5.62^{c}	4.44	4.865	5.60	4.88	4.294	3.50/5.00
Flash point, °C	169	131	102		180	172	168	26	167	181	139.7	158	182.5	101 min
Sulfur content, mg/kg	15	3.17			76	400	<100	4	50				6.2	10 max
Carbon residue (on 10% distillation residue), %	0.01				0.09		0.05	0.16		0.07	0.26		0.17	0.30 max
Cetane number	51.3	47.9	54.4		63		61	59.3	54		50	53.5	53.2	51 min
Sulfated ash content, %	0.020	0.007		<0.01	0.0023		0.02			0.0066	0.01		0.0021	0.02 max
Water content, mg/kg				424	11.1		500			300			465	500 max
Total contamination, mg/kg					53								12.8	24 max

Feedstock	Soybean soapstock	Acidulated soapstock	Acid oil	Olive acid oil	Acid oil	SBE (palm oil)	SBE	SBE	DD (palm oil)	DD (palm oil)	DD (rapeseed oil)	Chicken fat	Broiler rendering fat	EN14214 limits min/max
Technology[a]	B, BC, HC, Me	C, BC, SC, Me	B, BC, HC, Me	C, NC, AC, Me	C, EC, Me	B, AC, SC, Me	B, BC, HC, Me	B, EC, Me	C, AC, SC, Me	C, AC, HC, Me	B, TS, Me	B, TS, HC, Me	B, TS, HC, Me	
Property, unit														
Copper strip corrosion (3 h at 50 °C), rating	1a	1a			1					1	≤1		1a	Class 1 min
Oxidation stability at 110 °C (h)		4.3		1.74		14.6					2.37		3.82	6.0 min
Acid value, mg KOH/g	0.05	0.19		0.18	0.23		0.5		0.32	0.33	0.36	0.42	0.23	0.50 max
Iodine value, g I_2/100 g	129			62.3			27					81.14	93	120 max
Methanol content, %							0.01				0.30			0.20 max
Monoglyceride content, %						0.45				0.462	0.52		0.01	0.80 max
Diglyceride content, %						0.05				0.058	0.06		0.21	0.20 max
Triglyceride content, %						0.00				0.000			0.06	0.20 max
Free glycerol, %	0.00	0.007							0.038				0.01	0.02 max
Total glycerol, %	0.123	0.158			0.24				0.203				0.01	0.25 max

(continued)

Table 5.9 (continued)

Feedstock	Soybean soapstock	Acidulated soapstock	Acid oil	Olive acid oil	Acid oil	SBE (palm oil)	SBE	SBE	DD (palm oil)	DD (palm oil)	DD (rapeseed oil)	Chicken fat	Broiler rendering fat	EN14214 limits min/max
Technology[a]	B, BC, HC, Me	C, BC, SC, Me	B, BC, HC, Me	C, NC, AC, Me	C, EC, Me	B, AC, SC, Me	B, BC, HC, Me	B, EC, Me	C, AC, SC, Me	C, AC, HC, Me	B, TS, Me	B, TS, HC, Me	B, TS, HC, Me	
Property, unit														
Group I metals (Na + K), mg/kg		1.71											0.062	5.0 max
Group II metals (Ca + Mg), mg/kg													0.5	5.0 max
Phosphorus content, mg/kg		7					<10						1	4.0 max
Cloud point, °C	6	−1.6			−4			9		15			4	Not specified
Pour point, °C			−8			16		10	6	14	−2.8	3		Not specified
Higher heating value, MJ/kg			40.6	39.6		38.1	38.8						3	Not specified
Distillation range temperatures, °C		317	300–350					334		335	345.7			Not specified
Reference	[285]	[32]	[286]	[39]	[287]	[61]	[51]	[71]	[81]	[77]	[83]	[169]	[161]	

[a] *B* batch, *C* continuous, *TS* two step, *AC* acid catalyst, *BC* base catalyst, *NC* non-catalytic (supercritical) process, *HC* homogeneous catalysis, *SC* heterogeneous catalysis, *EC* enzyme catalysis, *Me* methanol

[b] At 25 °C

[c] At 30 °C

Table 5.10 Properties of biodiesel produced from WAFs

Feedstock	WAF	Beef tallow	Beef tallow	Beef tallow	Mutton tallow	Lard	Lard	Lard		Lard	Poultry fat	Chicken fat	Chicken fat	Chicken fat	Broiler rendering fat	EN14214 limits min/max
Technology[a]	B, AC, HC, Et	B, BC, HC, Me	B, BC, HC, Me	B, BC, HC, Me	B, TS, HC, Me	B, AC, HC, Me	B, TS, HC, Me	B, BC, SC, Me	B, BC, HC, Me	B, EC, Me	B, BC, HC, Me	B, TS, HC, Me	B, BC, SC, Me	B, TS, HC, Me	B, TS, HC, Me	
Property, unit																
FAME content, %			97	82.5		85.1	69.6–99.6	92.5	94.4		67.25				95.5	96.5 min
Density at 15 °C, kg/m^3	873	832[b]	872	870	882	873				877.4	877	883	870	879	882.1	860/900
Viscosity at 40 °C, mm^2/s	7.06[b]	4.89	5.3	5.35	4.75	5.08	4.64–7.73	4.59	4.71	4.84	6.86	4.94	5.4	4.88	4.294	3.50/5.00
Flash point, °C	<25	152	156.7	171		147				143.5	172	171.8	174	158	182.5	101 min
Sulfur content, mg/kg	230														6.2	10 max
Carbon residue (on 10% distillation residue), %										0.21			0.024		0.17	0.3 max
Cetane number			60.36		59								58.4	53.5	53.2	51 min
Sulfated ash content, %										0.002			0.03		0.0021	0.02 max
Water content, mg/kg				374.2		184	340–470	400	1100	200	1201	200			465	500 max

(continued)

Table 5.10 (continued)

Feedstock	WAF	Beef tallow	Beef tallow	Beef tallow	Mutton tallow	Lard	Lard	Lard		Lard	Poultry fat	Chicken fat	Chicken fat	Chicken fat	Broiler rendering fat	EN14214 limits min/max
Technology[a]	B, AC, HC, Et	B, BC, HC, Me	B, BC, HC, Me	B, BC, HC, Me	B, TS, HC, Me	B, AC, HC, Me	B, TS, HC, Me	B, BC, SC, Me	B, BC, HC, Me	B, EC, Me	B, BC, HC, Me	B, TS, HC, Me	B, BC, SC, Me	B, TS, HC, Me	B, TS, HC, Me	
Property, unit																
Total contamination, mg/kg															12.8	24 max
Copper strip corrosion (3 h at 50 °C), rating				1		1					1	1a			1a	Class 1 min
Oxidation stability at 110 °C, h													6.0		3.82	6.0 min
Acid value, mg KOH/g				0.2	0.3	0.22	1.13	0.25	0.04	0.12	0.55	0.22	0.8	0.42	0.23	0.5
Iodine value, g I_2/100 g				44.4	40	75.6	77	68	67		78.8			81.14	93	120
Linolenic methyl ester content (%)							1.4	0.9	1.0							12 max
Methanol content, %			0.1									0.01	0.06		0.01	0.20 max
Monoglyceride content, %	<0.1		0.13									0.56			0.21	0.80 max

Feedstock	WAF	Beef tallow	Beef tallow	Beef tallow	Mutton tallow	Lard	Lard	Lard		Lard	Poultry fat	Chicken fat	Chicken fat	Chicken fat	Broiler rendering fat	EN14214 limits min/max
Technology[a]	B, AC, HC, Et	B, BC, HC, Me	B, BC, HC, Me	B, BC, HC, Me	B, TS, HC, Me	B, AC, HC, Me	B, TS, HC, Me	B, BC, SC, Me	B, BC, HC, Me	B, EC, Me	B, BC, HC, Me	B, TS, HC, Me	B, BC, SC, Me	B, TS, HC, Me	B, TS, HC, Me	
Property, unit																
Diglyceride content, %	<0.05		0.12									0.09			0.06	0.20 max
Triglyceride content, %	<0.05		0.07									0.12			0.01	0.20 max
Free glycerol, %	<0.005		0.01									0.02	0.004		0.01	0.02 max
Total glycerol, %	<0.1		0.33									0.19			0.062	0.25 max
Group I metals (Na + K), mg/kg			<2.63	2		17.2					46.8		5		0.5	5.0 max
Group II metals (Ca + Mg), mg/kg													2		1	5.0 max
Phosphorus content, mg/kg					16								100		4	4.0 max
Cloud point, °C	5											3	14	3		Not specified
Pour point, °C	3	15	14.3	10	−5	5				7	3	2	12.3		3	Not specified

(continued)

Table 5.10 (continued)

Feedstock	WAF	Beef tallow	Beef tallow	Beef tallow	Mutton tallow	Lard	Lard	Lard		Lard	Poultry fat	Chicken fat	Chicken fat	Chicken fat	Broiler rendering fat	EN14214 limits min/max
Technology[a]	B, AC, HC, Et	B, BC, HC, Me	B, BC, HC, Me	B, BC, HC, Me	B, TS, HC, Me	B, AC, HC, Me	B, TS, HC, Me	B, BC, SC, Me	B, BC, HC, Me	B, EC, Me	B, BC, HC, Me	B, TS, HC, Me	B, BC, SC, Me	B, TS, HC, Me	B, TS, HC, Me	
Property, unit																
Higher heating value, MJ/kg	38.76			40.23		40.10				36.5	39.58	40.17	39.34			Not specified
Distillation range temperatures, °C			307–344							352.5						Not specified
Reference	[98]	[107]	[106]	[112, 113]	[135]	[112, 113]	[139]	[249]		[123]	[112, 113]	[137, 138]	[250]	[160]	[161]	

[a] *B* batch, *C* continuous, *TS* two step, *AC* acid catalyst, *BC* base catalyst *HC* homogeneous catalysis, *SC* heterogeneous catalysis, *EC* enzyme catalysis, *Me* methanol, *Et* ethanol

[b] At 20 °C

Table 5.11 Properties of biodiesel produced from WCOs

Feedstock	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	EN14214 limits min/max
Technology[a]	B, BC, HC, Et	B, BC, HC, Me	B, BC, HC, Me	B, BC, HC, Me	B, BC, SC, Me	B, BC, SC, Me	B, AC, HC, Et	B, TS, HC, Me	B, TS, HC, Et	B, TS, HC, Me	C, EC, Me	B, AC-NC, Me	
Property, unit													
FAME content, %		98.2	90	97.7	96.8	99.6		96	97		91.1		96.5 min
Density at 15 °C, kg/m³	870	844	880	888.3[b]	844	865	873.7	882.2	854.8	890	892.4		860/900
Viscosity at 40 °C, mm²/s	5.03	4.7	4.89	2.35	4.9	5.4	14.94[c]	4.68	4.98	4.23	9.12[a]	2.25–3.1	3.50/5.00
Flash point, °C	164	159	120	185	153	169	109			171	195		101 min
Sulfur content, mg/kg	2						180[d]			7	3		10 max
Carbon residue (on 10% distillation residue), %			4				0.3			0.2	0.15		0.30 max
Cetane number										54.5	68	55.45–56.1	51 min
Sulfated ash content, %											0.003		0.02 max
Water content, mg/kg	0.0		Trace	300						150	28.5		500 max
Total contamination, mg/kg											30		24 max
Copper strip corrosion (3 h at 50 °C), rating										1a			Class 1 min
Oxidation stability at 110 °C (h)													6.0 min
Acid value, mg KOH/g	0.29		0.43	0.48				0.5	0.8	0.48	0.12		0.50 max
Iodine value, g I_2/100 g								85.83	82.56				120 max

(continued)

Table 5.11 (continued)

Feedstock	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	EN14214 limits min/max
Technology[a]	B, BC, HC, Et	B, BC, HC, Me	B, BC, HC, Me	B, BC, HC, Me	B, BC, SC, Me	B, BC, SC, Me	B, AC, HC, Et	B, TS, HC, Me	B, TS, HC, Et	B, TS, HC, Me	C, EC, Me	B, AC-NC, Me	
Property, unit													
Methanol content, %													0.20 max
Monoglyceride content, %	0.29			2.34									0.80 max
Diglyceride content, %	0.19			0.0									0.20 max
Triglyceride content, %	0.06			0.0.									0.20 max
Free glycerol, %	0.022									0.008		0.006	0.02 max
Total glycerol, %	0.57									0.21		0.16	0.25 max
Group I metals (Na + K), mg/kg	66												5.0 max
Group II metals (Ca + Mg), mg/kg	1												5.0 max
Phosphorus content, mg/kg	2												4.0 max
Cloud point, °C	−1	−2	3	−3	−6	1	0	1	−2				Not specified
Pour point, °C	−16	−5	0	−19	−13	−4	0	−3	−6	1	−2	−4 to −1	Not specified
Higher heating value, MJ/kg				38.5		35.3	39.3	37.27	40.72	32.9			Not specified

Feedstock	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	WCO	EN14214 limits min/max
Technology[a]	B, BC, HC, Et	B, BC, HC, Me	B, BC, HC, Me	B, BC, HC, Me	B, BC, SC, Me	B, BC, SC, Me	B, AC, HC, Et	B, TS, HC, Me	B, TS, HC, Et	B, TS, HC, Me	C, EC, Me	B, AC-NC, Me	
Property, unit													
Distillation range temperatures, °C			213–348					350–380	350–380				Not specified
Reference	[209]	[203]	[210]	[205]	[203]	[221]	[180]	[288]	[288]	[289]	[37]	[243]	

[a] *B* batch, *C* continuous, *TS* two step, *AC* acid catalyst, *BC* base catalyst, *NC* non-catalytic (supercritical) process, *HC* homogeneous catalysis, *SC* heterogeneous catalysis, *EC* enzyme catalysis, *Me* methanol, *Et* ethanol

[b] At 25 °C

[c] At 20 °C

[d] Total sulfur

When compared to biodiesel from refined vegetable origin, biodiesel from WAFs has the advantage of the higher heating value and higher cetane number and the disadvantage of lower stability to oxidation, because of the absence of natural antioxidants, and higher cold filter plugging point, because of greater content of SFAs [137]. The flash point of WAF biodiesel was significantly higher than that of the standard limit [122, 123, 128, 129, 144, 158, 159]. With a high flash point, biodiesel is safer to handle, transport, and store. However, too high a flash point, as in the case of chicken fat and tallow biodiesel [128, 129, 158, 159], may cause ignition problems in the engine. Pour point (or cold filter plugging point, CFPP) is indicative of a high concentration of saturated fatty esters in the product and important for their use in low temperatures. Biodiesel obtained from beef tallow has a higher CFPP than the limit [122, 123, 128, 129]. The higher cetane number of WAF biodiesel than the specified minimum limit makes them attractive as an alternative fuel [122, 156, 291]. Teixeira et al. [123] observed the higher viscosity of WAF biodiesel than conventional diesel, which causes poor fuel amortization, incomplete combustion, and carbon deposition on the injector. Also, the higher viscosity of beef tallow biodiesel than the established limit is due to the high content of high molecular weight SFAs [122]. Compared to biodiesel obtained from different feedstocks, Mata et al. [128, 129] observed that the kinematic viscosities for lard and chicken fat biodiesel were higher than the standard limit. The same authors also observed that the water content of chicken fat biodiesel was very high, but lard biodiesel presented a low value. However, tallow biodiesel purified with water satisfied the standard maximum limit. Also, only for the purified tallow biodiesel, the amount of Na + K is within the standard limit. This parameter suggests that purification methods were not effective, leaving catalyst residues dissolved in the biodiesel. Comparing homo- and heterogeneously catalyzed processes of lard, Dias et al. [292] concluded that the acid value of the product was significantly lower when the homogeneous catalyst was used, and also, it was smaller than the maximum standard limit. Such differences were due to the fact that the homogeneous catalyst tends to react with FFAs to generated soaps, which reduced the acid value. It was noted that the viscosities of the products were similar independently of the type of process.

The properties of biodiesel produced from WCOs generally meet the biodiesel standard quality with some exception. A somewhat higher value of kinematic viscosity of WCO biodiesel than the standard limit is the result of the presence of dimeric FAMEs, which are formed from polymers incurred during the heating of oil [172] and higher content of unreacted AGs [293]. Phan and Phan [210] reported high carbon residue, which corresponded to the amount of AGs as well as FFAs, soaps, remaining catalyst, polymers (dimeric and polymeric methyl esters), and other impurities [293]. The high total sulfur content of 180 ppm in a WCO biodiesel [180] cannot be compared with standard limit since it includes sulfur and sulfate ash content. The acid value generally meets the biodiesel standard, with the exception of WCO ethyl esters, but its acid value is in the range of ASTM D-6751 biodiesel standard [288]. Density, flash point, cetane number, water content, iodine value, MAGs, DAGs, and TAGs content, as well as phosphorus and Ca + Mg content, are within the biodiesel standard limits. Free and total glycerol amounts are significant for defining the quality of biodiesel. A higher free glycerol content may cause problems during storage because of its separation or can lead to injector fouling or the higher aldehyde emissions [293]. Based on available data on WCO biodiesel characteristics, free and total glycerol are in one case outside of standard ranges [209]. Free glycerol can easily be removed by washing step, while bonded glycerol depends on AG content, and could be lowered by optimization of reaction conditions in order to achieve higher AG conversion or by further distillation of the product. The higher value of Na + K indicated the remaining of catalysts, which can be removed by washing biodiesel [209].

Generally, no change in engine operation was observed during the test in the case of biodiesels derived from soybean soapstock [285] and WCO [172]. Regarding the exhaust emissions, only the NO_x emission was increased [172, 285]. Particulate matter emission was significantly higher, and hydrocarbon emission was significantly lower for the soapstock biodiesel, compared to the biodiesel from soybean oil [285]. WAF biodiesel often reduces bot NO_x emission and particulate matter and provides greater lubricity [105]. A slight fried food smell was observed, when WCO biodiesel was used on a large scale with diesel fuel [172].

7 Economics of Biodiesel Production from Waste Oily Feedstocks

Various factors affect biodiesel production costs including oily feedstock, other reactants, conversion and purification processes, the scale of production, region, etc. The major economic factor is oily feedstock, which is about 75–80% of the total cost, followed by labor and chemicals (methanol and catalyst) [294]. Although economic considerations are of great importance for employing a process at the industrial scale, a few papers present cost analysis of biodiesel production from waste vegetable oils [48, 51, 78] and WCOs [3, 14, 48, 262, 295]. Process simulation and economic analysis were conducted using HYSYS [3, 262, 295] and Aspen Tech [14, 48, 295] software packages.

Haas [48] assessed the economic viability of biodiesel production from soapstock. An estimate of 0.41 US$/L was obtained from a model of an industrial plant with a capacity of 20–40 million L of biodiesel per year, which was nearly 25% less than the cost of biodiesel from refined soybean oil. Chongkhong et al. [78] estimated the cost of biodiesel production from palm fatty acid distillate of 0.62 US$/kg for the capacity of 72,000 kg/year. The main part (60%) of the overall production cost was the cost of the input raw material. Huang and Chang [51] performed an economic analysis for annual biodiesel production of 1000 tonnes from SBE residual oil and got the cost of 0.37 US$/L, which was lower than the estimated price of biodiesel produced from refined vegetable oils or WCOs (0.8–1.5 US$/L). They showed that the price of crude oil heavily affected the production cost and the investment return period since the chemicals were the predominant cost constituents. The production cost of biodiesel from animal fats is estimated to be 0.36 US$/L and is lower than the price of biodiesel from rapeseed and sunflower oils (0.39 US$/L and 0.62 US$/L, respectively) but higher than the price of soybean biodiesel (0.33 US$/L) [296]. This cost can be decreased if none of the pretreatment capital costs are allocated to the total production costs.

The estimated total production cost for the non-catalyzed process of WCO biodiesel production was 150 US$/tonne, 214 US$/tonne, and 442 US$/tonne (corresponding to biodiesel required selling price of 0.17 US$/L, 0.24 US$/L, and 0.52 US$/L) for plant capacity of 125,000 tonnes/year, 80,000 tonnes/year, and 8000 tonnes/year, respectively [14]. The total production cost of 574 US$/tonne for a plant capacity of 8000 tonnes/year was established by West et al. [262], while Lee et al. [295] reported a somewhat higher value of 725 US$/tonne for plant capacity 40,000 tonnes/year. The manufacturing cost for homogeneous alkali-catalyzed batch processes with a capacity of 7260 tonnes/year was estimated to be 598 US$/tonne in the case of the hot water purification process and 641 US$/tonne for vacuum FAME distillation process [297]. Higher production cost (884 US$/tonne) was established by Zhang et al. [3] for a plant with 8000 tonnes/year capacity. The cost of WCO biodiesel production in a homogeneous pretreated alkali-catalyzed process was reported to be 650 US$/tonne [262] and 875 US$/tonne [295]. The reported values of biodiesel production cost in the homogeneous acid-catalyzed processes are close: 595 US$/tonne [262] and 644 US$/tonne [3]. The biodiesel production cost in the heterogeneous acid-catalyzed process was nearly 18% less than the cost of biodiesel in the homogeneous one in the same plant capacity [262]. Sakai et al. [297] estimated the production cost for batch CaO-catalyzed processes of 584 US$/tonne and 622 US$/tonne for water washing and vacuum FAME distillation processes, respectively, which is almost the same compared to batch homogeneous (KOH) process with the same capacity [297].

8 Conclusion

At present, homogeneously catalyzed processes of edible oils are primarily used in the commercial biodiesel production, although a heterogeneous process is also applied. Due to the competition to the edible oil market, usage in the human diet and food industry, and insufficient quantities of edible oils for biodiesel production, the use of alternative oily feedstocks in biodiesel production has been focused. Therefore, special attention has been paid to cheap, nonedible, and low-quality oily feedstocks, such as waste oily by-products from an edible oil refinery, WAFs, and WCOs. Instead of being disposed into landfills with potential environmental hazards, these materials can be used for making biodiesel as an economically sustainable and ecologically acceptable product. The fuel properties of biodiesel derived from these waste oily materials are similar to those of biodiesel produced from refined vegetable oils and meet the biodiesel standard quality for all assayed parameters with some exceptions. Also, no change in engine operation was observed with biodiesel obtained from waste oily feedstocks. The price of this biodiesel depends on the input waste oily feedstock, but it is generally smaller than the cost of biodiesel from refined vegetable oils.

Although the two-step (acid/base) homogeneously catalyzed process seems to be useful for converting low-quality oily feedstocks having a high FFA content, present investigations of biodiesel production from these feedstocks are focused on developing novel technologies based on the application of solid catalysts, enzymes, or supercritical alcohol conditions. It might be expected that homogeneous catalysis will be replaced by these novel technologies. Future processes will involve, beside low-quality oily feedstocks: (a) cheap, active, stable, bifunctional, no leachable and reusable catalysts, (b) continuous operation, (c) as low power input as possible (lower pressure, temperature and alcohol-to-oil ratio), and (d) no environmental problem. It is probable that the future commercial process of biodiesel production will be a choice among solid catalysts, lipases, and non-catalytic processes. Nowadays, it is claimed that a one-step enzymatically catalyzed process is operated for biodiesel production from WCOs at the pilot scale.

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Glossary

Biodiesel Biodiesel is a form of diesel fuel derived from plants or animals and consisting of long-chain fatty acid esters.

Catalysis Catalysis is the process of increasing the rate of a chemical reaction by adding a substance known as a catalyst.

Cooking oils Cooking oil is plant, animal, or synthetic fat used in frying, baking, and other types of cooking.

Enzyme catalysis Enzyme catalysis is the increase in the rate of a process by a biological molecule, an “enzyme.”

Esterification Esterification is the general name for a chemical reaction in which two reactants (typically an alcohol and an acid) form an ester as the reaction product.

Fats Fat is a type of nutrient.

Transesterification Transesterification is the process of exchanging the organic group R'' of an ester with the organic group R' of an alcohol.

Vegetable oils Vegetable oils, or vegetable fats, are oils extracted from seeds, or less often, from other parts of fruits.

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Chapter 6
Physicochemical Treatment Consisting of Chemical Coagulation, Precipitation, Sedimentation, and Flotation

Lawrence K. Wang, Mu-Hao Sung Wang, Nazih K. Shammas, and Hermann H. Hahn

Contents

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Abstract This publication is a collection of a few authors' lecture materials of the Lenox Institute of Water Technology (LIWT) where the authors taught advanced humanitarian engineering courses and provided graduate education to international students around the world totally free of charge for decades. This publication has been timely assembled in memory of coauthors Professor Nazih K. Shammas and Professor Hermann H. Hahn without sufficient preparation time. Some omissions or repetitions among the authors' various publications are unavoidable. When a scholar leaves this world, he/she will be summarized as digital numbers and words, stored in the clouds, distributed through the Windows, and shown on the Internet. The scholar's life continuously lives whenever his/her publication is cited by other scholars. The subjects covered in this memoir-style publication are: chemistry of chemical coagulation and precipitation, electrical potential of negatively charged colloidal particles, effects of inter-particle forces on the stability of colloidal systems, relative coagulation power of electrolytes, optimum pH values for metallic coagulants, types of coagulating and precipitating chemicals, plug flow reactors, completely mixed continuous flow reactors, theories and principles of solid–water separation, rapid mixing basin design, flocculator design, sedimentation clarifier design, flotation clarifier design, streaming current monitor, and recent advances in partial or complete physicochemical process systems (PCPS) including chemical feeding, mixing, precipitation, coagulation, flocculation, clarification, filtration and disinfection. Design and applications of PCPS for wastewater and water treatment are introduced. The authors also introduce the US Environmental Protection Agency (USEPA) expected PCPS pretreatment results for treating the wastewaters from aluminum foundry die casting industry, metal finishing industry, iron and steel industry, textile mills, stream electric industry, inorganic chemical industry, ore mining and dressing industry, porcelain industry, paint manufacturing industry, coil coating industry, nonferrous metals industry, aluminum forming industry, battery industry, electrical and electronic industry, copper industry, organic chemical industry, auto industry, and laundries. Also introduced are: (a) the applications of dissolved air flotation

(DAF) clarification for replacing sedimentation clarification under certain engineering conditions, and (b) the availability of commercial DAF facilities (Supracell, Sandfloat, Sedifloat, Clari-DAF, AquaDAF, etc.) for treating general industrial effluents, specific petrochemical wastewater, turkey farm wastewater, and municipal drinking water. The case histories reported in this publication can be applied to any manufacturer's process equipment in any shape (rectangular or circular shape).

Keywords Theory · Principles · Industrial effluent treatment · Chemical coagulation · Chemical precipitation · Rapid mix · Flocculation · Clarification · Sedimentation · Dissolved air flotation · Design considerations · Physicochemical process system · Pretreatment · Aluminum foundry die casting industry · Metal finishing industry · Iron and steel industry · Textile mills · Stream electric industry · Inorganic chemical industry · Ore mining and dressing industry · Porcelain industry · Paint manufacturing industry · Coil coating industry · Nonferrous metal industry · Aluminum forming industry · Battery industry · Electrical and electronic industry · Copper industry · Organic chemical industry · Auto and laundries · Supracell · Sandfloat · Sedifloat · Clari-DAF · AquaDAF · Petroleum refinery · Turkey farm · Poultry plant · Municipal drinking water purification

Nomenclature

C	Solution concentration, mol/L or mg/L
C_D	Drag coefficient, no unit
C_s	Saturation concentration, mol/L or mg/L
C_T	Total carbonic species concentration, mol/L or mg/L
d/dt	Derivative with respect to reaction time
DF	Driving force
E_B	Bearing efficiency, %/100
E_D	Drive efficiency, %/100
G	Velocity gradient, s^{-1}
k	Reaction rate constant
L	Length between two points of tubular reactor
n	Particle or chemical agent concentration
N_i	Influent concentration
N_e	Effluent concentration (also corresponding to the concentration within the reactor)
N_0	Particle or reagent concentration at time $t = 0$
N_t	Concentration at time 't'
P	Water power, ft lb/s
P_H	Brake horsepower, ft lb/s
Q	Rate of flow through the reactor

r	Relative velocity of paddles, ft/s
s	Crystal surface area
T	Absolute temperature in kelvin, K, °C + 273
t	Detention time
t	L/v time elapsed between two points of tubular reactor
u	Absolute viscosity of liquid, lb s/ft^2, 2.089×10^{-5} at 20 °C
v	Velocity, ft/s
V	Volume, cu ft

1 Introduction

1.1 Summary

Chemical treatment is considered as a useful tool for: (a) pretreatment of harmful wastes, (b) early removal of non-dissolved precipitating substances, (c) reduction of load fluctuations, (d) combating bulking activated sludge, (e) polishing effluents, and (f) phosphorous removal. Chemical treatment as a rule means addition of chemicals. Such chemicals are usually inorganic (like iron or aluminum salts) or organic (such as cationic, anionic, or nonionic polymers). These chemicals cause precipitation and/or aggregation (i.e., coagulation and flocculation) of the suspended phase in the wastewater system under consideration. The addition of chemicals in the phase of chemical treatment changes water constituents into a form that improve removal by all liquid–solid separation processes.

This publication describes the effects of chemicals upon particle aggregation and the interrelationship of the aggregation with the chemical precipitation, coagulation, flocculation, sedimentation and flotation processes. The chemical used include inorganic, mostly metal salt-type chemicals, and organic, mostly polymeric chemicals. Examples of inorganic chemicals that might come into consideration are: calcium (salts), iron III (salts), and aluminum (salts). Organic coagulants—or better—flocculants are of the following types: low-molecular-weight substances with (opposite) charges, high molecular weight material adsorbing on oppositely charged surfaces and high-molecular-weight material adsorbing on surfaces with a charge of the same sign (possibly due to some intermediary reaction). For practical design and operation, the following recommendations are made on the effects on the detention time distribution: flow rate relative to volume, energy dissipation in the reactor (relative to the energy introduced with the throughput), stirrer type and geometry (relative to the reaction chamber), inflow and outflow configuration (relative to the geometry of the reactor), compartmentalization of the reactor, and baffles and other flow directing devices in the reactor (relative to the reactor geometry).

The process of aggregation, i.e., formation of larger (better separable) solids from small suspended solids, has traditionally been designed and operated to ensure a maximum efficiency in terms of aggregate growth. Aggregate growth means increase of average particle diameter for better removal in a liquid–solid separation process, such as, sedimentation or flotation.

This publication introduces also the theory, principles, design procedures, and application of partial or complete physicochemical process system consisting of chemical feeding/mixing, precipitation, coagulation/flocculation, clarification (sedimentation or flotation), filtration (sand, multi-media, GAC, DE, membrane), and disinfection.

1.2 Process Introduction

Classical waste water treatment, developed primarily for domestic wastewater, employs unit processes from the catalog of the mechanical and biological treatment. Such processes are reflected in the following elements of treatment plants [1, 2]:

1. Screens
2. Grit chambers
3. (Primary) Sedimentation or flotation tanks
4. Activated sludge or trickling filter units
5. (Secondary) Sedimentation or flotation tanks

The advantages of this concept of wastewater treatment are non-specificity, robustness, and acceptable cost [3].

The disadvantages of such treatment plants are vulnerability toward poisonous material, difficulties in following load fluctuations, lack of specificity, and non-flexibility in terms of re-orientation of the treatment concept.

Chemical treatment of wastewater, i.e., the removal or inactivation of constituents of the wastewater phase, has existed before today's concept of treatment was developed. Subsequently, it has been utilized and developed further in the realm of treating waters in the industrial sector. Today, chemical treatment is considered as a useful tool for [4, 5]:

1. Pretreatment of harmful wastes
2. Early removal of non-dissolved precipitating substances
3. Reduction of load fluctuations
4. Combating bulking activated sludge
5. Polishing effluents
6. Phosphorous removal

The extraordinary rise of the chemical sales for the water and wastewater industry is a witness to this. Chemical treatment as a rule means addition of chemicals. Such chemicals cause acid–base reactions, coordination reactions, and oxidation–reduction reactions. In the context of this discussion—i.e., primarily directed to the more nonspecific treatment of a larger number of wastewater constituents—only such chemicals are considered further which cause acid–base reactions in the sense of the definition by Lewis. The acid–base reactions considered here can take place in the aqueous phase or on surfaces [6].

Such chemicals are usually inorganic (like iron or aluminum salts) or organic (such as cationic, anionic, or nonionic polymers). These chemicals cause precipitation and/or aggregation (i.e., coagulation and flocculation) of the suspended phase in the wastewater system under consideration. The addition of chemicals in the phase of chemical treatment changes water constituents into a form that improves removal by all liquid–solid separation processes.

Chemical treatment, therefore, is incomplete without additional steps of solids removal, nutrient removal, disinfection, desalination, and final polishing. Unit processes to be considered for this are:

1. Screening
2. Sedimentation clarification
3. Flotation clarification
4. Filtration (sand, multi-media, DE, GAC, or membrane)
5. Disinfection (chlorine, ozone, UV, AOP)

The abbreviations listed above are: DE = diatomaceous earth; GAC = granular activated carbon; UV = ultra violet; and AOP = advanced oxidation process. Both sedimentation and flotation are discussed in detail in this publication. Screening, filtration and disinfection are discussed in detail elsewhere [7–10].

The application of flotation in water or wastewater treatment has many advantages over the sedimentation, such as:

1. High efficiency under high loading conditions
2. Very good flexibility in terms of loading rate and type of water or wastewater
3. Low investment cost (in combination with load-proportional operating costs, which are somewhat higher)

Both sedimentation and flotation are the clarification processes that have proven very valuable in various instances of water or wastewater treatment. Yet, flotation has not been applied to that degree in domestic water or wastewater treatment that would be expected on the basis of its known advantages. Thus, a transfer of this process into the field of domestic water or wastewater treatment could and should lead to significant savings and gains in treatment efficiencies [6].

Chemical addition and clarification (either sedimentation or flotation) can be seen as two separate unit processes. They do affect each other. However, the addition of chemicals might change the character of the flotation system by altering the nature of the dissolved phase. Such alterations will affect the particle–bubble contact. The addition of pressurized water, for instance, as is necessary in flotation may introduce additional energy, which can change the collision rate of the aggregating particles [11].

It is within the scope of this chapter to describe the effects of chemicals upon particle aggregation and the interrelationship of the aggregation process with the clarification process. A basic understanding of the process of clarification, in particular, in terms of the mechanical realization of this process in treatment plants, is presupposed.

Points of chemical addition and therefore points of application of the clarification process in the classical domestic treatment plant are:

1. Preceding the actual treatment plant (precede treatment)
2. Into/prior to the primary clarification tank (pretreatment)
3. Into/prior to the secondary clarification tank (simultaneous treatment)
4. Past the mechanical-biological treatment plant into a third stage (posttreatment)
5. For the treatment, i.e., conditioning, of sludge (sludge treatment)

In addition to the areas of application described here, it is reasonable to assume that chemical addition and clarification might be a useful tool in the treatment of stormwater overflow.

Aspects to be considered in the decision for one or another point of application are:

1. Type of wastewater and its constituents to be removed
2. Characteristics of the loading of the treatment plant
3. Frequency and amplitude of load fluctuations
4. Existing treatment steps
5. Goal of wastewater treatment and requirements for discharge
6. Installed or intended facilities for sludge handling and sludge utilization

2 Chemistry of Aggregation

2.1 Reason for Suspended Particles to Remain Suspended

2.1.1 Surface Charge Phenomena

1. Surface charge from lattice imperfections
2. Surface charge from adsorbed ion phenomena
3. Surface charge from surface chemical reactions in general

Most particular matter in natural waters and in wastewater appears to have a negative charge at neutral pH values or slightly basic conditions [12].

2.1.2 Repulsion Forces

Particles with charges of equal sign will repel each other. The repulsion forces increase with decreasing distance between the particles.

2.1.3 Attraction Forces (London—van der Waals)

Through non-compensated charge or potential effects, the matter presents itself as disordered dipoles. Ordering of these dipoles can lead to overall organization and thus to dipole (or magnet-type) effects manifested to the outside. Dipole elements in small particles might become ordered by the approach of such particles to each other. This means that decreasing distances between two particles will lead to increased order respectively increased attraction [13, 14].

2.1.4 Resultant Force/Energy Balance

Both the repulsive energy and attraction energy between two approaching particles (spheres) increase with decreasing particle distance. Since both energy terms change in a different way with particle distance, the resultant or net energy also changes with particle distances.

Upon particle approach, the repulsive energy increases faster than the attractive energy. The result is an increasing energy barrier which disappears at very close particle distances.

2.2 Double-Layer Compaction

2.2.1 What Is a So-Called Counter-Ion and What Are Its Effects?

The increase in concentration in so-called counter-ions leads to a much more intensive compensation of the surface charge, i.e., the (repulsive) effect of the surface charge is felt only at much shorter distances.

2.2.2 How Do Counter-Ions of Different Charge Affect the Charge Compensation? (Or the Schulze–Hardy Rule)

The effects of differently charged counter-ions can be expressed by changes in approximate “thickness” of the so-called double layer (i.e., the two layers are the surface charge and the compensating counter-ion charge).

At counter-ion concentration of 0.01 mol/L, the thickness for a monovalent ion is 1000 Å and for a divalent ion 500 Å only. At counter-ion concentration of 100 mol/L, the thickness for a monovalent ion is 10 Å and for a divalent ion 5 Å [15].

2.2.3 What Happens When the Concentration of the Counter-Ion Is Increased to Very High Values?

With increasing salt concentrations (i.e., counter-ion concentrations), the diffuse part of the double layer is compacted. It is also seen that there is a finite thickness, which cannot be reduced further. Even large concentrations of coagulating salts will not lead to a reversal of charge or potential. (Such charge or potential reversals are described in Sect. 2.4.)

2.2.4 Dosing Effect

For practical purposes, one can conclude that dosing problems do not exist if a certain minimum concentration is attained (the concentration is independent of the particle concentration), that overdosing does not lead to reduced efficiency, and that the coagula formed are of relatively dense nature.

2.3 Chemical Coagulation

2.3.1 Chemical Coagulation Process Description

Colloids are small enough to pass through ordinary filters, such as paper and sand, but are large relative to ions in size, diffuse very slowly and will not pass through membranes. As a result, colloidal particles can be readily removed by membrane filtration, but require chemical coagulation prior to their efficient removal by ordinary flocculation, clarification, and filtration.

As described in Sect. 2.1, in all chemical coagulation processes, there are surface chemical reactions causing dissolved species to be adsorbed to a surface or removed from it. Similarly, charged species may be attracted to a surface for physical reasons. Such chemisorption (Case 1) or physical adsorption (Case 2) may cause a direct change in the surface charge (*surface potential*). These effects are to be distinguished from charge compensation as discussed in Sect. 2.2. Examples of such changes in surface charge, as opposed to compensation of surface charge can be represented as follows [12].

It is possible to describe the relationship between ions in solution and those attached onto a surface in a quantitative way by an adsorption isotherm. (An adsorption isotherm describes the surface coverage as function of the equilibrium concentration in the solution phase for a given and constant temperature.) Vice versa it is also possible to clarify whether adsorption occurs by testing whether such adsorption isotherms do explain the observed behavior.

As the mechanism of adsorption states, the amount of material adsorbed increases with increasing amounts added (in an exponential way as illustrated for instance by the Langmuir isotherm). Thus, it is possible to adsorb such amounts of oppositely charged ions that the original surface charge of the particle is completely balanced, i.e., neutralized, and the particle appears to have a zero charge. Furthermore, one must note that the surface concentration available, i.e., the surface of the particles in suspension, directly affects the amount of material adsorbed: at constant salt additions, the amount of surface coverage (or change in charge) will decrease with increasing particle concentrations (more precisely with increasing surface concentrations).

At increased coagulant dosages, i.e., high equilibrium concentration of the oppositely charge ion, the extent of adsorption may be such that the original surface charge is not only eliminated but reversed. An originally negatively charged particle can thus become positively charged. This causes high stability, again. Such increase in stability with very high coagulant dosages of adsorbing ions resulting from charge reversal is referred to as *restabilization*.

From a practical point of view, the following conclusions for chemical coagulation are significant:

1. The necessary chemical dosage depends on the original particle charge and the particle concentration.
2. The pH value is of great significance to the overall chemical coagulation system.
3. Constant dosage leads necessarily to fluctuating efficiency when applied under real-world conditions.
4. High chemical dosages may lead to restabilization.
5. The resulting coagulant is dense (similar to the products of the process described under Sect. 2.2).

2.3.2 Chemical Coagulation Principles

The stability of colloidal particulate matter is dependent on their electrokinetic property. Colloidal particles acquiring similar primary charges develop repulsive forces that keep them apart and prevent their agglomeration. The primary electrical charges could be either negative or positive. However, the majority of colloids that exist in aqueous systems are negatively charged. A colloidal system as a whole does not have a net charge. Negative primary charges on colloidal particles are balanced by positive counter-ions near the solid–liquid interface and in the adjoining dispersion medium. In a similar fashion, positively charged particles are counter balanced by negative ions present in the surrounding water. This natural inclination toward achieving electrical neutrality and counterbalance of charges results in the formation of an electric double layer around colloidal particles.

The electric double layer, which comprises the charged particle and surrounding counter-ions, is illustrated in Fig. 6.1. The total potential at the surface of primary charged particle is termed the Nernst potential. The dense layer of counter-ions fixed on the surface of the primary particle is called the Stern layer. The outer limit of this layer is defined by the surface of shear that separates the mobile portion of the colloid from the surrounding mixture of diffuse ions. In an electric field, the ions within the surface of shear will move with the particle as a unit. The concentrated counter-ions within the surface of shear reduce the net charge on the particle by an amount that is usually referred to as the Stern potential. Consequently, the potential is maximum at the surface of the primary particle, the Nernst potential, that decreases rapidly through the Stern layer resulting in a net overall charge on the particle at the surface of shear called the zeta potential. This potential determines the extent of repulsion between similarly charged particles and is commonly considered to be the major cause of the stability of a colloidal system. Further away from the surface of shear, both the concentration and potential gradients continue decreasing, but at a more gradual drop, until the potential approaches the point of electrical neutrality in the surrounding solution.

The counter-ions of the Stern layer are concentrated in the interfacial region owing to electrostatic attraction. However, these ions tend to be more loosely attached, as they are located at distances further away from the particle surface as a result of the potential gradient. Consequently, any thermal agitation may cause these less strongly held ions to diffuse away toward the bulk of the dispersion medium. These two opposite forces, electrostatic attraction and diffusion, give rise

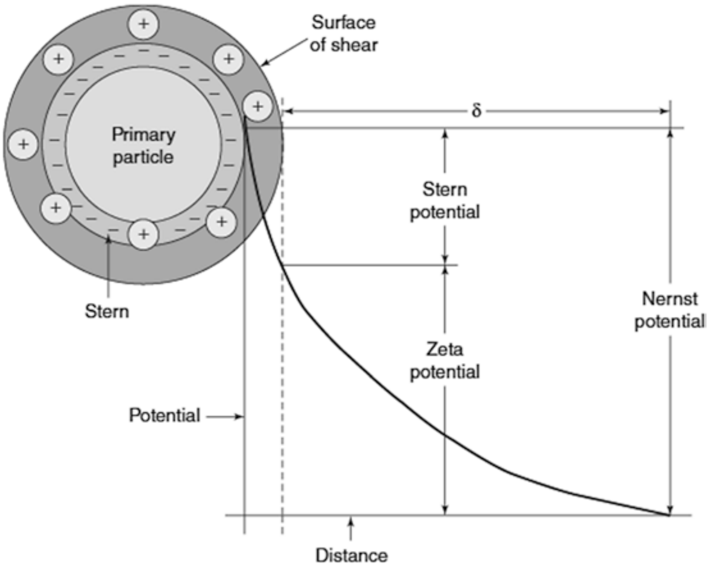


Fig. 6.1 Electrical potential of a negatively charged colloidal particle [8]

to the distribution of the potential over distance such that the highest concentration of counter-ions occurs at the particle interface and drops gradually with increasing distance. When the dispersion medium contains low concentration of ions (low ionic strength), the diffuse layer will be spread over a wide distance, as shown in Fig. 6.1. The consequence of this smallness in size and mass and largeness in surface area is that in colloidal suspensions: (a) gravitational effects are negligible, and (b) surface phenomena predominate.

Because of their large surface, colloidal particles have the tendency to adsorb various ions from the surrounding medium that impart to the colloids an electrostatic charge relative to the bulk of surrounding water. The developed electrostatic repulsive forces prevent the colloids from coming together and, consequently, contribute to their dispersion and stability.

When two similar primary charge particles drift toward each other, their diffuse layers start to interact leading to the production of a repulsive electrostatic force. The resulting repulsion between the approaching particles increases as the particles get closer. Such charged particles may not be able to collide at all if their charges are high enough. Ultimately, as illustrated in Fig. 6.2, the colloidal stability depends on the relative strength of the above electrostatic forces of repulsion and the forces of attraction.

The forces of attraction are due to van der Waals forces. All colloidal particles, irrespective of their composition, sign or magnitude of charge, or the composition of the dispersion medium, possess such attractive forces. They arise from the following: (a) electronegativity of some atoms is higher than for others in the same molecule; (b) vibration of charges within one atom creates a rapidly fluctuating dipole; and (c) approaching particles induce vibrations in phase with each other.

The above results in an attractive force between the two oppositely oriented dipoles. The magnitude of the force varies inversely with distance between particles, increasing rapidly with decreasing distance (see Fig. 6.2). If particles come close enough for these forces to take over, they will adhere.

The other factor, in addition to van der Waals attractive forces, tending to destabilize a colloidal system is Brownian movement. This is due to the random motion of colloids brought about by their bombardment by molecules of the dispersion medium. The outcome of the movement is to impart kinetic energy to the colloidal particles. Higher energy particles moving in a random fashion tend to collide eventually.

Figure 6.2 illustrates the relationship of forces that exist between colloidal particles as a function of the separation distance. The net resultant force is obtained by the summation of the respective electrostatic repulsive force and van der Waals attractive force. When the resultant repulsion energy exceeds the kinetic energy (Fig. 6.2a), the particles will not coagulate and the dispersion is stable. When the kinetic energy is larger than the repulsion energy (Fig. 6.2b), the dispersion is unstable and the particles will coagulate. Consequently, if it is required to destabilize and coagulate a stable dispersion, then the electrostatic repulsion energy between the particles must be lowered and/or the kinetic energy of the particles must be raised.

Destabilization of colloidal particles is accomplished by chemical coagulation through the addition of hydrolyzing electrolytes such as metal salts and/or synthetic

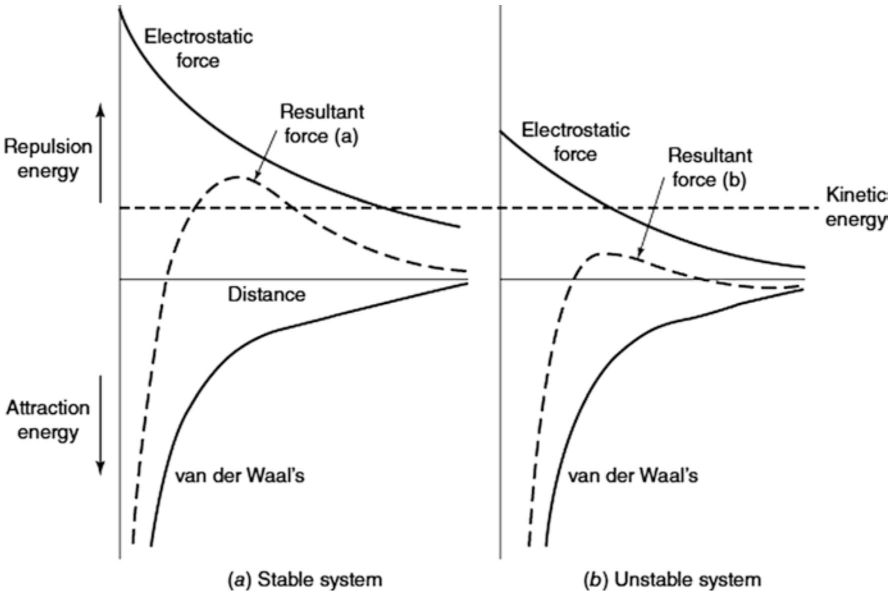


Fig. 6.2 Effect of inter-particle forces on the stability of a colloidal system [8]

organic polymers. Upon being added to the water, the action of the metal salt is complex. It undergoes dissolution, the formation of complex highly charged hydrolyzed metal coagulants (hydroxyoxides of metals), interparticle bridging, and the enmeshment of particles into flocs. Polymers work either on the basis of particle destabilization or bridging between the particles.

The destabilization process is achieved by the following four mechanisms of chemical coagulation:

1. Double-layer compression
2. Adsorption and charge neutralization
3. Entrapment of particles in precipitate
4. Adsorption and bridging between particles

2.4 Chemical Precipitation

2.4.1 Chemical Precipitation Process Description

Precipitation is a chemical unit process in which undesirable soluble metallic ions and certain anions are removed from water or wastewater by conversion to an insoluble form. It is a commonly used treatment technique for removal of heavy metals, phosphorus, and hardness. The procedure involves alteration of the ionic equilibrium to produce insoluble precipitates that can be easily removed by sedimentation.

Chemical precipitation is always followed by a solid separation operation that may include coagulation and/or sedimentation, or filtration to remove the precipitates. The process can be preceded by chemical reduction in order to change the characteristics of the metal ions to a form that can be precipitated [16–139].

The chemical equilibrium relationship in precipitation that affects the solubility of the component(s) can be achieved by a variety of means. One or a combination of the following processes induces the precipitation reactions in a water environment.

Hydroxide Precipitation

Dissolved heavy metal ions can be chemically precipitated as hydroxide for removal by physical means such as sedimentation or filtration. The process uses an alkaline agent to raise the pH of the water that causes the solubility of metal ions to decrease and thus precipitate out of the solvent. The optimum pH at which metallic hydroxides are least soluble varies with the type of metal ion as shown in Fig. 6.3. A simple form of the hydroxide precipitation reaction may be written as:

$$\mathrm{M}^{2+} + 2\left(\mathrm{OH}\right)^{-} = \mathrm{M}\left(\mathrm{OH}\right)_2$$

The product formed is an insoluble metal hydroxide. If the pH is below the optimum of precipitation, a soluble metal complex will form:

$$\mathrm{M}^{2+} + \mathrm{OH}^{-} = \mathrm{M}\left(\mathrm{OH}\right)^{+}$$

Hydroxide precipitation is also affected by the presence of organic radicals that can form chelates and mask the typical precipitation reaction:

$$\mathrm{M}^{2+} + \mathrm{OH}^{-} + n\mathrm{R} = \mathrm{M}\left(\mathrm{R}\right)_n \mathrm{OH}^{+}$$

Reagents commonly used to effect the hydroxide precipitation include alkaline compounds such as lime or caustic soda (sodium hydroxide). Lime in the form of quicklime or un-slaked lime, CaO, and hydrated lime, $\mathrm{Ca(OH)_2}$, can be used. Lime is generally made into wet suspensions or slurries before introduction into the treatment system. The precise steps involved in converting lime from the dry to the wet stage will vary according to the size of the operation and the type and form of lime used. In the smallest plants, bagged hydrated lime is often charged manually into a batch-mixing tank with the resulting “milk-of-lime” (or slurry) being fed by means of a solution feeder to the treatment process. Where bulk hydrate lime is used, some type of dry feeder charges the lime continuously to either a batch or continuous mixer. A solution feeder transfers lime to the point of application. With bulk quicklime, a dry feeder is also used to charge a slaking device, where the oxides are converted to hydroxides, producing a paste or slurry. The slurry is then further diluted to milk-of-lime before being fed by gravity or pumping into the process. Dry feeders can be of the volumetric or gravimetric type. Caustic soda, in the form of

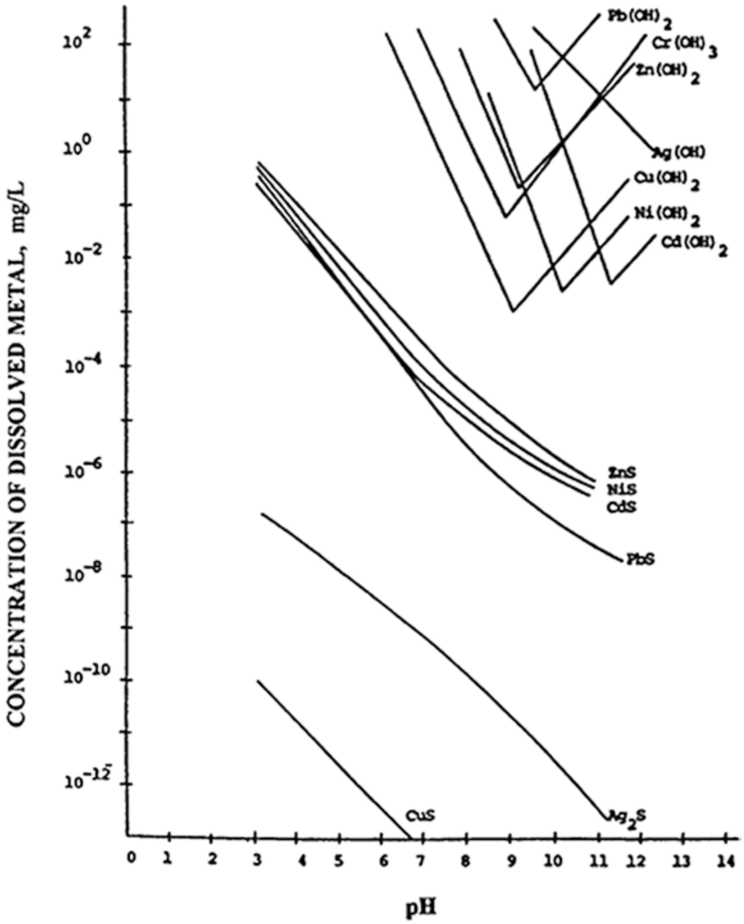


Fig. 6.3 Solubility of metal hydroxides and sulfides as a function of pH [8]

6–20% aqueous solution, is fed directly to the treatment system and does not require any dispensing and mixing equipment. The treatment chemicals may be added to a flash mixer or rapid-mix tank, or directly to the sedimentation device. Because metal hydroxides tend to be colloidal in nature, coagulation agents may also be added to facilitate settling.

Sulfide Precipitation

Both "soluble" sulfides such as hydrogen sulfide or sodium sulfide and "insoluble" sulfides such as ferrous sulfide may be used to precipitate heavy metal ions as insoluble metal sulfides. Sodium sulfide and sodium bisulfide are the two chemicals commonly used, with the choice between these two precipitation agents being strictly an economic one. Metal sulfides have lower solubilities than hydroxides in the alkaline pH range and also tend to have low solubilities at or below the neutral pH value (Fig. 6.3).

The basic principle of sulfide treatment technology is similar to that of hydroxide precipitation. Sulfide is added to precipitate the metals as metal sulfides, and the sludge formed is separated from solution by gravity settling or filtration. Several steps enter into the process of sulfide precipitation:

1. Preparation of sodium sulfide. Although there is often an abundant supply of this product from by-product sources, it can also be made by the reduction of sodium sulfate. The process involves an energy loss in the partial oxidation of carbon (such as that contained in coal) as follows:

$$\mathrm{Na_2SO_4} + 4\mathrm{C} = \mathrm{Na_2S} + 4\mathrm{CO_2}\left(\mathrm{gas}\right)$$

$$\text{Sodium sulfate} + \text{carbon} = \text{sodium sulfide} + \text{carbon dioxide gas}$$

2. Precipitation of the pollutant metal (M) in the waste stream by an excess of sodium sulfide:

$$\mathrm{Na_2S} + \mathrm{MSO_4} = \mathrm{MS}\left(\mathrm{precipitate}\right) + \mathrm{Na_2SO_4}$$

$$\text{Sodium sulfide} + \text{metallic sulfate} = \text{metallic sulfide} + \text{sodium sulfate}$$

3. Physical separation of the metal sulfide in thickeners or clarifiers, with reducing conditions maintained by excess sulfide ion.
4. Oxidation of excess sulfide by aeration:

$$\mathrm{Na_2S} + 2\mathrm{O_2} = \mathrm{Na_2SO_4}$$

$$\text{Sodium sulfide} + \text{oxygen} = \text{sodium sulfate}$$

Because of the toxicity of both the sulfide ion and hydrogen sulfide gas, the use of sulfide precipitation may require both pre- and posttreatment and close control of reagent additions. Pretreatment involves raising the pH of water to between 7 and 8 to reduce the formation of obnoxious hydrogen sulfide gas. The pH adjustment may be accomplished at essentially the same point as the sulfide treatment, or by the addition of a solution containing both sodium sulfide and a strong base (such as caustic soda). The posttreatment consists of oxidation by aeration or chemical oxidation to remove excess sulfide, a toxic substance.

A recently developed and patented process to eliminate the potential hazard of excess sulfide in the effluent and the formation of gaseous hydrogen sulfide uses ferrous sulfide as the sulfide source. The fresh ferrous sulfide is prepared by adding sodium sulfide to ferrous sulfate. The ferrous sulfide slurry formed is added to water to supply sufficient sulfide ions to precipitate metal sulfides, which have lower solubilities than ferrous sulfide. Typical reactions are:

$$\mathrm{FeS} + \mathrm{Cu}^{2+} = \mathrm{CuS} + \mathrm{Fe}^{2+}$$

Ferrous sulfide + copper ion = insoluble copper sulfide + iron ion

$$FeS + Ni(OH)_2 = Fe(OH)_2 + NiS$$

Ferrous sulfide + nickel hydroxide = ferrous hydroxide + insoluble nickel sulfide

A detention time of 10–15 min is sufficient to allow the reaction to go to completion. Ferrous sulfide itself is also a relatively insoluble compound. Thus, the sulfide ion concentration is limited by the solubility of ferrous sulfide, which amounts to about 0.02 mg/L, and the inherent problems associated with conventional sulfide precipitation are minimized.

Cyanide Precipitation

Cyanide precipitation, although a method for treating cyanide in wastewater, does not destroy the cyanide molecule, which is retained in the sludge that is formed. Reports indicate that during exposure to sunlight, the cyanide complexes can break down and form free cyanide. For this reason, the sludge from this treatment method must be disposed of carefully. Cyanide may be precipitated and settled out of wastewater by the addition of zinc sulfate or ferrous sulfate, which forms zinc ferrocyanide or ferro- and ferri-cyanide complexes. In the presence of iron, cyanide will form extremely stable cyanide complexes.

Carbonate Precipitation

Carbonate precipitation may be used to remove metals either by direct precipitation using a carbonate reagent such as calcium carbonate or by converting hydroxides into carbonates using carbon dioxide. The solubility of most metal carbonates is intermediate between hydroxide and sulfide solubilities; in addition, carbonates form easily filtered precipitates.

Coprecipitation

In coprecipitation, materials that cannot be removed from solution effectively by direct precipitation are removed by incorporating them into particles of another precipitate, which is separated by settling, filtration, or dissolved air flotation (DAF).

Technology Status and Many Other Chemical Precipitation Processes

Chemical precipitation of metal hydroxides is a classical water and wastewater treatment technology and is used by most industrial waste treatment systems. Chemical precipitation of metals in the carbonate form is used in water softening and in commercial applications to permit metal recovery and water reuse. Full-scale commercial sulfide precipitation units are operational at numerous industrial installations. Cyanide precipitation is used at several coil-coating plants. Many other chemical precipitation processes are further introduced in Sect. 2.4.4 Process Applications and Evaluation, and Sect. 2.4.5 Chemical Precipitation Process: Application Examples.

2.4.2 Chemical Precipitation Principles

Chemical precipitation processes perform by adjusting concentrations and other conditions, so that the ionic constituents that are to be removed change from a dissolved ionic phase to a solid salt. Precipitation of salts is a fairly rapid process and thus tends to be close to equilibrium. Accordingly, the remaining concentration of the ionic species in solution is controlled by the solubility of the solid phases present, and the theory of precipitation processes is described mostly by the principles of solubility equilibria. The readers are referred to the literature for the details of reaction equilibria, solubility equilibria, ionic strength and activity, and the examples of ionic strength and common ion effect [20, 95].

Soluble Complex Formation

Metals are acids in the Lewis sense. As such, they compete with protons and with each other for available bases, such as hydroxides. This competitive tendency increases with increasing valence of the metal and decreasing size of the metal atom. The "naked" metal ion, such as Fe^{3+} or Cd^{2+}, is rapidly hydrated in water, forming what is called the aquo complex. Under appropriate conditions, the aquo complexes will have a tendency to combine with hydroxides to form hydroxo complexes. For example, cadmium species can have charges ranging from plus two, Cd^{2+}, to minus two, $Cd(OH)_4^{2+}$.

Metals of higher valence (four or more) may also tend to form "oxo complexes." For example, hexavalent chromium forms the anionic oxo complex chromate, CrO_4^{2+}, or dichromate, $Cr_2O_7^{2-}$.

In general, as the oxidation state of the metal increases and the radius decreases, the pH at which hydroxo complexes dominate over aquo, or oxo dominate over hydroxo, decrease. It must be noted that the effect of valence is much stronger than that of size.

The hydroxo and oxo complexes are in equilibrium with any precipitates present and can be modeled using the solubility product expression just as the aquo ions. However, other complexing agents may be present, and in many cases, the solubility should be experimentally determined. For example, in natural waters, copper can form complexes with carbonate ions, with ammonium ions, and with dissolved organic matter. In plating solutions, hexametaphosphate and cyanide are added specifically because their complexation behavior is desired for purposes of controlling the plating process.

Hydroxo complexes are also strongly removed by adsorption on solids, whether those solids are precipitates of the particular metal or not.

Different metal ions can form soluble complexes with each other. Copper, in particular, seems to be implicated often in this type of behavior. Solutions of zinc cyanide and copper cyanide resulted in significantly increased zinc solubility and a shift in the pH of minimum solubility. Dilute mixtures of copper and chromium plating solutions also resulted in increased copper solubility.

Complexes other than those described here may be important, particularly polynuclear complexes. Some of these may be intermediates in the formation of precipitates, and thus are not at equilibrium. Consequently, some metal ion solutions "age" over a period of days or weeks, changing their precipitation behavior.

There is a tendency for solids with a smaller solubility product to be more likely to form soluble complexes. This has been observed with metal sulfides to the point that those with the lowest solubility products exhibited the greatest solubility. Thus, solubility based on the solubility product expression must be used carefully, and the formation of the soluble complexes often should be taken into account.

pH Effect

The most important competing reaction is the dissociation of water into H^+ and OH^-, primarily because metal hydroxides are fairly insoluble. Another reason for this is the formation of soluble complexes, which has been discussed above. Thus, the solubility of the metal usually decreases as pH increases (hydroxide concentration increases), until the formation of soluble hydroxide complexes becomes significant, and then the total solubility begins to increase with pH. In general, there will be either a single pH of minimum metal solubility or a pH range of minimum solubility. The following are the predicted pH ranges of minimum solubility for the metal species of aluminum, cadmium, chromium, copper, iron, lead and zinc:

Metal	Solubility (mg/L)	pH range
Al^{3+}	0.00055	6.2
Cd^{2+}	0.60	10.5–13.0
Cr^{3+}	0.04	7.0
Cu^{2+}	0.03	7.5–11.5
Fe^{3+}	0.00006	7.0–10.0
Pb^{2+}	16.5	10.0
Zn^{2+}	0.13	9.5

Solubility Diagrams

The solubility of metal precipitates is controlled largely by the pH (see Fig. 6.3). A graphical solubility diagram can concisely express the relationship between pH and solubility. The development of a solubility diagram requires knowledge of the solubility product constants for the dissolution of each solid phase present in each soluble species. The total solubility is just the sum of the solubilities due to each dissolution reaction.

2.4.3 Chemical Precipitation Kinetics

Once the possibility of precipitation is established by the equilibrium considerations described above, it is necessary to determine the factors that govern the rate of precipitation. Process design hinges upon the rate, as the slower the process occurs, the larger the size of reactors necessary to accomplish the degree of conversion desired.

The driving force for precipitation can be expressed as the degree of oversaturation:

$$\mathrm{DF} = C / C_\mathrm{s}$$

where DF = driving force, C = solution concentration (mol/L or mg/L), and C_s = saturation concentration (mol/L or mg/L). If DF is less than 1, the solution is undersaturated and no precipitation will occur. At DF = 1.0, the solution is saturated and will be in equilibrium with any salt present. If DF is greater than 1, the solution is supersaturated, and if it is much greater than 1, then the salt should precipitate out of solution. This is termed the "labile" regime. However, if the solution is only slightly supersaturated, precipitation may occur very slowly, if at all. A solution in this regime is called "metastable." The boundary between the labile and metastable regimes is somewhat arbitrary and will depend on the particular salt involved. Metastable solutions have been observed for DF as high as 10. The presence of a seed crystal can cause rapid precipitation of metastable solutions to occur.

The formation of a precipitate consists of three steps: (a) nucleation, (b) crystal growth, and (c) aging.

Nucleation

Nucleation is the condensation of ions to very small particles. This process requires a DF significantly different from 1. It depends on a mutual attraction between dissolved neutral salt molecules. In natural waters, nucleation will be promoted by the presence of a foreign particle, termed a heteronucleus. It acts by adsorbing solute molecules, decreasing the DF needed for precipitation to occur at a significant rate.

Crystal Growth

Crystal growth is the depositing of material upon previously formed nuclei. Growth proceeds by a sequence of steps: transport to the crystal surface by convection and diffusion, adsorption onto the surface, and reaction or formation of the crystal lattice bonds.

The rate of crystal growth is usually limited either by the diffusion step or by the reaction step, and mostly by the former. The rate depends on which step is limiting. For diffusion-limited crystal growth, the rate law is approximately first order:

$$\mathrm{d}C / \mathrm{d}t = -ks\left(C - C_{\mathrm{s}}\right)$$

where k = rate coefficient, dependent upon the amount of mixing and s = crystal surface area.

If the process is reaction-rate limited, the rate expression may be other than first order and will not depend on mixing. For example, sodium chloride has been found to be first order, silver chloride is second order, and silver chromate is third order.

Aging

“Ripening,” or aging, refers to slow changes in the crystal structure that occur over time. Fresh precipitates are small and have a relatively disordered structure with more crystal defects and inclusions of impurities. A slow process of re-solution and precipitation effects a rearrangement into larger, pure crystals having a lower solubility. In fact, any finely divided precipitate is not, strictly speaking, in equilibrium. True thermodynamic equilibrium will minimize the surface area of the crystals, ultimately resulting in the formation of a single, large crystal. Thus, solubility product constants measured using fresh precipitates may be larger than values obtained with ripened solids.

Also, as mentioned above, slow-forming polynuclear complexes may be intermediates in the formation of precipitates. Thus, even the solution may need to age in order to achieve equilibrium.

Complexing agents present in solution may affect the rate of precipitation even if they do not have an effect upon the solubility. Organic complex formers, in particular, may slow down precipitation, as well as influence the crystal form that results.

Adsorption and Coprecipitation

As described above, precipitation from metastable solutions can be promoted by the presence of foreign solid particles owing to adsorption. Adsorption can be primarily of a physical nature, due to van der Waals forces or pi bonds, or chemical. Metal ions adsorb primarily by ion exchange, which is a form of chemisorption. Metals are also strongly removed by activated carbon adsorption.

Solids with oxide surfaces can act as weak acids and bases in solution and are protonated and deprotonated in response to pH, ionizing the surface. The surface ions function as ion exchange sites. Increasing the pH increases the adsorption of cations and decreases adsorption of anions. The adsorption capacity will change from 0% to 100% of the adsorbent's total capacity over a narrow range of one or two pH units. The location of this "pH adsorption edge" also depends on the concentration of the adsorbent. The presence of competing adsorbents will either shift the pH adsorption edge or reduce the capacity of the adsorbent for a particular ion. Complexing agents can either increase or decrease adsorption. They may decrease adsorption by stabilizing the ion in solution. Alternatively, they may increase it by forming complexes that adsorb stronger than the ion alone. For example, cyanide can strongly increase adsorption of nickel ions at high pH values.

Coprecipitation refers to the simultaneous removal of an ion with the precipitation of another, with which it does not form a salt. The mechanism may be the inclusion of one ion as impurity in the crystal structure of the other or due to adsorption on the surfaces of the other's crystals. Thus, coprecipitation can be used to remove metals at concentrations that are already below their minimum solubility. For example, precipitation of ferric nitrate at a pH above 7.0 was found to remove approximately 95% of 5.0×10^{-7} mol/L solution of cadmium. Another application is the removal of radium using lime-soda ash softening.

Coprecipitation has been used to explain the decreased solubility of zinc in the presence of trivalent chromium and divalent and/or tetravalent nickel from plating solutions. Mixed copper and nickel-plating solutions had substantially lower solubilities at pH below 10. Copper and chromium-plating solutions with 200–500 mg/L of each metal also resulted in reduced copper solubility, but at lower initial concentrations, higher solubility resulted, apparently due to complex formation.

2.4.4 Process Applications and Evaluation

The principles described above find application in a number of ways. The particular reactions that are used in common precipitation technologies depend not only on the ion to be removed and the type of counter-ion used, but also on the presence of competing reactions and facilitating reactions (e.g., oxidation or reduction). The most important types of precipitation processes will be described here.

Chemical precipitation can be used to remove metal ions such as aluminum, antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, molybdenum, tin, and zinc. The process is also applicable to any substance that can be transformed into an insoluble form, for example, fluorides, phosphates, soaps, and sulfides.

Hydroxide Precipitation

This is the workhorse of precipitation processes. Many metal cations are removed easily as the hydroxide. The process consists of simply raising the pH to the range of minimum solubility with a strong base such as sodium hydroxide (NaOH), lime (CaO), or slaked lime [$Ca(OH)_2$].

The base dosage can be determined by titration or by calculation based on equilibrium considerations, if the water to be treated is characterized well enough. Of course, if the buffer capacity of the water is too great, the chemical dosage required may be large enough that some other precipitation process might be more economical, or even some other type of process entirely, such as ion exchange or reverse osmosis.

Waters containing mixtures of metals to be removed present special problems, because the pH corresponding to optimum removal for all species may not coincide. In this case, either a tradeoff must be made between removals of the various metals, or the treatment must be applied in stages, each one optimized for removal of a particular metal or group of metals.

Hydroxide precipitation and particularly the use of lime to cause chemical precipitation has gained widespread use in industrial waste treatment because of its ease of handling, its economy, and its effectiveness in treatment of a great variety of dissolved material. Industries and utilities using hydroxide precipitation include:

1. Inorganic chemical manufacturing
2. Metal finishing
3. Coil coating
4. Copper forming
5. Aluminum forming
6. Foundries
7. Explosives manufacturing
8. Steam electric power plants
9. Photographic equipment and supplies
10. Pharmaceutical manufacturing
11. Rubber processing
12. Porcelain enameling
13. Battery manufacturing
14. Iron and steel manufacturing
15. Nonferrous metal manufacturing
16. Coal mining
17. Electrical and electronic components
18. Ore mining and dressing
19. Publicly owned treatment works (POTW)

The most common treatment configuration is pH adjustment and hydroxide precipitation using lime or caustic following by settling for solids removal. Most plants also add a coagulant or flocculent prior to solids removal.

Carbonate Precipitation

Carbonate precipitation has long been the method of choice for the removal of calcium hardness from water. More recently, carbonate has been proposed for the removal of heavy metals from wastewater. The reason for this is that hydroxide precipitation may yield large sludge volumes, which may be difficult to settle and filter, and is also due to the additional precipitation of gypsum if sulfate is present and lime is used. In some cases, carbonate sludges settle and filter better than hydroxide sludges, and the treatment can be carried out at a lower pH.

Carbonate may in some cases decrease the solubility of metals, while increasing it in others. The effect depends on the particular metal and the pH at which the treatment is carried out. The effect may be calculated by applying the equilibrium approach discussed earlier, although the actual results may differ somewhat from the theoretical values.

Cadmium was predicted to have a minimum solubility of 0.011 mg/L at pH 9 and a total carbonic species concentration $C_T = 7.3$ mg/L. This is both a lower solubility and lower pH than obtained with hydroxide alone: 0.60 mg/L cadmium concentration at pH from 10.5 to 13.0. Furthermore, experimental values were somewhat lower and showed a further reduction above pH 9. It was also found that cadmium solubility was much more sensitive to total carbonic species concentration than to pH. All of these factors favor carbonate for the removal of cadmium over hydroxide precipitation.

The situation is quite different for copper. Both theory and experiment show an increase in solubility, particularly at pH less than about 9–10. Above pH 10, carbonate had little effect.

Lead shows even more complicated behavior with respect to carbonate. Experimental results indicate a strong sensitivity to carbonate concentration, such that even trace amount greatly reduced the solubility. At higher levels of carbonate, the effect was very different at different pH values. For example, at pH 6 increasing total carbonic species concentration decreased lead solubility, while at pH 9 it increased it. From theoretical predictions, the minimum solubility occurs at a pH near 9 with total carbonic species concentration, C_T at about 10^{-4} mol/L.

Zinc solubility is reduced significantly by the presence of carbon dioxide, especially at pH less than 9. The experimentally measured effect is less than that theoretically predicted, but is still substantial. It is possible that zinc carbonate is formed quite slowly, and thus may not be practical under treatment conditions.

There is no advantage in using carbonate precipitation for zinc or nickel removal, and the sludges produced are not denser or easier to filter. Cadmium can be precipitated at a lower pH as its carbonate than as its hydroxide and will result in sludge that can be flitted at about twice the rate. Lead can also be removed by carbonate precipitation at a lower pH than it could by hydroxide, and produces a denser sludge with better filtration characteristics. Treatment of wastes containing a mixture of metals was found to behave equivalently to those with single metals, with respect to both hydroxide and carbonate precipitation.

Carbonate precipitation is sometimes used to precipitate metals, especially where precipitated metals are to be recovered. Carbonate ions also appear to be particularly useful in precipitating lead and antimony. Coprecipitation is used for radium control in the uranium industry (a subcategory of ore mining and dressing). Radium sulfate ($RaSO_4$) is coprecipitated by the addition of barium chloride, which in the presence of sulfate ion forms barium sulfate precipitates. Coprecipitation of molybdate anion, which is not removed effectively by hydroxide or sulfide precipitation, can be carried out by the addition of ferric sulfate or ferric chloride, which forms ferric hydroxide precipitates at an acid pH. Vanadium is also subject to coprecipitation with ferric hydroxide.

Sulfide Precipitation

Metal sulfide precipitation has the advantages of lower metal solubility, smaller sludge volume, and insensitivity to the presence of chelating agents. Preliminary studies have also indicated that sulfide sludge have fewer tendencies to leach metal ions than hydroxide sludge do. However, there are disadvantages of odor and toxicity control, and contamination of the effluent with sulfide, which exerts an oxygen demand on receiving waters. The higher chemical cost of sulfide treatment is balanced by its ability to attain higher treatment efficiencies.

Sulfide is also capable of acting as a reducing agent to convert hexavalent chromium to the trivalent form. Under alkaline conditions the chromium can then be removed as the hydroxide precipitate. If ferrous sulfide is used, the products of the reduction and precipitation are chromic and ferric hydroxide sludge and elemental sulfur.

Two basic types of sulfide dosing exist: the soluble-sulfide method and insoluble-sulfide method. Odor problems and sulfide contamination of the effluent are caused by excessive sulfide dosage and are mainly a problem with the soluble-sulfide delivery method. In this method Na_2S or NaHS is added to the wastewater. Dosage control is achieved by the analysis of residual soluble metal concentration. Feedback control by specific ion electrodes for sulfide has been demonstrated in the laboratory. The precipitated particles are very small and require coagulants and flocculants for efficient sedimentation.

The insoluble-sulfide delivery method overcomes the control problem for sulfide precipitation. The source of sulfide ions is a sparingly soluble metal sulfide with a low solubility. This salt liberates its sulfide, as the metal to be removed consumes it by precipitation. Two forms of this method have been developed: the ferrous sulfide process by Permutit Company and a calcium sulfide process developed by Kim and Amodeo [21].

In the Permutit process, called Sulfex, FeS is produced onsite by mixing $FeSO_4$ with NaHS. H_2S gas emission from this part of the process may require control measures using NaHS. The dosage is determined by jar tests and usually requires two to four times the stoichiometric amount of FeS. This may result in large chemical costs and in the generation of large amounts of sludge, almost three times as much as a hydroxide precipitation process.

The calcium sulfide process is another insoluble-sulfide method. The CaS is available in a stable, dry, solid form. When mixed with water, it forms an equimolar solution of calcium hydroxide and calcium bisulfate, $Ca(HS)_2$. Passing H_2S gas through lime slurries can also produce the solution on-site. The generation process can be controlled by pH control, as can the dosage to the precipitation process itself. This process has been demonstrated at the pilot and full scale for treatment of wastes from a wire manufacturing plant containing dissolved copper in an aqueous emulsion.

In chemical industry, sulfide precipitation use has mainly been to remove mercury, lead, and silver from wastewater, with less frequent use to remove other metal ions. Sulfide precipitation is also used to precipitate hexavalent chromium (Cr^{6+}) without prior reduction to the trivalent state (Cr^{3+}), as is required in the hydroxide process. Sulfide precipitation is being practiced in the following industries:

1. Photographic equipment and supplies
2. Inorganic chemicals manufacturing
3. Coal mining
4. Textile mills
5. Nonferrous metal manufacturing
6. Ore mining and dressing

Most of the chlor-alkali industries (subcategory of the inorganic chemical manufacturing) apply this technology to remove lead or mercury from its waste streams. Most metal sulfides are less soluble than hydroxides and, in general, the precipitates are frequently more dependably removed from wastewater. Sulfide precipitation has potential for use as a polishing treatment after hydroxide precipitation and sedimentation to remove residual metals. This way one can obtain higher treatment efficiencies of sulfide removal at a lower chemical cost.

Cyanide Precipitation

Cyanide precipitation can be used when cyanide destruction is not feasible because of the presence of cyanide complexes that are difficult to destroy. This technology is being used in the coil coating industry.

Magnesium Oxide Precipitation

Magnesium oxide (MgO) treatment produces a MgO-hydroxide sludge that has a lower solubility than hydroxide sludge alone. The sludge is also relatively compact and tends to cement together upon standing, which inhibits resuspension of metal ions. The chemical costs are higher than for hydroxide precipitation, but as for sulfide removal, the process can be used after conventional treatment with lime.

Chemical Oxidation–Reduction Precipitation

Occasionally, metal ions present in a wastewater are in an oxidation state that is quite soluble. Changing the oxidation state in these cases may result in an ion with low solubility with respect to an appropriate treatment process. Examples of this are the reduction of hexavalent chromium (Cr^{6+}) to the trivalent state (Cr^{3+}) and the oxidation of ferrous ion (Fe^{2+}) and manganese (Mn^{2+}) to ferric (Fe^{3+}) and magnesium (Mg^{2+}) forms, which form insoluble precipitates. In an unusual process, sodium borohydride has been used to reduce heavy metals to the elemental state, yielding a compact precipitate for lead, silver, cadmium, and mercury. Reduction is best done in the absence of organic compounds. For details, the readers are referred to the literature [8] dealing with chemical oxidation and reduction.

Lime/Soda-Ash Softening

This is one of the most common softening processes for the removal of hardness from potable or industrial water. Because the process is discussed in literature [21] (recarbonation and softening) in detail, it will not be covered here.

Phosphorus Precipitation

Phosphorus must often be removed from wastewater to protect surface water from its fertilizing effect. Phosphorus is present in water in three main forms: phosphate, PO_4^{3-}, is the simplest and is the form most easily removed by precipitation, phosphate can be condensed into the polymeric polyphosphate form, and organic forms may also be present. These complex forms are also removed during precipitation, but the mechanisms are complicated and include adsorption onto other flocs.

Phosphate precipitation is carried out primarily with aluminum, iron, and calcium cations [8]. Theoretical stoichiometric dosages are not reliable indications of actuarial requirements, so dosages must be empirically measured.

Aluminum combines with phosphate to form aluminum phosphate, $AlPO_4$. The source of aluminum ions can be alum (aluminum sulfate) or sodium aluminate ($Na_2Al_2O_4$). Alum usage consumes alkalinity and therefore may decrease the pH. Low-alkalinity wastewater may require addition of alkalinity. Sodium aluminate, on the other hand, contributes to alkalinity, tending to increase the pH.

The optimum pH for the removal of phosphate by aluminum is between 5.5 and 6.5. The minimum solubility of aluminum phosphate is approximately 0.01 mg/L PO_4^{3-}, phosphorous at pH 6.

The stoichiometric requirement is 1 mol of aluminum ions per mole of phosphate. However, higher dosage is usually required for adequate removal efficiency. For example, for municipal wastewater, a 38% excess was found to provide only 75% phosphorus reduction, while 72% excess was required to remove 85% of the phosphorus, and 130% excess was necessary to remove 95%. The removal of phosphorus with aluminum has also been found to help with the removal of copper, chromium, and lead.

Iron can be used for phosphate removal in either the ferrous (Fe^{2+}) or ferric (Fe^{3+}) forms. Both have been found experimentally to give similar results with similar molar ratios, in spite of their differing stoichiometry. However, the two forms have distinct pH optima, the optimum for precipitation as ferric phosphate is at pH from 4.5 to 5.0, although significant removal is obtained at higher pH. The optimum for precipitation with ferrous ion is at about pH 8, and remains good as low as pH 7.

Calcium can be added to water in the form of lime to precipitate phosphate as hydroxyapatite. The removal efficiency increases with pH, achieving 80% removal at pH below 9.5.

Other Chemical Precipitation Processes

A wide variety of less common applications have been developed. The removal of ammonium fluoride using limestone has been studied [22]. Calcium chloride has also been used for fluoride removal [20]. Mercury was removed using a process combining sodium sulfide and ferric chloride in two stages [23]. Humic substances have been reported to be removed in lime softening [24]. Heavy metals can be removed from municipal wastewater, without removing the organic suspended and settleable solids, by coprecipitation on sand grains with calcium carbonate and calcium hydroxyapatite in an upflow expanded bed [25]. This enables the organics to be removed subsequently in conventional processes and yield sludge with lower metal concentrations.

Chemical Precipitation Process: Advantages and Limitations

Chemical precipitation has proven to be an effective technique for removing many industrial wastewater pollutants. It operates at ambient conditions and is well suited to automatic control. The use of chemical precipitation may be limited because of interference of chelating agents and other chemical interference possible when mixing wastewater and treatment chemicals, or because of the potentially hazardous situation involved with the storage and handling of chemicals.

Hydroxide precipitation is most commonly used in industry and produces a high-quality effluent when applied to many waste streams (particularly when followed by flocculation and filtration). Often, coprecipitation of a mixture of metal ions will result in residual metal solubilities lower than those that could be achieved by precipitating each metal at its optimum pH. Some common limitations of the hydroxide process are as follows:

1. The theoretical minimum solubility for different metals occurs at different pH values (Fig. 6.3). For a mixture of metal ions, it must be determined whether a

single pH can produce sufficiently low solubilities for the metal ions present in the wastewater.

2. Hydroxide precipitates tend to resolubilize if the solution pH is increased or decreased from the minimum solubility point; thus, maximum removal efficiency will not be achieved unless the pH is controlled within a narrow range.
3. The presence of complexing ions, such as phosphates, tartrates, ethylenediaminetetraacetic acid (EDTA), and ammonia, may have adverse effects on metal removal efficiencies when hydroxide precipitation is used.
4. Hydroxide precipitation usually makes recovery of the precipitated metals difficult because of the heterogeneous nature of most hydroxide sludge.

Lime for hydroxide precipitation has gained widespread use because of its ease of handling, economy, and treatment effectiveness for a great variety of dissolved materials. However, if there is sulfate ion present in the wastewater, gypsum (calcium sulfate) will be formed. This increases sludge production, may cause a scaling problem in pipelines, and may clog dual media filters. Using caustic soda is more expensive, but it generally eliminates the scaling problem. Total dissolved solids will increase in wastewater treated with caustic soda as a result of the formation of sodium salt.

Sulfide precipitation has been demonstrated to be an effective alternative to hydroxide precipitation for removing various heavy metals from industrial wastewaters. The major advantage of the sulfide precipitation process is that because of the extremely low solubility of metal sulfides, very high metal removal efficiencies can be achieved. Additional advantages of sulfide precipitation are as follows:

1. The sulfide process has the ability to remove chromate and dichromate without preliminary reduction of chromium to its trivalent state.
2. The high reactivity of sulfides with heavy metal ions and the insolubility of metal sulfides over a broad pH range are attractive features compared with the hydroxide precipitation process.
3. Sulfide precipitation, unlike hydroxide precipitation, is relatively insensitive to the presence of most chelating agents and eliminates the need to treat these wastes separately.

The major limitations of the sulfide precipitation process are the evolution of toxic hydrogen sulfide fumes and the discharge of treated wastewater containing residual levels of sulfide. Other factors include:

1. Sulfide reagent will produce hydrogen sulfide fumes when it comes into contact with acidic wastes. Maintaining the pH of solution between 8 and 9.5 and providing ventilation of treatment tanks can control this problem.
2. As with hydroxide precipitation, excess sulfide ion must be present to drive the precipitation reaction to completion. Because the sulfide ion itself is toxic, sulfide addition must be carefully controlled to maximize heavy metals precipitation with a minimum of excess sulfide to avoid the necessity of posttreatment. Where excess sulfide is present, aeration of the effluent stream would be necessary to oxidize residual sulfide to the less harmful sodium sulfate (Na_2SO_4).

3. The cost of sulfide precipitation is high in comparison with hydroxide treatment, and disposal of metallic sulfide sludge may pose problems.

The use of ferrous sulfide (insoluble-sulfide process) as a source of sulfide reduces or virtually eliminates the problem of hydrogen sulfide evolution. The use of ferrous sulfide, however, requires reagent consumption considerably higher than stoichiometric and produces significantly larger amounts of sludge than either the hydroxide or soluble-sulfide treatment processes.

Chemical Precipitation Process: Reliability

Hydroxide and sulfide chemical precipitation are highly reliable, although proper monitoring and control are required. The major maintenance needs involve periodic upkeep of equipment for monitoring, automatic feeding, and mixing, and other hardware.

Chemical Precipitation Process: Chemicals

1. Hydroxide precipitation: Quicklime, CaO, hydrated lime, $Ca(OH)_2$, and liquid caustic soda, NaOH
2. Sulfide precipitation: sodium sulfate, Na_2SO_4, sodium sulfide, Na_2S, and ferrous sulfate, $FeSO_4$
3. Cyanide precipitation: zinc sulfate, $ZnSO_4$, and ferrous sulfate, $FeSO_4$
4. Carbonate precipitation: calcium carbonate, $CaCO_3$, and carbon dioxide, CO_2

Chemical Precipitation Process: Residuals

Chemical precipitation generates solids that must be removed in a subsequent treatment step, such as sedimentation or filtration. Sulfide sludges are less subject to leaching than hydroxide sludge. However, the long-term impacts of weathering and of bacterial and air oxidation of sulfide sludges have not been evaluated.

Chemical Precipitation Process: Performance

The performance of chemical coagulation/precipitation depends on several variables. The most important factors affecting precipitation effectiveness are:

1. Maintenance of an alkaline pH throughout the precipitation reaction and subsequent settling
2. Addition of a sufficient excess of treatment ions to drive the precipitation reaction to completion

3. Addition of an adequate supply of sacrificial ions (such as ion or aluminum) to ensure precipitation and removal of specific target ions
4. Effective removal of precipitated solids

The US Environmental Protection Agency (USEPA) expected chemical coagulation/precipitation process performances for treating various industrial effluents are presented in Appendixes 1.1–1.23, and selectively explained in the subsequent sections Chemical Precipitation Process: Application Examples (Application Examples 1–16).

Proper control of pH is absolutely essential for favorable performance of precipitation/sedimentation technologies. This is clearly illustrated by solubility curves for selected metal hydroxides and sulfides as shown in Fig. 6.3. Hydroxide precipitation is effective in removing arsenic, cadmium, trivalent chromium, copper, iron, manganese, nickel, lead, and zinc. Sulfide treatment is superior to hydroxide treatment for removal of several metals and is very effective for removal of mercury and silver. As shown by theoretical solubilities of hydroxides and sulfides of selected metals (Appendix 1.24), sulfide precipitation is highly effective in removal of cadmium, cobalt, copper, iron, mercury, manganese, nickel, silver, tin, and zinc. Estimated achievable maximum 30-day average concentrations of several heavy metals under different chemical precipitation and solid removal technologies are shown in Appendix 1.25. The estimated achievable concentration is based on the performance data reported in literatures [26–40].

2.4.5 Chemical Precipitation Process: Application Examples

Examples of heavy metal removals by chemical precipitation and chemical coagulation are briefly summarized in this section. Chemical precipitation includes at least hydroxide precipitation, sulfide precipitation, iodide precipitation, carbonate precipitation, sulfate precipitation, phosphate precipitation, and coprecipitation. Chemical coagulation includes at least alum coagulation, ferric chloride coagulation, ferric sulfate coagulation, polyaluminum chloride (PAC) coagulation, aluminum chlorohydrate (ACH) coagulation, and polymer coagulation. Supplemental unit process, such as sedimentation, dissolved air flotation, multimedia filtration, ion exchange, adsorption, biosorption, and membrane filtration, are discussed. Special emphasis of this section is placed on: (a) summarizing typical examples of various chemical precipitation and chemical coagulation processes; (b) discussing continuous soluble sulfide precipitation (SSP), continuous insoluble sulfide precipitation (ISP), conventional batch soluble sulfide precipitation, conventional batch insoluble sulfide precipitation, sequencing batch reactor soluble sulfide precipitation (SBR-SSP), sequencing batch reactor insoluble sulfide precipitation (SBR-ISP), sequencing batch reactor soluble sulfide flotation (SBR-SSF), sequencing batch reactor insoluble sulfide flotation (SBR-ISF), membrane reactor soluble sulfide precipitation (MR-SSP), membrane reactor insoluble sulfide precipitation (MR-ISP); and (c) discussing recent developments in sulfide precipitation. The readers are referred to the literature for the detailed theories, principles, applications, and costs of chemical precipitation (including SSP and ISP) and chemical coagulation for heavy metals from industrial effluents [1–93, 95–151].

EXAMPLE 1: CHEMICAL COAGULATION/PRECIPITATION FOR INDUSTRIAL WASTE TREATMENT

It has been known that the chemical precipitation process is technically and economically feasible for treating the following industrial effluents [26–45]:

1. Foundries
2. Metal finishing
3. Iron and steel manufacturing
4. Textiles
5. Steam electric power plants
6. Inorganic chemical manufacturing
7. Ore mining and dressing
8. Porcelain enameling
9. Paint and ink formulation
10. Coil coating
11. Nonferrous metal manufacturing
12. Aluminum forming
13. Battery manufacturing
14. Electrical and electronic components
15. Copper coating
16. Organic and inorganic wastes
17. Auto and other laundries

Conduct a literature search, and present the treatability data sheets for the chemical industries listed above.

Solution
The treatability data sheets shown in Appendixes 1–23 provide performance data from studies on the above industries and/or waste streams using chemical precipitation in combination with various solid separation processes including flocculation, sedimentation, and filtration.

EXAMPLE 2: CHEMICAL COAGULATION/PRECIPITATION AND SOLID SEPARATION PROCESSES

The chemical coagulation/precipitation process is commonly used in conjunction with either sedimentation (such as Appendixes 1–3, 5, 6, 9–11, and 14–23) or filtration (such as Appendixes 4, 7, and 8) for removal of chemically produced precipitates (or flocs). List and explain other combinations of separation processes that can be used in conjunction with chemical coagulation/precipitation. The processes and their combinations should be feasible from both technical and economical viewpoints.

Solution

Other feasible process combinations include at least the following [43–93]:

1. Chemical precipitation + sedimentation + filtration
2. Chemical precipitation + flotation
3. Chemical precipitation + flotation + filtration
4. Chemical precipitation + ultrafiltration (UF)
5. Chemical precipitation + ultrafiltration + reverse osmosis (RO)
6. Chemical precipitation + fabric filtration (cartridge filter) + RO
7. Chemical precipitation + physical chemical sequencing batch reactor (PCSBR)
8. Chemical precipitation + PCSBR + filtration
9. Chemical precipitation + PCSBR + membrane filtration (NF, UF, and/or RO)
10. Chemical precipitation + filtration + granular activated carbon (GAC)
11. Chemical precipitation + flotation + GAC
12. Chemical precipitation + biological treatment process
13. Biological treatment process + chemical precipitation
14. Chemical precipitation + sedimentation + filtration + ion exchange
15. Chemical precipitation + flotation + filtration + ion exchange

Each process combination mentioned above may include chemical coagulation, if necessary, and can be a conventional continuous process, or an innovative physical chemical sequencing batch process (PCSBR) [9, 88].

The most common filtration process is rapid sand filtration, although slow sand filtration is an option. Membrane filtration includes nanofiltration (NF), microfiltration (MF), ultrafiltration (UF), and reverse osmosis (RO), of which at least one is needed in the process system.

The flotation process can be one or more of the following: dissolved air flotation, dispersed air flotation, electroflotation, ion flotation, precipitate flotation, and foam separation.

The biological treatment process can be, but is not limited to, activated sludge, trickling filter, rotating biological contactors, sequencing batch reactor, and membrane bioreactor.

Conventional sequencing batch reactor (SBR) is a biological treatment process, while innovative physicochemical sequencing batch reactor (PCSBR) is a newly developed physicochemical treatment process [9, 95].

EXAMPLE 3: CHEMICAL PRECIPITATION, CHEMICAL COAGULATION, AND THEIR COMBINATION

Explain the difference between the chemical precipitation process and the chemical coagulation process, and discuss the combined chemical coagulation–precipitation process.

Solution

Chemical precipitation is a chemical unit process in which undesirable soluble metallic ions and certain anions are converted to insoluble form and then removed from water or wastewater. Typically, soluble ions, such as soluble heavy metal ions, or soluble phosphate ions, are converted to insoluble solids by a soluble chemical precipitating agent in a process reactor containing aqueous solution. The resulting insoluble solids that are formed in the chemical precipitation process reactor are called precipitates. In other words, in a pure chemical precipitation process, a "soluble precipitating agent" chemically reacts with one or more "soluble ionic pollutants," forming "insoluble precipitates." The aqueous solution in the reactor is the water or wastewater to be treated for removal of ionic pollutants.

Chemical precipitation itself is only a conversion process converting soluble ionic pollutants (heavy metals, hardness, phosphate, etc.) into insoluble precipitates which must be further removed by a series of posttreatment processes, such as sedimentation, flotation, and filtration. Normally, chemical precipitation is suitable for treating certain industrial effluent containing mainly ionic chemicals (such as metal finishing wastewater and high phosphate mining wastewater) or high hardness water.

It is a commonly used treatment technique for removal of heavy metals, phosphorus, and hardness. The procedure involves alteration of the ionic equilibrium to produce insoluble precipitates that can be removed easily by a solid-separation operation that may include coagulation/flocculation and/or sedimentation, flotation, filtration, or a membrane process to remove the precipitates.

Theoretically speaking that undesirable pollutants to be removed by chemical precipitation are soluble cations and/or anions, not the colloids like color, turbidity, lignin, TSS, BOD, COD, etc.

Chemical precipitation process can be called hydroxide precipitation, sulfide precipitation, iodide precipitation, carbonate precipitation, chloride precipitation, sulfate precipitation, phosphate precipitation, etc., if the soluble precipitating agent contains/produces soluble hydroxide ions, sulfide ions, iodide ions, carbonate ions, chloride ions, sulfate ions, phosphate ions, respectively. There are two types of sulfide precipitation: (a) soluble sulfide precipitation (SSP) and (b) insoluble sulfide precipitation (ISP). In case ferrous iron sulfide is used in an ISP reactor, the process can also be called iron sulfide precipitation.

Figure 6.3 shows that most of the precipitated heavy metal hydroxides are amphoteric in nature, so the pH of wastewater must be carefully controlled at optimum range during hydroxide precipitation process. When more than one heavy metals are targeted for removal at the same time, some heavy metals cannot achieve their best precipitation results based on their solubility, since different heavy metal hydroxides have different optimum pHs for precipitation.

A serious disadvantage of hydroxide precipitation is that any presence of chelating agents in the wastewater will interfere with the hydroxide precipitating agent to precipitate soluble heavy metals. Technically speaking, a chelate, or a chelating agent, is a chemical that will form a joint-compound with one or more intended heavy metals, and with the intended purpose of keeping the heavy metals in the solution. Commonly used chelating agents include phosphate, EDTA, ammonia, cyanide, and citrate, which each may form a complex chelate-metal compound, so the targeted heavy metal ions may be kept in solution.

Chemical coagulation and flocculation are terms often used together to describe the physicochemical process of suspended particle aggregation, resulting from chemical additions to water or wastewater. Technically, coagulation involves the reduction of electrostatic surface charges and the formation of complex hydrous oxide. Coagulation is essentially instantaneous in that the only time required is that necessary for dispersing the chemicals in solution. Flocculation is the time-dependent physical process of the aggregation of solids into particles large enough to be separated by sedimentation, flotation, filtration, or any of the membrane processes. For particles in the colloidal and fine supercolloidal size ranges (less than 1–2 pm), natural stabilizing forces (electrostatic repulsion and physical repulsion by absorbed surface water layers) predominate over the natural aggregating forces (van der Waals forces) and the natural mechanism that tends to cause particles contact (Brownian motion). The purpose of coagulation is to overcome the above repulsive forces and, hence, to allow small particles to agglomerate into larger particles, so that gravitational and inertial forces will predominate and effect the settling of the particles. The process can be grouped into two sequential mechanisms: (a) Chemically induced destabilization of the repulsive surface-related forces, thus allowing particles to stick together when contact between particles is made, and (b) chemical bridging and physical enmeshment between the non-repelling particles, thus allowing for the formation of large particles.

In a chemical coagulation process operation, a coagulant (such as alum, polyaluminum chloride, ferric chloride, and aluminum chlorohydrate) that forms positively charged colloids electrochemically neutralizes the negatively charged colloidal pollutants (such as TSS, BOD, color colloids, turbidity, microorganisms, lignins, tannins, and NOM) to form stabilized, neutralized, insoluble flocs. The insoluble flocs must be further processed by flocculation, clarification, filtration, etc. for removal. Normally, chemical coagulation is suitable for treating water or wastewater containing various colloidal pollutants. In case water or wastewater contains both ionic pollutants (heavy metals, phosphates, hardness, etc.) and colloidal pollutants (NOM, TSS, BOD, color, turbidity, tannins, microorganisms, etc.), a combined chemical precipitation–coagulation process system is applied to the target water or wastewater for adequate treatment [1–95, 100–114, 140–151]. The readers are referred to the literature for various unit operations and unit processes which may be used with chemical precipitation and/or chemical coagulation together to form a complete water or wastewater treatment system [1, 95, 96, 100–112, 125–129, 137].

In water treatment systems, the lime softening process for hardness removal is normally a chemical precipitation process. However, if the raw water contains high concentration of color colloids, chemical coagulation will be involved, and the water purification process is a combined chemical coagulation/precipitation process system for total water treatment. In a chemical wastewater treatment system, if an industrial wastewater stream contains mainly ionic heavy metals, then this chemical treatment system (involving the use of chemical precipitating agents) is a typical chemical precipitation process aiming at ionic heavy metals removal. If the metal containing industrial effluent is mixed with municipal wastewater, for instance, the combined wastewater stream will contain both ionic heavy metals and colloidal organic pollutants. Treatment of this combined wastewater stream for removing both heavy metals and organic pollutants (BOD, COD, TSS, NOM, etc.) using chemical coagulants/precipitating agents may be a combined chemical coagulation/precipitation process.

EXAMPLE 4: REMOVAL OF TOXIC SOLUBLE LEAD IONS (PB(II)) FROM AN INDUSTRIAL EFFLUENT BY HYDROXIDE PRECIPITATION, SULFIDE PRECIPITATION, AND IODIDE PRECIPITATION

Write chemical reactions for lead removal assuming (a) sodium hydroxide, sodium sulfide, and sodium iodide are used as the precipitating agents in hydroxide precipitation, sulfide precipitation, and iodide precipitation, respectively; (b) the industrial effluent contains nitrate ions and (c) the pH is adjusted to optimum as required.

Solution

Removal of soluble lead ions (Pb^{2+}) from an industrial effluent by hydroxide precipitation using soluble sodium hydroxide:

$$\mathrm{Pb}\left(\mathrm{NO}_3\right)_2(\mathrm{aq})+2\mathrm{NaOH}(\mathrm{aq})\rightarrow \mathrm{Pb}\left(\mathrm{OH}\right)_2(\mathrm{s})+2\mathrm{NaNO}_3(\mathrm{aq})$$

Removal of soluble lead ions (Pb^{2+}) from an industrial effluent by sulfide precipitation using soluble sodium sulfide:

$$\mathrm{Pb}\left(\mathrm{NO}_3\right)_2(\mathrm{aq})+\mathrm{Na}_2\mathrm{S}(\mathrm{aq})\rightarrow \mathrm{PbS}(\mathrm{s})+2\mathrm{NaNO}_3(\mathrm{aq})$$

Removal of soluble lead ions (Pb^{2+}) from an industrial effluent by iodide precipitation using soluble sodium iodide:

$$\mathrm{Pb}\left(\mathrm{NO}_3\right)_2(\mathrm{aq})+2\mathrm{NaI}(\mathrm{aq})\rightarrow \mathrm{PbI}_2(\mathrm{s})+2\mathrm{NaNO}_3(\mathrm{aq})$$

EXAMPLE 5: REMOVAL OF SOLUBLE BARIUM IONS (BA(II)) FROM AN INDUSTRIAL EFFLUENT BY SULFATE PRECIPITATION

Write a chemical reaction for barium removal assuming (a) sodium sulfate is used as the precipitating agent in sulfate precipitation; (b) the industrial effluent contains chloride ions; and (c) the pH is adjusted to optimum as required.

Solution

Removal of soluble barium ions (Ba^{2+}) from an industrial effluent by sulfate precipitation using soluble sodium sulfate:

$$\mathrm{BaCl}_2(\mathrm{aq})+2\mathrm{Na}_2\mathrm{SO}_4(\mathrm{aq})\rightarrow \mathrm{BaSO}_4(\mathrm{s})+2\mathrm{NaCl}(\mathrm{aq})$$

EXAMPLE 6: REMOVAL OF SOLUBLE SILVER IONS (AG(I)) FROM AN INDUSTRIAL EFFLUENT BY CHLORIDE PRECIPITATION

Write a chemical reaction for silver removal assuming (a) sodium chloride is used as the precipitating agent in chloride precipitation; (b) the industrial effluent contains nitrate ions; and (c) the pH is adjusted to optimum as required.

Solution
Removal of soluble silver ions (Ag^+) from an industrial effluent by chloride precipitation using soluble sodium chloride:

$$\mathrm{AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)}$$

EXAMPLE 7: REMOVAL OF SOLUBLE COPPER IONS (CU(II)), NICKEL IONS (NI(II)), ZINC IONS (ZN(II)), CHROMIUM IONS (CR(III)), AND CADMIUM IONS (CD(II)) FROM AN INDUSTRIAL WASTEWATER BY HYDROXIDE PRECIPITATION (OR LIME PRECIPITATION)

(a) Write chemical reactions and discuss treatment system efficiencies for these heavy metal removal using lime and assuming the wastewater pH is adjusted to optimum as required; (b) discuss the difference of lime application and sodium hydroxide application; and (c) discuss the expected treatment efficiencies for removing these heavy metals.

Solution
Removal of soluble heavy metals from a wastewater by hydroxide precipitation using lime:

$$\mathrm{Cu(NO_3)_2(aq) + Ca(OH)_2(aq) \rightarrow Cu(OH)_2(s) + Ca(NO_3)_2(aq)}$$

$$\mathrm{Ni(NO_3)_2(aq) + Ca(OH)_2(aq) \rightarrow Ni(OH)_2(s) + Ca(NO_3)_2(aq)}$$

$$\mathrm{Zn(NO_3)_2(aq) + Ca(OH)_2(aq) \rightarrow Zn(OH)_2(s) + Ca(NO_3)_2(aq)}$$

$$\mathrm{2Cr(NO_3)_3(aq) + 3}Ca\mathrm{(OH)_2(aq) \rightarrow 2Cr(OH)_3(s) + 3Ca(NO_3)_2(aq)}$$

$$\mathrm{Cd(NO_3)_2(aq) + Ca(OH)_2(aq) \rightarrow Cd(OH)_2(s) + Ca(NO_3)_2(aq)}$$

Either sodium hydroxide or hydrated lime can be used in hydroxide precipitation process for heavy metal removal. Comparatively, hydrated lime is less expensive for wastewater treatment applications.

The following are expected treatment qualities if clarification and filtration are used after lime is mixed with the wastewater for chemical precipitation:

1. Chemical precipitation + clarification = Cu (0.2–1.5 mg/L), Ni (0.5–2.5 mg/L), Zn (0.2–1.5 mg/L), Cr (0.1–1.0 mg/L), Cd (0.2–1.5 mg/L).

2. Chemical precipitation + clarification + filtration = Cu (0.05–0.5 mg/L), Ni (0.25–1.5 mg/L), Zn (0.05–1.0 mg/L), Cr (0.05–0.5 mg/L), Cd (0.05–1.0 mg/L). The clarification process can be either sedimentation clarification or dissolved air flotation (DAF) clarification.

EXAMPLE 8: ADVANTAGES, DISADVANTAGES, PROCESS PROBLEMS, CORRECTION MEASURES AND APPLICATIONS OF HYDROXIDE PRECIPITATION USING LIME OR SODIUM HYDROXIDE FOR REMOVING MORE THAN ONE HEAVY METAL IONS FROM AN INDUSTRIAL WASTEWATER

Discuss (a) the advantages and disadvantages of using lime or sodium hydroxide in hydroxide precipitation, and (b) the problems, correctional measures, and applications of hydroxide precipitation.

Solution

Both lime and sodium hydroxide are common chemicals for heavy metals removal from wastewater treatment by hydroxide precipitation. Comparatively, the former (lime) is cheap, less toxic, popular, less corrosive, difficult to feed, and easy to dewater high quantity of sludge, and the latter (sodium hydroxide) is more expensive, very toxic, extremely corrosive, easy to feed, and difficult to dewater smaller quantity of sludge.

The precipitated metal hydroxide (insoluble solids) may resolubilize if the wastewater pH increases or decreases from the optimum pH value because these precipitated metal hydroxides are amphoteric. There are at least three options for precipitating more than one heavy metal ions with different optimum pH: (a) optimize pH for precipitating one targeted heavy metal ion to meet the overall industrial effluent standards; (b) find a compromise pH for simultaneous precipitation of more than one metal ions; and (c) operate the chemical precipitation process as a two-stage or multi-stage system, so the heavy metals can be precipitated in stages.

The hydroxide precipitation process is very popular in industrial effluent treatment. The problems of hydroxide precipitation include not only the above differences in metal ions' optimum pH for precipitation, but also the presence of chelating agents in certain industrial effluents. Ammonia, phosphates, and EDTA are chelating agents commonly used in metal plating solutions. These chelates hold metals in solution, not allowing metals to precipitate easily. There are at least six corrective methods of addressing the chelate problem: (a) precipitate metals at high pH, greater than 10, if all possible and metal precipitation results are still acceptable; (b) use calcium chloride to enhance chelate separation; (c) use ferrous sulfate which the chelate prefers over the heavy metal to be precipitated; (d) use a reducing agent, such as sodium borohydride, to convert the heavy metal from the ion back to the metal; (e) use sodium dimethyldithiocarbamate (DTC), or sodium polythiocarbonate (PTC) that can steal the targeted heavy metal from the chelating agent; DTC is an organic sulfur chemical compound, not pH sensitive in chelated wastewater control (any pH above 3), non-amphoteric, but is a very toxic agricultural insecticide or industrial biocide; while PTC is comparatively much less toxic meeting NPDES toxicity test requirements, produces 50% less sludge than DTC, lime or iron chemistries, and requires lower dosing of flocculant chemistry for water–solid separation; (f) use sulfide precipitation instead of hydroxide precipitation.

According to Appendixes 5–11, 15–17, and 21, hydroxide precipitation using lime has been successfully applied to treating the industrial effluents of iron and steel plants, textile mills, steam electric plants, inorganic chemical plants, base-metal mines, ore mining and dressing plants, coil coating plants, non-ferrous metals plants, and copper manufacturing plants. It has been known from the same source (Appendix 14) that hydroxide precipitation using sodium hydroxide has been successfully applied to treating a coil coating plant (aluminum subcategory).

EXAMPLE 9: REMOVAL OF HEAVY METALS FROM INDUSTRIAL EFFLUENTS BY COMBINED CHEMICAL PRECIPITATION, COAGULATION, FLOCCULATION, CLARIFICATION, AND FILTRATION

Discuss the theory, principles, and applications of combined chemical precipitation, coagulation/flocculation, clarification, and filtration for removing heavy metals from industrial effluents.

Solution

Combined chemical precipitation, coagulation/flocculation followed by clarification and filtration is commonly applied to heavy metal removal from industrial effluents containing both ionic pollutants (heavy metal ions, phosphate ions, etc.) and negatively charged colloidal pollutants (TSS, BOD, F&G, tannins, NOM, etc.). Coagulation is a chemical process involving the use of coagulants for destabilizing the colloids in water by neutralizing the electrical charges/forces that keep them apart. Common coagulants include aluminum sulfate, aluminum chloride, polyaluminum chloride (PAC), polyferric sulfate (PFS), polyacrylamide (PAM), ferrous sulfate, ferrous chloride, ferric chloride, sodium aluminate, aluminum chlorohydrate (ACH or Chemchlor), polymer, amphoteric polyelectrolyte, lignosulfonate, etc. which individually or in combination with precipitants and other coagulants, can effectively treat an industrial effluent for removal of heavy metals, BOD, TSS, F&G, microorganisms, tannins, lignins, etc. Flocculation is a physical process in which the coagulants form bridges between the flocs (including the precipitants and chemical coagulant flocs), bind these fine flocs and TSS together, and grow the floc sizes gradually during slow mixing in a reactor. After the flocs grow to a desirable size, the flocculator effluent discharges to a series of water–solid separation processes, such as clarification (i.e., sedimentation or flotation), gravity filtration, membrane filtration, and diatomaceous earth precoat filtration for insoluble flocs separation and final polishing. Detailed theory and principles of chemical precipitation, coagulation, flocculation, clarification (sedimentation clarification or flotation clarification), filtration (multimedia filtration, diatomaceous earth precoat filtration, membrane filtration) can be found from the literature [5, 20, 106–110, 126–129, 137–139].

According to Appendixes 1, 12, 13, 22, and 23, the combined chemical precipitation–coagulation process systems using sodium hydroxide-alum, lime-polymer, and aluminum sulfate-polymer, have been successfully applied to treating the wastewaters from foundry industry, porcelain manufacturing plant, paint manufacturing plant, organic and inorganic chemical plant, and auto laundries.

It has been noted that chemical precipitation is a pretreatment to chemical coagulation. Initially soluble aluminum coagulants (such aluminum sulfate and polyaluminum chloride) and soluble iron coagulants (such as ferric chloride and ferric sulfate) are precipitated by the alkalinity precipitating agents (such as sodium hydroxide, calcium hydroxide, and sodium bicarbonate) to form insoluble aluminum hydroxide precipitates and insoluble ferric hydroxide precipitates, respectively, at the optimum pH in a chemical precipitation process. The insoluble aluminum hydroxide precipitates and insoluble ferric hydroxide precipitates are the so-called chemical flocs bearing positive charges. Subsequently, the positively charged colloidal chemical flocs neutralize the negatively charged colloidal pollutants, forming the neutralized and stabilized insoluble bigger complex flocs in a chemical coagulation process. The bigger complex flocs that are further enhanced by flocculation are then ready to be separated by the posttreatment processes such as clarification and filtration. Accordingly, in most cases, we are using the combined chemical precipitation–coagulation for water or wastewater treatment.

Further, aluminum sulfate has been frequently applied to a typical combined chemical precipitation–coagulation wastewater treatment plant as both (a) a precipitating agent for phosphate precipitation (i.e., soluble aluminum ion + soluble phosphate ion = insoluble aluminum phosphate precipitate) and (b) a coagulating agent for coagulation of other pollutants (i.e., positively charged colloidal aluminum hydroxide flocs + negatively charged insoluble TSS-BOD flocs = insoluble charge-neutralized bigger complex flocs). The resulting aluminum phosphate precipitate and bigger complex flocs are then removed by the subsequent clarification (sedimentation or flotation) and filtration.

EXAMPLE 10: CONTINUOUS SOLUBLE SULFIDE PRECIPITATION (SSP) AND CONTINUOUS INSOLUBLE SULFIDE PRECIPITATION (ISP)

Discuss the chemical processes and applications of continuous soluble sulfide precipitation and continuous insoluble sulfide precipitation.

Solution

Applications of continuous SSP (SSP) and continuous ISP (ISP) for removal of heavy metals, such as Co(II), Zn(II), Cd(II), Pb(II), Ag(I), Cu(II), Ni(II), and Cr(VI) are illustrated in Fig. 6.3. Theoretically, both continuous SSP and continuous ISP are well-established processes for removing heavy metal ions from wastewater. In a continuous SSP process, selective-ion electrodes are used for controlling the dosages of soluble sulfide reagent (either sodium sulfide (Na_2S) or sodium hydrosulfide (NaHS)), in turn, preventing sulfide reagent overdose and eliminating its associated odor problem.

In a continuous ISP process, freshly prepared, slightly soluble, but practically insoluble ferrous sulfide (FeS) slurry is used to supply the sulfide ions, as needed, to precipitate the unwanted heavy metal ions from water. As sulfide ions are consumed in an ISP reactor, additional FeS will dissociate to maintain the equilibrium concentration of sulfide ions; therefore, hydrogen sulfide odor pollution can be significantly reduced. Applications of continuous ISP for precipitation of Co(II), Zn(II), Cd(II), Pb(II), Ag(I), Cu(II), and Ni(II) and for reduction of Cr(VI) to Cr(III) for sequent chemical precipitation are also fully described in the following sections.

EXAMPLE 11: REMOVAL OF SOLUBLE COPPER IONS (CU(II)), NICKEL IONS (NI(II)), ZINC IONS (ZN(II)), CHROMIUM IONS (CR(III) AND CR(VI)), AND CADMIUM IONS (CD(II)) FROM AN INDUSTRIAL WASTEWATER BY CONTINUOUS SOLUBLE SULFIDE PRECIPITATION (SSP) USING SODIUM SULFIDE (Na_2S)

Write chemical reactions for the above intended heavy metal removals.

Solution

Removal of soluble heavy metals from a wastewater by continuous soluble sulfide precipitation (CSSP) using sodium sulfide:

$$\mathrm{Cu(NO_3)_2(aq) + Na_2S(aq) \rightarrow CuS(s) + 2NaNO_3(aq)}$$

$$\mathrm{Ni(NO_3)_2(aq) + Na_2S(aq) \rightarrow NiS(s) + 2NaNO_3(aq)}$$

$$\mathrm{Zn(NO_3)_2(aq) + Na_2S(aq) \rightarrow ZnS(s) + 2NaNO_3(aq)}$$

$$\mathrm{2Cr(NO_3)_3(aq) + 3Na_2S(aq) \rightarrow Cr_2S_3(s) + 6NaNO_3(aq)}$$

$$\mathrm{Cd(NO_3)_2(aq) + Na_2S(aq) \rightarrow CdS(s) + 2NaNO_3(aq)}$$

$$\mathrm{2H_2CrO_4(aq) + 3Na_2S(aq) + 8H_2O(aq) \rightarrow 2Cr(OH)_3(s) + 3S(s) + 4H_2O(aq) + 6NaOH(aq)}$$

EXAMPLE 12: REMOVAL OF SOLUBLE COPPER IONS (CU(II)), NICKEL IONS (NI(II)), ZINC IONS (ZN(II)), CHROMIUM IONS (CR(III) AND CR(VI)), AND CADMIUM IONS (CD(II)) FROM AN INDUSTRIAL WASTEWATER BY CONTINUOUS SOLUBLE SULFIDE PRECIPITATION (SSP) USING SODIUM HYDROSULFIDE (NAHS)

Write chemical reactions for the above intended heavy metal removals and discuss treatment system efficiencies assuming the wastewater pH is adjusted to optimum as required.

Solution

Removal of soluble heavy metals from a wastewater by continuous soluble sulfide precipitation (CSSP) using sodium hydrosulfide:

$$\mathrm{Cu(NO_3)_2(aq) + NaHS(aq) \rightarrow CuS(s) + NaNO_3(aq) + HNO_3(aq)}$$

$$\mathrm{Ni(NO_3)_2(aq) + NaHS(aq) \rightarrow NiS(s) + NaNO_3(aq) + HNO_3(aq)}$$

$$\mathrm{Zn(NO_3)_2(aq) + NaHS(aq) \rightarrow ZnS(s) + NaNO_3(aq) + HNO_3(aq)}$$

$$\mathrm{2Cr(NO_3)_3(aq) + 3NaHS(aq) \rightarrow Cr_2S_3(s) + 3NaNO_3(aq) + 3HNO_3(aq)}$$

$$\mathrm{Cd(NO_3)_2(aq) + NaHS(aq) \rightarrow CdS(s) + NaNO_3(aq) + HNO_3(aq)}$$

$$\mathrm{2H_2CrO_4(aq) + 3NaHS(aq) + 8H_2O(aq) \rightarrow 2Cr(OH)_3(s) + 3S(s) + 7H_2O(aq) + 3NaOH(aq)}$$

Either sodium sulfide (Na_2S) or sodium hydrosulfide (NaHS) can be used in continuous soluble sulfide precipitation (CSSP) process for heavy metal removal.

The following are the expected treatment qualities if clarification (sedimentation or flotation) and filtration are used after sulfide-containing precipitating agent (either sodium sulfide or sodium hydrosulfide) is mixed with the wastewater for chemical precipitation: (a) chemical precipitation + clarification = Cu (0.05–0.5 mg/L), Ni (0.25–1.5 mg/L), Zn (0.05–1.0 mg/L), Cr (0.05–0.5 mg/L), Cd (0.05–1.0 mg/L); (b) chemical precipitation + clarification + filtration = Cu (0.01–0.2 mg/L), Ni (0.05–0.5 mg/L), Zn (0.01–0.25 mg/L), Cr (0.01–0.2 mg/L), Cd (0.01–0.25 mg/L). The clarification process can be either sedimentation clarification or dissolved air flotation clarification.

EXAMPLE 13: ADVANTAGES, DISADVANTAGES, PROCESS PROBLEMS, CORRECTION MEASURES, AND APPLICATIONS OF SULFIDE PRECIPITATION USING SOLUBLE SODIUM SULFIDE, SOLUBLE SODIUM HYDROSULFIDE, OR INSOLUBLE FERROUS SULFIDE FOR REMOVING MORE THAN ONE HEAVY METAL IONS FROM AN INDUSTRIAL WASTEWATER

Discuss (a) the advantages and disadvantages of using soluble and insoluble sulfide precipitating agents in continuous soluble sulfide precipitation (SSP) and continuous insoluble sulfide precipitation (ISP); (b) the problems, correctional measures, and applications of sulfide precipitation.

Solution

The readers are referred to Fig. 6.3. It can be seen that the biggest advantages of using sulfide precipitation (either SSP or ISP) instead of hydroxide precipitation are: (a) the solubility of all heavy metal sulfide compounds (MS) is much lower than the solubility of equivalent heavy metal hydroxide compounds $M(OH)_2$; (b) the optimum pH for sulfide precipitation of all heavy metals is almost the same, pH = 11, so it is convenient to remove all heavy metals at one optimum pH, and there is no need to use a multi-stage precipitation system for accommodating the pH differences of many targeted heavy metals that require simultaneous treatment for removal; (c) sulfide precipitation is often preferred for treating wastewater containing chelating agents because the sulfide ion may steal heavy metals from a chelated complex compound; (d) trivalent Cr(III) ion as Cr^{3+} and hexavalent Cr(VI) as CrO_4^{2-} can be precipitated from in the same reactor by either continuous or batch SSP using soluble sodium sulfide (or sodium hydrosulfide) or continuous or batch ISP using insoluble ferrous sulfide, and (e) toxic hydrogen sulfide odor problem is significantly reduced when using continuous or batch ISP using insoluble ferrous sulfide.

The disadvantages of sulfide precipitation process (in comparison with hydroxide precipitation) are: (a) all sulfide compounds have more negative environmental impacts than lime, sodium hydroxide, etc.; (b) treatment costs of sulfide precipitation are higher than that of hydroxide precipitation; and (c) sulfide precipitation must be precisely control, otherwise it may produce toxic hydrogen sulfide (H_2S) gas in lethal concentrations.

Of course, it has been discussed earlier that the use of insoluble FeS in insoluble sulfide precipitation (ISP) may significantly reduce the toxic hydrogen sulfide problem, but care must still be taken for environmental monitoring. ISP is also called iron sulfide precipitation when using FeS.

The sulfide precipitation process has been successfully applied to metal finishing plants for treating their tough wastewater containing more than one toxic heavy metals, hexavalent chromium, chelating agents, etc.

EXAMPLE 14: CONVENTIONAL BATCH REACTOR AND SEQUENCING BATCH REACTOR FOR SSP AND ISP

Discuss conventional batch reactor and sequencing batch reactor for SSP and ISP.

Solution

The chemical reactions of batch soluble sulfide precipitation (batch SSP) and batch insoluble sulfide precipitation (batch ISP) are identical to that of continuous soluble sulfide precipitation (continuous SSP) and continuous insoluble sulfide precipitation (continuous ISP), respectively. Accordingly, the heavy metal removal/reduction efficiencies, advantages, and disadvantages of batch SSP and batch ISP are expected to be similar to that of their respective continuous SSP and continuous ISP, respectively.

Conventional batch reactors (batch SSP and batch ISP) have been used for operating small biological systems, or small physicochemical systems for decades. Recently, physicochemical sequencing batch reactors (physicochemical SBR) have been patented and commercially developed for full-scale industrial and municipal wastewater treatment. Wang et al. have developed (a) enclosed physicochemical sequencing batch reactor (SBP), (b) sequencing batch sedimentation (SPS), (c) sequencing batch flotation (SBF), and (d) sequencing batch exchanger (SBE) for removing heavy metals as well as other organic and/or inorganic pollutants [129, 137, 152]. When the above physicochemical sequencing batch reactors are applied to sulfide precipitation, they can be a sequencing batch reactor insoluble sulfide precipitation (SBR-ISP), a sequencing batch reactor soluble sulfide flotation (SBR-SSF), a sequencing batch reactor insoluble sulfide flotation (SBR-ISF), etc. depending on the configurations of the process reactor. If a membrane filtration unit is used for posttreatment, the entire process system can be a membrane reactor soluble sulfide precipitation (MR-SSP), or a membrane reactor insoluble sulfide precipitation (MR-ISP).

A case history of chromium recovery from the spent tannery at Germanakos SA Tannery near Athens, Greece, can be found from the literature [129, 137].

The mechanical reactor and process control equipment for conventional biological sequencing batch reactor (BIO-SBR) are commercially available. With minor modifications, commercial BIO-SBR process equipment and monitoring equipment can be readily adopted as the process and monitoring equipment of physicochemical sequencing batch reactor (PC-SBR) for either SSP or ISP. Similarly, with minor modification, commercial membrane bioreactor process and monitoring equipment can be readily adopted as the process and monitoring equipment of physicochemical membrane filtration reactor [138, 139].

EXAMPLE 15: REMOVAL OF SOLUBLE HEXAVALENT CHROMIUM ION (CR(VI)) FROM AN INDUSTRIAL WASTEWATER USING INSOLUBLE FERROUS SULFIDE (FES) IN A SEQUENCING BATCH REACTOR INSOLUBLE SULFIDE PRECIPITATION (SBR-ISP) OR A CONTINUOUS INSOLUBLE SULFIDE PRECIPITATION (ISP)

Write chemical reactions for the above intended removal of trivalent chromium ions and hexavalent chromium ions and discuss treatment system efficiencies assuming the wastewater pH is adjusted to optimum as required.

Solution

The chemical reactions for chromium(VI) ion removal in a batch reactor or a continuous reactor are identical. The chemical reactions are written in below:

$$H_2CrO_4\left(aq\right)+FeS\left(s\right)+4H_2O\left(aq\right)\rightarrow Cr\left(OH\right)_3\left(s\right)+Fe\left(OH\right)_3\left(s\right)+S\left(s\right)+2H_2O\left(aq\right)$$

The big advantage of the ISP process (either batch reactor or continuous reactor) is the ability of the sulfide and ferrous ions to reduce hexavalent chromium to its trivalent state, which eliminates the need to segregate and treat chromium wastewaters separately. Under alkaline conditions, the chromium(VI) ion is reduced to chromium(III), forming insoluble chromium hydroxide precipitate $Cr(OH)_3$ (s). Both divalent iron (Fe^{2+}) and divalent sulfide (S^{2-}) are oxidized to insoluble $Fe(OH)_3$ precipitate and insoluble sulfur (S) precipitate, respectively.

Laboratory wastes frequently contain both trivalent chromium ions and hexavalent chromium ions [3, 4]. Insoluble sulfide precipitation (ISP) using ferrous sulfide can remove both trivalent chromium ions and hexavalent chromium ions in a one-stage process reactor.

EXAMPLE 16: BIOLOGICALLY INDUCED SULFIDE PRECIPITATION IN WASTEWATER COLLECTION SYSTEM, NATURAL SYSTEM, AND PROCESS SYSTEM

Discuss biologically induced sulfide precipitation process.
Industrial wastewater collection system of SSP or ISP usually contain some sulfide ions or hydrogen sulfide gas. Municipal wastewater collection system may also contain sulfide ions and/or hydrogen sulfide due to anaerobic biological reactions of sulfate reduction bacteria. Sulfide precipitation by the addition of iron salts is a common practice for sulfide and odor control in wastewater collection systems [27].

Sulfate reduction bacteria in sediments of an estuary may play a role in exporting hydrogen sulfide and threatening a major fish rearing habitat. Richards and Pallud studied the kinetics of sulfate reduction and sulfide precipitation rate in an estuary in Pescadero, California, USA [132].

The idea of sulfate reduction bacteria in the wastewater collection system and the natural system have led to development of bioreactors for sulfate reduction, in turn, for sulfide ion production and sulfide precipitation of heavy metals [134–136]. A new approach to study iron sulfide precipitation kinetics, solubility, and phase transformation has been proposed by Liu et al. [124]. Investigation of biologically induced sulfide precipitation for heavy metal removal and environmental conservation is a new research subject.

2.5 *Flocculation*

Flocculation is understood to be a process where aggregates of lower density are formed in a three-dimensional way. Particles are not destabilized on an individual basis and do not collide individually as described in the concept of coagulation. In this example, the particles rather find themselves incorporated into a three-dimensional network (the picture of a sponge may illustrate this).

Flocculation is accomplished by long-chain molecules or ions. Frequently, organic polymers are used for flocculation. Along with the molecular weight, the charge of such molecules is of great significance for their use as flocculants. There are [5, 141]: (a) cationic polymers; (b) anionic polymers; and (c) non-ionic polymers. Figure 6.4 shows a typical configuration of a cationic polyelectrolyte (cationic polymer) in solution.

To explain the observations made with polymer-induced aggregation, as-called *bridging model* has been invoked. Long-chain molecules adsorb (for reasons described above) with one end to one particle and with the other end to another one. Thus, there must always be free adsorption sites on the particle surface in order to allow bridge formation. At higher flocculant concentration surface coverage becomes so high that no longer free adsorption sites for molecules extending from other particles are available. A schematic representation of the bridging model for destabilization of colloids by polymers and subsequent flocculation actions is shown in Fig. 6.5.

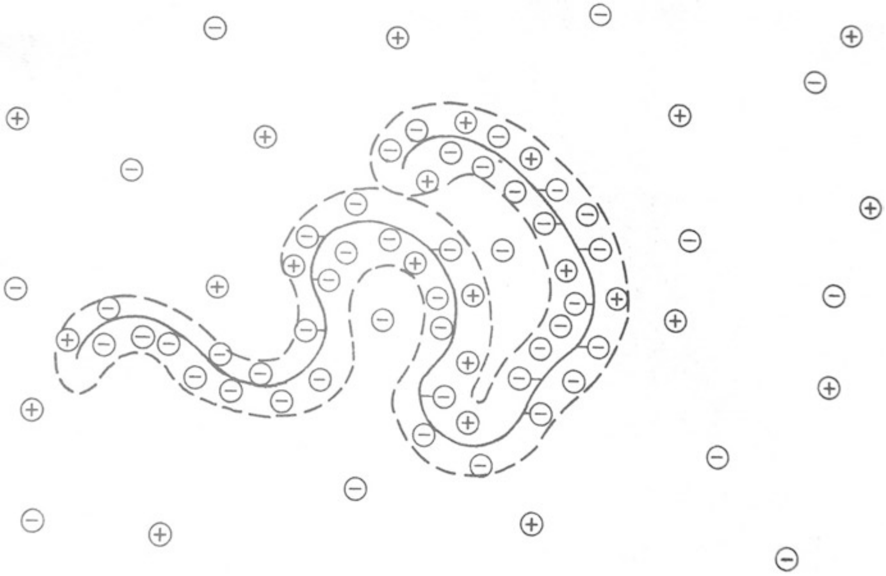


Fig. 6.4 Typical configuration of a cationic polyelectrolyte in solution (USEPA)

There is also another mechanism that can be invoked for the explanation of aggregation phenomena observed with shorter chain molecules. This so-called *Patch Model* stipulates that the (in this case oppositely) charged molecules will adsorb onto the particle surface and change the surface charge [1, 5].

From a practical point of view, the following may be said about the use of flocculants:

1. The amount of chemicals added is crucial to the success of the process.
2. The pH value, controlling the surface charge and the adsorption process, must be observed.
3. Overdosing may cause restabilization.
4. The intensity of mixing in the phase of flocculant addition is to be controlled carefully.
5. The resulting products, i.e., the floccules, are usually less dense than the coagulant.

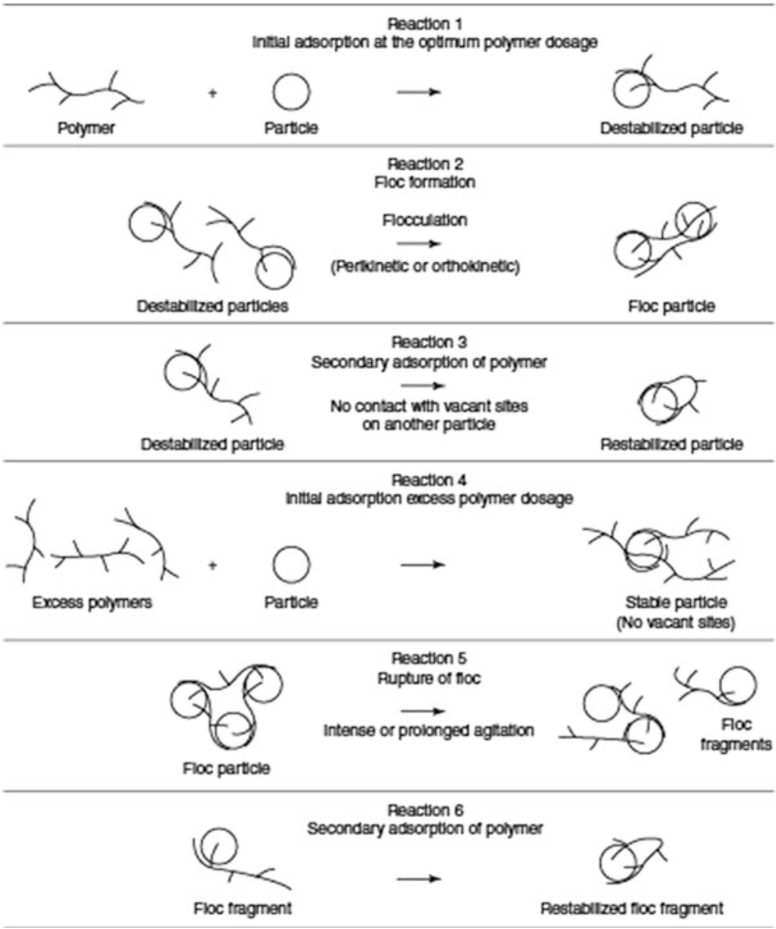


Fig. 6.5 Bridging model for the destabilization of colloids by polymers (USEPA)

2.6 Particle Removal by Enclosure in Coagulation and Precipitation Products

In water and wastewater treatment, frequently metal ions (i.e. metal salts) are used. These metal ions will hydrolyze. They will also react with the acid–base system "water" and form hydroxo complexes. These reactions are shown schematically below.

$$\begin{aligned}
Al^{+3} + H_2O &= Al(OH)^{+2} + H^+ \\
Al(OH)^{+2} + H_2O &= Al(OH)_2^{\ +} + H^+ \\
Al(OH)_2^{\ +} + H_2O &= Al(OH)_3(s) + H^+ \\
Al(OH)_3(s) + OH^- &= Al(OH)_4^{\ -}
\end{aligned}$$

A standard jar test is normally required to ensure that an optimum pH condition for chemical coagulation can be obtained. At average dosages and the most frequently observed pH conditions, metal-hydroxide formation will occur.

It is significant in what way this equilibrium point is reached. (It must be pointed out that in a strictly thermodynamic sense, there will be no equilibrium between metal-hydroxide and the dissolved species in such short time as is provided in those technical systems that are discussed here.) If the domain of insolubility is reached for a given total metal concentration by increasing pH from originally acidic values to neutral values, then there will be kinetic intermediaries that resemble those positively charged metal-hydroxo complexes. Analogous observations can be made when approaching the domain of insolubility from very high pH values; this may lead to negatively charged intermediaries.

In all real systems such as wastewater, one will rarely be able to distinguish between coagulation/flocculation and precipitation. Both the processes will occur simultaneously with a rate and to an extent that is determined by the composition of the dissolved phase. The significance of the precipitation phenomena for wastewater treatment processes lies in the fact that metal-hydroxide precipitates may and will incorporate suspended particles into the newly formed solid phase.

From a practical point of view, the following may be said about precipitation:

1. Under most conditions, hydroxide formation is favored.
2. Hydroxide formation means additional consumption of chemicals.
3. Hydroxide formation support suspended material removal, in particular such suspensions that might not respond to classical aggregation processes.
4. The resulting products do not show great strength.
5. The resulting products have a higher water content.

3 Types of Chemicals

In many instances, the reactors for liquid–solid separation do exist, and the overall plant efficiency can be increased by an improvement of the separability of the solids, i.e., inducing aggregation of particles [142].

The most important decision in such instances is point of chemical addition and dosage of chemical. For this reason, the selection of chemicals deserves great interest, be it for the optimization of the clear water quality or of the sludge characteristics or for reasons of operational reliability and robustness.

As will become clear from the following discussion, the various chemicals available to the operator of the wastewater treatment plant have significantly different effects and also significantly different consequences for the overall purification process. Therefore, it is necessary to describe briefly each of the chemical types used today [8–10].

3.1 Types of Chemicals Used

There are basically inorganic, mostly metal salt-type, chemicals and organic, mostly polymeric, chemicals used in today's water technology [5, 143].

Inorganic chemicals that might come into closer consideration are:

1. Calcium (salts)
2. Iron III (salts)
3. Aluminum (salts)

In addition to this clay type, substances are used to support the aggregation process, such as bentonite. These clay-type suspensions might either cause co-coagulation (i.e., a positively charged suspension is coagulated by a negatively charged sol) or improve the reaction kinetics. The latter phenomenon is explained by an increase in particle number and also by an increase in particle collision per unit time.

Organic coagulants—or better—flocculants are of the type:

1. Low-molecular-weight substances with (opposite) charges
2. High-molecular-weight material adsorbing on oppositely charged surfaces
3. High-molecular-weight material adsorbing on surfaces with a charge of the same sign (possibly due to some intermediary reaction)

3.2 Differences in Reactivity of Coagulating and Precipitating Chemicals

3.2.1 Calcium

1. Effects: coagulation due to counter-ion effect (precipitation of calcium is negligible)
2. Remarks: no problems with overdosing, high amounts of chemicals needed, higher pH values used in actual operation, larger amounts of solids (sludge) are produced, dewatering of these solids is not too problematic

3.2.2 Fe(III)/Al

1. Effects: counter-ion coagulation at lower pH values and surface charge reduction (coagulation) at higher pH values of about 5–7. At even higher pH values, hydroxide precipitation will occur.
2. Remarks: at low pH values, the necessary dosage is relatively low, at intermediate pH values, the system is very pH sensitive but very effective in terms of necessary dosing, at higher pH values, large amounts of chemicals are needed for

the precipitate formation. Overdosing in a sense of decreasing effectivity at increased dosage rates becomes a problem when the system is to be operated at intermediate pH values. The amount of solids forming and the problems in dewatering the resulting sludge are large when the system is operated at the hydroxide formation stage while at all other conditions these aspects are non-problematic. Fe(II) is a less-efficient coagulant. However, if oxidized or oxidizable, it is an economic one.

3.2.3 Polyaluminum

1. Effects: change of surface charge through adsorption of highly charged low-molecular-weight hydroxo complexes
2. Remarks: conditions for application as above for Fe(III)/Al at intermediate pH values, pH sensitivity less pronounced.

3.2.4 Polymers

For cationic, lower molecular weight, the effects and remarks are:

1. Effects: modification of surface charge through adsorption of material
2. Remarks: close similarity to (inorganic) polyaluminum in dosing requirements and effects

For cationic, high molecular weight, the effects and remarks are:

1. Effects: bridging through adsorption of long-chain molecules at more than one particle surface
2. Remarks: very low dosage requirements, the pH regime must be closely controlled, when overdosing occurs then the sign of the (charged) surface charge is reversed and restabilization begins, aggregates formed are voluminous and frequently show unsatisfactory dewatering properties.

For anionic, high molecular weight, the effects and remarks are:

1. Effects: bridging between particles that frequently carry a charge of the same sign, intermediary reactions with other constituents of the dissolved phase is assumed (for instance with Ca^{2+}).
2. Remarks: very low dosage requirements, the pH regime must not be controlled as closely as described above since charge variations do not have such effects, similarly dosing must not be controlled as accurately as above mentioned, solids (sludge) characteristics as mentioned above.

For non-ionic, high molecular weight, the effects and remarks are:

1. Effects: bridging between particles (see above).
2. Remarks: pH effects completely disappeared (for practical purposes), all other conditions as above described.

3.2.5 Summary in Terms of Flocs Strength

1. Strong: polymer flocs in general
2. Medium: counter-ion coagulated aggregates formed due to hydroxo complex adsorption, similarly flocs formed on the basis of low-molecular-weight polymer adsorption
3. Weak: enmeshment in hydroxide precipitates

3.3 Coagulating and Precipitating Aids

In practice, flocculating reagents are frequently employed not separately and independently but in conjunction with coagulating chemicals. In this instance one postulates that the mostly inorganic coagulants initiate the aggregation process leading to the formation of small flocs. The organic flocculants lead the process of aggregation to the formation of very large (for instance visible) flocs and therefore aid the coagulation process.

This practice is coupled very often with a delayed dosing of the coagulant aid, such that the initiation of floc growth is well on the way.

3.4 Chemical Selection in Practical Applications

The basic principles of reactivity of the different chemicals have been described before. The following remarks are intended to serve predominantly the operator of a coagulation/flocculation plant. Under conditions of day-to-day operation, it is important to know how sensitive the process reacts to fluctuations in dosage or how stable the aggregates are with respect to shear stress, etc. This is to be described in brief in the following paragraphs.

3.4.1 Calcium/Ca^{2+}

1. Effects (mechanisms): coagulation due to counter-ion presence; to a reduced extent also calcium hydroxide precipitation.
2. Remarks: high pH values are required, higher dosages are necessary, larger amounts of solids are produced (i.e., sludge produced).

3.4.2 Iron(III)/Fe^{3+} and Aluminum/Al^{3+}

1. Effects (mechanisms): (a) at pH values below 4 coagulation due to counter ion presence; (b) at pH values below 6–7 coagulation due to surface charge compensation from the adsorption of hydroxo complexes; and (c) at pH values where

precipitation occurs, i.e., pH 6 for Fe(III) and pH 7 for Al, there will be an enmeshment of particles into precipitates.
2. Remarks: for case (a), lower dosages required and no problem with overdosing; for case (b), very low dosages required, very high pH sensitivity, significant problem when overdosing occurs; for case (c), higher metal ion dosages necessary, no problem of overdosing if pH values are kept in the range of hydroxide precipitation.

3.4.3 Polyaluminum

1. Effects (mechanisms): coagulation due to surface charge compensation, which is adsorption of polynuclear aluminum hydroxo species.
2. Remarks: (a) Very low dosages required; (b) Significant problem with imprecise dosing; (c) Lesser pH sensitivity than in case of in situ formed aluminum hydroxo complexes.

3.4.4 Polymers

For cationic polymers (lower molecular weight), the effects and remarks are:

1. Effects (mechanism): coagulation due to surface potential chance from the adsorption of highly charged species
2. Remarks: operating conditions as for polyaluminum or aluminum-hydroxo complexes

For cationic polymers (high molecular weight), the effects and remarks are:

1. Effects (mechanisms): bridge formation due to the adsorption of long-chain polymeric substances onto more than one suspended solution
2. Remarks: (a) There is a definite pH optimum; (b) The problem of overdosing still exists and results in this case from high degree of surface coverage at higher polymer dosages; (c) The resulting (three-dimensional) floes cause voluminous amounts of sludge; (d) The sludge handling properties of the separated solids are frequently not very satisfactory.

For anionic (mostly of high molecular weight), the effects and remarks are:

1. Effects (mechanisms): bridging supported most likely by surface chemical reactions of calcium or magnesium ions, present in the aqueous phase, leading to a reduction of charge and/or adsorption of the oppositely charged polymers.
2. Remarks: (a) Slight pH dependence (lower than in case of cationic polymers); (b) Dosing sensitivity less evident than in case of cationic polymers; (c) Due to unknown mechanisms process not in all instances successful.

For non-ionic (mostly of high molecular weight), the effects and remarks are:

1. Effects (mechanisms): bridging due to adsorption of longer chain molecules at more than one surface

2. Remarks: (a) Next to no pH effect; (b) All other conditions as described for high-molecular-weight polymers.

3.5 *Simultaneous Coagulation and Precipitation*

Coagulation is the formation of larger aggregates from solid substances, i.e., no change in phase. Precipitation, the formation of solid, non-dissolved species, implies a phase transition. In chemical terms coagulation and precipitation are distinctly different processes.

In wastewater systems, however, in particular when metal ions (metal salts as coagulants) are used, both processes might occur simultaneously. To what extent these two different processes occur and with what reaction rate they proceed depend upon the composition of the dissolved phase. This dissolved phase is very complex and changing in its nature in wastewater systems.

In particular, in the presence of phosphate ions, for instance, precipitation will prevail. If for instance the hydroxide ions predominate, then metal hydroxides will be primarily formed. Under conditions of intermediate pH values, dissolved hydroxo complexes will be formed leading to coagulation.

All pathways will be followed simultaneously but to a different extent and with possibly different reaction rate. And, furthermore, there are chances from one pathway to another, if the chemical situation does allow this. Such switches are illustrated by the possibility or even necessity to complete a precipitation step in practice by coagulation or flocculation step.

3.6 *The Role of Adsorption*

Chemical addition in this discussion leads by definition only to a chance of phase or to aggregation/fIoc formation. It does not allow per se the elimination or modification of substances that do not precipitate or coagulate. However, in practical applications, one has observed that constituents of the dissolved phase that do not belong to either of the above-mentioned categories are also reduced in their concentration. The most plausible explanation is a *sorption process* which is favored by the very large specific surfaces formed for instance in metal hydroxide precipitation [8, 144, 145].

It is reasonable therefore to expect such adsorption processes to occur in situations where solid surfaces are formed or reformed and where surface-active species are available (as is the case in wastewater). Examples of such elimination by adsorption onto coagulated solids are heavy metal removal or DOC reduction in wastewater systems treated with coagulants.

4 Types of Process Reactors

4.1 Plug Flow and Completely Mixed Continuous Flow Reactors

In order to understand what is happening in real aggregation reactors, as well as in flotation units, it is expedient to define two *ideal* or extreme situations of reactor dynamics or reactor flow [8, 146]: plug flow (PF) and completely mixed continuous flow reactors [8, 147].

The PF reactor distinguishes itself by the fact that no mining takes place between neighboring (fluid) elements. They move independent of each other through the reactor. Such reactors are, for instance, tubular reactors or rivers (from certain points of view) or the reaction chambers preceding the so-called *auto-analyzers*.

The completely mixed continuous flow (CMCF) reactor ideally is the very opposite of the plug flow reactor; here each additional fluid (or reacting) element is, upon entering the reactor, immediately completely mixed with all other elements that entered this reactor earlier. Examples of such reactors are equalization or neutralization basins or also activated sludge reactors if designed as completely mixed units.

The behavior of these reactors can also be illustrated by recording the movement of a tracer substance through the system. Such tracer materials are usually not dosed continuously but rather added on an *impulse* or pulse basis.

Quite clearly such a pulse moves by definition unchanged through the PF reactor since there is no mixing with neighboring elements and therefore no dilution (if one assumes that no other reaction takes place). If one envisions a tubular reactor with one port for tracer addition and another one for sampling, then the time T elapsing until the slug of tracer appears (completely) equals the detention or reaction time in the system.

The CMCF reactor shows a very different characteristic [147]. Here the slug of tracer is, upon entering, immediately mined with the total content of the reactor. All fluid (or reacting) elements entering later will be mixed in completely and lead to a *dilution* of the tracer in the reactor. The tracer concentration monitored at the outlet of the reactor will therefore decrease with time. It can be shown that the concentration change follows an exponential decrease. Similarly, as for the decay of a radioactive substance one can formulate a half-life time. One can monitor for this concentration and determine in this way the actual detention or reaction time of the system.

If one superimposes a reaction rate over the hydraulic characteristics of these systems, then again there will be differences in the progress of the reaction for different times. For illustration's sake, a first-order reaction rate process is assumed.

$$\mathrm{d}/\mathrm{d}t\left(n\right) = -k \cdot n,$$

where

n = particle or chemical agent concentration
k = reaction rate constant
$\mathrm{d}/\mathrm{d}t$ = derivative with respect to reaction time

In a PF reactor, this reaction will proceed to an extent that can be predicted from the integrated rate law.

$$N_t = N_0 e^{-kt},$$

where

N_0 = particle or reagent concentration at time $t = 0$
N_t = concentration at time "t"
$t = L/v$ time elapsed between two points of tubular reactor

If one draws this curve as function of the reaction time one finds a logarithmic decrease in the final concentration with increased reaction time.

In a CMCF reactor, the same reaction will proceed differently; in particular, the reaction endpoint after specified reaction time has elapsed will change in a different way from the above reactor. Or in other words, increase of reaction time will lead to different results in terms of reaction end point in the CMCF reactor.

The effect can be seen from the following mass-balance equation:

$$\text{Inflow} - \text{Change Due to Reaction} - \text{Outflow} = \text{Overall Change},$$

and for a steady state equilibrium with the assumption of no overall-change one finds:

$$QN_\mathrm{i} - kN_\mathrm{e}V - QN_\mathrm{e} = V\,\mathrm{d}N/\mathrm{d}t,$$

where

V = volume
Q = rate of flow through the reactor
N_i = influent concentration
N_e = effluent concentration (also corresponding to the concentration within the reactor)

Frequently, for technical systems, there is a steady state for which one then finds $\mathrm{d}N_\mathrm{e}/\mathrm{d}t = 0$ and consequently

$$N_\mathrm{e} = N_\mathrm{i}/(k_t + 1).$$

The effect of prolonged reaction or detention time upon the reaction end point is significantly different from the logarithmic one for the PF reactor.

4.2 Detention Time Characteristics in Real Reactors

The reactors distinguish themselves by different stirring and possibly by the existence of baffles, etc. The effluent concentration changes in a different way in both reactors if measured with time.

In the instance of the reactors without stirring and baffles, the effluent concentration is for a longer period of time close to zero; then it increases rapidly to higher values, and finally it drops rather rapidly again to zero. The pattern resembles the PF reactor characteristics.

The intensively stirred reactor (without baffles) shows an immediate reading on the effluent concentration scale. This reading or concentration is reduced monotonously with increased time. The pattern very much resembles the CFCM reactor characteristics.

It is important to note that neither pattern completely repeats the characteristics of the two ideal reactors discussed above. Furthermore, it should be mentioned that it is very difficult to design reaction chambers such as neither one of the ideal reactors results or is approached (with the exception of the pipe flow reactor).

The actually observed detention time distribution can be explained in qualitative terms as a combination of plug flow reactor and continuous flow completely mixed reactor. In some instances, it was possible to describe a real reactor (i.e., observations on the so-called *displacement curves*) in quantitative terms as a combination of PF and CFCM reactors. Such combination entails arrangements of several reactor units in series and in parallel.

For practical design (and operation), the following recommendations may be made on the basis of the above-described phenomena. The detention time distribution is affected by:

1. Flow rate relative to volume
2. Energy dissipation in the reactor (relative to the energy introduced with the throughput)
3. Stirrer type and geometry (relative to the reaction chamber)
4. Inflow and outflow configuration (relative to the geometry of the reactor)
5. Compartmentalization of the reactor
6. Baffles and other flow directing devices in the reactor (relative to the reactor geometry)

In the past, these parameters have not been controlled closely or extensively, whether in the phase of reactor design or for the repeated optimization during operation. This is true for both types of application, aggregation reactors and flotation reactors. Frequently, a *sweeping* effect of chemicals used in the aggregation reaction and the flotation reaction has masked possible problems resulting from non-optimal design (and operation). Yet, presently it appears necessary and also possible to exploit reactor dynamics more extensively in order to save chemicals or to attain higher degrees of efficiency.

4.3 Recommendation for Stepwise Design of Coagulation/Precipitation and Flocculation Reactors

1. The design objective is for instance a reactor that converts a known suspension (i.e., of known average particle diameter) into one with a larger diameter in order to guarantee removal by a liquid–solid separation process such as sedimentation or flotation.
2. In the next step, experiments of an exploratory nature are to be performed which should show the possibilities for aggregating the suspension (and the necessary type and amount of chemicals).
3. Then from the idealized rate law, an estimate is made for the necessary detention time and the required power input. Both parameters must only be estimated within certain ranges. They are also interdependent: a high energy input will lead to a lower necessary reaction time and vice versa. Estimates for these parameters can also be taken from the literature.
4. Now the reactor geometry has to be determined (after the overall size has been set by the determination of the detention or reaction time). This should and can only be done by "scale-model" experiments. By such experiments, all effects will be evaluated.
5. It is important to point out that the scale-up of these models is difficult and critical and that there exist no rules for this scale-up. Depending upon the situation, one can choose between various dimensionless or characteristic numbers, such as the Froude number or the Reynolds number (for the reactor or the zrelated scale-up number [148].
6. Finally, it must be stated that jar test-type experiments on the potential for aggregation of the suspension should be used to optimize the operation. Such optimization will be necessary again and again if the characteristics of the influent suspension will change. The analysis can also help to overcome possible shortcomings of the design.

5 Products of Aggregation: The Liquid Phase

The process of aggregation, i.e., formation of larger (better separable) solids from small suspended solids, has traditionally been designed and operated to ensure a maximum efficiency in terms of aggregate growth. Aggregate growth means increase of average particle diameter and therefore better removal in all liquid–solid separation.

In many instances of practical application of this process, one has accomplished this goal but also obtained large amounts of solids that cause great difficulties in separation and dewatering. Thus, today one will have to design and operate the aggregation process such that both products, the liquid phase (i.e., the original focus in design and operation) and the solid phase (i.e., the sludge to be expected), will correspond to certain standards.

There is much experience and experimental evidence available for the optimization of the aggregation process in order to obtain a very good clear water quality. This will be presented and interpreted in the following paragraphs. The second objective, i.e., to produce not too large amounts of separable and treatable sludge, is presently the aim of several laboratory and technical investigations. The little evidence available for the optimal setting of design and operational to attain this goal is to be presented in the next chapter.

5.1 The Average Quality of the Liquid Phase

Aggregation accomplishes the formation of larger suspended solids from small suspended material. It has been pointed out earlier that in wastewater systems aggregation frequently is initiated by the addition of metal ions (metal salts). Thus, depending upon the composition of the dissolved phase, there will be more or less pronounced precipitation of substances that form insoluble complexes with the added metal ion (for instance, Me-phosphate).

When discussing the efficiency of the process in terms of clear water quality, then one has to bear in mind that only aggregating and precipitating substances will be affected. It has also been indicated earlier that there is adsorption onto the freshly formed solid surface when aggregation and precipitation processes occur. Thus, also adsorbing substances will be affected in their concentration by this process.

At the same time, it must be pointed out and emphasized that none of the constituents of the dissolved phase of a wastewater system will be removed or altered if those substances are not amenable to precipitation and/or adsorption. Nitrogen species are a case in point. They will not be removed in any instance of chemical dosing that has been described here.

For practical purposes, one can conclude that the addition of coagulating and precipitating chemicals leads to: (a) reduction of non-dissolved substances (nearly completely); (b) reduction of dissolved matter of mostly inorganic anionic nature (with high degree of efficiency); and (c) reduction of dissolved organic matter that precipitates and/or adsorbs (with medium efficiency).

It is important to point out that any quantitative information on removal efficiencies or on effluent quality can only and must be problem specific. There are so many interfering reactions that it is difficult to predict for an unknown or un-investigated wastewater system the type and extent of all processes that might occur. A general listing of process efficiency data that might be desirable for the design engineer is not possible. However, one can inspect efficiency data reported in the literature, evaluate and discuss them within the context of the specific situation, and derive from these orders of magnitude for the process efficiency to be expected.

The progress of the process is measured in agreement with the above-described principles in terms of (a) turbidity reduction and/or (b) reduction in filter residue and/or (c) decrease in the concentration of specific ions (e.g., phosphate, heavy metals), and/or (d) decrease in biochemical/chemical oxygen demand (filtered or unfiltered sample).

These are by far not at all parameters that one would select on the basis of the known process efficiencies. However, routine analysis during (treatment) plant operation usually does not allow more specific investigations, such as chance in particle size distribution (very specific for the description of this process) or reduction in specific organic substances.

Furthermore, it must be pointed out that from a practical point of view such parameters should be listed in more than one dimension, for instance, as: (a) first statistical moment (mean, etc.) of distribution of effluent concentrations and/or (b) second statistical moment (standard deviation, etc.) of distribution of effluent concentration and/or (c) similar measures for (relative) concentration reduction in the effluent.

Each measure will describe a different aspect of process efficiency and operation. And each might be of particular importance under different conditions.

5.2 The Selection of Physical Parameters in View of Optimal Quality of Liquid Phase

The exact description or analysis of the physical parameters under conditions of plant operation is not only difficult but rarely done. Thus, more theory-oriented measures have to be translated into practical terms. In most instances, the following conditions will show good to optimal results:

1. Intensive mixing of coagulation/flocculation chemicals with energy input values significantly greater than s^{-1}. In this phase, even high stirring rates/energy input will not cause negative effects.
2. Floc or aggregate preserving stirring of lower intensity with a magnitude of 100–200 s^{-1}. Here, the material to be aggregated will influence the absolute size of the energy input that should be considered optimal. It is also conceivable to adjust the energy input in this phase to the changing floc quality. This is done in practice by reducing the stirring speed in two or more steps in subsequent reactor compartments.
3. Reaction times necessary in the phase of chemical addition is mostly less than 1–2 min at maximum. Reaction times in the stage of aggregate growth, depending upon the energy input, they can range from 2 to 20 min. Here it must be pointed out that increased reaction time will lead to higher process yield, i.e., better floc growth. Yet, larger flocs are more susceptible to destruction in shear flow. Increase of reaction time must therefore always be seen in conjunction with the actual energy input (expressed as energy dissipation per unit volume reactor space).

4. A combined optimization of energy input and reaction time (i.e., the product of Gt) has proven useful for practical purposes.

These practice-oriented recommendations for the setting of physical parameters usually lead to optimal aggregates growth, i.e., optimal quality of the liquid phase after separation of the aggregates. As will be described later (see Sect. 6), such settings must not necessarily lead to a solid phase that has good qualities in terms of sludge handling, i.e., sedimentation/flotation or thickening or dewatering.

5.3 Actual Plant Efficiency Data as Reported from Process Operation

As indicated above, the use of precipitating or coagulating chemicals is always then commendable when the following wastewater constituents are to be controlled: (a) suspended solids, which are registered in the parameter turbidity or filter residue and (b) suspended or dissolved adsorbing organic substances, which are registered in the parameter BOD or COD, and (c) dissolved inorganic substances with the metal ion.

This practical limitation of the process to the control of only some wastewater constituents has been documented in practice in the treatment of textiles industry waste [149], dairy wastewater [150], and the removal of impurities from seawater [151]. It has also been shown that there are always several processes occurring at the same time when metal ions (or coagulants) are added to a wastewater system. As stated before, it depends upon the relative preponderance of the specific wastewater constituents, which specific reaction pathway is favored.

When discussing process efficiency in real system, it is also necessary to point out that coagulation/flocculation and the competing precipitation process depend on their success upon the subsequent step of liquid–solid separation. Thus, in all discussions, it is assumed that there is an optimal unit process of solids separation available.

Furthermore, one must be aware of the limitations of the process in terms of not controlling non-adsorbing or non-precipitating or non-coagulating substances. One group of wastewater constituents that is discussed intensively in wastewater pollution control is the nitrogen compounds. Dosing chemicals that cause precipitation/coagulation will not significantly affect the concentration of any nitrogenous substance even if liquid–solid separation is an optimal one.

The comparison of plant efficiency of a mechanical biological plant built to the standard of “generally available technology” with efficiency data for such a mechanical biological plant that is supported by chemical dosing is given in the literature [3, 16, 17]. It is very clear that the addition of chemicals leads to a significant increase in the quality of performance.

In addition to the absolute increase in the removal or reduction rate of undesirable waste water constituents, there is also an increase in the stability of the performance, i.e., a reduction in the scattering of the efficiency data when chemicals are used. Cumulative frequency distributions obtained for plants with chemical dosing show a much steeper line, i.e., a lower standard deviation than those lines obtained or observed with mechanical biological treatment alone.

The observed improvement of plant performance, i.e., the reduction in fluctuations of the effluent concentrations results from two phenomena: (a) Inflow fluctuations are dampened by the frequently flow-proportional operated chemical dosing and (b) the process of precipitation/coagulation allows a rather rapid response to known or anticipated load fluctuations such as from stormwater run-off, etc.

This possibility of stabilizing or equalizing the plant effluent is by far not yet realized to its utmost. The automation of this particular process is at best at its beginning. Contrary to the traditional biological processes, this chemical process is described and controlled by analyses that are readily and rapidly feasible. And there is already some experience in such plant control.

Finally, it should be pointed out that all other reactions in the course of the wastewater treatment process will profit from the addition of a treatment step that leads to load reduction and to an evening-out of load fluctuations. Thus, the overall plant performance of such plants where chemicals are used for precipitation/coagulation is more than linearly improved.

6 Products of Aggregation: The Solid Phase

It has been pointed out in the preceding section that there is a new focus in wastewater treatment on *simultaneous optimization of the quality of the liquid phase and the solid phase*. This means that a process is no longer operated such that the effluent quality is optimal without consideration for the amount and characteristics of the resulting solid phase. Today, one rather selects a specific output quality for the liquid phase, the ‘necessary condition’ to be observed in the operation, and then optimizes the process such that the resulting solids are easily separated, thickened and dewatered.

If one looks at the process of aggregation (and liquid-solid separation) in a more basic way, then one understands that the amount and quality of solids produced depend on a significant degree upon the kind of chemical added (including the solvent used for dosing the chemicals) and also the more physical conditions of mixing energy and aggregation promoting. It is clear that these are design and operation variables that will affect or even control the solid phase produced by the processes discussed here.

6.1 Amounts of Solids Produced

The amount of solids produced—in the terminology of the operator the "amount of sludge produced"—depends upon: (a) the (mostly solid) wastewater constituents removed; (b) the amount of chemicals (added and) removed with the formed aggregates; and (c) the water (from chemicals dosing and from the waste water phase) incorporated into the aggregates that are removed.

One can formulate a *mass balance* on the basis of this observation. Such a mass balance would read as follows:

$$\begin{array}{lclclcl} \text{Total} & & \text{Most of} & & \text{Substances} & & \\ \text{amount} & = & \text{chemicals} & + & \text{eliminated} & + & \mathrm{H_2O} \\ \text{of solids} & & \text{added} & & \text{from water} & & \\ \text{generated} & & (90-99\%) & & (\mathrm{N,PO_4}) & & \end{array}$$

or in more mathematical terms:

$$\text{Volume} = f(\text{solids, water})$$

or

$$\text{Volume} = f(\text{absolute amount solids, solid content}).$$

The absolute amount of solids incorporated into the sludge is readily determined from the difference between inflow concentration of those substances that are affected and their respective effluent concentration. These parameters are routinely monitored in any plant operation.

Furthermore, the amount of chemicals added and not discharged with the process effluent is to be included into the solid balance. In most practical situations, the amount of coagulant remaining in the treated water is not monitored (with the exception of water purification technology in the field of drinking water supply). Here one will have to rely on estimates of the amount of chemicals incorporated into the aggregates. As indicated above in the verbally formulated mass balance, this fraction is very high and can be estimated for all practical purposes to be about 90–95%.

The second variable listed in the functional description (or prediction) of the sludge volume is the solid content. This is certainly the most sensitive parameter and also the most difficult parameter to be determined. However, solid content is a standard parameter for the characterization of sludge quality. Thus, it is determined on a routine basis. There is a large amount of empirical evidence available in the literature. It was observed that [5, 8]: (a) the solid content depends upon the amount of chemical (and the type) added; (b) the solid content decreases with increasing amounts of the most frequently used iron or aluminum salts; (c) the solid content can be improved if the inorganic coagulant is substituted in part by organic coagulant (aid) or more precisely called ‘flocculation’; and (d) the absolute size of the solids content is lower than that of the so-called primary sludge and in the same order of magnitude as that of the secondary sludge.

With these two variable sets, one can attempt a prediction on the amount of sludge to be expected when chemicals are added to improve the performance of a wastewater treatment process. The quality of such prognoses by showing for comparison’s sake the actually observed sludge volume. The prediction is undoubtedly satisfactory. (One must point out that the measurement of the second parameter entering the above-described function, the solid content, is not easily reproduced, i.e., yields fluctuating results.)

6.2 Sludge Characteristics

There are four coals in sludge treatment in the realm of waste water technology: (a) volume reduction (sedimentation or flotation); (b) stabilization (here not considered); (c) dewatering (by belt or filter press); and (d) disinfection (here not considered).

These requirements for the ultimate sludge usage or deposit are attained by different unit processes. For all these processes, the volume and the characteristics of the sludge are decisive. Thus, in addition to the prediction of the sludge volume to be expected, the average qualities of this sludge fraction must be known in order to design and operate sludge handling installations. The most important processes prior to the incineration of chemical sludge are thickening and dewatering. Thus, parameters describing the thickening properties and the dewatering characteristics must be known or assessed.

Prior to the presentation of average quality parameters for the sludge it is necessary to state that in most practical instances the chemical sludge is not treated separately from the primary and secondary sludge. Thus, the properties of the sludge fractions to be treated are only in part determined by those of the here discussed chemical sludge fraction.

Furthermore, it must be said that there are numerous possibilities to design a sludge handling installation, due to the larger number of phases in the treatment process and due to the great diversity of unit processes available to accomplish these goals. The above-mentioned survey has produced results that indicate the existence of more than 25 distinctly different variations. Again, it is not possible to present data or information that could be considered representative or indicative of standard conditions. The data to be given in the following paragraphs are intended to serve as illustration.

The survey also led to the insight that there is no uniform and predictable chance in the sludge properties when precipitating/coagulating chemicals are used. If one analyzes the data from this survey in great detail, then one finds the operational conditions as well as the process of liquid–solid separation determine not only amount but also the properties of the resulting solids.

The sedimentation properties of the wastewater solids are changed by the addition of chemicals. Since the velocity of sedimentation depends upon the specific gravity of the suspensor as well as upon the density/porosity of the aggregate, it is reasonable to postulate that so-called primary, i.e., non-aggregated particle sediment more rapidly than hydroxide flocs or composites of hydroxide and biological flocs. The reason is the increased inclusion cf water into the solids aggregate. The worsening of the sedimentation properties as a rule are paralleled by an improved floatability of these aggregates of biological and chemical sludge particles.

There is one exception to this worsening of the sedimentation properties upon the addition of chemicals. This is the use of inorganic reagents, i.e., metal ions to combat bulking sludge. In this instance, the velocity of separation by sedimentation is increased. Bulking sludge might be controlled better by the use of flotation as standard liquid-solid separation process, however.

One must also take into consideration, when discussing liquid–solid separation by sedimentation, that the use of chemicals leads to an increase in the removal of suspended solids. Thus, one could expect increased sludge volume indices for the biological excess sludge when pre-precipitation/coagulation is used: here all particles that might be enhancing the specific gravity of the biological floc have been removed in the preceding step. Plant observations have indicated that this effect exists but is of no great significance.

From the discussions on the principles of the process, it becomes clear that one has to distinguish between the different points of application. The following conclusions are of particular importance for the design and operation of treatment plants: (a) any addition of chemicals prior to or into the primary sedimentation tank, i.e., pretreatment leads to increased sludge volume after 120 min sedimentation time, i.e., reduced sedimentation velocity; (b) a similar decrease in the sedimentation velocity with increased chemical dosage has been observed, when chemicals are dosed past the biological unit, i.e., posttreatment; and (c) only in the case of dosing chemicals prior to or into the secondary sedimentation tank (i.e., simultaneous treatment), there is an improvement of the sedimentation velocity.

Note: it is not possible to conclude from this that there is necessarily an improvement of the flotation tendency when the sedimentation characteristics are worsened.

Another interesting and promising operational measure to control sludge handling properties is the variation of the stirring rate and stirring time. The literature [18] shows data from operating plant and pilot plant studies, where the separation characteristics (i.e., the settled volume after 120 min) are improved if the energy input is increased.

The Camp number can be increased either by intensifying the energy dissipation, usually done by increasing the rotational speed of the stirring device, or by increasing the stirring time or the residence time. Investigations on the effect of varying the stirring rate and keeping the detention time constant have shown the feasibility of this concept.

A possible explanation of the effect of increased CAMP numbers might be the destruction and recombination of aggregates in reactors with high detention times and/or with high shear rates. It is known that upon destruction and recombination denser aggregates result. This increased density leads to increased floc stability, and also increased sedimentation velocity. A similar observation for a coagulation–flotation system does not exist. One might speculate, however, that increased aggregate strength will also further the robustness of the flotation separation (while the slight increase in specific gravity might easily be overcome by the correction of the air–solid ratio).

The next phase after solid separation is the sludge thickening, i.e., a separation of the water that is included in between the individual particles that form an aggregate. Thickening might well be the most decisive process in the whole line of sludge handling: malfunctioning thickeners lead to reduced volume reduction and by this to a (volumetric) overloading of all subsequent processes. Thickening has been accomplished in the past by sedimentation technique. Here, however, the flotation process [19] has entered the field, competed successfully and in part substituted the gravity thickeners.

Thickening properties, i.e., separation of included water fractions could be quantified by the same measures as those used to describe the liquid–solid separation. In this discussion, the solid content of the thickened sludge (after a defined and constant time of thickening) has been selected for the description of these properties. The change of the thickening properties, i.e., solid content, as a consequence of changed operational conditions has been studied and observed that [19]: (a) the less water containing primary sludge reaches the highest end concentration of solids—corresponding to a medium, volume reduction; (b) the secondary sludge with usually high water content also reach very high-end concentration of solids—corresponding to a very high volume reduction; and (c) the tertiary sludge with the usually high water content reaches a lower-end concentration of solids—corresponding to a medium volume reduction.

Decisive factors for these changes are among others the (a) organic content, (b) chemical content, (c) average particle size, and (d) three-dimensional floc network of the sludge. Naturally, it is very difficult to quantify these effects or even to explain observation evidence for the correctness of these statements and therefore for the usefulness of recommendations, that are based on these parameters.

After separation of solids and thickening of the sludge, the solid fraction usually has to be dewatered further for reasons of transport, for the building-in in landfills and for incineration (if applicable).

Dewatering properties are also difficult to evaluate. As in other unit processes, there is a discrepancy between the concept of the process and the feasibility of analysis. In the case of sludge dewatering, two types of analysis have proven useful: (a) the measurement of a specific filter resistance (higher analytic effort, better interpretation of process) and (b) the measurement of a capillary suction time, the time that pore water leaving the filter cake needs to move in a defined filter paper over a specified distance (easily determined but difficult in process-oriented interpretation).

The result of technical and pilot plant-type investigations shows the change in the capillary suction time for varying chemical dosage and for the three different points of application of chemicals [19]. It is seen that: (a) in all instances, the capillary suction time is reduced, i.e., the dewatering quality improved, when more chemicals are added; and (b) the improvement of the dewatering characteristics upon increased chemical dosage is most pronounced in the instance of tertiary sludge, i.e., sludge from post-precipitation/coagulation.

Such improvement might have been anticipated in the case of precipitation/coagulation with metal ions. These reagents have been used successfully in the sludge treatment process for the so-called chemical conditioning: the addition of these chemicals prior to a dewatering step has led to improved efficiency of almost any dewatering process equipment (vacuum filters, belt filters, filter presses, etc.).

7 Design Considerations, Performance Evaluation, and Process Management of Rapid Mixing, Flocculation, and Clarification

7.1 Rapid Mixing, Flocculation, and Clarification

Rapid mixing and flocculation are used in series to optimize chemical treatment of wastewater. Rapid mixing is done in a small tank with a mechanical mixing device. Sometimes the mixing is done with other equipment such as baffled channels, hydraulic jump mixers, pneumatic (compressed air) mixing, or in-line static mixing devices. The most common type of mixing device is the rotating turbine mixer; propellers are normally used for small volumes, such as the mixing tanks in chemical feed systems. Paddles are usually used for flocculation agitation.

Flocculation helps the suspended particles to stick together to make larger clumps of particles, known as flocs, which will separate out easily in either sedimentation clarifiers or dissolved air flotation clarifiers. Flocculation is usually done by controlled agitation or slow mixing of the coagulated wastewater in a tank which contains mechanical agitation devices such as rotating paddles, vertical turbines or vertical reciprocating mechanisms. The most common type used is the rotating paddle on a wheel equals 25% of the water depth of the basin, or the total paddle area is less than 15–20% of the cross-sectional area of the water (depth × width). The range of speeds at the outside edge of the paddles (peripheral speed) is 0.5–4 feet per second (fps). The flocculation of the suspended particles is caused by the small eddy currents that are formed at the trailing (back) edge of the paddles, turbine blades, or reciprocating caps.

Clarification is either gravitational settling or dissolved air flotation related to physicochemical processes. Chemical clarification almost always follows the rapid mix-flocculation steps.

7.2 Design Criteria

The principal criteria by which the rapid mixing equipment is sized are the velocity gradient, *G*, and the detention time. Once these have been selected, the type of mixer and impeller is selected, and the horsepower can be computed. Typical values for *G* and the detention times are given in Table 6.1. For these values, the horsepower averages about 0.5 HP per MGD (million gallons per day) for a turbine. The design for a 10 MGD rapid mixer is shown in Table 6.2.

The principal criteria for the design of the flocculation equipment are also the velocity gradient, *G*, and the detention time. The type of mixers used will depend upon the wastewater and process flexibility. The flocculation basin is typically divided into 2–4 zones, each with a different *G* value. Typical *G* values for a three zoned system are 100, 60, and 20, with the percentage volumes for the respective zones of 30%, 30%, and 40%. Velocities through the flocculation basin should range from 0.35 to 1 ft/s. Detention times for flocculation typically range from 20 to 40 min. The design criteria for a 10 MGD plant flow are shown in Table 6.3. Flocculation velocity gradients for various applications are shown in Table 6.4. The clarifiers are sized on the basis of the overflow rate and detention time or water depth. The overflow rate for the sedimentation clarifiers is based on the chemical coagulant used. Typical design values for sedimentation clarification of a lime-treated wastewater for a 10 MGD plant flow are shown in Table 6.5.

Table 6.1 Velocity gradients (*G*) for rapid mixing (USEPA) 1 fps/ft = 1 mps/m

Application	*G* fps/ft or s^{-1}
In-line, instantaneous blending	3000–4000
Rapid mixing	
20 s contact time	700–1000
30 s contact time	650–900
Longer contact time	500–700

Table 6.2 Typical design for a 10-MGD rapid mixing process unit (USEPA).
1 feet = 1 ft = 0.3048 m;
1 inch = 1 in = 2.54 cm;
1 ft^3/min = 0.0283 m^3/min

Detention time at maximum flow, minutes	1.1
Width, feet	11
Water depth, feet	8.5
Volume, cubic feet	1030
Propeller diameter, inches	38
Propeller capacity, cubic feet per minute	2060
Shaft speed, revolutions per minute	100
Motor horsepower	5
Velocity gradient, *G*, s^{-1}	360

Table 6.3 Typical design for a 10-MGD flocculator (USEPA). 1 cu ft = 1 cubic feet = 1 ft^3 = 0.0283 cubic meter = 0.0283 m^3

Detention time, minutes	45
Width, feet	30
Water depth, feet	10
Length, feet	140
Volume of tank, cubic feet	41,778
Mixing zones	
Zone 1, cu ft	12,500
Zone 2, cu ft	12,500
Zone 3, cu ft	16,788
Velocity gradient, *G*	
Zone 1, s^{-1}	100
Zone 2, s^{-1}	60
Zone 3, s^{-1}	20

Table 6.4 Velocity gradients (*G*) for flocculation basins (USEPA) 1 fps/ft = 1 mps/m

Application	*G* fps/ft or s^{-1}
Flocculation	
Tertiary wastewater	100[a] taper to 40
Turbidity/color removal—no solid recirculation.	100[a] taper to 40
Turbidity/color removal—solid contact reactors (5%—vol in suspension)	150[a] taper to 50
Softening—solid contact reactors (10%—vol in suspension)	200[a] taper to 100
Softening—ultra high solid contact (20–40%—vol in suspension)	400[a] taper to 250

[a] Drive layout should provide for alternate speeds, allowing selective downward variation from the maximum values shown

Table 6.5 Typical design for a 10-MGD sedimentation clarifier (USEPA). 1 MGD = 3.785 MLD; 1 gpd/ft^2 = 0.0408 m^3/day/m^2; 1 ft^2 = 0.092903 m^2; 1 ft = 0.3048 m

Type of coagulant	Lime
Number of tanks	2
Overflow rate, gpd/ft^2	903
Detention time, h	2
Total surface area, ft^2	11,083
Diameter of tanks, ft	84
Depth of tank, ft	10

7.3 Performance Evaluation

The rapid mix, flocculation, and clarification operations are typically considered together and are ultimately judged on the suspended solids and phosphorus removal efficiencies. Typical removal efficiencies have been determined and are shown in Table 6.6. A clarification process shown in Table 6.6 can be either sedimentation or dissolved air flotation (DAF).

To check these operations, the simple computations can be made, as shown in Sect. 8, Design and Analysis of a Combined Rapid Mixing, Flocculation, and Sedimentation Clarification. The equations used are shown in Table 6.7. For easier solution, the poser equations have also been presented in graphical form in Fig. 6.6. Table 6.8 gives correction factors.

7.4 Process Management of a Complete Physicochemical Process System

The recommended sampling and laboratory tests are shown in Fig. 6.7 for the rapid mix, flocculation, and sedimentation clarification operations. In case a dissolved air flotation clarification is used instead of a sedimentation clarification, Fig. 6.7 should be modified slightly as follows: (a) a dissolved air flotation (DAF) clarifier should be shown in Fig. 6.7 instead of a sedimentation clarifier; (b) sludge upflow to chemical sludge treatment processes (instead of sludge underflow to chemical sludge treatment processes); and (c) subnatant clarifier effluent to next main flow treatment process (instead of supernatant clarifier effluent to next main flow treatment process). Typically, the solid concentrations from a clarifier range between 1% and 2% for sedimentation clarification, and about 2–3% for dissolved air flotation

Table 6.6 Typical phosphorus removal efficiencies (USEPA)

		Range in percent removals	
Chemical coagulant	Application location	Without filtration	With filtration
Lime	Tertiary	95–97	97–99
Lime + ferric	Tertiary	96–98	98–99
Alum	Primary clarification	75–90	
Ferric chloride	Primary clarification	70–90	
Ferric chloride	Secondary clarification	83	
Ferric sulfate	Aeration basin	91	
Alum	Aeration basin	75–85	
Ferric chloride	Aeration basin	75–85	
Lime	Primary clarification	75–90	
Lime + ferric	Primary clarification	90–95	
Lime + ferric	Trickling filter efficiency	93.5	

Table 6.7 Equations used to evaluate rapid mixing and flocculation systems (USEPA)

Energy for mixing by mechanical means	
Water power = $P = G^2 V u$	Where
	P = water power, ft lb/s
	G = velocity gradient, s^{-1}
	V = volume of tank, cu ft
	u = absolute viscosity of liquid, lb s/sq ft
	$=2.089 \times 10^{-5}$ at 20 °C
Brake horsepower	
$P_H = \dfrac{P}{500 \times E_D \times E_B}$	E_D = drive efficiency, %/100
	E_B = bearing efficiency, %/100
	P_H = brake horsepower, HP
Substituting for constants	
Velocity gradient = 4589.4 P/V	
Flocculator paddle area	
$A = \dfrac{2P}{C_D r^3} = \dfrac{561.2 P_H}{v^3}$	A = paddle area, sq ft
	P = water power, ft lb/s
	C_D = drag coefficient = 1.8
	=mass density of liquid, lb s^2/ft^4
	=62.4
	r = relative velocity of paddles, ft/s
	=0.75 v
	v = velocity of paddle tip, fps

clarification. A complete physicochemical process system consists of chemical feeding/mixing, precipitation, coagulation/flocculation, clarification (sedimentation or flotation), filtration (sand, multi-media, DE, GAC, or membrane), and disinfection. The readers are referred to the literature [7–10, 73, 91, 109, 126, 128, 159] concerning the details of filtration and disinfection.

8 Design and Analysis of a Combined Rapid Mixing, Flocculation, and Sedimentation Clarification System

EXAMPLE 17: DESIGN OF A FIVE-MGD PHYSICOCHEMICAL WASTEWATER TREATMENT PLANT FOR PHOSPHORUS REMOVAL USING THE USEPA METHOD

Solution

1. Collect the required base information for the rapid mix, flocculation, and clarifiers.

   Plant flow rate = 5 MGD
   Phosphorus influent concentration = 10 mg/L as P
   Phosphorus effluent concentration = 0.6 mg/L as P

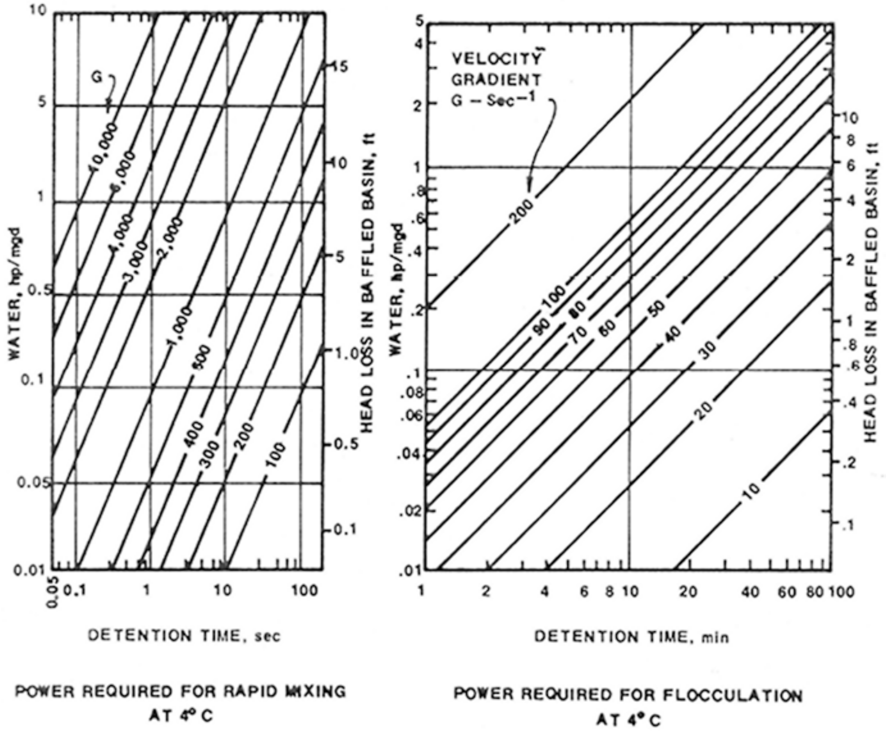


Fig. 6.6 Power requirements for rapid mixing and flocculation (USEPA). 1 hp = 0.7457 kw = 10.7 kg-cal/min; 1 mgd = 1 MGD = 3.785 MLD; 1 ft = 0.3048 m

Rapid mix tank dimensions = 2 tanks at 6′ × 6′ × 6′ water depth
Rapid mixer horsepower = 1 HP per tank
Flocculator dimensions = 2 tanks of 40′ × 20′ × 10′ water depth
Paddle area = 47 sq ft
Mixer horsepower = First stage = 2 HP, Second stage = 1/2 HP
Clarifier diameter = 60 ft
Number of clarifiers = 2
Depth of clarifier tank = 12 ft

2. Compute detention time and velocity gradient for rapid mix.
   Volume = 2 × 6′ × 6′ × 6′ = 432 cu ft

$$\text{Detention time} \quad = \frac{432 \times 7.48 \times 24 \times 60 \times 60}{5\ \text{MGD}}$$
$$= 56\ \text{s}$$

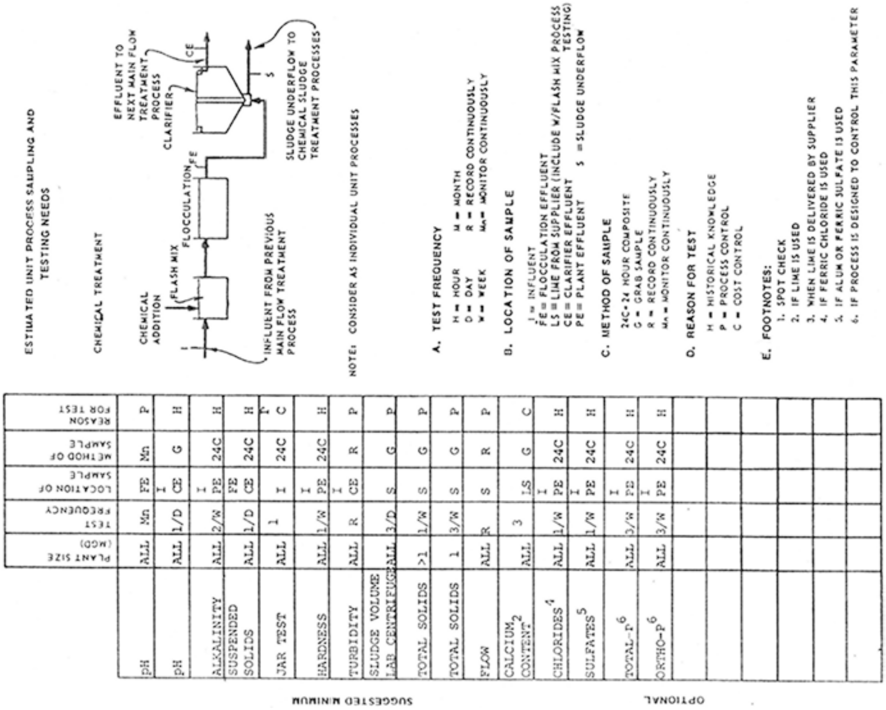
Table 6.8 Temperature corrections (USEPA). Multiple values obtained from accompanying graphs for 4 °C by temperature correction factor stated below to determine horsepower or velocity gradient at any other temperature. 1 MGD = 3.785 MLD;
1 HP = 0.7457 kw

	Temperature correction factor	
Water temperature, °C	HP per MGD	G, s^{-1}
0	1.14	0.937
1	1.11	0.948
2	1.07	0.966
3	1.03	0.985
4	1.00	1.00
5	0.981	1.02
6	0.940	1.03
7	0.914	1.05
8	0.889	1.06
9	0.863	1.08
10	0.838	1.09
11	0.811	1.11
12	0.794	1.12
13	0.774	1.14
14	0.748	1.16
15	0.729	1.17
16	0.716	1.18
17	0.696	1.20
18	0.678	1.21
19	0.669	1.22
20	0.646	1.24
21	0.629	1.26
22	0.615	1.28
23	0.600	1.29
24	0.586	1.31
25	0.572	1.32
26	0.559	1.34
27	0.547	1.35
28	0.535	1.37
29	0.523	1.39
30	0.512	1.40

Water horsepower = 2 × 0.8 = 1.6 HP

$$\begin{aligned}\text{Velocity gradient}, G &= 4589.4 \times P / V \\ &= 4589.4 \times 2 / 432 \\ &= 312\ \text{s}^{-1}\end{aligned}$$

Water HP/MGD = 0.32
From the curve (Fig. 6.6), using 0.32 and 56 s, $G = 260$



NOTE: CONSIDER AS INDIVIDUAL UNIT PROCESSES

SUGGESTED MINIMUM

OPTIONAL

	PLANT SIZE (MGD)	TEST FREQUENCY	LOCATION OF SAMPLE	METHOD OF SAMPLE	REASON FOR TEST
pH	ALL	Mn	FE	Mn	P
pH	ALL	1/D	I CE	G	H
ALKALINITY	ALL	2/W	I PE	24C	H
SUSPENDED SOLIDS	ALL	1/D	FE CE	24C	H
JAR TEST	ALL	1	I	24C	P C
HARDNESS	ALL	1/W	I PE	24C	H
TURBIDITY	ALL	R	I CE	R	P
SLUDGE VOLUME LAB CENTRIFUGE	ALL	3/D	S	G	P
TOTAL SOLIDS	>1	1/W	S	G	P
TOTAL SOLIDS	1	3/W	S	G	P
FLOW	ALL	R	S	R	P
CALCIUM CONTENT[2]	ALL	3	LS	G	C
CHLORIDES[4]	ALL	1/W	I PE	24C	H
SULFATES[5]	ALL	1/W	I PE	24C	H
TOTAL-P[6]	ALL	3/W	I PE	24C	H
ORTHO-P[6]	ALL	3/W	I PE	24C	H

A. TEST FREQUENCY

H = HOUR		M = MONTH	
D = DAY		R = RECORD CONTINUOUSLY	
W = WEEK		M_A = MONITOR CONTINUOUSLY	

B. LOCATION OF SAMPLE

I = INFLUENT
FE = FLOCCULATION EFFLUENT
LS = LIME FROM SUPPLIER (INCLUDE W/FLASH MIX PROCESS TESTING)
CE = CLARIFIER EFFLUENT
PE = PLANT EFFLUENT
S = SLUDGE UNDERFLOW

C. METHOD OF SAMPLE

24C = 24 HOUR COMPOSITE
G = GRAB SAMPLE
R = RECORD CONTINUOUSLY
M_A = MONITOR CONTINUOUSLY

D. REASON FOR TEST

H = HISTORICAL KNOWLEDGE
P = PROCESS CONTROL
C = COST CONTROL

E. FOOTNOTES:

1. SPOT CHECK
2. IF LIME IS USED
3. WHEN LIME IS DELIVERED BY SUPPLIER
4. IF FERRIC CHLORIDE IS USED
5. IF ALUM OR FERRIC SULFATE IS USED
6. IF PROCESS IS DESIGNED TO CONTROL THIS PARAMETER

Fig. 6.7 Estimated unit process sampling and testing needs (USEPA)

Correction factor from Table 6.8 for 20 °C = 1.24

G value = 1.24 × 260 = 322 s^{-1}

3. Compute detention time, velocity gradient, and check paddle area for flocculation.

$$\begin{aligned}\text{Total volume} &= 2\times 40'\times 20'\times 10' = 16{,}000\ \text{cu ft}\\ &= 8000\ \text{cu ft per basin}\end{aligned}$$

$$\begin{aligned}\text{Detention time} &= \frac{16{,}000\times 7.48\times 24\times 60}{5\ \text{MGD}}\\ &= 34.5\ \text{min}\end{aligned}$$

Assumed two flocculation stages, using half volume of each tank (from Table 6.7)

$$\begin{aligned}\text{First stage } G &= 4589.4P/V\\ &= 4589.4\times 2/4000\\ &= 102.6\ \text{s}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Second stage } G &= 4589.4\times 0.5/4000\\ &= 51.3\ \text{s}^{-1}\end{aligned}$$

Check value from graph (Fig. 6.6).

$$\text{Ratio of water HP / MGD} = \frac{2\times 0.8}{2.5} = 0.64$$

Using 0.64 and detention time of 17 min
From graph (Fig. 6.6), $G = 88\ \text{s}^{-1}$
Correction factor to 20 °C from Table 6.8 = 1.24
$G = 1.24 \times 88 = 109\ \text{s}^{-1}$
Check paddle area using equations from Table 6.7.

$$\begin{aligned}\text{Paddle area, } A &= \frac{561.2P_{\text{H}}}{V^3}\\ &= \frac{561.2\times 2}{3^3}\\ &= 41.5\ \text{sq ft}\end{aligned}$$

4. Determine overflow rate and detention time for the clarifier.

$$\text{Surface area} = \frac{2\times D^2(3.1416)}{4}$$

$$\text{Surface area} = \frac{2\times 60\times 60\times 3.1416}{4} = 5655\ \text{ft}^2$$

$$\text{Overflow rate} = \frac{5\times 10^6}{5655} = 884\ \text{gpd/ft}^2$$

$$\begin{aligned}\text{Volume} &= \text{Surface area}\times\text{depth}\\ &= 5655\times 12\times 7.48 = 507{,}593\ \text{gal}\end{aligned}$$

$$\text{Detention time} = \frac{507{,}593}{5\times 10^6}\times 24 = 2.44\ \text{h}$$

Check paddle area as percent of cross-section area.

$$\text{Percent} = \frac{41.5\times 100}{20\times 10} = 20.8\%$$

9 Sedimentation Versus Dissolved Air Flotation for Wastewater and Water Treatment

9.1 Sedimentation Clarification Design and Applications

9.1.1 Sedimentation Configurations and Design Criteria

Sedimentation is a clarification process that relies upon gravity to remove suspended solids (chemical flocs, biological flocs, silts, etc.) from an aqueous stream. The fundamentals of a sedimentation process includes: (a) a basin or container of sufficient size to maintain the liquid to be treated in a relatively quiescent state for a specified period of time; (b) a means of directing the liquid to be treated into the above basin in a manner conducive to settling; and a means of physically removing the settled particles from the liquid (or liquid from the settled particles). Sedimentation can be carried out as either a sequencing batch reactor (SBR) process or a continuous flow process in lined impoundments, conventional settling basins, clarifiers, and high-rate gravity settlers for water purification or wastewater treatment. Figures 6.8 and 6.9 illustrate two different design configurations of rectangular sedimentation basins. In natural sedimentation ponds, the liquid is merely decanted as the particles accumulate on the bottom of the pond. Backhoes, draglines, or siphons are used periodically to remove settled solids.

Sedimentation basins and clarifiers usually employ a built-in solid collection and removal device such as a sludge scraper and draw-off mechanism shown in Figs. 6.8 and 6.9. Normal rectangular sedimentation basins usually employ a belt-like collection mechanism and are mainly used for the removal of truly settleable particles from liquid. Circular sedimentation clarifiers are also common. Circular sedimentation clarifiers are usually used in applications involving chemical coagulation/precipitation and flocculation as well as clarification. Many package sedimentation clarifiers are equipped with separate zones for chemical mixing and precipitation, flocculation, and sedimentation.

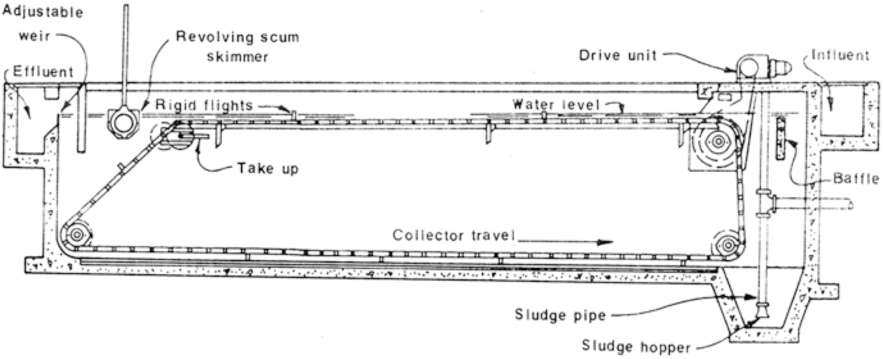


Fig. 6.8 Rectangular sedimentation basin with a chain sludge collector (USEPA)

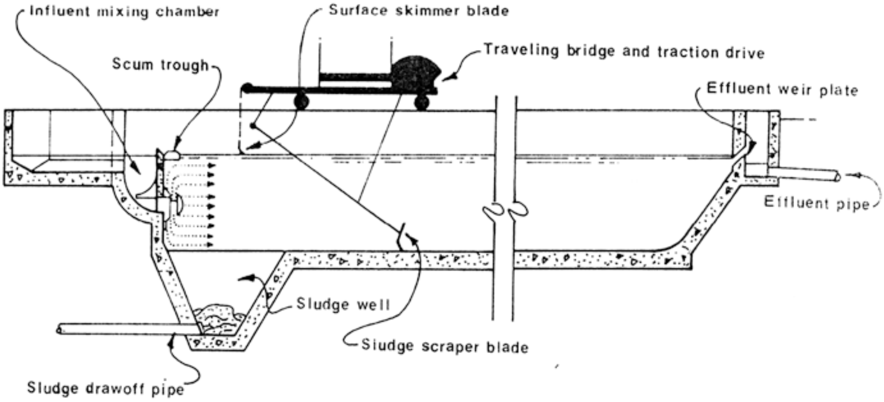


Fig. 6.9 Rectangular sedimentation basin with a traveling bridge sludge collector (USEPA)

Sedimentation clarification process is commonly applied to aqueous water or wastewater influents with high suspended solid loadings. This may include contaminated raw water (i.e., a water source for drinking water treatment), chemical coagulation/precipitation effluent, surface run-off, collected leachate or landfill toe seepage, dredge slurries, and effluents from biological treatment. Sedimentation is also required as a pretreatment step for many chemical processes, including carbon adsorption, ion exchange, stripping, reverse osmosis, and filtration. This technology is applicable to the removal of suspended solids heavier than water. Suspended oil droplets or oil-soaked particles may not settle out and may have to be removed by some other means. Some sedimentation units are fitted with skimmers to remove oil and grease that float to the water surface. However, these would not be effective in removing emulsified oils [1, 8–10, 20–40, 82, 95, 105, 106, 110, 111, 143–146, 153–155].

Sedimentation design is frequently considered in terms of ideal settling. The ideal settling theory results in the following equation for surface loading or overflow rate [1].

$$V_o = Q / A$$

where V_o = settling velocity; Q = flow through the basin; and A = surface area of the sedimentation basin.

Sedimentation basin loadings (Q/A) are often expressed in terms of gallons per day per square foot. Thus, under ideal settling conditions, sedimentation is independent of basin depth and detention time and depends only on the flow rate, basin surface area, and properties of the particles.

However, sedimentation does not perform according to ideal settling conditions, since settling is affected by such conditions as turbulence, and bottom scour. Therefore, removal of particles is dependent on basin depth and detention time as well as flow rate surface area and particle size. The performance of a sedimentation basin on a suspension of discrete particles can be calculated, but it is not possible to calculate sedimentation basin performance for a suspension of flocculating. Laboratory settling tests, however, may be performed to predict sedimentation basin performance.

The surface loading rates for sedimentation following chemical treatment vary considerably from one application to another. This wide variation emphasizes the importance of testing and pilot work in designing sedimentation facilities. In addition to the hydraulic loading rate, other design criteria include: solid loading rate, depth, detention time, weir loading rate, and length/width ratio for rectangular basins.

As a solid–water separation process, sedimentation provides a reliable means to remove suspended matter from a waste stream, provided the suspended matter is settleable and the treatment process including the use of flocculants/coagulants has been appropriately designed from laboratory settling tests. Clarifiers are capable of removing 90–99% of the suspended solids. Efficiencies for total suspended solid (TSS) removal normally, however, range from 50% to 70%. With some coagulation and precipitation sludges, the efficiency may be higher but seldom reaches 99%.

In terms of operation and performance, sedimentation employs readily available equipment and is relatively easy to operate. The process is versatile in that it can be applied to almost any liquid water stream or waste stream containing TSS. It can also be easily integrated into a more complex treatment system as a pre- or post-treatment method. Sedimentation is non-selective and nondestructive, resulting in a large volume of potentially contaminated sludge that may require further treatment and disposal. The typical hydraulic loading rate of sedimentation basins following chemical treatment are: (a) 20,000–24,000 L/day/m^2 (500–600 gpd/ft^2) when alum is used as a coagulant/precipitant; (b) 29,000–33,000 L/day/m^2 (700–800 gpd/ft^2) when iron is used as a coagulant/precipitant; and (c) 57,000–65,000 L/day/m^2 (1400–1600 gpd/ft^2) when lime is used as a coagulant/precipitant. For wastewater primary and secondary sedimentation clarifications, the sedimentation hydraulic loading rates range from 8000 to 120,000 L/day/m^2 (200–3000 gpd/ft^2), so an environmental engineer must either determine the rate based on a pilot plant experiment or based on the professional association's standard rates, such as the Ten State Standards [156, 157].

The following is a list of important provisions described in the Recommended Standards for Wastewater Treatment Works [156] for the design of sedimentation tanks. These standards are called Ten State Standards for Wastewater Treatment Works.

1. The inlet channel should have a velocity of at least 0.30 m/s (1 ft/s) at one-half the design flow.
2. The minimum length of the tank should be 3 m (10 ft). The mechanically cleaned settling tank should be as shallow as possible but not less than 2.1 m (7 ft) deep. The final clarifier for activated sludge to be not less than 2.5 m (8 ft) deep.
3. Provide scum removal facilities in all wastewater sedimentation tanks.

4. Weir overflow rate should not exceed 10,000 gpd/ft for 1 MGD or smaller plants and 15,000 gpd/foot for larger plants. In metric units, this corresponds to 124,000 L/day/m for 3.8 ML/day or smaller plants and 186,000 L/day/m for larger than 3.8 ML/day plants.
5. The surface overflow rates for primary tanks of capacity greater than 3.8 ML/day (1 MGD) shall not exceed 41,000 L/day/m^2 (1000 gpd/ft^2) at average design flow.
6. The surface overflow rates for primary tanks of capacity 3.8 ML/day (1 MGD) or less shall not exceed 24,000 L/day/m^2 (600 gpd/ft^2).
7. Multiple settling tanks are required in all plants of 380,000 L/day (100,000 gpd) or more.
8. Surface overflow rates for final settling tanks depend on the type of secondary treatment at the plant and the size of the plant. For conventional activated sludge plants, the overflow rate shall not exceed 800 gpd/ft^2 for plants of over 1.5 MGD, 700 gpd/ft^2 for plants 0.5–1.5 MGD, and 600 gpd/ft^2 for plants up to 0.5 MGD. In metric units, this corresponds to 32,600 L/day/m^2 for plants of over 5.7 ML/day, 28,500 L/day/m^2 for plants 1.9–5.7 ML/day, and 24,400 L/day/m^2 for plants up to 1.9 ML/day.
9. Surface overflow rate for an intermediate settling tank following fixed film processes shall not exceed 61,000 L/day/m^2 (1500 gpd/ft^2) at peak hourly flow.
10. The detention time for final sedimentation tanks in conventional activated sludge plants shall be 3 h for up to 0.5 MGD plants, 2.5 h for 0.5–1.5 MGD plants and 2.0 h for over 1.5 MGD plants. In metric units, this corresponds to 3 h for up to 1.9 ML/day plants, 2.5 h for 1.9–5.7 ML/day plants, and 2.0 h for over 5.7 ML/day plants.

9.1.2 Sedimentation Design

EXAMPLE 18: DESIGN OF A 20 MGD SEDIMENTATION TANKS WITH 2 HOUR OF DETENTION TIME ACCORDING TO TEN STATE STANDARDS

Solution

1. Capacity of sedimentation tank required:

$$V = Qt$$

$$V = 20\times10^6 \frac{\text{gal}}{\text{day}}\times\frac{\text{day}}{24\ \text{h}}\times 2\text{h} = 29{,}800\ \text{gal}$$

$$= 29{,}800\ \text{gal}\times 7.48 = 222{,}800\ \text{ft}^3$$

Assume an effective depth of 8 ft

Area of tank required = 222,800/8 = 27,850 ft^2

2. Rectangular tank dimensions:

Assume number of tanks to be provided = 6

The width of the tank should be based on the availability of sludge collection equipment.

Assume the working width of units to be 40 ft

$$\text{Length of each tank} = \frac{27{,}850}{6 \times 40} = 116\ \text{ft}$$

Provide six tanks of dimensions 120 ft × 40 ft × 8 ft

3. Check for overflow rate

   Area of each tank = 120 × 40 = 4800 ft^2

$$\begin{aligned}\text{Overflow rate} &= \frac{(20/6) \times 10^6}{4800} \\ &= 695\ \text{gpd}/\text{ft}^2, \text{ which is acceptable}\end{aligned}$$

4. Check for horizontal flow velocity

$$\begin{aligned}\text{Velocity} &= \frac{\text{length of tank}}{\text{detention time}} \\ &= \frac{120\ \text{ft}}{2 \times 60\ \text{min}} = 1.0\ \text{ft}/\text{min}, \text{ which is acceptable}\end{aligned}$$

5. Weir overflow rate

   According to Ten State Standards, the maximum weir overflow rate allowed is 15,000 gpd/ft.

   So, weir length required for each tank

$$= \frac{(20/6) \times 10^6}{15{,}000} = 222\ \text{ft}$$

Let n be the number of additional overflow weir troughs then,
$(2n + 1) \times 40 = 222$
$n = 2.28$

6. Provide three additional troughs.

$$\text{Weir overflow rate} = \frac{(20/6) \times 10^6}{(3 \times 2 + 1) \times 40} = 11{,}900\,\text{gpd}/\text{ft}, \text{ which is acceptable}$$

9.1.3 Sedimentation Applications

Sedimentation is a very reliable unit process for water clarification, wastewater primary clarification, wastewater secondary/tertiary clarification and sludge gravity thickening. It is important to note that the design criteria for each specific application (water clarification, wastewater primary clarification, wastewater secondary/tertiary clarification, or sludge gravity thickening), the design criteria, and design procedures will be different. The readers are referred to the Ten State Standards, engineering books, and local governmental agency's guidelines, etc. for design or analysis of a specific sedimentation design project [1, 2, 8, 39, 144, 145, 153–157]. Since sedimentation is a well-established process, there is no need for environmental engineers to conduct a pilot plant demonstration prior to process design and equipment installation as long as the required design specifications are met.

The applications of sedimentation for water treatment, wastewater treatment, and sludge thickening are reported in the literature [1, 8–10, 20–40, 82, 95, 105, 106, 110, 111, 143–146, 153–155]. It can be used as one of the reliable unit processes in a water treatment plant (WTP) or a wastewater treatment plant (WWTP) for the treatment of raw water, municipal wastewater, industrial effluent, storm run-off water, etc. Appendixes 1.1–1.23 document some of the sedimentation applications.

Selection of sedimentation for water or wastewater treatment is an easy decision, if there are plenty of land space and construction funds available, except that following situations: (a) the influent has too much light weight oil and grease (O&G); (b) the influent has too much rising sludges; and (c) the separated sludge has high recyclable value, such as titanium dioxide, paper fibers, and plastics. Once the valuable suspended solids are mixed with the contaminants in the settled sludge, this settled sludge will have no value because the further separation cost will be too high.

9.2 Dissolved Air Flotation Clarification Design and Applications

9.2.1 DAF Configuration and Design Criteria

Dissolved air flotation (DAF) is used to remove suspended solids by flotation (rising) by decreasing their apparent density. The DAF process consists of saturating a portion or all of the water or wastewater feed, or a portion of recycled effluent with air at a pressure of 25–70 lb/square inch in a pressurization device, such as the air dissolving tube (ADT) shown in Fig. 6.10, or equivalent pressurized retention tank. The pressurized water or wastewater is held at this pressure for 0.5–3.0 min in an ADT (or a pressurized retention tank) and then released to atmospheric pressure to the flotation chamber. The sudden reduction in pressure results in the release of microscopic air bubbles which attach themselves to oil and suspended particles (i.e., chemical flocs and/or biological flocs) in the water/wastewater in the flotation chamber. This results in agglomeration which, due to the entrained air, has greatly increased vertical rise rates of about 0.5–2.0 ft/min. The floated materials rise to the surface to form a froth layer (scum or float). Specially designed flight scrapers, or rotating scoops, or other skimming devices continuously remove the froth layer. The retention time in the flotation chambers is usually about 20–60 min for conventional rectangular DAF (Fig. 6.11) and 3–15 min for innovative high-rate DAF (such as Supracell shown in Fig. 6.12, or Sandfloat shown in Fig. 6.13). The latest development of AquaDAF (Fig. 6.14) and Clari-DAF (Fig. 6.15) is also very impressive in terms of high-rate flotation. The effectiveness of dissolved air flotation depends upon the attachment of bubbles to the suspended oil and other particles which are to be removed from the waste stream. The air to solid ratio (A/S ratio) is about 0.01–0.1 kg/kg. The DAF overflow rate is normally controlled at a range of 500–8000 gal/day/ft^2. The attraction between the air bubble and particle is primarily a result of the particle surface charges and bubble-size distribution [152, 158–162].

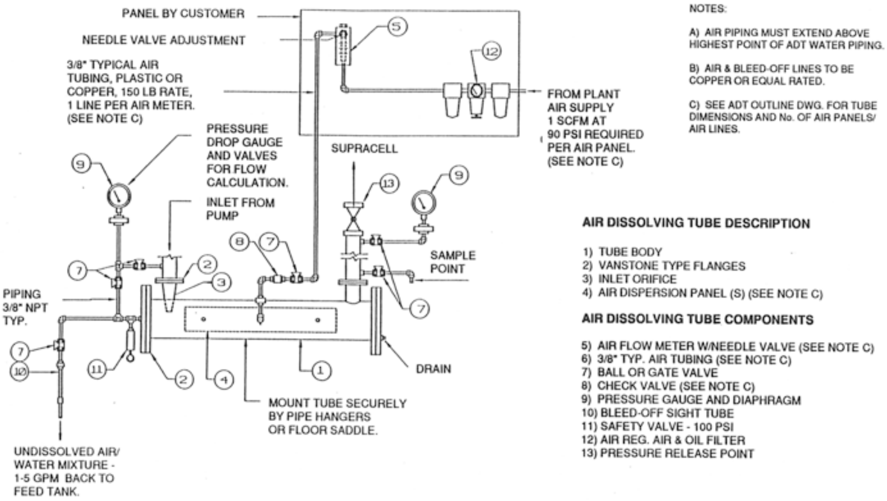


Fig. 6.10 Typical air dissolving tube system of a flotation clarifier [158]

The more uniform the distribution of water and micro-bubbles, the shallower the flotation unit can be. Generally, the depth of effective flotation units is between 4 and 9 ft. The surface sludge layer can in certain cases attain a thickness of many inches and can be relatively stable for a short period. The layer thickens with time, but undue delays in removal will cause a release of particulates back to the liquid.

The DAF units can be round, square or rectangular. In addition, gases other them air can be used. The petroleum industry has used nitrogen, with closed vessels, to reduce the possibilities of fire. DAF has been used for many years to thicken activated sludge in wastewater treatment plants, but has now been significantly improved, modified for drinking water treatment, industrial effluent treatment, wastewater primary flotation clarification, and secondary flotation clarification. Alum ($Al_2(SO_4)_3 \cdot 14H_2O$), ferric chloride ($FeCl_3$), and polymers can be added to aid in the coagulation/precipitation process prior to the actual flotation step [152, 158–161].

The following table presents the expected percent removal for the separation of total suspended solids (TSS) and oil and grease (O&G):

Percent removal (without chemicals)	Percent removal (with chemicals)
Suspended solids, 40–65	80–93
Oil and grease, 60–80	85–99

The DAF systems have been found to be very reliable. However, chemical pretreatment is essential, without which DAF units are subject to variable influent conditions, resulting in widely varying performance.

The advantage of DAF clarification over sedimentation clarification is that DAF requires very little use of land. In normal water purification or municipal wastewater clarification using DAF, the air released in the DAF unit is unlikely to strip

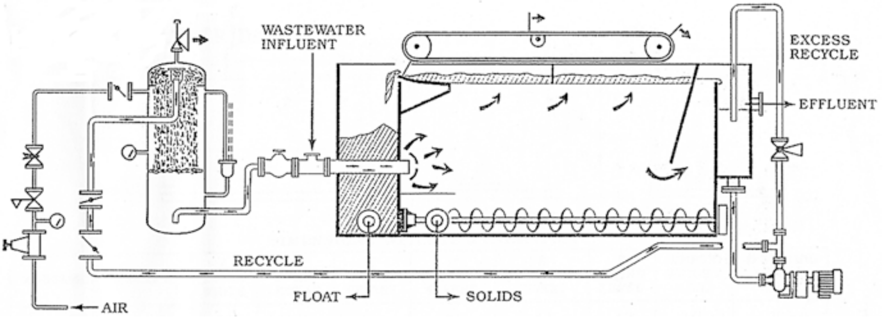


Fig. 6.11 Typical rectangular dissolved air flotation system [11]

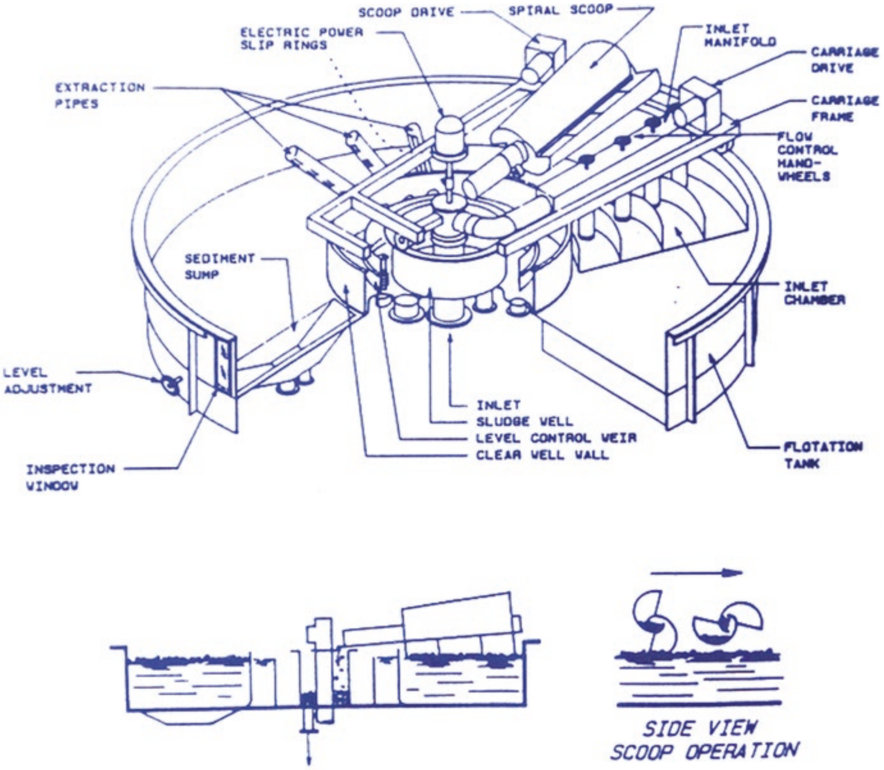
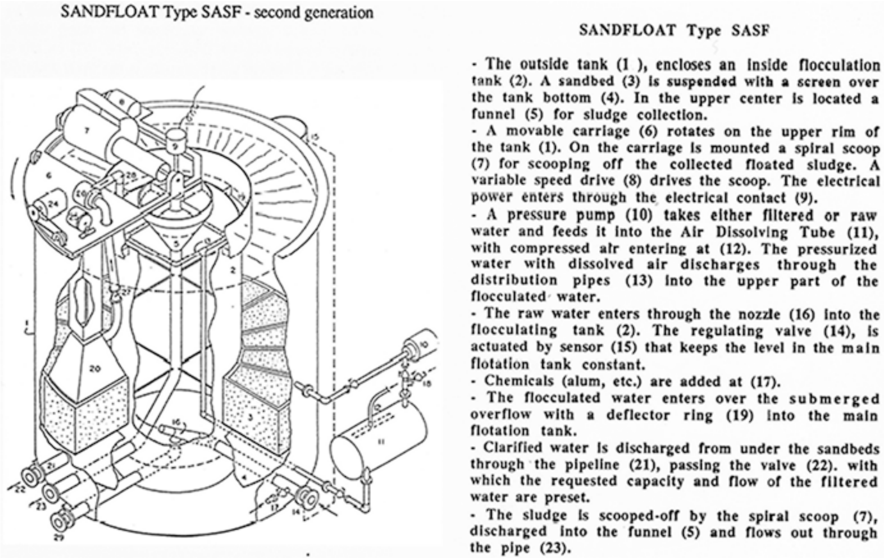


Fig. 6.12 Circular dissolved air flotation clarifier (Supracell; DAF) [158]



SANDFLOAT Type SASF - second generation

SANDFLOAT Type SASF

- The outside tank (1), encloses an inside flocculation tank (2). A sandbed (3) is suspended with a screen over the tank bottom (4). In the upper center is located a funnel (5) for sludge collection.
- A movable carriage (6) rotates on the upper rim of the tank (1). On the carriage is mounted a spiral scoop (7) for scooping off the collected floated sludge. A variable speed drive (8) drives the scoop. The electrical power enters through the electrical contact (9).
- A pressure pump (10) takes either filtered or raw water and feeds it into the Air Dissolving Tube (11), with compressed air entering at (12). The pressurized water with dissolved air discharges through the distribution pipes (13) into the upper part of the flocculated water.
- The raw water enters through the nozzle (16) into the flocculating tank (2). The regulating valve (14), is actuated by sensor (15) that keeps the level in the main flotation tank constant.
- Chemicals (alum, etc.) are added at (17).
- The flocculated water enters over the submerged overflow with a deflector ring (19) into the main flotation tank.
- Clarified water is discharged from under the sandbeds through the pipeline (21), passing the valve (22). with which the requested capacity and flow of the filtered water are preset.
- The sludge is scooped-off by the spiral scoop (7), discharged into the funnel (5) and flows out through the pipe (23).

Fig. 6.13 Circular chemical coagulation/precipitation, flocculation, dissolved air flotation and filtration package plant (Sandfloat; DAFF) [158]

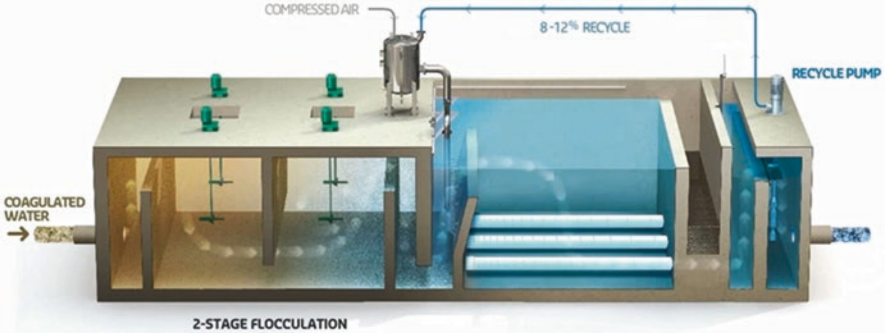


Fig. 6.14 Rectangular chemical coagulation/precipitation, flocculation and dissolved air flotation package plant (AquaDAF) [161]

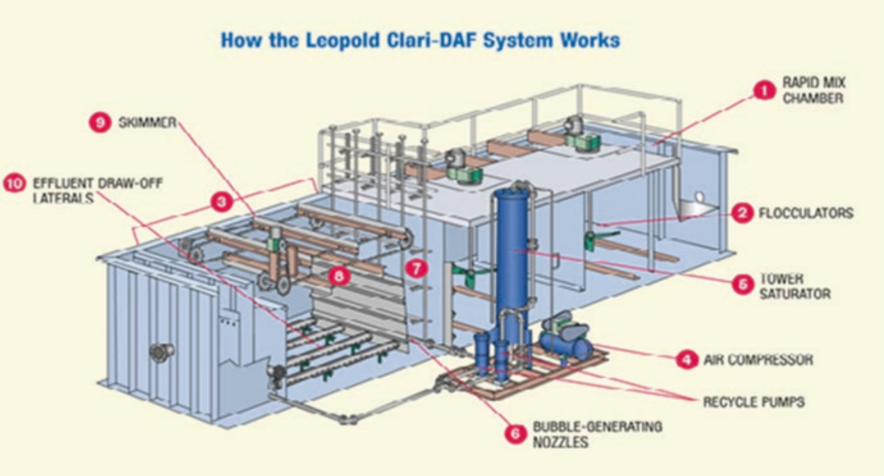


Fig. 6.15 Rectangular chemical coagulation/precipitation, flocculation and dissolved air flotation package plant (Clari-DAF) [160]

volatile organic component (VOC) material into the air. When treating industrial wastewater containing high concentrations of VOCs, a canopy-type enclosure on the top of DAF clarifier may remove any toxic gases released from the DAF units.

The Ten State Standards [156, 157] and most of the government agency's design guidelines do not cover the criteria and procedures of flotation clarifier design. At present, dissolved air flotation (DAF) is still considered as an alternative environmental technology requiring tentative design, cost estimation, and pilot plant demonstration for the review and consideration by the customers and approving government agencies. The tentative design will show the intended customers and government agencies the flotation clarifier's footprint, and approximate installation costs and operation costs. A pilot plant demonstration project will prove flotation's technical feasibility for treating a specific water or wastewater for removing certain targeted pollutants and will also generate enough data for future full-scale flotation process design, plant operation, and accurate cost estimation. The readers are referred to the literature [1, 7–11, 16, 20, 62, 103, 107, 108, 138, 139, 152, 158–161] and the DAF equipment manufacturers for both technical and economical feasibilities of various DAF processes.

9.2.2 Dissolved Air Flotation Application Examples

Selection of dissolved air flotation (DAF) instead of sedimentation for water or wastewater treatment is a challenge because sedimentation is a well-established conventional clarification process. DAF is selected for water or wastewater clarification when one or more of the following conditions occur: (a) there is a land space limitation or site problem that will prevent the use of sedimentation; (b) there is no sufficient budget available, and cost saving is required; (c) the influent has too much light weight oil and grease (O&G); (d) the influent has too much rising sludges; and (e) the separated sludge has high recyclable value, such as titanium dioxide, paper fibers, plastics, and precious metals. A combined DAF–sedimentation clarifier (such as Sedifloat) may selectively float valuable suspended solids for recovery, but settle the heavy unwanted contaminants.

Mobility may be another factor when a DAF is chosen over sedimentation because a DAF clarifier is much smaller than a comparable sedimentation clarifier when treating the same hydraulic flow. It has been demonstrated that mobile DAF treatment plant may be built on a boat, a truck, or a train for emergency, military, temporary, or seasonal water supply, wastewater treatment, storm water treatment, or groundwater decontamination at different locations or times [11, 158]. The following sections illustrate a few application examples of DAF.

EXAMPLE 19: INDUSTRIAL EFFLUENT TREATMENT WHEN THERE ARE SPACE/SITE/LOCATION LIMITATIONS

Solution

Figure 6.16 shows the size and detention time comparisons between an innovative circular combined dissolved air flotation and sedimentation clarifier (Sedifloat) and a conventional circular sedimentation clarifier when treating an identical wastewater flow. Apparently, the footprint (area), volume, and detention time of a Sedifloat unit in comparison with an equivalent conventional sedimentation clarifier is much smaller. For municipalities, usually large land spaces are available in their reserved

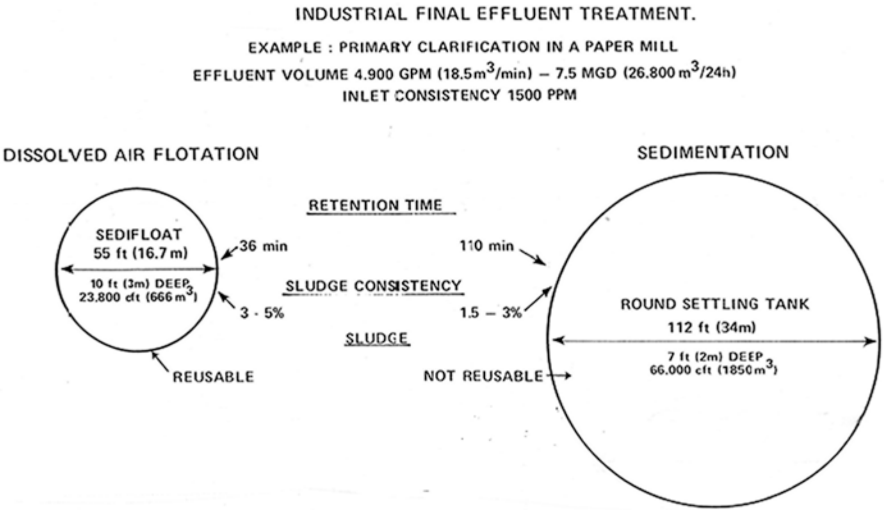


Fig. 6.16 Comparison between an innovative circular combined dissolved air flotation and sedimentation clarifier (Sedifloat) and a conventional circular sedimentation clarifier when treating the same wastewater flow [162]

Fig. 6.17 Two elevated light weight shallow circular dissolved air flotation clarifiers with zero footprint [162]

rural areas, and there are sufficient municipal construction funds. So, adoption of conventional sedimentation by consulting engineers for water or wastewater clarification will be an easy and logical decision. For industries, usually there are limited land spaces, and/or limited installation funds available. The plant engineers and managers are constantly searching for innovative and inexpensive process equipment to fit their needs.

Figure 6.17 shows that the innovative Supracell DAF clarifier has very shallow depth and light unit weight, such that it can be installed anywhere, such as on a building top, with almost zero foot-print. A Supracell DAF clarifier can also be installed on the top of Sandfloat DAF–filtration clarifier (or any other process unit) for space-saving water processing (Fig. 6.18), or on a small boat for lake water restoration [152].

EXAMPLE 20: CHEMICAL COAGULATION AND COMBINED DAF–SEDIMENTATION CLARIFICATION FOR TREATING TURKEY FARM WASTEWATER AND REMOVING BOTH LIGHT- AND HEAVY-WEIGHT POLLUTANTS SIMULTANEOUSLY

Solution

There is a situation that some agricultural wastewater (such a wastewater from a turkey farm) contains both very light weight oil and grease (O&G), and very heavy

Fig. 6.18 Two stage DAF-DAFF (Supracell-Sandfloat) system for advanced treatment and space saving [158]

weight silts and dirt. Then a combined DAF and sedimentation clarifier, shown in Figs. 6.19 and 6.20, will be an ideal engineering solution [162].

Figure 6.21 shows the flow diagram of a chemical coagulation and clarification process system consisting of screening, mixing/flocculation, and combined circular DAF–sedimentation clarification, and involving the use of lime, alum, and polymer as the coagulants. The actual case history is for Jaindl's Turkey Farm, located in Allentown, PA, USA. The turkey farm's wastewater flow was 100,000 gpd (gallons per day). The poultry farm's effluent is discharged to a municipal wastewater treatment plant (WWTP) for further treatment.

EXAMPLE 21: MULTIPLE DAF UNITS FOR MULTIPLE TREATMENT PURPOSES OF OIL SEPARATION, SULFIDE PRECIPITATION, SLUDGE THICKENING, BIOLOGICAL SLUDGE SEPARATION, TERTIARY TREATMENT, AND WASTEWATER RECLAMATION AT A PETROLEUM REFINING PLANT

Solution

The attached process flow sheet (Fig. 6.22) illustrates how multiple DAF clarifiers (such as Supracell, or equivalent) and combined DAF–filtration clarifiers (such as Sandfloat, or equivalent) solve the wastewater pretreatment problem at a petroleum

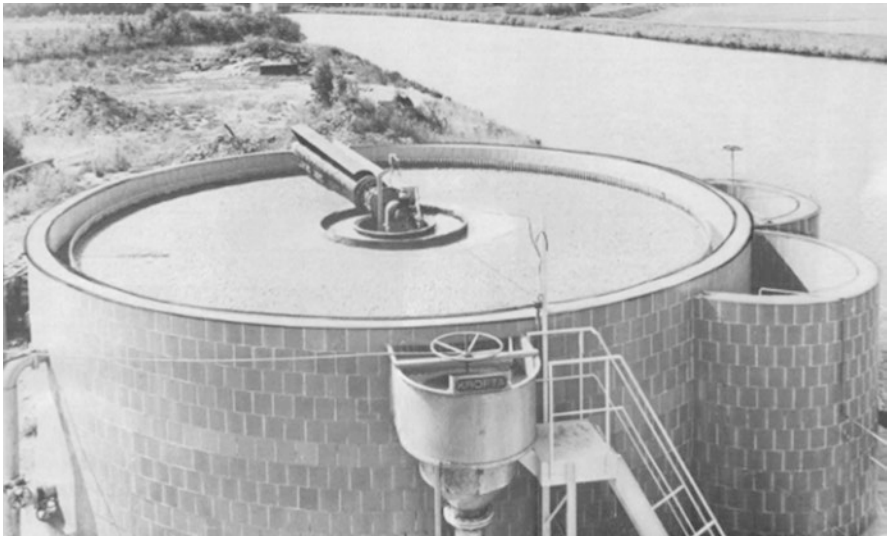
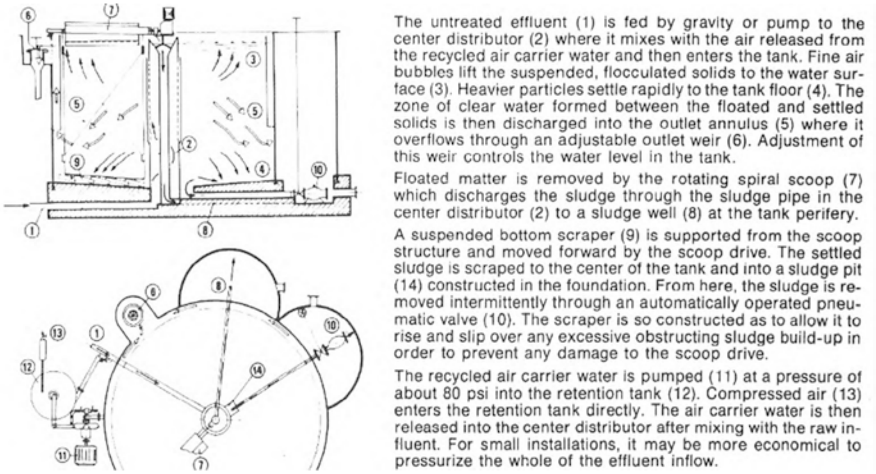


Fig. 6.19 Combined dissolved air flotation and sedimentation clarifier (Sedifloat) with an acid resistance brick construction [162]



The untreated effluent (1) is fed by gravity or pump to the center distributor (2) where it mixes with the air released from the recycled air carrier water and then enters the tank. Fine air bubbles lift the suspended, flocculated solids to the water surface (3). Heavier particles settle rapidly to the tank floor (4). The zone of clear water formed between the floated and settled solids is then discharged into the outlet annulus (5) where it overflows through an adjustable outlet weir (6). Adjustment of this weir controls the water level in the tank.

Floated matter is removed by the rotating spiral scoop (7) which discharges the sludge through the sludge pipe in the center distributor (2) to a sludge well (8) at the tank perifery.

A suspended bottom scraper (9) is supported from the scoop structure and moved forward by the scoop drive. The settled sludge is scraped to the center of the tank and into a sludge pit (14) constructed in the foundation. From here, the sludge is removed intermittently through an automatically operated pneumatic valve (10). The scraper is so constructed as to allow it to rise and slip over any excessive obstructing sludge build-up in order to prevent any damage to the scoop drive.

The recycled air carrier water is pumped (11) at a pressure of about 80 psi into the retention tank (12). Compressed air (13) enters the retention tank directly. The air carrier water is then released into the center distributor after mixing with the raw influent. For small installations, it may be more economical to pressurize the whole of the effluent inflow.

Fig. 6.20 Combined dissolved air flotation and sedimentation clarifier (Sedifloat) process description [158]

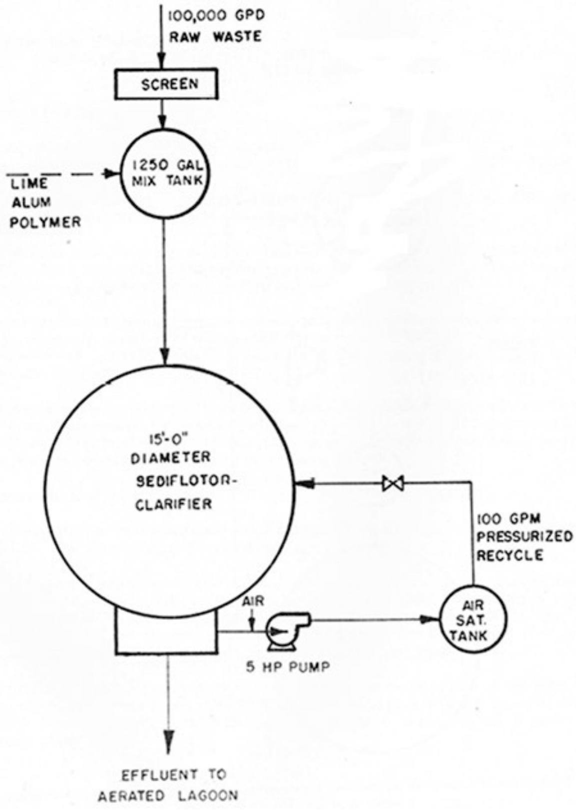


Fig. 6.21 Turkey farm wastewater treatment by chemical coagulation/precipitation and combined dissolved air flotation and sedimentation (Sedifloat) ([162]; USEPA)

refining plant in the USA. The petroleum refining plant generates multiple wastewater streams containing oil and grease, sulfide, phenol, caustics, storm-run off pollutants, cooling tower blowdowns, and sanitary wastewater pollutants.

From top to bottom of Fig. 6.22, it can be seen that the sulfide bearing spent caustic streams are treated in an oil separation unit where the collected oil flows to a slop oil tank, and the sludge discharges to the lagoons. Precipitating chemicals are added to the oil separator effluent for chemical precipitation of sulfides prior to dissolved air flotation clarification by Sandfloat, which is a combined DAF–filtration unit. The Sandfloat floated sludge is thickened and goes to a dewatering unit, while the Sandfloat effluent is mixed with the sludge lagoon effluent in an equalization pond prior to biological treatment. The bioreactors are aeration units (other trickling filters, rotating biological reactors, sequencing batch reactors, etc. will be equally effective) for bio-oxidation, nitrification, and denitrification. The bioreactor effluent is treated by a Supracell (or an equivalent DAF unit) for secondary flotation clarification. The Supracell effluent is collected in a tertiary pond prior to final disposal to

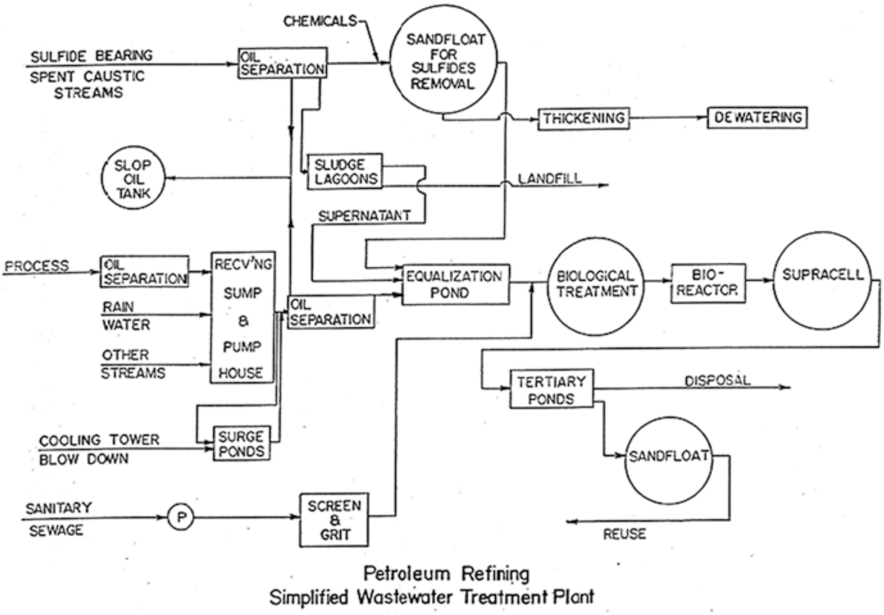


Fig. 6.22 Combined physicochemical and biological treatment of petroleum refinery wastewater streams [162]

a receiving stream or to a Sandfloat unit (or an equivalent DAF–filtration unit) for further water reclamation [162].

The left-middle of Fig. 6.22 is the petroleum refinery's less-polluted process water, rain water, and other streams, which are collected by a receiving sump in a pump house, while the cooling tower blow down goes to surge ponds, then to meet the pump house effluent together all for oil separation and further biological treatment. The petro-refining plant's sanitary sewage shown at the bottom-left of Fig. 6.22 is screened, its grit removed prior to biological treatment. The entire combined physicochemical and biological wastewater treatment system is very complex involving the use of unit processes of oil–water separation, screening, grit removal, equalization, lagoons, sulfide precipitation, multiple DAFs, filtration, thickening, dewatering, landfill, biological treatment, and tertiary water reclamation.

EXAMPLE 22: INTRODUCTION OF CLARI-DAF SYSTEMS (GREENVILLE, SOUTH CAROLINA TABLE ROCK/NORTH SALUDA PLANT, USA) FOR WATER PURIFICATION

Solution

The Greenville Water System draws water from three sources—Table Rock Reservoir on the South Saluda River, Poinsett Reservoir on the North Saluda River, and Lake Keowee. The Table Rock and Poinsett Reservoirs are both located in the foothills of the Blue Ridge Mountains in northern Greenville County, USA. The source waters were so clear that for more than 70 years, the water from the mountain reservoirs was unfiltered and only treated with chlorine. In the mid-1980s, the Adkins Filtration Plant using conventional sedimentation clarification technology for 30 MGD design capacity was built using Lake Keowee as its source water. This plant was expanded in 2003 to increase the capacity to 60 MGD using the same settling basin clarification technology. Because increasing regulations required all surface water systems to be filtered, a new state-of-the-art filter plant was placed in service in July 2000 to provide filtration for all of the water drawn from the Table Rock and Poinsett reservoirs. This new Table Rock/North Saluda filter plant, designed at 75 MGD, uses the Clari-DAF® system (Fig. 6.15) for clarification in the treatment scheme [160].

The Adkins Filter Plant is a conventional complete physicochemical process system which uses chemical coagulation, sedimentation, filtration, and disinfection to treat the source water. Alum is used as the coagulant, along with sodium hydroxide (caustic) for pH adjustment. Chlorine combined with ammonia is used for disinfection, while a zinc polyphosphate is added for corrosion control. Fluoridation is provided to prevent tooth decay. The Table Rock/North Saluda (TR/NS) Filter Plant is an innovative complete physicochemical process system which uses the flotation process, rather than sedimentation, for particle removal. The remaining processes and chemicals used are similar to those at the Adkins Plant. The raw water quality of the two plants is very similar, with low turbidity, low hardness, and low alkalinity. There is a significant difference in the footprint required for the processes at each facility while the energy requirement is similar for both processes.

Listed in Table 6.9 are the average water quality data for raw, clarified and finished water for the 2-year time period (August 2003 through July 2005). Table 6.10 compares the design criteria of the two processes.

Table 6.9 Average water quality data for Adkins and TR/NS filter plants

	Parameter		Adkins	TR/NS
Raw	pH	Unit	6.55	6.55
	Alkalinity	mg/L	8.89	6.95
	Temperature	°C	21.70	19.20
	Hardness	mg/L	5.00	4.20
	Turbidity	NTU	1.20	0.49
Clarified	Turbidity	NTU	0.37	0.20
	Chlorine	mg/L	1.70	0.20
Finished	pH	Unit	7.10	7.45
	Alkalinity	mg/L	10.70	8.70
	Temperature	°C	21.40	19.00
	Hardness	mg/L	5.25	4.40
	Turbidity	NTU	0.04	0.05
	Chlorine	mg/L	2.65	2.60

Table 6.10 Comparison of process design criteria at Adkins and TR/NS filter plants. 1 ft^2 = 0.0929 m^2; 1 MGD = 3.785 MLD

Process	Adkins (per basin)	TR/NS (per train)
Rapid mix		
Area (ft^2)	95	Inline static
Flow (MGD)	30	
Flocculation		
Area (ft^2)	5664	3684
Flow (MGD)	15	25
Clarification		
Area (ft^2)	28,438	3784
Flow (MGD)	15	25
Filtration (per filter)		
Area (ft^2)	1343	792
Flow (MGD)	11.25	6.87
Total plant		
Area (ft^2)	147,342	31,908
Flow (MGD)	60	75

Table 6.11 Average chemical dosages in Adkins and TR/NS filter plants

Parameter	Adkins	TR/NS	Diff	% Diff
Alum, mg/L	14.1	11.4	2.7	19
Caustic, mg/L	12.7	9.1	3.6	28
Chlorine, mg/L	7.7	3.2	3.5	45
Aq. ammonia, mg/L	1.4	0.6	0.8	57

The footprint for processing 60 MGD by the conventional settling basin system at Adkins is 147,342 ft^2. This results in a requirement of 2456 ft^2 per million gallons of water processed when producing 60 MGD. The total area for processing 75 MGD through the DAF system at Table Rock/North Saluda is 31,908 ft^2. This results in a requirement of 425 ft^2 per million gallons of water processed. By selecting the Clari-DAF® process, the land footprint requirement is reduced by 82.7%.

The average chemical dosages for the 2-year time frame of August 2003 through July 2005 are listed in Table 6.11.

Given the fact that the raw water turbidity was lower at TR/NS, it would be expected that the alum coagulant dosage would be higher. The lower the turbidity, the harder it is to clarify the water and, subsequently, the higher the inorganic coagulant dosage; however, the reduction at TR/NS is due to the fact that flotation can effectively remove smaller diameter solids. Some of the increased caustic feed at Adkins can be attributed to the higher alum feed that depresses the pH for coagulation. The increased chlorine and ammonia feed at Adkins is due to the fact that a higher clarified combined residual is maintained through the clarification process at Adkins to meet C_T requirements.

Filter performance data listed in Table 6.12 were collected from one filter at Adkins and one filter/train at TR/NS (three total filters) for the August 2003 to July 2005 time frame.

The average in-plant water usage rates (water for filter backwash, water-to-waste after backwash, sludge removal, etc.) for the same period are compared in Table 6.13.

There is a major difference and, therefore, an associated cost savings, due to reduced in-plant water usage. The overall cost of water accelerates with higher figures because the in-plant usage is water that has already been processed and, therefore, has an associated multiplied cost. Some of the differences are the result of shorter filter runs and additional backwash water required to wash the filter. In addition, some of the differences are associated with the sludge content of the solids removed from the Adkins conventional settling basin (<0.5%) vs. the DAF unit solids thickening (to >2%) for removal from the TR/NS flotation clarification process. The Adkins submerged sludge collector consumes 2.6 million gal of water per cycle per day. Table 6.14 compares the expenses incurred and the total water production at each treatment plant for the 2-year time frame (August 2003 through July 2005). There was a major reduction (56%) in cost per 1000 gal treated at the TR/NS plant.

Given similar raw water conditions and the ability to produce effluent water below MCL (maximum contaminant level), and given the potential of efficient sludge handling, selecting Clari-DAF® as a replacement for standard sedimentation

Table 6.12 Comparison of filter performance at Adkins and TR/NS filter plants. 1 $ft^2 = 0.0929\ m^2$; 1 MG = 3.785 ML

Parameter	Units	Adkins	TR/NS
Surface area	ft^2	1342	792
Total volume	MG	21.59	16.817
Average filter run	h	126	118
Average backwash	gal	294,458	269,125
Unit filter runtime Vol.	MG/ft^2	17,697	20,984
Backwash (%) range	%	0.77–2.41	0.88–2.42

Table 6.13 Comparison of in-plant water usage rate at Adkin and TR/NS filter plants

Parameter	Adkins	TR/NS	Diff	% Diff
% In-plant use	9.47	3.84	5.63	59.45

Table 6.14 Comparison of production costs at Adkins and TR/NS filter plants. 1 gal = 3.785 L

Parameter	Adkins	TR/NS	Diff	% Diff
Total flow × 10^6 (gal)	10,664	22,918	+12,254	+53
Treatment expense ($)	1,892,941	1,727,882	−165,059	−8.7
$/1000 gal	0.18	0.08	−0.10	−56

technology has resulted in significant chemical and operating cost savings. The advantages include:

1. The footprint required per million gallons was one sixth the size.
2. The chemical consumption was lower.
3. Unit Filter Runtime volumes were 18% longer.
4. In-plant water usage was 59% lower.
5. The total cost per 1000 gal was 56% lower.

EXAMPLE 23: INTRODUCTION OF AQUADAF AND RICTOR DAF SYSTEMS AROUND THE WORLD FOR WATER PURIFICATION

Solution

The latest advancements in DAF came out of Helsinki, Finland, and the Rictor Company in the mid-1990s. These process advancements further improved hydraulics and DAF geometry, even at turbulent flow conditions, and allow for design flotation rates from 25 to 40 m/h (10–16 gpm/ft^2).[2] Tanks are being designed wider due to limited tank lengths. Tanks are designed from 10 to 14 ft deep. The bottom of the flotation tank incorporates a perforated plate with orifices spread in a patented, non-uniform pattern. The density and diameter of holes are higher toward the inlet of the DAF and less so at the outlet, which allows for uniform collection of water and a consistent micro-bubble bed over the entirety of the flotation tank [161].

Currently branded the AquaDAF (Fig. 6.14) in North America, this technology made its debut in the US in 2000 in West Nyack, NY, USA, a 20-MGD water treatment plant. There are now more than 1.7 billion gal per day of high-rate, AquaDAF and Rictor systems installed around the world from the US to Canada, France, Finland, Brazil, China, Spain, Russia, Romania, Portugal, and the United Arab Emirates.

Table 6.15 shows the installation list of the AquaDAF systems (Fig. 6.14) and the predecessor DAF systems by Rictor. All of the installations since the Town of Tampere water treatment plant (WTP) in 2000 include the latest process enhancements of high-rate AquaDAF and Rictor systems. All installations preceding the Tampere system are conventional rate systems. The largest system AquaDAF system (208.3 MGD) was installed in the Haworth WTP in New Jersey, USA, in 2009, at a DAF loading rate of 16 gpm/ft^2. Most of the AquaDAF systems were installed for conventional drinking water pretreatment, several were for membrane filtration and desalination pretreatment, and two were for tertiary treatment of wastewater, including phosphorous removal. All AquaDAF and Rictor DAF systems are the innovative complete physicochemical process systems consisting of chemical feeding/mixing, precipitation, coagulation/flocculation, dissolved air flotation clarification, and disinfection unit processes.

Table 6.15 Installation list of AquaDAF® and Rictor DAF systems. 1 MGD = 3.785 MLD (Courtesy of SUEZ)

Plant	Country	State	Application	MGD	Start-up
Twin Oaks WTP	USA	California	Membrane Backwash	12.0	2020
Stony Brook WTP	USA	Connecticut	DW Clarification	4.4	2020
Haverhill	USA	Massachusetts	DW Clarification	16.1	2020
Paulding County	USA	Georgia	DW Clarification	18.0	2020
Williamstown WTP	USA	Kentucky	DW Clarification	4.0	2017
Carthage WTP	USA	North Carolina	DW Clarification	1.0	2017
Canmore WWTP	Canada	Alberta	Filter Backwash	1.0	2016
Broad Brook WFP	USA	Connecticut	DW Clarification	10.0	2014
Ebensburg WTP	USA	Pennsylvania	DW Clarification	1.1	2013
Roux-Canal WWTP	Belgium		Tertiary WW	4.6	2012
El Dorado	Brazil			50.8	2012
Grenoble	France			4.4	2012
La Houlme	France			1.3	2012
Evreux WWTP	France		Tertiary WW	3.8	2012
Canoe Brook WTP	USA	New Jersey	DW Clarification	15.0	2012
Al Dur	Bahrain		Desal Clarification	152.2	2011
Kokkola	Finland		Tertiary WW	7.9	2011
Amesbury WTP	USA	Massachusetts	Drinking Water (DW) Clarification	8.4	2011
Berea Municipal Utilities WTP	USA	Kentucky	DW Clarification	8.0	2009
Haworth WTP	USA	New Jersey	DW Clarification	208.3	2009
Claresholm WTP	Canada	Alberta	Membrane Pretreatment	3.0	2009
Hudson WWTP	USA	Massachusetts	Tertiary Phosphorous Removal	6.6	2009
Monistrol WTP	France		DW Clarification	4.4	2009
Wetaskiwin WTP	Canada	Alberta	DW Clarification	4.5	2008
Barcelona WTP	Spain	NA	Desalination Clarification	126.8	2008
Hameenlinna WWTP	Finland	NA	Tertiary WW	16.0	2008
La Segarra WTP	Spain	NA	DW Clarification	6.3	2008
Scottsdale Water Campus	USA	Arizona	Membrane Pretreatment	25.0	2008
White Tanks Regional WTP	USA	Arizona	DW Clarification	20.0	2008
Seneca WTP (Phase II)	USA	South Carolina	DW Clarification	6.0	2008
Jekaterinburg WTP	Russia	NA	DW Clarification	44.5	2007

(continued)

Table 6.15 (continued)

Plant	Country	State	Application	MGD	Start-up
UAE WTP	United Arab Emirates	Desalination Clarification	70.0		2007
Qingzhen	China	NA	DW Clarification	27.9	2007
Brasov WTP	Romania	NA	DW Clarification	45.7	2006
Macao Coloane	China	NA	DW Clarification	8.3	2006
Ville de Contrecoeur WTP	Canada	Quebec	DW Clarification	3.2	2006
Lac Etchemin WTP	Canada	Quebec	DW Clarification	0.6	2006
Monte Novo WTP	Portugal	NA	DW Clarification	7.0	2006
Turku, Finland	Finland	NA	DW Clarification	20.4	2006
Minera Escondida	Chile	NA	Desalination Clarification	24.5	2006
Apremont WTP	France	NA	DW Clarification	22.8	2005
Macao MSR2 WTP	China	NA	DW Clarification	15.9	2005
Utti WTP	Finland	NA	DW Clarification	5.1	2005
Seneca WTP (Phase I)	USA	South Carolina	DW Clarification	6.0	2005
Saint Brieuc WTP	France	NA	DW Clarification	6.5	2005
SSJID WTP	USA	California	Membrane Pretreatment	46.0	2004
Lake Deforest WTP	USA	New York	DW Clarification	20.0	2003
Manaus WTP	Brazil	NA	DW Clarification	75.0	2002
Town of Tampere WTP	Finland	NA	DW Clarification	19.0	2000
Joutseno WWTP	Finland	NA	NA	1.3	2000
Lappavesi Oy, Kuortane	Finland	NA	NA	1.0	1999
Butoniga WTP	Croatia	NA	NA	22.8	1999
Town of Vaasa WWTP	Finland	NA	NA	8.2	1997
United Paper Mills, Kajaani	Finland	NA	NA	3.6	1995
Cellulose and Paper Mill Veitsiluoto Oy, Kemi	Finland	NA	NA	6.4	1995
Tittesworth WTP	England	NA	NA	13.2	1994
Ogston WTP	England	NA	NA	11.9	1994
Town of Norrtalje, Sweden	Sweden	NA	NA	3.2	1992
Paper Mill, Veitsiluoto Oy, Oulu	Finland	NA	NA	6.5	1991
Voss Country WWTP	Norway	NA	NA	4.6	1990
Veitsiluoto Oy, Oulu	Finland	NA	NA	9.1	1990
Town of Tampere	Finland	NA	NA	9.5	1989
The commune of Sahalahti	Finland	NA	NA	1.0	1989
Kymmene Oy, Kaukas	Finland	NA	NA	3.2	1988
Svetogorsk, USSR	Russia	NA	NA	73.0	1988
Town of Vammala	Finland	NA	NA	1.5	1987

(continued)

Table 6.15 (continued)

Plant	Country	State	Application	MGD	Start-up
LSO Slaughter House, effluent	Finland	NA	NA	0.2	1985
Paper Mill Veitsiluoto Oy, Kemi	Finland	NA	NA	4.8	1984
Cellulose Mill Oy Metsa-Botnia Ab, Aanekoski	Finland	NA	NA	3.4	1984
Textile Mill Nanso Oy, Nokia	Finland	NA	NA	0.4	1983
Sugar Factory Suomen Sokeri Oy, Kantvik	Finland	NA	NA	2.6	1983
Power Plant Pohjolan Voima Oy, Kristiinankaupunki	Finland	NA	NA	0.7	1983
Town of Iisalmi	Finland	NA	NA	1.7	1982
Paper Mill Tampella Oy, Inkeroinen	Finland	NA	NA	1.2	1982
Town of Rauma	Finland	NA	NA	5.7	1981
Veitsiluoto Paper Mill	Finland	NA	NA	0.4	1980
Yhtyneet Paperitehtaat, The United Paper Mill	Finland	NA	NA	1.9	1980
Rauma Repola Paper Mill	Finland	NA	NA	7.7	1980
Veitsiluoto Bleached Paper Mill	Finland	NA	NA	0.4	1978
Town of Pieksamaki	Finland	NA	NA	2.7	1978
Town of Kristiinankaupunki	Finland	NA	NA	0.1	1977
The rural commune of Jyvaskyla	Finland	NA	NA	2.7	1977
Town of Uusikaupunki	Finland	NA	NA	1.9	1977
Town of Oulu	Finland	NA	NA	7.7	1976
Imatran Voima, Electric Steam Power Plant	Finland	NA	NA	1.6	1976
Town of Varkaus	Finland	NA	NA	2.5	1975
The Finnish State Railways	Finland	NA	NA	0.8	1975
Town of Pietarsaari	Finland	NA	NA	2.3	1974
Town of Vaasa	Finland	NA	NA	7.7	1973
Military Base Ylojarvi	Finland	NA	NA	0.3	1972
Varkaus co-operative dairy	Finland	NA	NA	0.1	1972
Town of Hamina	Finland	NA	NA	1.7	1971
Kymi Fine Paper Mill	Finland	NA	NA	1.9	1971
Town of Kristiinankaupunki	Finland	NA	NA	0.1	1971

(continued)

Table 6.15 (continued)

Plant	Country	State	Application	MGD	Start-up
Town of Sienajoki	Finland	NA	NA	6.9	1971
Town of Lohja	Finland	NA	NA	2.5	1970
Town of Uusikaupunki	Finland	NA	NA	1.5	1970
Lohja Cement and Lime Mill	Finland	NA	NA	1.5	1970
Varkaus co-operative	Finland	NA	NA	0.1	1970
Town of Kuopio	Finland	NA	NA	5.3	1969
Town of Oulu	Finland	NA	NA	5.7	1969
Rinnekoti Foundation	Finland	NA	NA	0.5	1969
Municipality of Karhula	Finland	NA	NA	1.5	1969
Tervakoski Condensator Paper Mill	Finland	NA	NA	2.9	1968
Council of Kiuruvesi	Finland	NA	NA	0.4	1968
Town of Vaasa	Finland	NA	NA	5.3	1968
Town of Nokia	Finland	NA	NA	0.2	1968
Town of Kristiinankaupunki	Finland	NA	NA	0.1	1967
Town of Oulu	Finland	NA	NA	2.9	1967
Town of Kuusankoski	Finland	NA	NA	1.5	1967

Notes: Installations including the Town of Tampere WTP (2000) and thereafter are high-rate AquaDAF and Rictor systems; the rest are conventional DAFs by Rictor
NA not available

Glossary

Coagulant A chemical (alum or iron salts) added to water to destabilize particles, allowing subsequent floc formation and removal by clarification (flotation or sedimentation) and/or filtration.

Coagulation A process of destabilizing charges of suspended and colloidal particles in water by adding chemicals (coagulants). In coagulation process, positively charged chemicals are added to neutralize or destabilize these negative charges and allow the neutralized particles to accumulate and be removed by clarification (flotation or sedimentation) and/or filtration.

Collector A device or system designed to collect filter backwash water, or other treatment unit.

Colloids Colloids are very small particles that have extremely large surface area. Colloidal particles are larger than atoms and ions but are small enough that they are usually not visible to the naked eye. They range in size from 0.001 to 10 μm, resulting in a very small ratio of mass to surface area.

Complete physicochemical process system A water or wastewater treatment system that consists of at least the unit processes of chemical feeding/mixing, precipitation, coagulation/flocculation, clarification (sedimentation or flotation), filtration (sand, multi-media, DE, GAC, or membrane), and disinfection.

Dispersion A uniform and maximum separation of extremely fine particles, often of colloidal size.

Dissolved air flotation (DAF) One of the dissolved gas flotation (DGF) processes when air is used for generation of gas bubbles. See dissolved gas flotation (DGF).

Dissolved gas flotation (DGF) It is a process involving pressurization of gas at 25–95 psig for dissolving gas into water, and subsequent release of pressure (to 1 atm) under laminar flow hydraulic conditions for generating extremely fine gas bubbles (20–80 μm) which become attached to the impurities to be removed and rise to the water surface together. The impurities or pollutants to be removed are on the water surface and are called float or scum which is scooped off by sludge collection means. The clarified water is discharged from the flotation clarifier's bottom. The gas flow rate is about 1% of influent liquid flow rate. The attachment of gas bubbles to the impurities can be a result of physical entrapment, electrochemical attraction, surface adsorption, and/or gas stripping. The specific gravity of the bubble-impurity agglomerate is less than 1, resulting in buoyancy or non-selective flotation (i.e., Save-All).

Floc Collections of smaller particles that have agglomerated together into larger, more separable, floatable or settleable particles as a result of the coagulation process.

Flocculation A water treatment unit process following coagulation that uses gentle stirring to bring suspended particles together so they will form larger, more separable (floatable or settleable) floc.

Flocculator A process device to enhance the formation of floc in a water. Mixing energy can be provided by slow turning mechanical means or head loss.

Physicochemical process system A water or wastewater treatment system consisting of only the chemical and mechanical unit processes.

Rapid mixing A water treatment unit process of quickly mixing a chemical solution uniformly through the process water.

Velocity gradient (*G*) A measure of the mixing intensity (in units of per second) in a water treatment process. Very high velocity gradients (greater than 300 s^{-1}) are used for complete mixing and dissolution of chemicals in a coagulation process, whereas lower values (less than 75 s^{-1}) are used in flocculation to bring particles together and promote agglomeration.

Appendix 1: Treatment of Foundry Industry Wastes by Chemical Precipitation with Sedimentation (Alum, Sodium Hydroxide, and Sulfuric Acid) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (alum, NaOH, H_2SO_4)				
Data source: Effluent guidelines			Data source status:	
Point source: Foundry industry			Not specified _____	
Subcategory: Aluminum foundry die casting			Bench scale _____	
Plant: 574–C			Full scale __×__	
Pretreatment/treatment: Emulsion Breaking/Chem. Ppt.				
Design or Operating Parameters				
Wastewater flow rate: 4.3 L/s			Type of sedimentation: Basin	
Unit configuration: Continuous operation				
Removal Data				
Sampling: Unspecified	Analysis: Data set 2 (v.7.3.12)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Toxic pollutants, μg/L				
Cyanide	BDL	BDL	NM	10
Lead	200	150	25	10
Zinc	1300	60	97	10
Bis(2-ethylhexyl) phthalate	5500	32	99	10
Butyl benzyl phthalate	690	BDL	99[a]	10
Di-*n*-butyl phthalate	74	BDL	93[a]	10
Diethyl phthalate	730	BDL	99[a]	10
2,4-Dimethylphenol	41	BDL	88[a]	10
Phenol	16	BDL	69[a]	10
p-Chloro-a-cresol	110	62	44	10
Benzo (a)pyrene	53	BDL	91[a]	10
Chrysene	780	10	99	10
Fluoranthene	370	BDL	98[a]	10
Fluorene	800	BDL	99[a]	10
Naphthalene	160	BDL	97[a]	10
Pyrene	80	BDL	94[a]	10
Methylene chloride	BDL	39	NM	10
1,1,1-Trichloroethane	ND	51	NM	10
Acenaphthalene	20	BDL	75	10
Tetrachloroethylene	ND	30	NM	10
Xylene	75	BDL	93[a]	10

BDL below detection limit, *NM* not meaningful, *ND* not detected; [a]Approximate value

Appendix 2: Treatment of Metal Finishing Industry Wastes by Chemical Precipitation with Sedimentation (USEPA)

Treatment Technology: Chemical precipitation with sedimentation	
Data source: EGD combined database	Data source status:
Point source: Metal finishing	Not specified _____
Subcategory: Common metals; precious metals; hexavalent chromium; cyanide, oils	Bench scale _____ Pilot scale _____
Plant: 36040	Full scale __×__
Pretreatment/treatment: Chem. Ox. (CN), Chem. Red. (Cr)/Chem. Ppt.,Sed. (clarifier)	
Design or Operating Parameters	
Wastewater flow rate: 107,000 m^3/day	Type of sedimentation: Clarifier
Unit configuration: Batch Chem. Ox. (CN); continuous Chem. Red. (Cr); clarifier—continuous operation	
Removal Data	

Sampling: 24-h composite, flow proportion	Analysis: Data set 1 (v.7.3.13)[a]			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L, except pH				
pH, minimum, unit	6.8			
pH, maximum, unit	7.1	9.1	NM	
Fluorides	4.5	5.7	NM	0.1
Phosphorus	2.2	0.07	97	0.003
TSS	100	11	89	5.0
TDS	960	1500	NM	5.0
Iron	1.3	0.07	95	0.005
Tin	0.08	0.06	25	
Oil and grease	20	BDL	88[c]	5.0
Gold	0.04	0.17	NM	
Toxic pollutants, µg/L				
Cadmium	5.0	5.0	0	2.0
Chromium	26,000	530	98	3.0
Copper	5900	69	99	1.0
Lead	53	BDL	72	30
Nickel	120,000	1400	99	6.0
Zinc	910	18	98	1.0
Cyanide, total	330	57	83	5.0
Hexavalent chromium	24,000	11	>99	5.0

Blanks indicate data not available; *BSL* below detection limit, *NM* not meaningful; [a]Plant data are a 3-day average; [b]Original source of data: Electroplating Pretreatment 1976–1977 (HS)

Appendix 3: Treatment of Metal Finishing Industry Wastes by Chemical Precipitation with Sedimentation (USEPA)

Treatment Technology: Chemical precipitation with sedimentation	
Data source: EGD combined database	Data source status:
Point source: Metal finishing	Not specified _____
Subcategory: Common metals; hexavalent chromium; cyanide; oil	Bench scale _____
	Pilot scale _____
Plant: 33024	Full scale __×__
Pretreatment/treatment: Chem. Ox. (CN), Chem. Red. (Cr)/Chem. Ppt., Sed. (clarifier)	
Design or Operating Parameters	
Wastewater flow rate: 303,000 m^3/day	Type of sedimentation: Clarifier
Unit configuration: Clarifier—continuous operation	
Removal Data	

Sampling: 8-h composite	Analysis: Data set 1 (v.7.3.13)[a]			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L, except pH				
pH, maximum, unit	8.5	8.5		
Fluorides	23	18	22	0.1
TSS	250	42	83	5.0
Tin	0.12	0.15	NM	
Iron	2.5	0.18	93	0.005
Manganese	0.07	0.14	NM	0.005
Oil and grease	22	18	18	5.0
Aluminum	22	2.2	90	0.005
Toxic pollutants, μg/L				
Cadmium	95	5.0	95	2.0
Chromium	340	70	79	1.0
Copper	1600	160	90	1.0
Lead	47	18	62	30
Nickel	96	19	80	6.0
Zinc	12,000	1100	91	1.0
Cyanide, total	1000	40	96	5.0
Hexavalent chromium	5.0	5.0	0	5.0
Mercury	1.0	1.0	0	0.1
Silver	2.0	4.0	NM	0.1/1.0

Blanks indicate data not available; *NM* not meaningful; [a]Original source of data: NAMPM

Appendix 4: Treatment of Metal Finishing Industry Wastes by Chemical Precipitation with Filtration (USEPA)

Treatment Technology: Chemical precipitation with filtration	
Data source: EGD combined database	Data source status:
Point source: Metal finishing	Not specified _____
Subcategory: Common metals; hexavalent chromium; cyanide; oils	Bench scale_____
	Pilot scale _____
Plant: 36041	Full scale __×__
Pretreatment/treatment: Chem. Ox. (CN), Chem. Red. (Cr)/Chem. Ppt., Filter	
Design or Operating Parameters	
Wastewater flow rate: 229,000 m^3/day	Filtration rate (hydraulic loading):
Unit configuration: Batch Chem. Ox.; batch Chem. Red.; continuous Chem. Ppt. and filter	
Removal Data	
Sampling: 24-h composite, flow proportion (unspecified)	Analysis: Data set 1 (v.7.3.13)[a]

Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L, except pH				
pH, maximum, unit	11	11		
Phosphorus	1.2	0.05	96	0.003
TSS	520	10	98	5.0
Iron	5.8	0.25	96	0.005
Tin	2.0	0.14	93	
Oil and grease	46	5.0	89	5.0
Toxic pollutants, μg/L				
Cadmium	42	6.0	86	2.0
Chromium	12,000	610	95	3.0
Hexavalent chromium	5.0	5.0	0	5.0
Copper	7500	440	94	1.0
Lead	140	32	77	30
Nickel	2600	44	98	6.0
Zinc	13,000	140	99	1.0
Cyanide, total	2000	400	80	5.0

Blanks indicate data not available; *NM* not meaningful; [a]Original source of data: Electroplating Pretreatment 1976–1977(HS)

Appendix 5: Treatment of Iron and Steel Industry Wastes (Combination Acid Subcategory) by Chemical Precipitation with Sedimentation (Lime) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (lime)				
Data source: Effluent guidelines			Data source status:	
Point source: Iron and steel			Not specified _____	
Subcategory: Combination acid			Bench scale _____	
Plant. I			Full scale __×__	
Pretreatment/treatment: Neutral./Chem. Ppt., Sed.				
Design or Operating Parameters				
Wastewater flow rate: 69.4 L/s			Type of sedimentation: Settling lagoon	
Unit configuration: Continuous operation				
Removal Data				
Sampling: Unspecified	Analysis: Data set 2 (v.7.3.5)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L				
TSS	560	130	77	
Dissolved iron	62	24	61	
Fluoride	33	9.1	72	
Toxic pollutants, µg/L				
Chromium	17,000	1800	89	
Copper	150	ND	100	
Nickel	6000	5200	13	
Zinc	750	240	68	

Blanks indicate data not available; *ND* not detected, *NM* not meaningful

Appendix 6: Treatment of Textile Mills Wastes (Knit Fabric Finishing Subcategory) by Chemical Precipitation with Sedimentation (Lime) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (lime)				
Data source: Effluent guidelines			Data source status:	
Point source: Textile mills			Not specified _____	
Subcategory: Knit fabric finishing			Bench scale __×__	
Plant: Unspecified			Pilot scale _____	
			Full scale _____	
Pretreatment/treatment: Unspecified/Chem. Ppt.				
Design or Operating Parameters				
Wastewater flow rate: Unspecified			Type of sedimentation: Unspecified	
Chemical dosages(s): Unspecified				
Mix detention time: Unspecified				
Flocculation detention time: Unspecified				
Unit configuration: Unspecified				
Removal Data				
Sampling: Unspecified	Analysis: Data set 2 (v.7.3.32)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent[a]	Effluent		
Toxic pollutants, μg/L				
Cadmium	10	ND	>99	
Chromium	930	80	91	
Copper	500	30	94	
Lead	100	ND	>99	
Nickel	50	ND	>99	
Silver	50	ND	>99	
Zinc	3200	110	97	

Blanks indicate data not available; *ND* not detected; [a]Sample taken from aeration basin at plant

Appendix 7: Treatment of Steam Electric Industry Wastes (Cooling Tower Blowdown Subcategory) by Chemical Precipitation with Filtration (USEPA)

Treatment Technology: Chemical precipitation with filtration (lime)				
Data source: Effluent guidelines			Data source status:	
Point source: Steam electric			Not specified _____	
Subcategory: Cooling tower blowdown			Bench scale __×__	
Plant: 5604			Pilot scale _____	
			Full scale_____	
Pretreatment/treatment: Unspecified/Chem. Ppt., Filtration				
Design or Operating Parameters				
Wastewater flow rate: Unspecified				
Chemical dosages(s): Add to pH >11.0				
Mix detention time: Unspecified				
Removal Data				
Sampling: Unspecified	Analysis: Data set 2 (v.7.3.31)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Toxic pollutants, μg/L				
Antimony	5	3	40	
Arsenic	7	<1	>86	
Chromium	2	<2	NM	
Copper	180	48	73	
Nickel	6	12	NM	
Silver	3	4	NM	
Zinc	780	140	82	
Beryllium	<0.5	<0.5	NM	
Cadmium	<0.5	<0.5	NM	
Lead	<3	<3	NM	
Mercury	<0.2	<0.2	NM	
Selenium	<2	<2	NM	
Thallium	<1	<1	NM	
Vanadium	24	77	NM	

Blanks indicate data not available; *NM* not meaningful

Appendix 8: Treatment of Steam Electric Industry Wastes (Ash Transport Water Subcategory) by Chemical Precipitation with Filtration (Lime) (USEPA)

Treatment Technology: Chemical precipitation with filtration (lime)				
Data source: Effluent guidelines			Data source status.	
Point source: Steam electric			Not specified _____	
Subcategory: Ash transport water			Bench scale __×__	
Plant: 1226			Pilot scale _____	
			Full scale _____	
Pretreatment/treatment: Sed. (ash pond)/Chem. Ppt., Filtration				
Design or Operating Parameters				
Wastewater flow rate: Unspecified				
Chemical dosages(s): Add to pH >11.0				
Mix detention time: Unspecified				
Unit configuration: Jar test				
Removal Data				
Sampling: Unspecified	Analysis: Data set 2 (v.7.3.31)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L				
TOC	<20	<20	NM	
Toxic pollutants, µg/L				
Antimony	7	10	NM	
Arsenic	9	1	89	
Cadmium	2.0	2.0	0	
Chromium	6	11	NM	
Copper	14	10	29	
Lead	4	<3	>25	
Mercury	<0.2	0.3	NM	
Nickel	5.5	6.0	NM	
Selenium	8	8	0	
Silver	0.5	0.4	20	
Zinc	7	2	71	
Beryllium	<0.5	<0.5	NM	
Thallium	<1	<1	NM	
Vanadium	78	78	0	

Blanks indicate data not available; *NM* not meaningful

Appendix 9: Treatment of Inorganic Chemicals Industry Wastes (Hydrofluoric Acid Subcategory) by Chemical Precipitation with Sedimentation (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (lime)				
Data source: Effluent guidelines			Data source status:	
Point source: Inorganic chemicals			Not specified _____	
Subcategory: Hydrofluoric acid			Bench scale _____	
Plant: 705			Pilot scale _____ Full scale __×__	
Pretreatment/treatment: Unspecified/Sed.				
Design or Operating Parameters				
Wastewater flow rate: Unspecified			Type of sedimentation: Unspecified	
Chemical dosages(s): Unspecified				
Mix detention time: Unspecified				
Flocculation detention time: Unspecified				
Unit configuration: 30–35% of effluent recycled, remaining effluent neutralized and discharged				
Removal Data				
Sampling: 72-h composite and grab	Analysis: Data set 1 (v.7.3.15)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Toxic pollutants, µg/L				
Antimony	10	1.9	81	
Arsenic	40	<9.7	>76	
Cadmium	9.7	1.6	84	
Chromium	390	47	88	
Copper	290	19	93	
Lead	50	23	54	
Mercury	5.8	0.48	92	
Nickel	560	<9.7	>98	
Thallium	2.6	1.1	58	
Zinc	240	53	78	

Blanks indicate data not available

Appendix 10: Treatment of Ore Mining and Dressing Industry Wastes (Base-Metal Mine Subcategory) by Chemical Precipitation with Sedimentation (Lime) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (lime)				
Data source: Effluent guidelines			Data source status:	
Point source: Ore mining and dressing			Not specified _____	
Subcategory: Base-metal mine			Bench scale _____	
Plant: Plant 3 of Canadian pilot plant study			Pilot scale __×__	
			Full scale _____	
Pretreatment/treatment: Unspecified/Chem. Ppt.				
Design or Operating Parameters				
Wastewater flow rate: Unspecified			Type of sedimentation:	
Unspecified chemical dosages(s): Unspecified				
Mix detention time: Unspecified				
Flocculation detention time: Unspecified				
Unit configuration: Two-stage lime addition				
Removal Data				
Sampling: 1 year	Analysis: Data set 4 (v.7.3.23)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent[a]	Effluent[b]		
Toxic pollutants, μg/L				
Copper	19,000	60	99	
Lead	1300	150	88	
Zinc	110,000	350	99	

Blanks indicate data not available; [a]Average value for raw mine water influent to pilot plant; [b]Effluent qualities during periods of optimized steady operation

Appendix 11: Treatment of Ore Mining and Dressing Industry Wastes (Lead/Zinc Mine Subcategory) by Chemical Precipitation with Sedimentation (Lime) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (lime)	
Data source: Effluent guidelines	Data source status:
Point source: Ore mining and dressing	Not specified _____
Subcategory: Lead/zinc mine	Bench scale _____
Plant: 3113	Pilot scale __×__
	Full scale _____
Pretreatment/treatment: None/Chem. Ppt.	
Design or Operating Parameters	
Wastewater flow rate: Unspecified	Type of sedimentation: Unspecified
Chemical dosages(s): Unspecified	
Mix detention time: Unspecified	
Flocculation detention times: Unspecified	
Unit configuration: Unspecified pH in clarifier: 9.1–9.7	

Removal Data				
Sampling: 4 days	Analysis: Data set 4 (v.7.3.23)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent[a]	Effluent		
Classical pollutants, mg/L				
TSS	112	33	71	
Toxic pollutants, μg/L				
Cadmium	230	25	89	
Copper	1500	100	93	
Lead	88	100	NM	
Zinc	71,000	<20	>99	

Blanks indicate data not available; *NM* not meaningful; [a]Average of seven observations

Appendix 12: Treatment of Porcelain Industry Wastes (Alum Subcategory) by Chemical Precipitation with Sedimentation (Lime, Polymer) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (lime, polymer)				
Data source: EGD combined database			Data source status:	
Point source: Porcelain			Not specified _____	
Subcategory: Alum			Bench scale _____	
Plant: 33077			Pilot scale _____	
			Full scale __×__	
Pretreatment/treatment: Equal./<u>Chem. Ppt.</u>, Sed. (tube/plate settler)				
Design or Operating Parameters				
Wastewater flow rate: 965 m^3/day			Type of sedimentation: Tube/ plate settler	
Chemical dosages(s): Lime: 47,200 kg/year				
Polymer: 320 kg/year				
Mix detention time: Unspecified				
Flocculation detention time: Unspecified				
Unit configuration: Continuous operation (16 h/day)				
Removal Data				
Sampling: 16-h composite, flow proportion (1 h)	Analysis: Data set 2 (v.7.3.16)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L, except pH				
pH, minimum, unit	8.9	9.4		
pH, maximum, unit	10.5	10.0		
Fluorides	1.8	2.0	NM	0.1
Phosphorus	12	0.89	92	0.003
TSS	53	ND	>99	5.0
Iron	2.0	0.038	98	0.005
Titanium	1.2	ND	>99	
Manganese	0.017	ND	>99	0.005
Phenols, total	0.006	ND	>99	0.005
Aluminum	1.2	ND	>99	0.04
Barium	.23	0.20	13	
Toxic pollutants, μg/L				
Cadmium	2900	57	98	2.0
Chromium, total	11	ND	>99	3.0
Copper	4.0	ND	>99	1.0
Lead	1200	ND	>99	30
Zinc	220	540	NM	1.0
Cyanide, total	160	ND	>99	5.0
Selenium	300	ND	>99	

Blanks indicate data not available; *ND* not detected, *NM* not meaningful

Appendix 13: Treatment of Paint Manufacturing Industry Wastes by Chemical Precipitation with Sedimentation (Alum, Polymer) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (alum, aluminum sulfate, polymer)	
Data source: Effluent guidelines	Data source status:
Point source: Paint manufacturing	Not specified _____
Subcategory: Unspecified	Bench scale _____
Plant: 24	Pilot scale _____
	Full scale __×__
Pretreatment/treatment: Neutral., Oil Sep./Chem. Ppt., Sed.	
Design or Operating Parameters	
Wastewater flow rate: 0.26–0.52 L/s	Type of sedimentation: Unspecified
Chemical dosages(s): Unspecified	
Mix detention time: Unspecified	
Flocculation detention time: Unspecified	
Unit configuration: Batch operation	

Removal Data

Sampling: Grab and composite — Analysis: Data set 1 (v.7.3.25)

Pollutant/parameter	Concentration[a]		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L				
BOD (5)	16,000	1100	25	
COD	56,000	11,000	69	
Total phenol	0.20	0.15	25	
Total solids	41	3	93	
Toxic pollutants, µg/L				
Ethylbenzene	1900	460	75	
Toluene	2900	2900	0	
Chloroform	48	26	40	
Methylene chloride	130,000	13,000	90	
1,1,2-Trichloroethane	<7	<11	NM	
1,1,1-Trichloroethane	380	<170	<55	
Phenol	ND	<10	NM	
Bis(2-ethylhexyl) phthalate	<10	ND	>99	
Tetrachloroethylene	740	ND	>99	
Trichloroethylene	<10	ND	>99	

Blanks indicate data not available; *NM* not meaningful; [a]Average of three samples, except total phenol: two samples

Appendix 14: Treatment of Coil Coating Industry Wastes (Alum Subcategory) by Chemical Precipitation with Sedimentation (Sodium Hydroxide, Lime) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (sodium hydroxide; lime)	
Data source: EGD combined database	Data source status:
Point source: Coil costing	Not specified _____
Subcategory: Alum	Bench scale _____
Plant: 13029	Full scale __×__
Pretreatment/treatment: None/Chem. Red. (Cr), Chem. Ppt., Sed. (tube/plate)	
Design or Operating Parameters	
Wastewater flow rate: 3930 L/day	Type of sedimentation! Tube/plate settler
Chemical dosages(s): NaOH: 8700 kg/year:	
$Ca(OH)_2$: 4300 kg/year	
Unit configuration: Tube/plate settler-continuous	
Removal Data	
Sampling: 24-h composite. Flow proportion (1 h)	Analysis: Data set 2 (v.7.3.9)

Pollutant/parameter	Concentration				Percent removal	Detection limits
	Influent			Effluent		
	200	201	Average			
Classical pollutants, mg/L, except pH						
pH, minimum, unit	11	3.1	7.0	8.3		
pH, maximum, unit	11	5.4	8.2	8.7		
Fluorides	0.43	340	170	44	74	0.1
Phosphorus	91		46	1.3	97	0.003
TSS	970	99	530	37	93	5.0
Iron	0.61	14	7.3	0.1	99	0.005
Oil and grease	2800	8.0	1400	20	98	5.0
Phenols, total	0.14	ND	0.07	0.2	71	0.005
Aluminum	970	99	530	5.1	99	0.04
Manganese	1.5	0.76	1.1	0.011.	99	0.005
Toxic pollutants, µg/L						
Cadmium	3.0	8.0	5.5	ND	>99	2.0
Chromium	180	660,000	330,000	2500	99	3.0
Copper	210	230	220	10	95	1.0
Lead	60	170	115	ND	>99	30
Nickel	ND	190	95	ND	>99	6.0
Zinc	280	38,000	19,000	69	>99	1.0
Bis(2-ethyhexyl) phthalate	220	62	140	BDL	96	10
Diethyl phthalate	410	68	240	3.0	99	10
Hexavalent chromium	ND	290,000	140,000	ND	>99	5.0

Blanks indicate data not available; *BDL* below detection limit, *ND* not detected, *NM* not meaningful

Appendix 15: Treatment of Coil Coating Industry Wastes (Steel Subcategory) by Chemical Precipitation with Sedimentation (Lime) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (lime)	
Data source: EGD combined database	Data source status:
Point source: Coil coating	Not specified _____
Subcategory: Steel	Bench scale _____
Plant: 46050	Full scale __×__
Pretreatment/treatment: Ion Exch./Chem. Red. (Cr), Equal., Chem. Ppt., Coag. Floc Sed.	
Design or Operating Parameters	
Wastewater flow rate: 156 m^3/day	Type of sedimentation: Tank
Unit configuration: Batch (8 h/day) Chem. Red. (Cr); continuous (24 h/day) Chem. Ppt	Hydraulic detention time: 16.0 h
Removal Data	
Sampling: Influent: (201–202) continuous 24-h composite, time proportion (1 h): effluent: batch (unspecified) composite, time proportion (3 h): (205) continuous (unspecified) composite, (253) batch-unspecified composite, flow proportion (1 day)	Analysis: Data set 2 (v.7.5.9)

Pollutant/parameter	Concentration						Percent removal	Detection limits
	Influent					Effluent		
	201	202	253	205	Average			
Classical pollutants, mg/L, except pH								
pH, minimum, unit	7.0	4.3	7.5	2.0[a]	5.2[a]	7.0		
pH, maximum, unit	7.4	5.0	7.5	6.9	6.9	7.0		
Fluorides	1.0	76	2.6	0.75	23	10	5.2	0.1
Phosphorus	22	11		0.6	17	1.6	90	0.003
TSS	160	70	870	110	150	8.0	95	5.0
Iron	0.82	1.4	7.2	0.60	1.1	0.17	84	0.005
Manganese	0.73	1.05	3.6	2.4	1.1	0.16	85	
Toxic pollutants, μg/L								
Chromium	ND	130	620,000	ND	18,000	24	>99	3.0
Copper	14	ND	43	11	11	3.0	73	1.0
Lead	180	ND	56	ND	110	ND	>99	30
Nickel	150	32,000	20,300	ND	9100	1400	85	4.0
Zinc	5300	65,000	370,000	230	31,000	440	95	1.0
Bis(2-ethyhexyl) phthalate	23	200	15	BDL	60	40	41	10
Diethyl phthalate	BDL	330	15	ND	91	40	56	10
Trichloroethylene	0.5	ND	ND	0.6	36	ND	>99	0.1
Hexavalent chromium	ND	60	330,000	ND	9500	ND	>99	5.0

Blanks indicate data not available; *BDL* below detection limit, *ND* not detected, *NM* not meaningful;
[a] Influent 202, 201, and 205 are coded as continuous raw waste, 253 is coded as batch

Appendix 16: Treatment of Nonferrous Metals Wastes (Columbium/Tantalum Subcategory) by Chemical Precipitation with Sedimentation (Lime) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (lime)				
Data source: Effluent guidelines			Data source status:	
Point source: Nonferrous metals			Not specified _____	
Subcategory: Columbium/tantalum			Bench scale _____	
Plants: Unspecified			Full scale __×__	
Pretreatment/treatment: None/Chem. Ppt.				
Design or Operating Parameters				
Wastewater flow rate: Unspecified			Type of sedimentation: Unspecified	
Chemical dosages(s): Unspecified				
Removal Data				
Sampling: 24-h and 72-h composite and grab	Analysis: Data set 2 (v.7.3.22)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L				
COD	16	8	50	
TSS	900	10	99	
Fluoride	4.5	2.5	44	
Aluminum	9.0	0.2	98	
Calcium	550	230	58	
Iron	120	0.3	>99	
Manganese	17	0.2	99	
Toxic pollutants, μg/L				
Cadmium	25	2	92	
Copper	110,000	700	99	
Nickel	60,000	500	99	
Zinc	27,000	200	99	

Blanks indicate data not available

Appendix 17: Treatment of Nonferrous Metals Wastes (Tungsten Subcategory) by Chemical Precipitation with Sedimentation (Lime) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (lime)				
Data source: Effluent guidelines			Data source status:	
Point source: Nonferrous metals			Not specified _____	
Subcategory: Tungsten			Bench scale _____	
Plant: Unspecified			Full scale __×__	
Pretreatment/treatment: None/Chem. Ppt.				
Design or Operating Parameters				
Wastewater flow rate: Unspecified			Type of sedimentation: Unspecified	
Chemical dosages(s): Unspecified				
Mix detention time: Unspecified				
Flocculation detention time: Unspecified				
Unit configuration: Unspecified				
Removal Data				
Sampling: 24-h and 72-h composite and grab	Analysis: Data set 2 (v.7.3.22)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L				
COD	300	53	82	
TSS	300	150	50	
Chloride	25,000	19,000	24	
Aluminum	3	0.5	83	
Iron	50	2	96	
Toxic pollutants, μg/L				
Arsenic	7000	80	99	
Cadmium	200	80	60	
Chromium	2000	50	98	
Copper	5000	70	99	
Lead	20,000	200	99	
Nickel	1000	100	90	
Zinc	2000	600	70	

Blanks indicate data not available

Appendix 18: Treatment of Aluminum Forming Industry Wastes by Chemical Precipitation with Sedimentation (USEPA)

Treatment Technology: Chemical precipitation with sedimentation				
Data source: Effluent guidelines			Data source status:	
Point source: Aluminum forming			Not specified _____	
Subcategory: Unspecified			Bench scale _____	
Plant: J			Full scale __×__	
Pretreatment/treatment: None/Equal., Chem Ppt., Sed.				
Design or Operating Parameters				
Wastewater flow rate: Unspecified			Type of sedimentation: Clarifier	
Chemical dosages(s): Unspecified				
Removal Data				
Sampling: composite	Analysis: Data set 2 (v.7.3.22)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L, except pH				
Oil and grease	86	15	99	
TOC	75	74	1	
Phenol	0.003	0.002	33	
pH, units	2.8	3.7	NM	
Toxic pollutants, µg/L				
Chromium	900,000	790,000	12	5
Copper	2,200,000	2,200,000	0	9
Lead	3200	1000	69	20
Nickel	2600	2400	8	5
Zinc	2,000,000	1,800,000	10	50
Fluoranthene	10	ND	>99	10
Methylene chloride	260	15	93	10
2,4-Dinitrophenol	37	ND	>99	10
N-nitrosodiphenylamine	67	ND	>99	10
Chrysene	10	ND	>99	10
Anthracene/phenanthrene	<26	BDL	NM	10
Pyrene	16	ND	>99	10

Blanks indicate data not available; *BDL* below detection limit, *ND* not detected, *NM* not meaningful

Appendix 19: Treatment of Battery Industry Wastes (Lead Subcategory) by Chemical Precipitation with Sedimentation (USEPA)

Treatment Technology: Chemical precipitation with sedimentation				
Data source: EGD combined database			Data source status:	
Point source: Battery			Not specified _____	
Subcategory: Lead			Bench scale _____	
Plant: 20993			Full scale __×__	
Pretreatment/treatment: Equal., Screen/Chem. Ppt., Sed. (clarifier). Polishing Lagoon				
Design or Operating Parameters				
Wastewater flow rate: Influent: 561,000 m^3/day; effluent: 552,000 m^3/day			Type of sedimentation: Clarifier	
Chemical dosages(s): Sodium hydroxide: 227,000 kg/year			Hydraulic loading rate: 693 L/h/m^2	
Mix detention time: Unspecified			Hydraulic detention time: 7 h	
Flocculation detention time: Unspecified			Weir loading rate: Unspecified	
Unit configuration: Continuous operation (24 h/day)			Type of sedimentation: Polishing lagoon	
Hydraulic detention time: 10.2 L/h/m^2			Hydraulic loading rate: 120 h	
Removal Data				
Sampling: 24-h composite, flow proportion	Analysis: Data set 2 (v.7.3.8)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L, except pH				
pH, minimum, unit	2.0	8.7		
pH, maximum, unit	2.4	9.1		
TSS	14	11	21	5.0
Iron	16	0.92	94	0.005
Manganese	120	44	63	
Strontium	33	27	18	
Toxic pollutants, μg/L				
Chromium	57	5.0	91	BDL
Copper	78	14	82	1.0
Lead	1400	130	91	30
Nickel	36	9.0	75	6.0
Zinc	120	BDL	>99	1.0
1,1,1-Trichloroethane	0.1[a]	0.1[a]	NM	0.1
Bis(2-ethylhexyl) phthalate	10	BDL	>99	10
Butyl benzyl phthalate	ND	BDL	NM	10
Methylene chloride	BDL	BDL	NM	1.0

Blanks indicate data not available; *BDL* below detection limit, *ND* not detected, *NM* not meaningful; [a]Approximate value

Appendix 20: Treatment of Electrical and Electronic Industry Waste by Chemical Precipitation with Sedimentation (Na_2CO_3) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (sodium carbonate)				
Data source: Effluent guidelines			Data source status:	
Point source: Electrical and electronic components			Not specified _____	
			Bench scale _____	
Subcategory: Unspecified			Pilot scale _____	
Plant: 30172			Full scale __×__	
Pretreatment/treatment: None/Chem. Ppt.				
Design or Operating Parameters				
Wastewater flow rate: 3.77 m^3/day			Type of sedimentation: Unspecified	
Chemical dosages(s): Sodium carbonate				
Mix detention time: Unspecified				
Flocculation detention time: Unspecified				
Unit configuration: 6610 L tank				
Removal Data				
Sampling: Three 24-h composite	Analysis: Data set 2 (v.7.3.11)			
Pollutant/parameter	Concentration[a]		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L, except pH				
Oil and grease	11	14	NM	
TOC	<1	160	NM	
TDS	<1	<1	NM	
TSS	190	17	91	
Phenol	0.01	0.06	NM	
Fluoride	160	76	52	
pH, units	<2	7.3	NM	
Calcium	88	29	67	
Magnesium	31	18	42	
Sodium	640	13,000,000	NM	
Aluminum	12	0.68	94	
Manganese	5.9	0.55	91	
Vanadium	0.16	0.024	65	
Boron	350	400,000	NM	
Barium	200	12,000	NM	
Molybdenum	1.6	0.17	89	
Tin	3.0	0.39	87	
Yttrium	17	<0.008	>99	
Cobalt	2.6	<0.120	>95	
Iron	1900	0.38	99	
Titanium	0.31	0.043	86	
Palladium	0.32	<0.003	>99	

Tellurium	0.29	0.013	96	
Platinum	0.09	0.02	78	
Toxic pollutants, μg/L				
Antimony	92	<15	>84	
Arsenic	250	10	96	
Beryllium	4	<1	>75	
Cadmium	1100	<5	>99	
Chromium	4700	27	99	
Copper	<50	48	NM	
Lead	890,000	1900	99	
Mercury	1	<1	NM	
Nickel	18,000	640	96	
Selenium	<20	<4	NM	
Silver	60	<2	>97	
Thallium	2		NM	
Zinc	1,500,000	11,000	99	
Cyanide	<3	<5	NM	

Blanks indicate data not available; *NM* not meaningful; [a]Values presented as "less than" the reported concentration are below detectable limits. They are not reported as BDL because the detection limit are variable in this industry

Appendix 21: Treatment of Copper Industry Wastes (Pickle Subcategory) by Chemical Precipitation with Sedimentation (Lime) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (lime)	
Data source: EGD combined database	Data source status:
Point source: Copper	Not specified _____
Subcategory: Pickle	Bench scale _____
Plant: 6070	Full scale __x__
Pretreatment/treatment: None/Chem. Ppt., Sed. (clarifier)	
Design or Operating Parameters	
Wastewater flow rate: 3000 m^3/day	Type of sedimentation: Clarifier
Unit configuration: Continuous operation (24 h/day)	
Removal Data	
Sampling: 24-h composite, flow proportion (1 h)	Analysis: Data set I (V.7.3.13)

Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L				
pH, minimum	1.0	5.0		
pH, maximum	3.2	7.0		
Fluorides	0.80	10	NM	0.1
Phosphorus	5.0	0.86	83	0.003
TSS	18	16	0	5.0
Iron	13	0.27	98	0.005
Oil and grease	4.0	1.0	75	5.0
Phenols, total	0.01	0.01	0	0.005
TOC	12	10	17	
Manganese	0.77	0.32	58	0.005
Toxic pollutants, μg/L				
Chromium	200	23	88	3.0
Copper	9400	220	98	1.0
Lead	430	ND	>99	30
Nickel	320	300	6	6.0
Zinc	74,000	1400	98	1.0
l,l,l-Trichloroethane	0.1	ND	NM	0.1
Chloroform	BDL	BDL	NM	1.0
Trichloroethylene	0.2	ND	>99	1.0
Toluene	1.0	ND	>99	1.0
Benzene	1.0	ND	>99	1.0

Blanks indicate data not available; *BDL* below detection limit, *ND* not detected, *NM* not meaningful

Appendix 22: Treatment of Organic and Inorganic Industry Wastes by Chemical Precipitation with Sedimentation (Alum) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (alum)				
Data source: Government report			Data source status:	
Point source: Organic and inorganic wastes			Not specified _____	
Subcategory: Unspecified			Bench scale _____	
Plant: Reichhold Chemical, Inc.			Pilot scale __×__	
			Full scale _____	
Pretreatment/treatment: Equal./Chem. Ppt.				
Design or Operating Parameters				
Wastewater flow rate: Unspecified			Type of sedimentation: Unspecified	
Chemical dosages(s): 650 mg/L (alum)				
Mix detention time: Unspecified				
Flocculation detention time: Unspecified				
Unit configuration: Unspecified				
Removal Data				
Sampling: 24-h composite	Analysis: Data set 2 (v.7.3.35)			
Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L				
BOD_5	2400	2200	8	
COD	3600	3500	3	
Total phenol	320	220	31	
Total phosphorus	49	43	12	
SS	140	28	80	
TS	4600	4300	6	
DS	4400	4300	2	
Sulfate	750	830	NM	
Sulfite	40	10	75	
Iron	40	ND	>99	
Nitrate	320	310	3	

Blanks indicate data not available; *ND* not detected, *NM* not meaningful

Appendix 23: Treatment of Auto and Laundry Industry Wastes (Power Laundries Subcategory) by Chemical Precipitation with Sedimentation (Alum, Polymer) (USEPA)

Treatment Technology: Chemical precipitation with sedimentation (alum, polymer)	
Data source: Effluent guidelines	Data source status:
Point source: Auto and other laundries	Not specified _____
Subcategory: Power laundries	Bench scale _____
Plant: N	Pilot scale _____
	Full scale __×__
Pretreatment/treatment: Screen, Equal./Chem. Ppt.	
Design or Operating Parameters	
Wastewater flow rate: 15.1 m^3/day	Type of sedimentation: Clarifier
Chemical dosages(s): Alum, 2800 mg/L; polymer, 200 mg/L	Hydraulic detention time: 0.33 day
Mix detention time: Unspecified	
Flocculation detention time: Unspecified	
Unit configuration: Circular clarifier, 4.92 m^3 with mix tank	
Removal Data	
Sampling: Composite and grab	Analysis: Data set 1 (v.7.3.1)

Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L				
BOD (5)	160	57	64	
COD	240	130	46	
TOC	63	40	37	
TSS	40	46	NM	
Oil and grease	15	4	73	
Total phenol	0.038	0.028	26	
Total phosphorus	7.0	1.6	77	
Toxic pollutants, μg/L				
Cadmium	51	12	76	2
Chromium	39	34	13	4
Copper	140	31	78	4
Lead	71	66	7	22
Nickel	55	50	9	36
Silver	14	11	21	5
Zinc	610	240	61	1
Phenol	ND	2	NM	0.07
Toluene	5	3	40	0.1
Tetrachloroethylene	2	100	NM	
Trichloroethylene	0.56	12	NM	0.5

Cyanide	<2	<2	NM	
Chloroform	ND	70	NM	5
Methyl chloride	ND	38	NM	0.4
Bis(2-ethylhexyl) phthalate	ND	67	NM	0.04
Butyl benzyl phthalate	ND	36	NM	0.03
Di-*n*-butyl phthalate	ND	7	NM	0.02
Di-*n*-octyl phthalate	ND	5	NM	0.89

Blanks indicate data not available; *BOL* below detection limit, *ND* not detected, *NM* not meaningful

Appendix 24: Theoretical Solubilities of Hydroxides, Carbonates, and Sulfides of Selected Metals in Pure Water

	Solubility of metal ion (mg/L)		
Metal	As hydroxide	As carbonate	As sulfide
Cadmium (Cd^{2+})	2.3×10^{-5}	1.0×10^{-4}	6.7×10^{-10}
Chromium (Cr^{3+})	8.4×10^{-4}		No precipitate
Cobalt (Co^{2+})	2.2×10^{-1}		1.0×10^{-8}
Copper (Cu^{2+})	2.2×10^{-2}		5.8×10^{-13}
Iron (Fe^{2+})	8.9×10^{-1}		3.4×10^{-5}
Lead (Pb^{2+})	2.1	7.0×10^{-3}	3.8×10^{-9}
Manganese (Mn^{2+})	1.2		2.1×10^{-3}
Mercury (Hg^{2+})	3.9×10^{-4}	3.9×10^{-2}	9.0×10^{-2}
Nickel (Ni^{2+})	6.9×10^{-3}	1.9×10^{-1}	6.9×10^{-8}
Silver (Ag^{+})	13.3	2.1×10^{-1}	7.4×10^{-12}
Tin (Sn^{2+})	1.1×10^{-4}		3.8×10^{-9}
Zinc (Zn^{2+})	1.1	7.0×10^{-4}	2.3×10^{-7}

Appendix 25: Estimated Achievable 30-Day Averages of Final Concentrations for Various Applied Technologies [23]

Final concentrations (mg/L)						
	Lime precipitation followed by filtration	Lime precipitation followed by filtration	Sulfide precipitation followed by filtration	Ferric coprecipitation followed by filtration	Soda ash addition followed by sedimentation	Soda ash addition followed by filtration
Antimony, Sb	0.8–1.5	0.4–0.8				
Arsenic, As	0.5–1.0	0.5–1.0	0.05–0.1			
Beryllium, Be	0.1–0.5	0.01–0.1				
Cadmium, Cd	0.1–0.5	0.05–0.1	0.01–0.1	<0.5		
Copper, Cu	0.05–1.0	0.4–0.7	0.05–0.5	<0.5		
Chromium, Cr(III)	0.0–0.5	0.05–0.5		0.01		
Lead, Pb	0.3–1.6	0.05–0.6	0.05–0.4	0.20	0.4–0.8	0.1–0.6
Mercury, Hg(II)	0.01–0.05		<0.01			
Nickel, Ni	0.2–1.5	0.05–0.2	0.1–0.5			
Silver, Ag	0.4–0.8	0.2–0.4	0.05–0.5			
Selenium, Se	0.2–1.0	0.1–0.5				
Thallium, Tl	0.2–1.0	0.1–0.5				
Zinc, Zn	0.5–1.5	0.4–1.2	0.02–1.2	0.02–0.5		

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Chapter 7
Water Quality Control of Tidal Rivers and Estuaries

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Abstract The authors introduce the basic and working mathematical models required for proper water quality control of tidal rivers and estuaries. The water quality parameters of conservative substances, reactive substances, sequentially reactive constituents, surface transfer coefficient, reaeration coefficient, deoxygenation coefficient, assimilation ratio, estuarine number, estuarine dispersion coefficient, and advective velocity are defined. Three types of working models are presented: (a) steady-state equations for waste concentrations in tidal rivers and estuaries resulting from a point source of pollution; (b) steady-state equations for waste concentrations in tidal rivers and estuaries resulting from a distributed source of pollution; (c) alternate working models and system identification for tidal rivers. Three practical examples are included in this book chapter for illustration of various applications of the working models.

Keywords Mathematical models · Water quality models · Water quality control · Tidal rivers · Estuaries · Water quality parameters · Basic models. Working models · Steady-state equations · Point source of pollution · Distributed source of pollution · Nonpoint source of pollution · Practical examples · Tam-Sui River, Taiwan · Biochemical oxygen demand model · Dissolved oxygen deficit model

Nomenclature

a	$\frac{K_d}{K_2 - K_d - K_3}\left(L_0 - \frac{K_s}{K_d + K_3}\right)$ in the moment method, a constant otherwise.
A	Average cross-sectional area of a surface water system, L^2
B	$\frac{K_d}{K_2}\left(\frac{K_s}{K_d + K_3} - \frac{\alpha}{K_d}\right)$ in the moment method
C	Conservative substance concentration, M/L^3
C_0	Maximum concentration of a conservative substance at the point source discharge location, M/L^3
D	Concentration of dissolved oxygen deficit, M/L^3
D_c	Critical (e.g., maximum) dissolved oxygen deficit, M/L^3
D_0	Dissolved oxygen deficit at the point source discharge, M/L^3
E	Longitudinal dispersion coefficient, L^2/T
$\bar{E}$	Turbulent dispersion vector, with components $\bar{E}_x$, $\bar{E}_y$, and $\bar{E}_z$
g_1	$(U/2E)(1 + m_1)$
g_2	$(U/2E)(1 + m_2)$
h	Average depth of receiving water at mean tide, L
j_1	$(U/2E)(1 - m_1)$
j_2	$(U/2E)(1 - m_2)$
J_1	$\frac{U}{2E} - \left(\frac{U^2}{4E^2} + \frac{K_d + K_3}{E}\right)^{1/2}$

J_2	$\frac{U}{2E}-\left(\frac{U^2}{4E^2}+\frac{K_2}{E}\right)^{1/2}$
K	First-order reaction rate, T^{-1} (base e)
K_a	Reaeration coefficient, T^{-1}
K_b	Coliform die-off rate, T^{-1} (base e)
k_d	CBOD deoxygenation rate, T^{-1} (base 10)
K_d	BOD decay rate, T^{-1} (base e)
K_L	Surface transfer coefficient, L/T
K_n	NBOD deoxygenation rate or nitrification rate, T^{-1} (base e)
K_p	Reaction rate of phosphorus in receiving water, T^{-1} (base e)
K_r	CBOD removal rate in receiving water, T^{-1} (base e)
K_s	Rate of BUD addition to the overlying water from the bottom deposits and/or from the local runoff, $M/L^3/T$
K_1	Decay rate, System 1, T^{-1} (base e).
K_2	Reaction rate of System 2 (e.g., reaeration coefficient K_a), T^{-1} (base e)
K_3	BOD settling rate, T^{-1} (base e)
K_{12}	Reaction rate between Systems 1 and 2 (e.g., deoxygenation rate K_d), T^{-1} (base e)
L	Concentration of reactive substances (e.g., UOD), M/L^3
L_{max}	Maximum concentration of reactive substances, M/L^3
L_0	Concentration of reactive substances (e.g., UOD) at the point source discharge, M/L^3
m_1	$[1 + 4K_1\ E/U^2]^{0.5} = [1 + 4N_1]^{0.5}$
m_2	$[1 + 4K_2\ E/U^2]^{0.5} = [1 + 4N_2]^{0.5}$
M_l	Longitudinal mass flux, $M/L^2/T$
M_t	Transverse mass flux, $M/L^2/T$
M_T	Total mass flux, $M/L^2/T$
M_v	Vertical mass flux, $M/L^2/T$
n	Numbers of observations
N	Estuarine number, N_1 for System 1 and N_2 for System 2
P_k	$K_s/(K_d + K_3)$
q	Lateral inflow per unit length, $L^3/T/L$
Q	Freshwater flow, L^3/T
R	Assimilation ratio
s	Slope of the dissolved oxygen deficit curve
S	Sources and sinks of substance C in the surface wider system, $M/L^3/T$
t	Time, T
U	Mean velocity or advective velocity, L/T
U_T	Average tidal velocity, L/T
w	Distributed source (e.g., nonpoint source) of pollution, M/T/L
W	Mass of point source pollution discharge rate, M/T, W_{tn} for total nitrogen, W_c for coliform, and W_{UOD} for UOD

x	Cartesian coordinate in the direction x
X	Downstream distance from the point source of pollution, L
X_c	Critical distance downstream where the critical dissolved oxygen deficit D_c occurs, L
X_l	Location of L_{max}, which is a distance measured from the center of a distributed source of pollution, L
X_p	Downstream distance of point source of pollution, L
y	Cartesian coordinate in the direction y
z	Cartesian coordinate in the direction z
α	Production rate of oxygen by photosynthesis, M/L^3/T
β	Order of moment = 0, 1, 2, …

1 Introduction

Estuaries are those water bodies in which a significant hydrodynamic transport mechanism is caused by astronomical tides and other similar mechanisms. For the purposes of water quality analysis, the "estuary" is that portion of the river that is under the influence of tidal action in which the dispersion factor is always significant. An official, more comprehensive definition is contained in Section 104 (n) (4) of the US Water Pollution Control Act Amendment of 1972 [1] and documented in a general chapter on "Surface Water Quality Analysis."

Estuaries normally consist of two sections that are characterized by the relative magnitude of advective flow to tidal mixing or dispersion. In purely estuarine systems, the upper reaches are referred to as tidal river reaches and characterized by a significant advective transport component. The downstream portion is generally dominated by tidal mixing and freshwater advective flow and is less important in transporting physical and chemical constituents. The length of the estuary may be much greater than the length of the salt water intrusion.

This report considers methods for evaluating water quality responses in estuaries and tidal rivers. Mathematical simulation and analysis of water quality are introduced. Practical examples useful to the environmental engineers in the initial development steps of the 208 water quality management plan [2] are provided by the US Environmental Protection Agency (USEPA), Cincinnati, Ohio, USA, and are presented in this report for demonstrating the analytical methods or both point nonpoint sources of pollution.

2 Water Quality Parameters

2.1 *Conservative Substances*

Conservative constituents are those that are not subject to reactive change and remain dissolved or suspended in the receiving water. Typical conservative constituents are total dissolved solids, total nitrogen, total phosphorus, total suspended solids, and other materials that decay at such slow rates that they may be regarded as conservative.

2.2 *Reactive Substances*

Nonconservative substances are subject to change within the receiving water as a result of physical, chemical, or biological reactions and can also be termed reactive constituents. Typical nonconservative substances include BOD, coliform bacteria, and nutrients. Although total nitrogen and phosphorus are treated as conservative on an annual average basis, they are considered reactive during the summer low flow period because of the algal uptake of the nutrients and their subsequent removal by sedimentation.

The reactions of reactive constituents in tidal rivers and estuaries are analyzed based on the following assumptions:

1. The reaction is first-order with a decay coefficient, K (see Table 7.1).
2. Steady-state conditions exist.
3. Constant coefficients exist, i.e., flow, cross-sectional area, reaction kinetics, and dispersion characteristics are all constant along the length of the estuary under investigation.

2.3 *Sequentially Reactive Constituents*

A sequentially reactive constituent, such as dissolved oxygen deficit (D), is affected or changed by the reacting constituents, such as ultimate oxygen demand (UOD).

Table 7.1 First-order range of reaction coefficients for tidal rivers and estuaries

Substance	Reaction coefficients, day^{-1}	K, base e, 20 °C
Coliform bacteria	2–4	(K_b)
BOD$_5$	0.2–0.5	(K_d or K_1)
Nutrients	0.1–0.25	(K_n or K_p)

Source: Ref. [3]

Table 7.2 Range of transfer and reaeration coefficients estimated for tidal rivers and estuaries (K_L in ft/day, K_2 in day^{-1})

	Average tidal velocity ft/s					
	1	1	1–2	1–2	2	2
Mean tidal depth, ft	K_L	K_2	K_L	K_2	K_L	K_2
10	4	0.5	5.5	0.6	7	0.8
10–20	3	0.2	4.5	0.3	6	0.4
20–30	2.5	0.1	3.5	0.14	5	0.2
30	2	0.06	2.5	0.08	4	0.12

Table 7.3 Assimilation ratio of tidal rivers and estuaries

	Assimilation ratio			
Reaeration coefficient, K_2, day^{-1}	$K_d = 0.2$	$K_d = 0.3$	$K_d = 0.4$	$K_d = 0.5$
0.08	0.40	0.27	0.20	0.16
0.15	0.75	0.50	0.38	0.30
0.30	1.50	1.00	0.75	0.60
0.60	3.00	2.00	1.50	1.20

2.4 Surface Transfer Coefficient, Reaeration Coefficient, and Deoxygenation Coefficient

The surface transfer coefficient (K_L, ft/day) is related to the volumetric reaeration coefficient (K_2, day^{-1}) by the depth,

$$K_2 = K_L / h, \tag{7.1}$$

where h is the average depth at mean tide in ft.

Table 7.2 shows the range of transfer and reaeration coefficients for tidal rivers and estuaries. Both K_L and K_2 are functions of the velocity (average tidal current) and depth of low.

The deoxygenation coefficient (K_d) ranges from 0.2 to 0.5, as shown in Table 7.1, assuming that the estuary is not shallower than about 5 ft.

2.5 Assimilation Ratio

The assimilation ratio (R) characterizes water quality in tidal rivers and estuaries and is a function of the reaeration coefficient (K_2) and the deoxygenation coefficient (K_d), as shown in Table 7.3. From Tables 7.2 and 7.3, it can be seen that the deep main channel estuaries (10–30 ft in depth) have assimilation ratios ranging from 0.2 to 0.8, while the shallower tidal tributaries (5–10 ft in depth) are in the range of 0.8–3.0. At the lower limits of the assimilation ratio, ranges are found in the more

Table 7.4 Range of estuarine number for tidal rivers[a]

	Estuarine number at various advective velocities[b]			
Tidal dispersion mi^2/day	0.5	1.0	2.0	4.0
2	2.4	0.6	0.15	0.04
5	6.0	1.5	0.38	0.10
10	12.0	3.0	0.75	0.19
20	24.0	6.0	1.50	0.75

[a] At BOD_5, reaction rate = 0.3 day^{-1}

[b] Unit of advective velocity = mi/day

Table 7.5 Classification of tidal rivers and estuaries ($K = 0.3\ day^{-1}$)

	Assimilation ratio, R		Estuary number, N	
Description	Average value	Range	Average value	Range
Large, deep, main channel in vicinity of mouth	0.3	0.1–0.5	5	5–30
Moderate navigation channel, upstream from mouth, saline, and large tidal tributaries	0.5	0.2–1.0	5	2–10
Minimum navigation upstream smaller saline or nonsaline tidal tributaries	1.0	0.5–2.0	2	0.5–5
Tidal tributaries, shallow, and nonsaline	2.0	1.0–3.0	1	0.2–2

restricted tidal bodies with lower velocity, higher temperatures, and plant effluents from secondary treatment or less. The upper limits include the free-flowing, higher velocity estuary, with more moderate water temperature and effluents from advanced treatment.

2.6 *Estuarine Number*

The estuarine number (N) is defined as

$$N = KE/U^2, \tag{7.2}$$

where E = the dispersion coefficient ranging from 1 to 20 mi^2/day and U = advective velocity ranging from 0.1 to 10 mi/day. The dispersion coefficient and advective velocity are discussed in subsequent subsections. The estuarine numbers developed from the practical ranges of E and U at $K = 3\ day^{-1}$ for BOD_5 are summarized in Table 7.4. For waste substances with higher reaction rates, the N value increases proportionally according to Eq. (7.2).

A summary of Tables 7.3 and 7.4 with approximate physical descriptions of the types of tidal rivers and estuaries is presented in Table 7.5. Tables 7.3, 7.4, and 7.5 are all abstracted from Ref. [3].

2.7 Estuarine Dispersion Coefficient

The primary difference between estuaries and the one-dimensional river flow situation is the dispersive mass transport resulting from the tidal mixing occasioned by tidal flow reversals. The longitudinal dispersion coefficient can be determined by the salinity gradient in an estuary system. An estimate of the dispersion coefficient may be obtained by plotting the salinity versus distance on semilog graphical paper, fitting straight line to the data, and obtaining *E*. Other field and mathematical methods for determination of *F* values are possible [4–8].

As discussed earlier, the practical range of the dispersion coefficient is from 1 to 20 mi^2/day. The upper limit describes the highly saline, high-tidal-velocity stretches in the vicinity of the estuarine mouth, while the lower limit applies to the upstream, nonsaline, low tidal sections of the estuary.

2.8 Advective Velocity

The advective velocity (U) associated with the freshwater flow is determined by dividing the freshwater flow (Q) by the average cross-sectional area (A).

3 Basic Mathematical Models

Since a summary of several popular estuary water quality models has been presented in another chapter entitled, "Surface Water Quality Control," this chapter will not be an exhaustive review. The objective here is to introduce and describe the basic dispersion process in an estuarine system.

The movement of water in an estuary is more complex than in nontidal streams principally because of tidal mixing and the timescale of estuarine response to continuous and intermittent loadings. In general, the water movement in an estuary can be divided into two major categories: bulk motion (e.g., freshwater flow and tidal flow) and turbulent motion (e.g., eddies). Soluble point-source and nonpoint source pollutants that are discharged to an estuary are transported along the flow direction by the bulk water motion and are spread out, both along and perpendicular to the direction of flow by the diffusive effects of the turbulent motion. By assuming that the mass flux (M/L^2/T) in a given direction is proportional to the concentration gradient in that direction, the total mass flux can be expressed by Eq. (7.3),

$$M_{\mathrm{T}} = M_{\mathrm{l}} + M_{\mathrm{v}} + M_{\mathrm{t}}, \tag{7.3}$$

where

$$\begin{aligned} M_1 &= \text{longitudinal mass flux}, \mathrm{M/L^2/T} \\ &= \left(U_x C - \bar{E}_x \,\partial C/\partial x\right) \end{aligned} \tag{7.3a}$$

$$\begin{aligned} M_\mathrm{v} &= \text{vertical mass flux}, \mathrm{M/L^2/T} \\ &= \left(U_y C - \bar{E}_y \,\partial C/\partial y\right) \end{aligned} \tag{7.3b}$$

$$\begin{aligned} M_\mathrm{t} &= \text{transverse mass flux}, \mathrm{M/L^2/T} \\ &= \left(U_z C - \bar{E}_z \partial C/\partial z\right) \end{aligned} \tag{7.3c}$$

C = soluble substance concentration, M/L^3
$\bar{E}_x$ = turbulent diffusion coefficient in longitudinal direction x, L^2/T
$\bar{E}_y$ = turbulent diffusion coefficient in vertical direction y, L^2/T
$\bar{E}_z$ = turbulent diffusion coefficient in transverse direction z, L^2/T
U_x = longitudinal bulk water velocity, L/T
U_y = vertical bulk water velocity, L/T
U_z = transverse hulk water velocity, L/T.

Equation (7.4) is mass balance equation derived from Eq. (7.3),

$$\frac{\partial C}{\partial t} = -\frac{\partial M_1}{\partial x} - \frac{\partial M_\mathrm{v}}{\partial y} - \frac{\partial M_\mathrm{t}}{\partial z} + S, \tag{7.4}$$

where t is the time, T and the term S (x, y, z, t) is added to account for external sources and sinks of substance C in the surface water system, M/L^3/T. The above equation is a second-order partial differential equation, constituting the general form of a three-dimensional time variable water quality model. Subject to appropriate boundary conditions and a knowledge of velocities and turbulent dispersion coefficients in longitudinal, vertical, and transverse directions, Eq. (7.4) can be solved to determine the spatial and temporal distribution of the concentration C. The computational effort required to solve the equation for realistic estuarine conditions, however, is enormous and costly. The common procedure adopted to simplify the problem is to average Eq. (7.4) over one or more of the space dimensions [9]:

1. Averaging vertically yields a two-dimensional plan model suitable for the investigation of wide vertically mixed estuaries and bays.
2. Averaging transversely yields a two-dimensional elevation model suitable for the study of narrow stratified estuaries.
3. Averaging both vertically and transversely yields a one-dimensional model suitable for estuaries that are well mixed both vertically and transversely.

The last one-dimensional model is commonly used for its comparative computational simplicity. Equation (7.4) can be reduced to the following basic equation for the one-dimensional estuary, after some regrouping of the advective and diffusive terms,

$$\partial C / \partial t = \left(E / A\right) \partial \left(A \partial C / \partial x\right) / \partial x - \left(Q / A\right)\left(\partial C / \partial x\right) \pm S, \tag{7.5}$$

where A = cross-sectional area of the estuary system, L^2

Q = net advective flow of the estuary system, L^3/T

E = estuarine dispersion coefficient, L^2/T.

Equation (7.5) defines the time rate of change of a pollutant in an estuary, with freshwater flow. There is no tidal velocity term since the analysis is restricted to slack water at high or low tide. The variable C in Eq. (7.5) may apply in general to any soluble substances including dissolved oxygen concentration. In the following sections, the term "C" will apply specifically to the concentration of conservative

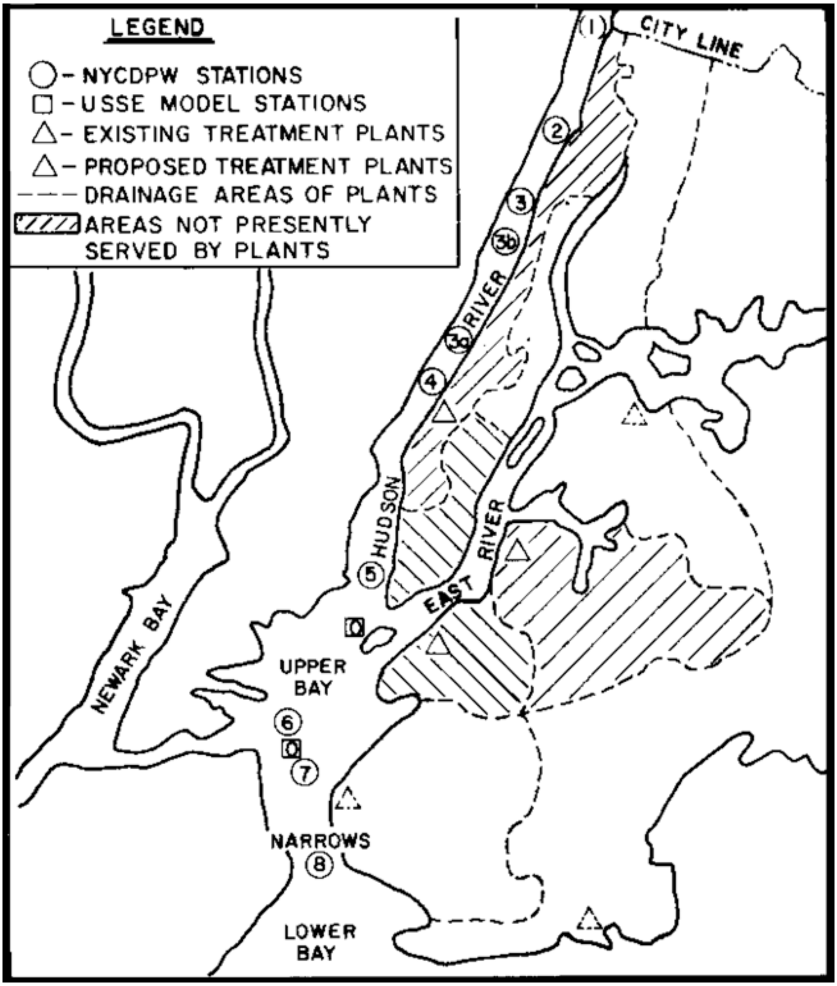


Fig. 7.1 Hudson River and East River in New York metropolitan area

substance, such as salinity or chlorides; the term "*L*" to any substance that decays in accordance with a first-order reaction and in particular to the concentration of the oxygen demanding material.

The majority of estuaries in which there are pollutional problems are probably of variable cross-sectional area. The area functions can be the liner, the power, and the exponential forms.

In order to simplify the water quality analysis problem further, the estuarine area may be assumed constant for considerable distances. Typical examples of estuaries whose areas may be assumed constant are Hudson River and East River in New York Metropolitan area, shown in Fig. 7.1. Assuming the sink term to be first-order decay, Eq. (7.5) becomes

$$\partial C/\partial t = E\left(\partial^2 L/\partial x^2\right) - U\left(\partial L/\partial x\right) - KL, \tag{7.6}$$

where K is the first-order reaction rate, T^{-1} (base e).

Section 4 presents working models derived from the general one-dimensional estuary model, Eq. (7.6), assuming that the cross-sectional area of channel is constant. Detailed derivation of the working models can be found elsewhere [9, 10]. Also presented are alternate working models [11–16] and system identification techniques for tidal rivers [8, 14, 15].

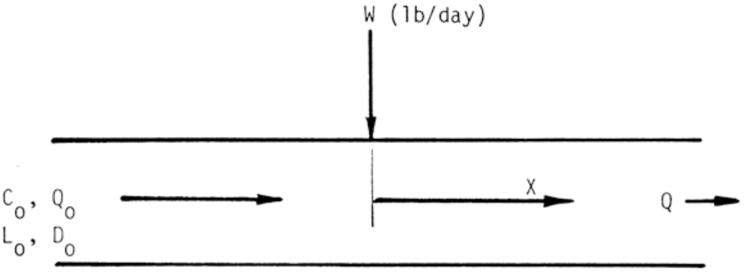
It should be noted that all working models presented in the next section are suitable for tidal rivers and estuaries only. The upstream nontidal portion of the receiving water system may be analyzed for its water quality by some mathematical models in a general chapter "Surface Water Quality Analysis," and by the US EPA models summarized in Tables 7.6 and 7.7. All water quality parameters are clearly defined in "Nomenclature" section.

Table 7.6 Pollutant concentrations in nontidal rivers resulting from a point source pollution

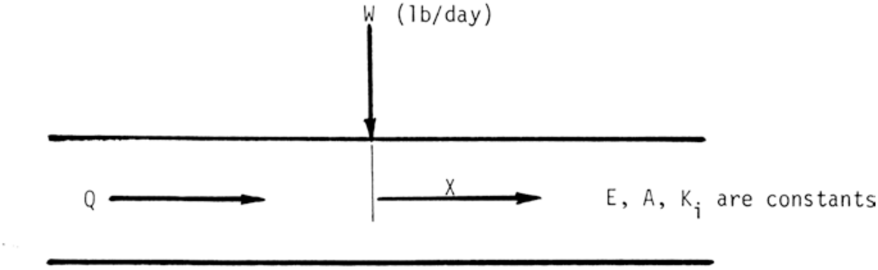
Conservative substances	$C = C_0 + W/Q$
Reactive substances	$L = L_0 \exp(-K_r X/U) + (W/Q)\exp(-K_r X/U)$
Sequentially reactive constituents	$D = D_0 \exp(-K_2 X/U)$ $+ L_0\left[K_d/(K_2 - K_r)\right]\left[\exp(-K_r X/U) - \exp(-K_2 X/U)\right]$ $+ (W/Q)\left[K_d/(K_2 - K_r)\right]\left[\exp(-K_r X/U) - \exp(-K_2 X/U)\right]$

Table 7.7 Pollutant concentrations in nontidal rivers resulting from a nonpoint source of pollution

Conservative substances	$C = C_0 + wX/Q$
Reactive substances	$L = L_0 \exp(-K_rX/U) + [w/(AK_r)][1 - \exp(-K_rX/U)]$
Sequentially reactive constituents	$D = D_0 \exp(-K_2X/U) + L_0[K_d/(K_2 - K_r)][\exp(-K_rX/U) - \exp(-K_2X/U)] + [w/(AK_r)][K_d/(K_2 - K_r)][K_rK_2^{-1}\exp(-K_2X/U) - \exp(-K_rX/U) + (K_2 - K_r)/K_2]$



(a) Non-tidal Rivers



(b) Tidal Rivers and Estuaries

Fig. 7.2 Discharge of point source of pollutants into a receiving water system

4 Working Models

4.1 Steady-State Equations for Waste Concentrations in Tidal Rivers and Estuaries Resulting from a Point Source of Pollution

The following working models are derived from the general estuary model in Sect. 3 and provided by the US EPA, Cincinnati, Ohio. Figure 7.2 illustrates the stream and estuary conditions. Figure 7.3 shows the distribution of waste concentrations in tidal rivers and estuaries resulting from a point source of pollution.

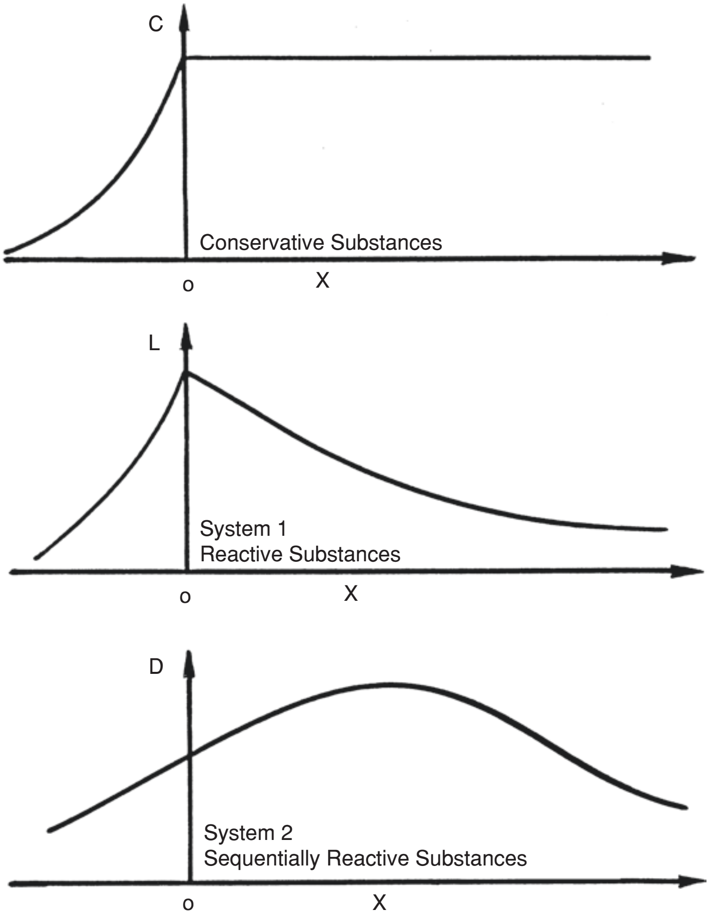


Fig. 7.3 Distribution of various types of waste substances in tidal rivers and estuaries resulting from a point source of pollution

1. *At Point Source of Discharge (X = 0)*

   (a) *Conservative Substances*. The maximum concentration of a conservative substance at the point source discharge location ($X = 0$) is simply the mass rate of waste discharge divided by the freshwater flow,

$$C_0 = W / Q, \tag{7.7}$$

   where C_0 = the maximum concentration of a conservative substance at the point source discharge location, M/L^3; W = mass of point source pollution discharge rate, M/T; Q = freshwater flow, L^3/T; and X = downstream distance from the point source of pollution, L.

   (b) *Reactive Substances (System 1)*. The concentration of reactive substances at the point source discharge (L_0, in M/L^3) can be calculated by Eq. (7.8),

$$L_0 = W/(Qm_1), \tag{7.8}$$

where K_1 = decay rate, System 1 (e.g., BOD), T^{-1};
E = dispersion coefficient, L^2/T; and

$$m_1 = \left[1 + 4K_1E/U^2\right]^{0.5}. \tag{7.9}$$

(c) *Sequentially Reactive Constituents (System 2)*. The dissolved oxygen deficit at the point source discharge (D_0, in M/L^3) can be calculated by Eq. (7.10),

$$D_0 = \left[L_0K_{12}/(K_2 - K_1)\right]\left[1 - m_1/m_2\right], \tag{7.10}$$

where K_2 = reaction rate, System 2 (e.g., reaeration rate), T^{-1}; K_{12} = reaction rate between Systems 1 and 2 (e.g., deoxygenation rate K_d), T^{-1}; and

$$m_2 = \left[1 + 4K_2E/U^2\right]^{0.5}. \tag{7.11}$$

2. *Upstream Reach ($X \le 0$)*

   (a) *Conservative Substances*. The concentration of conservative substances (C, in M/L^3) can be determined by

$$C = C_0 \exp(UX/E), \tag{7.12}$$

   where X = downstream distance from the point source of pollution, L.

   (b) *Reactive Substances (System 1)*. The concentration of reactive substances (L, in M/L^3) can be determined by

$$L = L_0 \exp(g_1X), \tag{7.13}$$

   where

$$g_1 = (U/2E)(1 + m_1). \tag{7.14}$$

   (c) *Sequentially Reactive Constituents (System 2)*. Dissolved oxygen deficit at any point upstream of the point source of pollution (D, in M/L^3)

$$D = \left[L_0K_{12}/(K_2 - K_1)\right]\left[\exp(g_1X) - m_1m_2^{-1}\ \exp(g_2X)\right], \tag{7.15}$$

   where

$$g_2 = (U/2E)(1 + m_2). \tag{7.16}$$

3. *Downstream Reach ($X \ge 0$)*

   (a) *Conservative Substances*

$$C = C_0 = W/Q. \tag{7.17}$$

   (b) *Reactive Substances (System 1)*

$$L = L_0 \exp(j_1X), \tag{7.18}$$

where

$$j_1 = (U/2E)(1 - m_1). \tag{7.19}$$

(c) *Sequentially Reactive Constituents (System 2)*. The dissolved oxygen deficit (D) at downstream distance X can be determined by Eq. (7.20),

$$D = \left[L_0 K_{12} / (K_2 - K_1)\right]\left[\exp(j_1 X) - m_1 m_2^{-1} \exp(j_2 X)\right], \tag{7.20}$$

where

$$j_2 = (U/2E)(1 - m_2), \tag{7.21}$$

and the critical distance (X_c, in L) where the critical dissolved oxygen deficit (D_c, in M/L^3) occurs can be determined by Eq. (7.22),

$$X_c = \ln\left[m_1(1 - m_2)m_2^{-1}(1 - m_1)^{-1}\right] / \left[(U/2E)(m_2 - m_1)\right]. \tag{7.22}$$

The critical dissolved oxygen deficit can then be calculated by

$$D_c = \left[L_0 K_{12} / (K_2 - K_1)\right]\left[\exp(j_1 X_c) - m_1 m_2^{-1} \exp(j_2 - X_c)\right]. \tag{7.23}$$

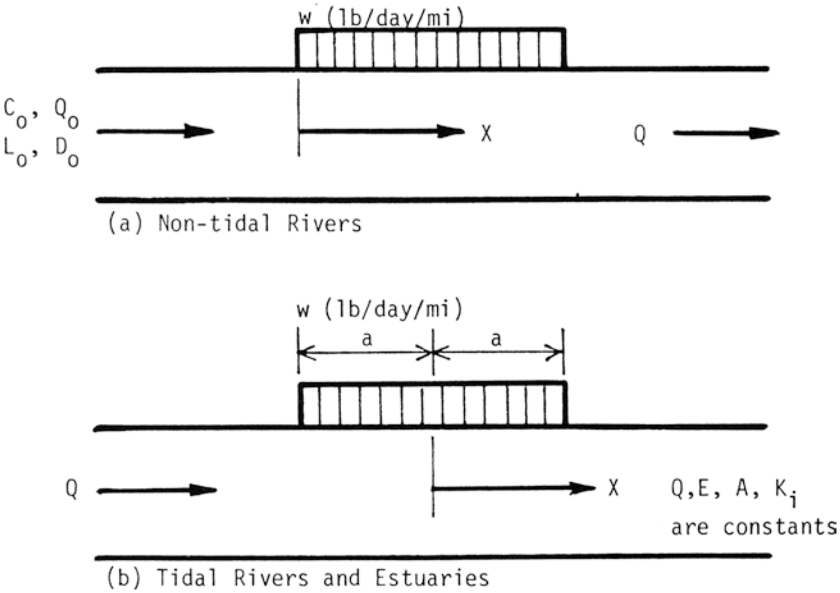


Fig. 7.4 Discharge of nonpoint source of pollutants into a receiving water system

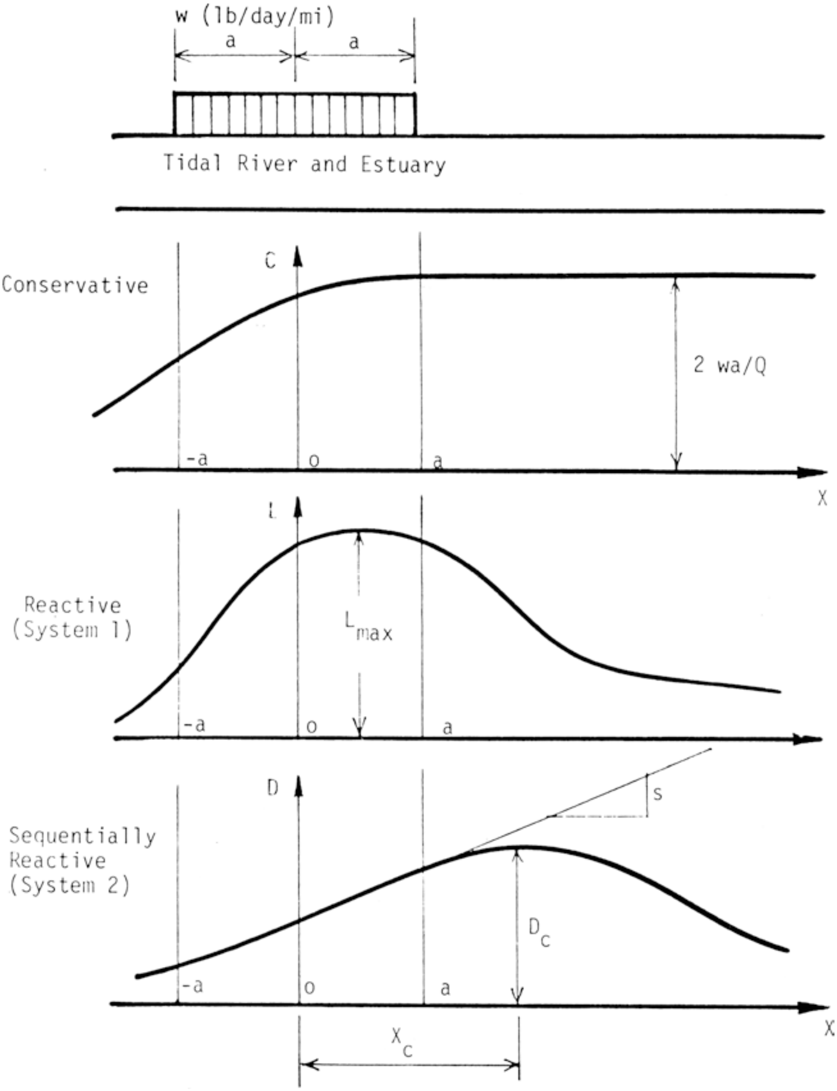


Fig. 7.5 Distribution of estuarine waste concentrations resulting from nonpoint Source of pollution

4.2 *Steady-Stale Equations for Waste Concentrations in Tidal Rivers and Estuaries Resulting from a Distributed Source of Pollution*

The following working models are also derived from the general estuary model in Sect. 3. They are provided by the US EPA, Cincinnati, Ohio. Figure 7.4 illustrates the tidal river and estuary conditions. Figure 7.5 shows the distribution of estuarine

Table 7.8 Location of maximum concentration for distributed sequentially reacting waste

$s = [\mathrm{d}D/\mathrm{d}x]$ at $X = a$		$s = \dfrac{e^{2aj_1} - 1}{m_1} - \dfrac{e^{2aj_2} - 1}{m_2}$ (7.65)
Value of s	Location of D_c	Implicit equation for X_c and for D_c, when $s = 0$
1. Positive	$X_c > a$	$\dfrac{e^{j_1(X_c+a)} - e^{j_1(X_c-a)}}{m_1} = \dfrac{e^{j_2(X_c+a)} - e^{j_2(X_c-a)}}{m_2}$ (7.66)
2. Negative	$X_c < a$	$\dfrac{e^{j_1(X_c+a)} - e^{g_1(X_c-a)}}{m_1} = \dfrac{e^{j_2(X_c+a)} - e^{g_2(X_c-a)}}{m_2}$ (7.67)
3. Zero	$X_c = a$	$D_c = \dfrac{W}{Q} . \dfrac{K_{12}}{K_2 - K_1} . \dfrac{e^{2aj_1} - 1}{m_1 j_1} - \dfrac{e^{2aj_2} - 1}{m_2 j_2}$ (7.68)

Source: US EPA

waste concentrations for conservative substances, reactive substances, and sequentially reactive constituents. Table 7.8 further lists equations for calculating X_c and D_c for distributed sequentially reactive wastes. It is assumed that the distributed source (or nonpoint source) of pollution (w, in lb/day/mi) is discharged into the receiving water according to Fig. 7.4 and has a total length of $2a$. The following subsections present the steady-state equations for three types of waste concentrations (C, L, and D) in three zones ($X \leq a$, $-a \leq X \leq +a$, and $X \geq a$) assuming that the flow, dispersion coefficients, cross-sectional area, and reaction rates are all constants and X is the downstream distance starting from the center of the distributed source of pollution.

1. *In the Reach Covered by the Distributed Source of Pollution* ($-a \leqq X \leqq +a$)

   (a) *Conservative Substances*

$$C = wa / Q + X / a + \left(E / aU\right)\left\{1 - \exp\left[UE^{-1}\left(X - a\right)^{-1}\right]\right\}. \tag{7.24}$$

   (b) *Reactive Substances (System 1)*

$$L = \frac{w}{Qm_1}\left[\frac{\exp\left[j_1\left(X + a\right)\right] - 1}{j_1} - \frac{\exp\left[g_1\left(X - a\right)\right] - 1}{g_1}\right]. \tag{7.25}$$

   (c) *Sequentially Reactive Constituents (System 2)*

$$\begin{aligned} D \quad &= \frac{w}{Q}\frac{K_{12}}{K_2 - K_1}\biggl\{\left[\frac{\exp\left[j_1\left(X + a\right)\right] - 1}{m_1 j_1} - \frac{\exp\left[g_1\left(X - a\right)\right] - 1}{m_1 g_1}\right] \\ &\quad - \left[\frac{\exp\left[j_2\left(X + a\right)\right] - 1}{m_2 j_2} - \frac{\exp\left[g_2\left(X - a\right)\right] - 1}{m_2 g_2}\right]\biggr\}. \end{aligned} \tag{7.26}$$

2. *Upstream Reach (X ≦ −a)*
   (a) *Conservative Substances*
   $$C=\{wE/(QU)\}\{\exp[U/E(X+a)]-\exp[U/E(X-a)]\}. \tag{7.27}$$
   (b) *Reactive Substances (System 1)*
   $$L=[w/(Qm_1g_1)]\{\exp[g_1(X+a)]-\exp[g_1(X-a)]\}. \tag{7.28}$$
   (c) *Sequentially Reactive Constituents (System 2)*
   $$D=\frac{w}{Q}\frac{K_{12}}{K_2-K_1}\{\frac{\exp[g_1(X+a)]-\exp[g_1(X-a)]}{m_1g_1}-\frac{\exp[g_2(X+a)]-\exp[g_2(X-a)]}{m_2g_2}\}. \tag{7.29}$$

3. *Downstream Reach (X ≧ +a)*
   (a) *Conservative Substances*
   $$C=2wa/Q. \tag{7.30}$$
   (b) *Reactive Substances (System 1)*
   $$L=[w/(Qm_1j_1)]\{\exp[j_1(X+a)]-\exp[j_1(X-a)]\}. \tag{7.31}$$
   (c) *Sequentially Reactive Constituents (System 2)*
   $$D=\frac{w}{Q}\frac{K_{12}}{K_2-K_1}\{\frac{\exp[j_1(X+a)]-\exp[j_1(X-a)]}{m_1j_1}-\frac{\exp[j_2(X+a)]-\exp[j_2(X-a)]}{m_2j_2}\}. \tag{7.32}$$

   Four equations in Table 7.8 are presented for estimation of the location of maximum concentration (X_c) and critical dissolved oxygen deficit (D_c) of distributed sequentially reactive wastes. The symbols in the table represent the slope of the dissolved oxygen deficit curve.

It should be noted that all water quality analyses are expected to be carried out using steady-state Eqs. (7.7)–(7.32) for calculating waste concentrations in estuaries with constant geometry, hydrology, and kinetics and having continuous pollutant inputs. For study areas having significantly varying geometry, flows, or kinetic rates (e.g., reaeration coefficients), appropriate analyses may be conducted to determine the sensitivity of the result to the varying parameters [11, 12].

4.3 Alternate Working Models and System Identification for Tidal Rivers

A procedure for systematic identification of characteristic parameters in water quality models by a moment method [8, 14, 15] is presented in detail. More specifically, the parameters identified in a steady-state tidal stream model include the reaeration coefficient (K_2), the coefficient of BOD settling rate and other variables (K_3), the longitudinal dispersion coefficient (E), the rate of BOD addition to the overlying water from the bottom deposits as well as the local runoff (K_s), and the oxygen production rate by photosynthesis (a). This section initially introduces the working models for tidal rivers and then presents the Moment Method. A mathematical model describing the effect of salinity on reaeration coefficients can be found in Appendix [17].

1. *BOD and DO Deficit Models*
   In a tidal river, the following two simplified mathematical models for BOD and DO deficit can be derived from Eq. (7.3) based on the assumptions of: the tidal river is under steady-state conditions; C can be BOD concentration or DO concentration; DO deficit is equal to the saturation DO concentration; DO deficit is equal to the saturation DO minus the DO in river water; and the tidal river system is well mixed vertically and horizontally, and thus, system segmentation is performed only along its main longitudinal axis,

$$E\frac{\mathrm{d}^2L}{\mathrm{d}X^2}-U\frac{\mathrm{d}L}{\mathrm{d}X}-\left(K_\mathrm{d}+K_3\right)L+K_\mathrm{s}=0, \tag{7.33}$$

$$\frac{E\mathrm{d}^2D}{\mathrm{d}X^2}-\frac{U\mathrm{d}D}{\mathrm{d}X}+K_\mathrm{d}L-K_2D-a=0, \qquad (7\ 34)$$

in which K_s is the rate of BOD addition to the overlying water from the bottom deposits and local runoff, a is the oxygen production rate by photosynthesis, E is the longitudinal dispersion coefficient, U is the net mean velocity of water flow, and X is the distance from the discharge point of pollutant. Integrating Eqs. (7.33) and (7.34) and substituting the initial and boundary conditions into them, one can obtain the following working mathematical models:

$$L=\left[L_0-\frac{K_\mathrm{s}}{K_\mathrm{d}+K_3}\right]\exp\left(J_1X\right)+\frac{K_\mathrm{s}}{K_\mathrm{d}+K_3}, \tag{7.35}$$

$$\begin{aligned} D &=\frac{K_\mathrm{d}}{K_2-K_\mathrm{d}-K_3}\left[L_0-\frac{K_\mathrm{s}}{K_\mathrm{d}+K_3}\right]\left[\exp\left(J_1X\right)-\exp\left(J_2X\right)\right] \\ &\quad+\frac{K_\mathrm{d}}{K_2}\left[\frac{K_\mathrm{s}}{K_\mathrm{d}-K_3}-\frac{\alpha}{K_\mathrm{d}}\right]\left[1-\exp\left(J_2X\right)\right]+D_0\exp\left(J_2X\right) \end{aligned}, \tag{7.36}$$

where

$$J_1 = \frac{U}{2E} - \left[\frac{U^2}{4E^2} + \frac{K_d + K_3}{E}\right]^{1/2}, \tag{7.37}$$

$$J_2 = \frac{U}{2E} - \left[\frac{U^2}{4E^2} + \frac{K_2}{E}\right]^{1/2}, \tag{7.38}$$

L_0 = the initial concentration of remaining ultimate BOD and D_0 = the initial concentration of dissolved oxygen deficit.

2. *Moment Method*

The moment method [8] is introduced in this section by defining

$$P_k = \frac{K_s}{K_d + K_3}, \tag{7.39}$$

$$a = \frac{K_d}{K_2 - K_d - K_3}\left[L_0 - \frac{K_s}{K_d + K_3}\right], \tag{7.40}$$

and

$$b = \frac{K_d}{K_2}\left[\frac{K_s}{K_d + K_3} - \frac{a}{K_d}\right]. \tag{7.41}$$

Equations (7.35) and (7.36) become

$$L = L_0 \exp(J_1 X) + P_k\left[1 - \exp(J_1 X)\right], \tag{7.42}$$

$$D = a\left[\exp(J_1 X) - \exp(J_2 X)\right] + b\left[1 - \exp(J_2 X)\right] + D_0 \exp(J_2 X), \tag{7.43}$$

in which a, b, and P_k are constants. Both L and D are the functions of X. Equations (7.42) and (7.43) can be multiplied by X^β ($\beta = 0, 1, 2 \ldots$), and the products are defined as the βth order moment about y axis. If there are n sets of observed data of L and X, by the theory of the moment method, the sum of moments on the right side of Eqs. (7.42) and (7.43) must be equal to the sum of the left side, that is,

$$\sum_1^n X^\beta L = \sum_1^n X^\beta \left\{L_0 \exp(J_1 X) + P_k\left[1 - \exp(J_1 X)\right]\right\}, \tag{7.44}$$

$$\begin{aligned}\sum_1^n X^\beta D &= \sum_1^n X^\beta \left\{a\left[\exp(J_1 X) - \exp(J_2 X)\right]\right\} \\ &\quad + b\left[1 - \exp(J_2 X)\right] + D_0 \exp(J_2 X)\end{aligned}. \tag{7.45}$$

Since L_0, P_k, a, b, and D_0 are all constants, Eqs. (7.44) and (7.45) can be rearranged as

$$\sum_1^n X^\beta L = L_0 \sum_1^n X^\beta \exp(J_1 X) + P_\mathrm{k} \sum_1^n X^\beta \left[1 - \exp(J_1 X)\right], \tag{7.46}$$

$$\begin{aligned}\sum_1^n X^\beta D &= a \sum_1^n X^\beta \left[\exp(J_1 X) - \exp(J_2 X)\right] \\ &+ b \sum_1^n X^\beta \left[1 - \exp(J_2 X)\right] + D_0 \sum_1^n X^\beta \exp(J_2 X)\end{aligned}. \tag{7.47}$$

Now, there are only two unknown parameters (P_k and J_1) in Eq. (7.46). If one takes the zero order ($\beta = 0$) and the first-order ($\beta = 1$) moments from Eq. (7.44), the following two equations are obtained:

$$\beta = 0, \quad \sum_1^n L = L_0 \quad \sum_1^n \exp(J_1 X) + P_\mathrm{k} \sum_1^n \left[1 - \exp(J_1 X)\right], \tag{7.48}$$

$$\beta = 1, \quad \sum_1^n LX = L_0 \quad \sum_1^n X \exp(J_1 X) + P_\mathrm{k} \sum_1^n X \left[1 - \exp(J_1 X)\right]. \tag{7.49}$$

P_k and J_1 can then be solved by the numerical methods from Eqs. (7.48) and (7.49). The advantage of taking the lower order moments (the zero and the first) for estimating parameters is that the calculation is very simple, and the error is less than that of the higher orders.

Similarly, it will be able to solve J_2, a, and b by taking the third-order moments from Eq. (7.47),

$$\begin{aligned}\beta = 0, \quad \sum_1^n D &= a \left[\sum_1^n \exp(J_1 X) - \sum_1^n \exp(J_2 X)\right] \\ &+ b \left[n - \sum_1^n \exp(J_2 X)\right] + D_0 \sum_1^n \exp(J_2 X)\end{aligned}, \tag{7.50}$$

$$\begin{aligned}\beta = 1, \quad \sum_1^n DX &= a \left[\sum_1^n X \exp(J_1 X) - \sum_1^n X \exp(J_2 X)\right] \\ &+ b \left[\sum_1^n X - \sum_1^n X \exp(J_2 X)\right] + D_0 \sum_1^n \exp(J_2 X)\end{aligned}, \tag{7.51}$$

$$\begin{aligned}\beta = 2, \quad \sum_1^n DX^2 &= a \left[\sum_1^n X^2 \exp(J_1 X) - \sum_1^n X^2 \exp(J_2 X)\right] \\ &+ b \left[\sum_1^n X^2 - \sum_1^n X^2 \exp(J_2 X)\right] + D_0 \sum_1^n X^2 \exp(J_2 X)\end{aligned}. \tag{7.52}$$

3. *Procedures for System Identification.* Equations (7.48)–(7.52) are nonlinear, but can be solved by the numerical methods or a graphical method. The procedures of calculation are listed below:
   (a) Rearrange Eqs. (7.48) and (7.49) and obtain Eqs. (7.53) and (7.54), respectively,

$$P_{\mathrm{k}} = \frac{\sum_{1}^{n} L - L_0 \sum_{1}^{n} \exp\left(J_1 X\right)}{n - \sum_{1}^{n} \exp\left(J_1 X\right)}, \tag{7.53}$$

$$P_{\mathrm{k}} = \frac{\sum_{1}^{n} LX - L_0 \sum_{1}^{n} \exp\left(J_1 X\right)}{\sum_{1}^{n} X - \sum_{1}^{n} X \exp\left(J_1 X\right)}. \tag{7.54}$$

   (b) Substitute the observed data of X, L, L_0, and n into Eqs. (7.53) and (7.54).
   (c) Assume a suitable J_1 value and substitute it into Eqs. (7.53) and (7.54) in order to calculate the P_{k} values. Repeat this procedure for different assumed values of J_1.
   (d) Plot the calculated P_{k} values against the assumed J_1 values on an arithmetic graphical sheet and obtain two curves; the point of intersection gives the solutions of P_{k} and J_1.
   (e) From Eq. (7.50), Eq. (7.55) is derived.

$$b = \frac{\sum_{1}^{n} D - a\left[\sum_{1}^{n} \exp\left(J_1 X\right) - \sum_{1}^{n} \exp\left(J_2 X\right)\right] - D_0 \sum_{1}^{n} \exp\left(J_2 X\right)}{n - \sum_{1}^{n} \exp\left(J_2 X\right)}. \tag{7.55}$$

   Equations (7.56) and (7.57) are then derived by substituting Eq. (7.55) into Eqs. (7.51) and (7.52),

$$\begin{aligned} a \;=& \left\{\left[n - \sum_{1}^{n} \exp\left(J_2 X\right)\right]\left(\sum_{1}^{n} DX\right) + \left[\sum_{1}^{n} \exp\left(J_2 X\right) - \sum_{1}^{n} X\right]\sum_{1}^{n} D \right. \\ & \left. + D_0\left[\sum_{1}^{n} \exp\left(J_2 X\right)\sum_{1}^{n} X - n\sum_{1}^{n} X \exp\left(J_2 X\right)\right]\right\} \\ & \div \left\{ n\left[\sum_{1}^{n} X \exp\left(J_1 X\right) - \sum_{1}^{n} X \exp\left(J_2 X\right)\right] \right. \\ & + \sum_{1}^{n} \exp\left(J_2 X\right)\left[\sum_{1}^{n} X - \sum_{1}^{n} X \exp\left(J_1 X\right)\right] \\ & \left. + \sum_{1}^{n} \exp\left(J_1 X\right)\left[\sum_{1}^{n} X \exp\left(J_2 X\right) - \sum_{1}^{n} X\right]\right\} \end{aligned} \; . \tag{7.56}$$

$$\begin{aligned} a \ &= \{\left[n-\sum_1^n \exp\left(J_2X\right)\right]\left(\sum_1^n DX^2\right)+\left[\sum_1^n X^2\exp\left(J_2X\right)-\sum_1^n X^2\right]\sum_1^n D \\ &\quad + D_0\left[\sum_1^n \exp\left(J_2X\right)\sum_1^n X^2 - n\sum_1^n X^2\exp\left(J_2X\right)\right]\} \\ &\quad \div\{n\left[\sum_1^n X^2\exp\left(J_1X\right)-\sum_1^n X^2\exp\left(J_2X\right)\right] \\ &\quad + \sum_1^n \exp\left(J_2X\right)\left[\sum_1^n X^2 - \sum_1^n X^2\exp\left(J_1X\right)\right] \\ &\quad + \sum_1^n \exp\left(J_1X\right)\left[\sum_1^n X^2\exp\left(J_2X\right)-\sum_1^n X^2\right]\} \end{aligned} \quad . \tag{7.57}$$

(f) The procedures for solving the parameters of J_2 and a are similar to that for solving J_1 and P_k [described in procedures (c) and (d)].

(g) Obtain the b value by substituting J_2 and P_k values into Eq. (7.55).

It is important to know that the values of J_1, J_2, a, b, and P_k that can be calculated from Eqs. (7.48)–(7.52) are not real parameters of water quality. The real parameters are K_2, K_3, K_s, α, and F; these should be further evaluated by Eqs. (7.37)–(7.41).

From Eqs. (7.37) and (7.38), Eqs. (7.58) and (7.59) are derived,

$$K_3 - J_1{}^2E = -\left(UJ_1 \pm K_d\right), \tag{7.58}$$

$$K_2 - J_2{}^2E = -J_2U. \tag{7.59}$$

By simplifying Eqs. (7.39)–(7.41), one can obtain Eqs. (7.60)–(7.62), respectively,

$$P_kK_3 - K_s = -P_kK_d, \tag{7.60}$$

$$aK_2 - aK_3 = K_d\left(a + L_0 - P_k\right), \tag{7.61}$$

$$bK_2 + \alpha = K_dP_k. \tag{7.62}$$

Equations (7.58)–(7.62) are linear equations with five unknowns. It is easy to evaluate K_2, K_3. K_s, a, and E except when the following determinant equals zero:

$$\begin{vmatrix} 0 & 1 & 0 & 0 & -J_1^2 \\ 1 & 0 & 0 & 0 & -J_2^2 \\ 0 & -P_k & -1 & 0 & 0 \\ a & -a & 0 & 0 & 0 \\ b & 0 & 0 & 1 & 0 \end{vmatrix} = 0. \tag{7.63}$$

The solutions of Eq. (7.63) are

$$L_0 = P_\mathrm{k} = K_\mathrm{s} / \left(K_\mathrm{d} + K_3\right) \text{ and } J_1 = J_2,$$

i.e., the parameters cannot be determined by any method under these conditions.

5 Recent Development

Anthropogenic perturbations of agricultural, domestic, or industrial origin have increased the N and P loadings in the hydrographical networks, resulting in the local eutrophication of coastal marine water masses. Exceptional phytoplankton blooms are observed in a large number of coastal areas, and these have generally been attributed to enhanced inputs from terrestrial sources. For instance, harmful algal blooms have increased dramatically in recent years in the coastal regions around the world, leading to phenomena such as “brown” or “red” tides. In the eutrophic coastal waters, a recurrent phenomenon is a massive bloom of the colony forming [18]. In addition, global climate change is one of the most important effects on the phytoplankton growth [19]. The accumulation of large amounts of sludge and foam occurs on many beaches, also leading to serious environmental and ecological problems. It has been demonstrated that the magnitude of harmful algal blooms in coastal area is ultimately related to the inorganic nitrogen supply, i.e., the bloom is nitrogen limited, left over after an early spring growth of a silica-controlled diatom community. As a result, the nutrient regeneration dynamics are very sensitive to the riverine nitrogen fluxes reaching the sea [20, 21].

The understanding and prediction of coastal eutrophication, therefore, should rely on a careful quantitative estimation of these seaward fluxes [22–26]. Salinity is an important indicator for water quality and aquatic ecosystem in tidal rivers. The increase of salinity intrusion in a river may have an adverse effect on the aquatic environment system. Parameters in the neural network model trained until the model predictions matched well with the observations will be validated for predicting another independent dataset [27]. Recent attention has also been paid to toxic substances, especially for, such as, metals, PAHs, and PCBs at sufficiently high levels to depress growth of some benthic macroinvertebrates [28, 29]. In a large number of ecosystems in general and in particular regions [30, 31], a major component of the land-ocean interface consists of estuaries, which render the task of flux quantification much more difficult.

The application of GIS (geographic information system) mapping techniques has facilitated the simplification and presentation of a complex and highly heterogeneous dataset. The maps of the average concentrations of determinands produced by the technique are vital for an understanding of the broad-scale characteristics and controls on water quality in a major drainage system. The maps have permitted visual inspection of relationships between elements from a spatial perspective. Oguchi et al. mapped for key inorganic chemical determinands using a GIS system to examine the spatial variability in river water quality [32]. The resultant maps revealed the major factors affecting the general characteristics of regional water quality. The database compiled by using GIS maps of estuaries and their catchments makes it useful for categorizing biological relationships between estuaries, human population, land use, and land tenure data to assess the level of anthropogenic disturbance to each estuary [33, 34]. It provides a host of other research possibilities in relation to regional water quality, particularly when combined with other large-scale spatial datasets such as land use and geology and with more detailed and specialized monitoring and process-focused research [35, 36].

In estuaries, the residence time of solutes and nutrients within the estuarine domain is fairly long, allowing for extensive and complex biogeochemical transformations of the nutrient species as they move along the estuarine gradient. The estimation of seaward fluxes is further complicated by the fact that steady state is rarely approached because the hydrodynamic forcings prevailing at the estuarine boundaries are of a fundamentally variable nature; also, these fluctuations generate important constituent storage or depletion within the estuary during significant periods of time [37]. Ideally, transient physical phenomena should be taken into account in the flux estimation along with the complex transformations taking place within the estuaries [38]. A turbulence depth-averaged (depth-integrated) two-equation closure model may be satisfactorily adopted for the demands of engineering practice [39, 40].

Temperature and turbidity play a key environmental, ecological, and morphological role within an estuary, and the magnitude of the annual temperature cycle is important in determining the range of fauna and flora [41–43]. Parameters of longitudinal distributions of pH and total alkalinity and their variability in estuaries are closely linked through the inorganic carbon cycle. First, the extent of particle-water exchange for many constituents, e.g., metals, is pH-dependent, and therefore, marked variations in pH can affect environmental transport pathways of these materials. Second, estuaries and shallow seas are zones of carbon cycling and storage and may be quantitatively important to ocean-atmosphere exchanges of CO_2 [44]. It will be highly recommended to utilize multiparameter studies to quantify the fluxes of energy and materials into coastal zone from rivers. Investigation on variability of salinity, temperature, turbidity, and suspended chlorophyll and some data on nutrient-salinity relationships had been a good attempt [45, 46].

6 Practical Examples

6.1 Example 6.1: Field Investigation of Tam-Sui River, a Tidal River Located in Taipei, Taiwan, China

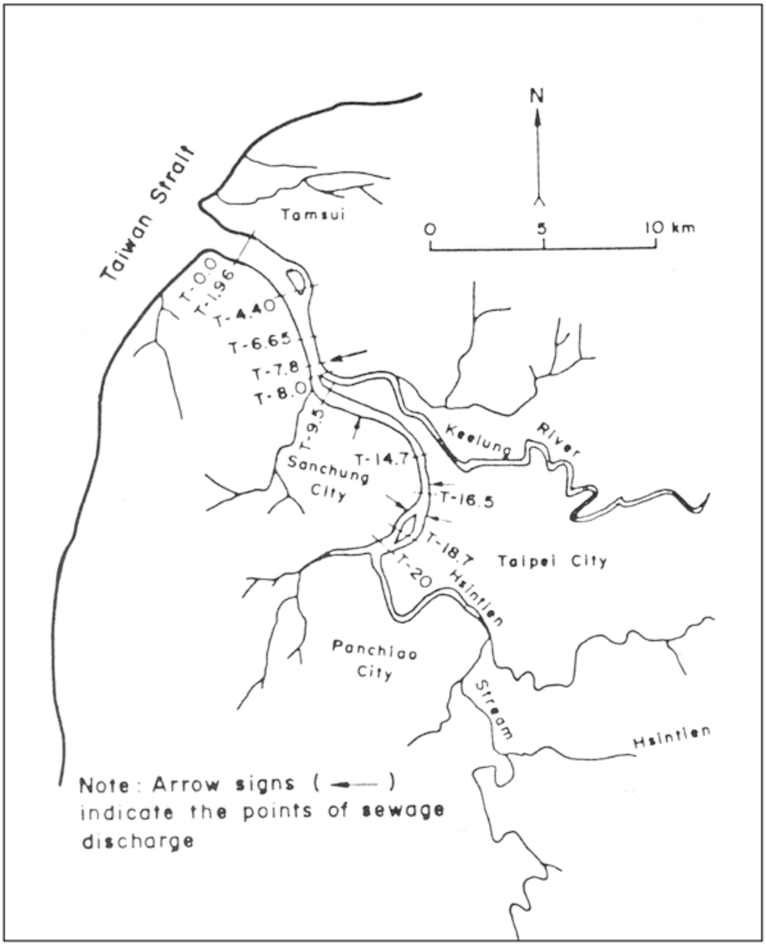
Figure 7.6 shows its geographical location, sampling Stations, tributaries, and point sources of pollution. The length of the river is about 20 km. There are two main tributaries, Keelung River and Hsintien Stream, which discharge their flows into Tam-Sui River at 8 km and 20 km, respectively, from Tam-Sui's mouth. The estuary is used mainly for recreation. Tam-Sui River is divided into two sections according to its hydraulic conditions. Section I is from Stations T-20.0 to T-8.0, while Section II is from Stations T-8.0 to T-0.0 (the numbers represent the distance in kilometers from the river mouth). The mean velocities (U) are 7.56 km/day and 4.58 km/day for Sections I and II, respectively. Both sections are affected by tidal action.

Partial field data are listed in Table 7.9. The five water quality parameters, K_2, K_3, K_s, a, and E, are estimated by a moment method [8, 14, 15].

Solution It is seen from Table 7.9 that the initial concentrations of first-stage ultimate BOD (L_0) are 5.76 mg/L for Section I and 7.97 mg/L for Section II. The initial concentrations of dissolved oxygen deficit (D_0) are 5.6 mg/L for Section I and 3.7 mg/L for Section II.

The average k_d (28 °C, base 10) values that are weighted by distance are 0.142 day^{-1} for Section I and 0.150 day^{-1} for Section II. Both are calculated with the data in Column 6, Table 7.9.

1. *Tam-Sui River, Section I*
   By assuming J_1 values ranging from −0.01 to −1.00, two sets of P_k values are calculated by Eqs. (7.53) and (7.54) and listed in Table 7.10. The assumed J_1 values are then plotted against the two sets of calculated P_k values, and therefore, two curves (J_1 vs. P_k) are obtained, as shown in Fig. 7.7. It is seen from the figure that two curves do not intersect each other; thus, there is no solution for J_1 and P_k for Section I.
   There are no sanitary sewerage systems in the Cities of Taipei and Sanchong. The untreated raw sewage from the two cities is discharged into Section I of Tam-Sui River (Stations T-20.0 to T-8.0) at several points, as shown in Fig. 7.6. It is concluded that the water quality of this section is not suitable for modeling unless the section is divided into several smaller parts.
2. *Tam-Sui River, Section II*
   Section II is suitable for water quality modeling and therefore is described in detail. Figure 7.6 shows that the major point source of organic pollution is from Station 7.8, where L_0 and D_0 have been estimated to be 7.97 mg/L and 3.7 mg/L, respectively. There are five sampling Stations providing water quality data, as shown in Table 7.9; therefore, n is equal to 5. The average values of U and K_d (28 °C, base 10) for this section are 4.58 km/day and 0.150 day^{-1}, respectively.
   By substituting the observed data of X, L, L_0, and n and the assumed J_1 values into Eqs. (7.53) and (7.54), two sets of P_k values are calculated and listed in Table 7.11. For example, P_k values are calculated to be 2.21741 and 2.22578 by Eqs. (7.53) and (7.54), respectively, when J_1 is assumed to be −0.250.
   With the data in Table 7.11, the relationship of J_1 and P_k in Tam-Sui River, Section II, is plotted in Fig. 7.8. The solutions for P_k and J_1 are 2.290 and −0.257, respectively, obtained according to the procedure outlined in Sect. 4.3, step 3.
   By substituting the observed data of X, D, D_0, and n and the assumed J_2 values into Eqs. (7.56) and (7.57), two sets of "a" values are calculated and listed in



Note: Arrow signs (⟵) indicate the points of sewage discharge

Fig. 7.6 Tam-Sui river and its sampling station [15]

Table 7.12. For example, when J_2 is assumed to be −0.130, the calculated "*a*" values are −2.37126 and −2.37069 by Eqs. (7.56) and (7.57), respectively.

The relationship of J_2 and a in Section II of Tam-Sui River is then graphically illustrated in Fig. 7.9. The solutions of J_2 and a are −0.132 and −2.450, respectively, obtained according to the procedure outlined in Sect. 4.3, step 3.

By choosing the D, D_0, X, and n values from Table 7.9 and substituting D, D_0, X, n, a, J_1, and J_2 into Eq. (7.55), the value of "*b*" can then be calculated to be −0.631 according to Eq. (7.55).

Knowing $L_0 = 7.97$ mg/L, $U = 4.58$ km/day, K_d (28 °C, base 10) = 0.15 day^{-1}, $J_1 = -0.257$, $P_k = 2.290$, $J_2 = -0.132$, $a = -2.450$, and $b = 0.631$, one could then determine the real water quality parameters using Eqs. (7.58)–(7.62),

Table 7.9 Water quality data of Tam-Sui River during summer, 1969 [15]

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Section	Section	X	BOD[a] (5-day, 28 °C), mg/L	DO[a] (28 °C), mg/L	k_d, 28 °C (base 10), day^{-1}	Saturated DO[b] at 28 °C, mg/L	L, mg/L	D, mg/L
I	T-18.70	0	5.30	2.30	0.22	7.90	5.76	5.60
	T-16.50	2.20	5.30	1.80	0.14	7.90	6.62	6.10
	T-14.70	4.00	6.00	2.35	0.12	7.90	8.02	5.55
	T-9.50	9.20	5.40	3.25	0.14	7.75	6.75	4.50
II	T-7.80	0	6.55	3.85	0.15	7.55	7.97	3.70
	T-6.65	1.15	5.05	4.05	0.15	7.52	6.14	3.47
	T-4.45	3.35	4.35	4.80	0.15	7.24	5.29	2.44
	T-1.35	6.45	2.70	5.00	0.15	7.14	3.29	2.14
	T-0.00	7.80	2.40	5.48	0.15	6.75	2.92	1.27

[a] Tidal average

[b] Corrected by chloride concentration and atmospheric pressure

Table 7.10 The values of P_k with respect to J_1 for the first section of Tam-Sui river

	Calculated P_k			Calculated P_k	
Assumed J_1	Eq. (7.53)	Eq. (7.54)	Assumed J_1	Eq. (7.53)	Eq. (7.54)
−0.01	33.36878	25.53210	−0.55	7.35015	7.16679
−0.05	12.04294	10.36976	−0.60	7.31791	7.15017
−0.10	9.40154	8.50963	−0.65	7.29135	7.13674
−0.15	8.53574	7.91242	−0.70	7.26924	7.12574
−0.20	8.11150	7.62821	−0.75	7.25066	7.11662
−0.25	7.86239	7.46710	−0.80	7.23493	7.10899
−0.30	7.69990	7.36598	−0.85	7.22154	7.10255
−0.35	7.58631	7.29799	−0.90	7.21006	7.09710
−0.40	7.50292	7.24990	−0.95	7.20019	7.09245
−0.45	7.43946	7.21453	−1.00	7.19166	7.08846
−0.50	7.38982	7.18768			

$$K_3 - \left(-0.257\right)^2 E = -\left[4.58\left(-0.257\right) + 0.15 \times 2.3\right], \tag{7.58}$$

$$K_2 - \left(-0.132\right)^2 E = 0.132 \times 4.58, \tag{7.59}$$

$$2.290K_3 - K_s = -2.290 \times 0.15 \times 2.3, \tag{7.60}$$

$$-2.450K_2 + 2.450K_3 = 0.15 \times 2.3$$

$$\left(-2.450 + 7.97 - 2.290\right), \tag{7.61}$$

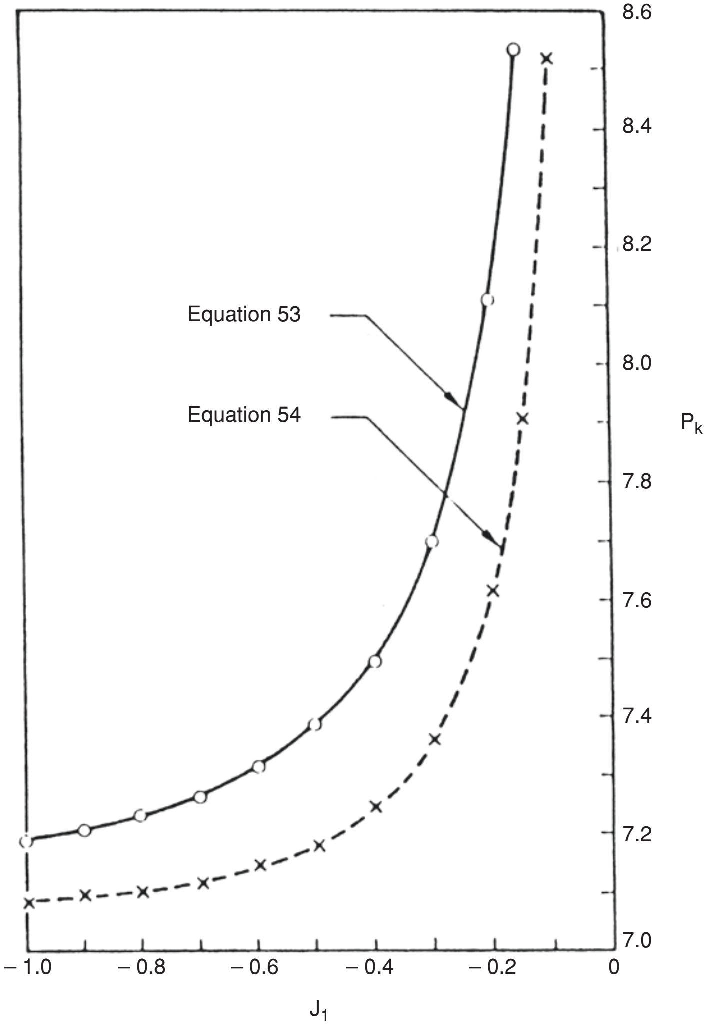


Fig. 7.7 The relationships of J_1 and P_k in Tam-Sui River, Section I (Stations T-9.5 to T-18.7)

$$-0.631K_2 + \alpha = 0.15 \times 2.3 \times 2.290. \tag{7.62}$$

The solutions of the above five simultaneous linear equations are K_2 (28 °C, base e) = 0.69 day^{-1}; K_3 (28 °C, base e) = 1.14 day^{-1}; K_s = 3.40 mg/L/day; α = 1.22 mg/L/day; and E = 4.7 km^2/day.

The preceding computations yielded the following two specific mathematical models for Tam-Sui River, Section II:

Biochemical Oxygen Demand Model

$$L = 5.680\exp(-0.257X) + 2.290. \tag{7.35a}$$

Table 7.11 The values of P_k with respect to J_1 for the second section of the Tam-Sui river

	Calculated P_k			Calculated P_k	
Assumed J_1	Eq. (7.53)	Eq. (7.54)	Assumed J_1	Eq. (7.53)	Eq. (7.54)
−0.050	−9.63830	−8.56550	−0.280	2.50776	2.47081
−0.100	−2.12766	−1.66788	−0.290	2.59008	2.53925
−0.150	0.62831	0.82950	−0.300	2.66642	2.60221
−0.200	1.52174	1.62268	−0.310	2.73737	2.66026
−0.210	1.68928	1.76946	−0.320	2.80346	2.71388
−0.220	1.84064	1.90134	−0.330	2.86515	2.76351
−0.230	1.97797	2.02029	−0.340	2.92284	2.80951
−0.240	2.10306	2.12798	−0.350	2.97689	2.85222
−0.250	2.21741	2.22578	−0.360	3.02761	2.89194
−0.260	2.32228	2.31488	−0.370	3.07531	2.92893
−0.270	2.41876	2.39627	−0.380	3.12022	2.96343

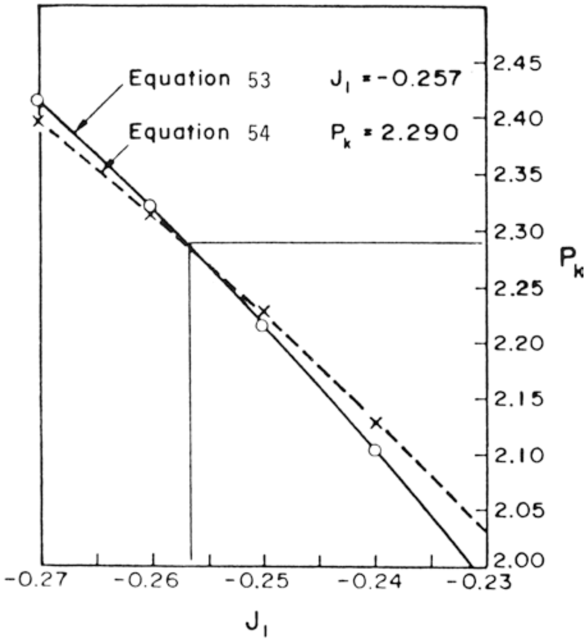


Fig. 7.8 The relationships of J_1 and P_k in Tam-Sui River, Section II (Stations T-0.0 to T-7.8)

Dissolved Oxygen Deficit Model

$$D = 6.781\exp(-0.132X) - 2.450\exp(-0.257X) - 0.631, \tag{7.36a}$$

which are derived from Eqs. (7.35) and (7.36) because the values of L_0, K_s, E, K_d, K_2, K_3, J_1, J_2, α, D_0, and U are all known or identified.

After the Biochemical Oxygen Demand Model (Eq. 7.35a) and the Dissolved Oxygen Deficit Model (Eq. 7.36a) for a target stream are developed, environmental engineers and planners can use them to determine the remaining concentration of first-stage ultimate BOD (L) and the concentration of dissolved oxygen

Table 7.12 The values of a with respect to J_2 for the second section of the Tam-Sui river

	Calculated a			Calculated a	
Assumed J_2	Eq. (7.56)	Eq. (7.57)	Assumed J_2	Eq. (7.56)	Eq. (7.57)
−0.090	−1.19604	−1.18092	−0.145	−3.03142	−3.03926
−0.095	−1.13073	−1.29701	−0.150	−3.29304	−3.30425
−0.100	−1.43281	−0.42060	−0.155	−3.58055	−3.59543
−0.105	−1.56315	−1.55248	−0.160	−3.89792	−3.91692
−0.110	−1.70239	−1.69352	−0.165	−4.25008	−4.27360
−0.115	−1.85167	−1.84464	−0.170	−4.64284	−4.67149
−0.120	−2.01197	−2.00698	−0.175	−5.08392	−5.11826
−0.125	−2.18463	−2.18178	−0.180	−5.58240	−5.62327
−0.130	−2.37108	−2.37055	−0.185	−6.15055	−6.19880
−0.135	−2.57293	−2.57499	−0.190	−6.80359	−6.86045
−0.140	−2.79230	−2.79710	−0.195	−7.56237	−7.62919

deficit (D) at any downstream distance X. Columns 1, 2, and 4 of Table 7.13 indicate the stations, the observed BOD, and the observed DO deficit, respectively, which can also be found in Table 7.9. Columns 3 and 5 indicate the BOD and DO deficit values estimated by Eqs. (7.35a) and (7.36a), respectively. It should be noted that Station T-7.80 is considered to be a starting point, and thus, $X = 0$ mi at Station T-7.80 and $X = 7.8$ mi at Station T-0.00. It can be seen that the estimated L and D values are in close agreement with the observed L and D values. The BOD Model and the DO Deficit Model are accepted under 5% and 1%, respectively, of significance levels according to the chi-square test.

It is then concluded that the moment method is an effective method in estimating the characteristic parameters of steady-state stream models. The errors are very small if the numbers of parameters in the models are five or less. The procedure for system identification is mathematically simple. Water quality parameters can be estimated easily by using an electronic computer. When necessary, the sensitivities of various water quality parameters can also be determined [16, 47].

6.2 *Example 6.2: Low Flow Analysis for a Continuous Point Source Discharge*

The following are the given information:

Freshwater low flow (Q) = 50 ft^3/s,
Mean water depth (h) = 10 ft,
Average cross-sectional area (A) = 2000 ft^2,
Average tidal velocity (U_T) = 0.6 knots,
Dispersion coefficient (E) = 2 mi^2/day,
$K_1 = K_r = 0.25\ \text{day}^{-1}$,
$K_{12} = K_d = K_r$,
$K_2 = K_a$,

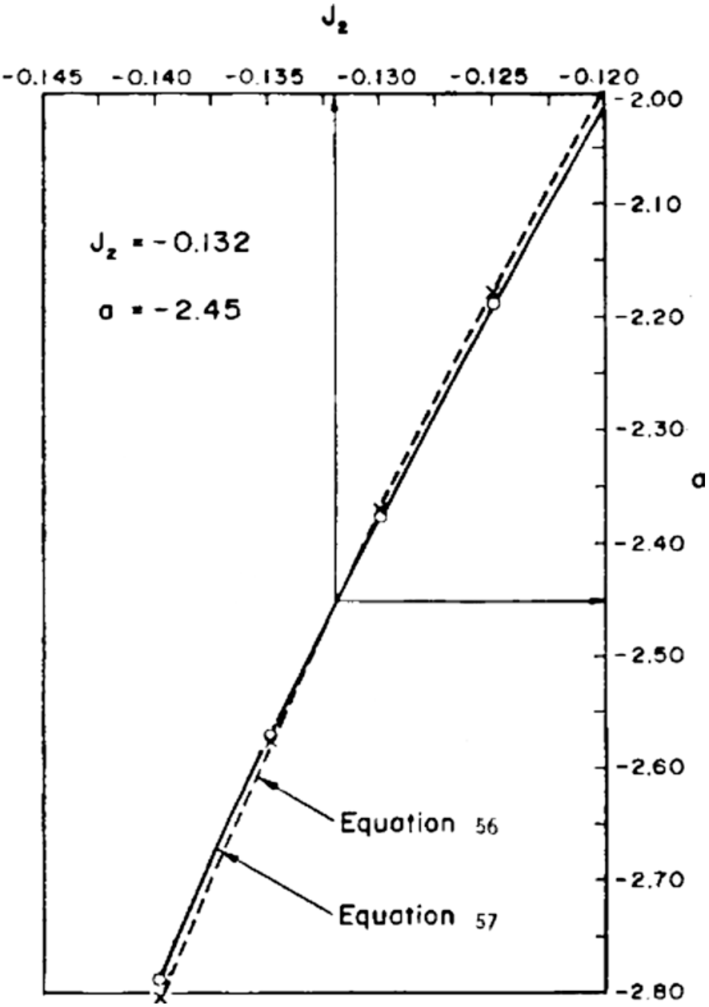


Fig. 7.9 The relationships of J_2 and a in the Tam-Sui river, Section II (stations T-0.0 to T-7.8)

$K_b = 2$ day^{-1},
$K_L = 4$ ft/day,
PS (i.e., point source) effluent flow = 10 ft^3/s,
PS effluent total nitrogen = 20 mg/L,
PS effluent UOD = 120 mg/L,
PS effluent total coliform = 1000 MPN/100 mL.

Figure 7.10 shows both actual and idealized estuarine systems. Determine the following important water quality parameters and models under low freshwater flow conditions:

Table 7.13 Evaluation of biochemical oxygen demand and dissolved oxygen models

	Biochemical oxygen demand, mg/L		Dissolved oxygen deficit, mg/L	
Station	Observed *L*	Estimated *L*	Observed *D*	Estimated *D*
T-7.80	7.97	7.97	3.70	3.70
T-6.65	6.14	6.52	3.47	3.37
T-4.45	5.29	4.69	2.44	2.69
T-1.35	3.29	3.37	2.14	1.80
T-0.00	2.92	3.06	1.27	1.46

Source: Refs. [14] and [15]

1. Total nitrogen concentrations at

$$X = 0, \quad X \leqq 0, \quad \text{and} \quad X \geqq 0,$$

2. Total coliform concentrations at

$$X = 0, \quad X \leqq 0, \quad \text{and} \quad X \geqq 0,$$

3. Dissolved oxygen deficit at

$$K = X_c, \quad X \leqq 0, \quad \text{and} \quad X \geqq 0,$$

where X = downstream distance from the source of pollution and X_c = critical distance where the DO deficit is maximum.

Solution

1. *Determination of Total Nitrogen Concentrations: Average freshwater velocity*

$$(U) = Q/A = 50/2000 = 0.025 \text{ ft/s} = 0.41 \text{ mi/day},$$

$$1(\text{ft}^3/\text{s})(\text{mg/L}) = 1(\text{cfs})(\text{mg/L}) = 5.4 \text{ lb/day},$$

$$W_{tn} = W = (10)(20)(5.4) = 1080 \text{ lb/day},$$

$$C_{max} = C_0 = W/Q \tag{7.7}$$

$$C_{max} = 1080/(50 \times 5.4)$$
$$C_{max} = 4.0 \text{ mg/L} \qquad \text{at } X = 0'$$

$$C = C_0 \exp(UX/E) \tag{7.12}$$

$$C = 4\exp(0.41X/2),$$

$$C = 4\exp(0.205X) \text{ at } X \leqq 0,$$

$$C = C_0 = 4 \text{mg/L} \qquad \text{at } X \geqq 0 \tag{7.17}$$

2. *Determination of Total Coliform Concentrations*

$$\text{Estuary number}(N) = K_b E/U^2, \tag{7.2}$$

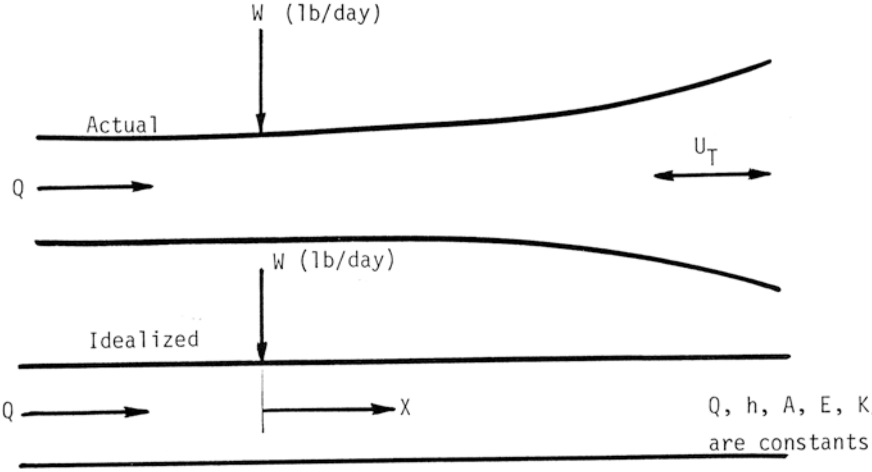


Fig. 7.10 Example of an estuary with a single-point source of pollution

$$N = \left(2\ \text{day}^{-1}\right)\left(2\ \text{mi}^2/\text{day}\right)/\left(0.41\ \text{mi}/\text{day}\right)^2 = 23.8,$$

$$m_1 = \left(1+4N\right)^{0.5} = \left(1+4\times 23.8\right)^{0.5} = 9.81, \tag{7.9}$$

$$j_1 = \left(U/2E\right)\left(1-m_1\right), \tag{7.19}$$

$$\begin{aligned} j_1 &= \left(0.41/2\times 2\right)\left(1-9.81\right) \\ &= -0.903\text{mi}^{-1} \end{aligned},$$

$$g_1 = \left(U/2E\right)\left(1+m_1\right) \tag{7.14}$$

$$\begin{aligned} g_1 &= \left(0.41/2\times 2\right)\left(1+9.81\right) \\ g_1 &= +1.108\,\text{mi}^{-1} \end{aligned},$$

Total coliform discharge (W_c) = W,

$$W = \left(10\text{ft}^3/\text{s}\right)\left(1000\text{MPN}/100\text{mL}\right),$$

$$L_{\max} = L_0 = W/\left(Qm_1\right) \tag{7.8}$$

$$\begin{aligned} L_{\max} &= \left(10\ \text{ft}^3/\text{s}\right)\left(1000\ \text{MPN}/100\ \text{mL}\right)/\left[\left(50\ \text{ft}^3/\text{s}\right)\left(9.81\right)\right] \\ L_{\max} &= 20\ \text{MPN}/100\text{mL}\quad \text{at}\ X=0 \end{aligned},$$

$$L = L_0\exp\left(j_1 X\right) \tag{7.18}$$

$$L = 20\exp(-0.930X) \quad \text{at}\, X \geqq 0,$$

$$L = L_0 \exp(g_1 X) \tag{7.13}$$

$$L = 20\exp(1.108X) \quad \text{at}\, X \leqq 0.$$

3. *Determination of Dissolved Oxygen Deficit Concentrations Average tidal velocity (U_T) = 0.6 knots*

$$\begin{aligned} U_\mathrm{T} &= (0.6\,\text{naut.mi/h})\,(1.15\,\text{stat.mi/naut.mi})\left[88\,\text{ft/s/}(60\text{mi/h})\right], \\ &= 1\,\text{ft/s} \end{aligned}$$

$$\text{Mean water depth}\,(h) = 10\text{ft},$$

$$K_\mathrm{L} = 4\,\text{ft / day},$$

$$K_2 = K_\mathrm{a} = K_\mathrm{L} / h = 4/10 = 0.4\,\text{day}^{-1}, \tag{7.1}$$

$$N_1 = K_1 E / U^2 = (0.25 \times 2)/(0.41)^2 = 2.974, \tag{7.2}$$

$$m_1 = (1 + 4N_1)^{0.5} = 3.591, \tag{7.9}$$

$$N_2 = K_2 E / U^2 = (0.4 \times 2)/(0.41)^2 = 4.759, \tag{7.2}$$

$$m_2 = (1 + 4N_2)^{0.5} = 4.476, \tag{7.11}$$

$$j_1 = (U/2E)(1 - m_1) \tag{7.19}$$

$$\begin{aligned} j_1 &= \left[0.41/(2 \times 2)\right](1 - 3.591) \\ j_1 &= -0.266\ \text{mi}^{-1} \end{aligned},$$

$$j_2 = (U/2E)(1 - m_2) \tag{7.21}$$

$$\begin{aligned} j_2 &= \left[0.417(2 \times 2)\right](1 - 4.476) \\ j_2 &= -0.356\ \text{mi}^{-1} \end{aligned},$$

$$g_1 = (U/2E)(1 + m_1) \tag{7.14}$$

$$\begin{aligned} g_1 &= \left[0.41/(2 \times 2)\right](1 + 3.591) \\ g_1 &= 0.471\,\text{mi}^{-1} \end{aligned},$$

$$g_2 = (U/2E)(1+m_2) \tag{7.16}$$

$$\begin{aligned} g_2 &= [0.41/(2\times 2)](1+4.476), \\ g_2 &= 0.561\,\text{mi}^{-1} \end{aligned}$$

$$W_{\text{UOD}} = W = \text{UOD discharged} = (10)(120)(5.4) = 6480\,\text{lb/day},$$

$$X_c = \frac{\ln\left[m_1(1-m_2)m_2^{-1}(1-m_1)^{-1}\right]}{(U/2E)(m_2-m_1)} \tag{7.22}$$

$$\begin{aligned} X_c &= \frac{\ln\left[3.591(1-4.476)4.476^{-1}(1-3.591)^{-1}\right]}{(0.41/2\times 2)(4.476-3.591)}, \\ X_c &= 0.811\,\text{mi} \end{aligned}$$

$$\begin{aligned} L_0 &= W/Qm_1 \\ &= 6480/(50\times 5.4\times 3.591), \\ &= 6.68\,\text{mg/L} \end{aligned}$$

$$K_{12} = K_d = 0.25\,\text{day}^{-1},$$

$$D_c = \left[L_0K_{12}/(K_2-K_1)\right]\left[\exp(j_1X_c) - m_1m_2^{-1}\exp(j_2X_c)\right] \tag{7.23}$$

$$\begin{aligned} D_c &= [6.68\times 0.25/(0.4-0.25)]\times[\exp(-0.266\times 0.811) \\ &\quad -3.591(4.476)^{-1}\times\exp(-0.356\times 0.811)], \\ D_c &= 11.14(0.2049) \\ D_c &= 2.28\,\text{mg/L} \quad \text{at } X = X_c \text{ or critical point} \end{aligned}$$

$$D = \left[L_0K_{12}/(K_2-K_1)\right]\left[\exp(g_1X) - m_1m_2^{-1}\exp(g_2X)\right] \tag{7.15}$$

$$\begin{aligned} D &= [6.68\times 0.25/(0.4-0.25)]\times[\exp(0.471X) \\ &\quad -3.591(4.476)^{-1}\exp(0.561X)], \\ D &= 11.14[\exp(0.471X) - 0.802\exp(0.561X)] \quad \text{at } X \leqq 0 \text{ or upstream} \end{aligned}$$

$$D = \left[L_0K_{12}/(K_2-K_1)\right]\left[\exp(j_1X) - m_1m_2^{-1}\exp(j_2X)\right] \tag{7.20}$$

$$D = \left[6.68 \times 0.25/(0.4 - 0.25)\right] \times [\exp(-0.266X) - 3.591(4.476)^{-1}\exp(-0.356X)] .$$
$$D = 11.14\left[\exp(-0.266X) - 0.802\exp(-0.356X)\right] \quad \text{at } X \geqq 0 \quad \text{or downstream}$$

6.3 Example 6.3: Investigation of an Estuary with Multiple Waste Sources

The following are the given information:

Freshwater low flow (Q) = 50 ft^3/s,
Freshwater summer average flow (Q) = 300 ft^3/s,
Freshwater summer storm flow (Q) = 900 ft^3/s,
Mean water depth (h) = 10 ft,
Average cross-sectional area (A) = 5000 ft^2,
Average tidal velocity (U_T) = 0.2 knots,
Dispersion coefficient (E) = 2 mi^2/day,
$K_1 = K_r = 0.25\ \text{day}^{-1}$,
$K_{12} = K_d = K_r$,
$K_2 = K_a$,
$K_b = K_1 = 2\ \text{day}^{-1}$,
PS (i.e., point source) effluent flow = 20 ft^3/s,
PS effluent total coliform = 10,000 MPN/100 mL,
PS effluent UOD = 160 mg/L,
NPS (i.e., nonpoint source) UOD = 80 mg/L,
NPS total coliform concentration = 3×10^5 MPN/100 mL,
NPS summer average flow = 20 ft^3/s,
NPS summer storm flow = 100 ft^3/s,
NPS distribution = uniformly distributed over 4 mi.

Figure 7.11 shows the actual and idealized estuarine systems. Determine the following important water quality parameters and models under the stated freshwater flow conditions:

1. Total coliform and UOD of PS and NPS under three freshwater flow conditions: low, summer average, and summer storm flow.
2. Total coliform concentrations at Milepoints 38–60 under summer storm conditions (see Fig. 7.11 for milepoints and definitions of X and X_p).
3. Maximum total coliform concentration and its location in terms of milepoint (MP) under summer storm conditions.
4. Dissolved oxygen deficit (D) at Milepoints 27–60 under summer average flow conditions.
5. Maximum dissolved oxygen deficit and critical distance.

Solution

1. *Determination of Total Coliform and UOD under Various Flow Conditions.*
   Total coliform of PS (ft^3/s MPN/100 mL) = (flow, ft^3/s) × (concentration, MPN/100 mL)
   Total coliform of NPS (ft^3/s MPN/100 mL/mi) = (flow, ft^3/s) (concentration, MPN/100 mL)/(distributed length, mi)
   UOD of PS (lb/day) = 5.4 (flow, ft^3/s) (concentration, mg/L)
   UOD of NPS (lb/day/mi) = 5.4 (flow, ft^3/s) (concentration, mg/L)/(length, mi)
   The answers are summarized below:

Flow conditions	Point source, *W*	
	Total coliform, ft^3/s MPN/100 mL	UOD, lb/day
Low	20 × 10,000	20 × 160 × 5.4 = 17,280
Summer average	20 × 10,000	20 × 160 × 5.4 = 17,280
Summer storm	20 × 10,000	20 × 160 × 5.4 = 17,280
Flow conditions	Nonpoint source, *w*	
	Total coliform, ft^3/s MPN/100 mL	UOD, lb/day/mi
Low	0	0
Summer average	–	20 × 80 × 5.4/4 = 2160
Summer storm	$100 \times 3 \times 10^5/4 = 7.5 \times 10^6$	–

2. *Determination of Total Coliform Concentrations at Various Milepoints under Summer Storm Conditions*

$$Q = 900\ \text{ft}^3/\text{s},$$

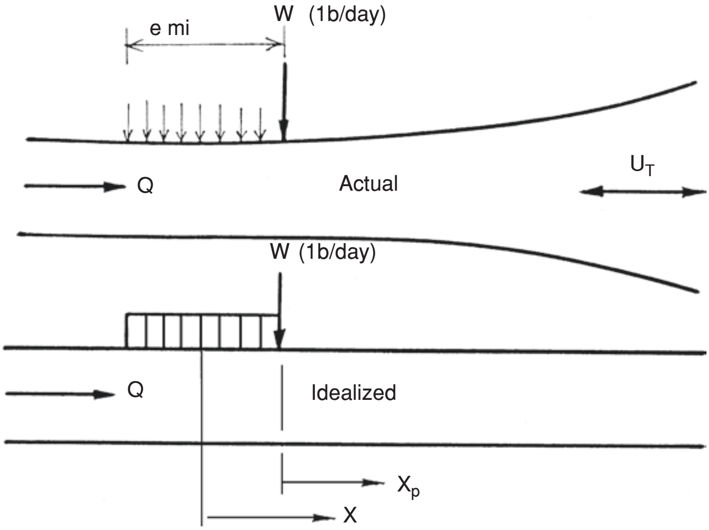


Fig. 7.11 Estuary with both point source and nonpoint sources of pollution

$$U = Q/A = \left(900/5000\right)16.4 = 2.95\ \text{mi/day},$$

$$E = 2\ \text{mi}^2\text{/day},$$

$$K_\text{b} = 2\ \text{day}^{-1},$$

$$N = 2\times 2/\left(2.95\right)^2 = 0.46, \tag{7.2}$$

$$m_1 = \left(1+4\times 0.46\right)^{0.5} = 1.685, \tag{7.9}$$

$$g_1 = \left[2.95/\left(2\times 2\right)\right]\left(1+1.685\right) = 1.98\ \text{mi}^{-1}, \tag{7.14}$$

$$j_1 = \left[2.951\left(2\times 2\right)\right]\left(1-1.685\right) = -0.505\ \text{mi}^{-1}, \tag{7.19}$$

Coliform concentrations from PS
$X_\text{p} = 0$ at MP 52 (see Fig. 7.11),

$$W = \left(20\ \text{ft}^3\text{/s}\right)\left(10{,}000\ \text{MPN/100 mL}\right),$$

$$L_0 = W/\left(Qm_1\right), \tag{7.8a}$$

$$\begin{array}{l} L_0 = \left(20\times 10000\right)/\left(900\times 1.685\right) \\ L_0 = 132\ \text{MPN/100mL} \qquad \text{at}\ X_\text{p} = 0 \end{array},$$

$$L = L_0\exp\left(g_1X_\text{p}\right) \tag{7.13a}$$

$$L = 132\ \exp\left(-0.505X_\text{p}\right) \quad \text{at}\ X_\text{p} \leqq 0,$$

$$L = L_0\exp\left(j_1X_\text{p}\right) \tag{7.18a}$$

$$L = 132\exp\left(-0.505X_\text{p}\right) \quad \text{at}\ X_\text{p} \geqq 0,$$

Using Eqs. (7.13a) and (7.18a), the PS data in the first three columns of Table 7.14 can be completed. The maximum coliform concentration caused by the PS is 132 MPN/100 mL at $X_\text{p} = 0$ according to Eq. (7.8a).

Coliform concentrations from NPS

$X = 0$ at MP 54 (see Fig. 7.11), $a = 2$ mi,

$$\begin{array}{l} w = \left(100\ \text{ft}^3/\text{s}\right)\left(3\times 10^5\ \text{MPN}/100\ \text{mL}\right)/\left(4\ \text{mi}\right) \\ w = 7.5\times 10^6\,(\text{ft}^3/\text{s})\,(\text{MPN}/100\ \text{mL})/\text{mi} \end{array},$$

$L \quad \text{at}\ X \leqq -a\ \left(\text{or} \leqq -2\right)$

$$L = \left[w/(Qm_1g_1)\right]\{\exp\left[g_1(X+a)\right] - \exp\left[g_1(X-a)\right]\} \tag{7.28}$$

$$L = \left[7.5\times10^6/\left(900\times1.685\times1.98\right)\right]\times\{\exp\left[1.98(X+2)\right] \\ -\exp\left[1.98(X-2)\right]\}$$

$$L = 2498\left\{\exp\left[1.98(X+2)\right] - \exp\left[1.98(X-2)\right]\right\}, \tag{7.28a}$$

L at $X \geqq a$ (or $X \geqq 2$)

$$L = \left[w/(Qm_1j_1)\right]\{\exp\left[j_1(X+a)\right] - \exp\left[j_1(X-a)\right]\} \tag{7.31}$$

$$L = \left[7.5\times10^6/\left(-0.505\times900\times1.685\times1.98\right)\right]\times\{\exp\left[-0.505(X+2)\right] \\ -\exp\left[-0.505(X-2)\right]\}$$

$$L = -9793\left\{\exp\left[-0.505(X+2)\right] - \exp\left[-0.505(X-2)\right]\right\}, \tag{7.31a}$$

L at $-a \leqq X \leqq a$ (or $-2 \leqq X \leqq 2$)

$$L = \frac{w}{Qm_1}\left[\frac{\exp\left[j_1(X+a)\right]-1}{j_1} - \frac{\exp\left[g_1(X+a)\right]-1}{g_1}\right], \tag{7.25}$$

$$L = \frac{7.5\times10^6}{900\times1.685}\left[\frac{\exp\left[-0.505(X+2)\right]-1}{-0.505} - \frac{\exp\left[1.98(X-2)\right]-1}{1.98}\right],$$

$$L = 4946\left[\frac{\exp\left[-0.505(X+2)\right]-1}{-0.505} - \frac{\exp\left[1.98(X-2)\right]-1}{1.98}\right]. \tag{7.25a}$$

Using Eqs. (7.28a), (7.31a), and (7.25a), the NPS data in Columns 1, 4, and 5 of Table 7.14 can be completed. Finally, the total coliform concentration caused by both PS and NPS is calculated and listed in Column 6 of the same table.

3. *Determination of* Maximum *Total Coliform* Concentration *and its Location*
Maximum total coliform from PS

$$L_{\max} = L_0 = 132 \text{ MPN/100mL at } X_p = 0,$$

according to Eq. (7.8a)
Maximum total coliform from NPS. $L_{\max}$ is located at (see Fig. 7.5):

$$X_1 = a/m_1, \tag{7.64}$$

where X_1 is the location of $L_{\max}$ and

Table 7.14 Total coliform analysis of an estuary with multiple waste sources under summer storm flow conditions[a]

MP	PS X_p	PS L	NPS X	NPS L	Total L, MPN/100 mL
60	−8	0	−6	1	1
58	−6	0	−4	48	48
57	−5	0	−3	345	345
56	−4	0	−2	2498	2498
55	−3	0	−1	6375	6375
54	−2	3	0	8677	8680
53	−1	18	10	9794	9812
52.81	−0.81	26	12	9834[b]	9860
52	0	132[b]	14	8495	8627
51	1	80	16	5126	5206
50	2	48	1	3094	3142
49	3	29	1.19	1867	1896
48	4	18	2	1127	1145
47	5	11	3	680	691
46	6	6	4	410	416
45	7	4	5	248	252
44	8	2	6	149	151
42	10	1	7	54	55
40	12	0	8	20	20
38	14	0	9	7	7
Column: (1)	(2)	(3)	(4)	(5)	(6)

[a] Example 7.3

[b] Maximum concentration

$$0 \leqq X_1 \leqq a\,.$$

Therefore,

$$X_1 = 2/1.685 = 1.19\ \text{mi} = X\,,$$

$$L_{\max} = 9834\ \text{MPN/100 mL}\,. \tag{7.25a}$$

Maximum total coliform from PS and NPS, From Table 7.14,

$$L_{\max} = 9860\ \text{MPN/100 mL},$$

$$\text{at}\ X = 1.19\ \text{mi or MP} = 52.81.$$

4. *Determination of Dissolved Oxygen Deficit at Milepoints 27–60 under Summer Average Conditions*

$h = 10\,\text{ft}$	$N_1 = 0.516$,
$Q = 300\,\text{ft}^3/\text{s}$	$m_1 = 1.750$,
$U = 0.984\,\text{mi/day}$	$g_1 = 0.677\,\text{mi}^{-1}$,
$E = 2\,\text{mi}^2/\text{day}_1$	$j_1 = -0.1845\,\text{mi}^{-1}$,
$K_1 = K_r = 0.25\,\text{day}^{-1}$	$N_2 = 0.826$,
$K_L = 4\,\text{ft/day}$	$m_2 = 2.075$,
$K_2 = K_a = K_1/h = 4/10 = 0.4\,\text{day}^{-1}$	$g_2 = 0.756\,\text{mi}^{-1}$,
$K_{12} = K_d = K_r = 0.25\,\text{day}^{-1}$	$j_2 = -0.264\,\text{mi}^{-1}$.

D from PS:
$W = 17{,}280$ lb/day from Step 1,

$$L_0 = 17{,}280/\left(300 \times 1.75 \times 5.4\right) = 6.095\,\text{mg/L}, \tag{7.8}$$

D at $X_p \leqq 0$

$$\begin{aligned} D = &\left[6.095 \times 0.25 / \left(0.4 - 0.25\right)\right] \\ &\times \left[\exp\left(0.677 X_p\right) - 1.75 \times 2.075^{-1} \exp\left(0.756 X_p\right)\right], \end{aligned} \tag{7.15a}$$

D at $X_p \geqq 0$

$$\begin{aligned} D = &\left[6.095 \times 0.25 / \left(0.4 - 0.25\right)\right] \\ &\times \left[\exp\left(-0.1845 X_p\right) - 1.75 \times 2.075^{-1} \exp\left(-0.264 X_p\right)\right], \end{aligned} \tag{7.20a}$$

$$\begin{aligned} X_c = &\ln\left[1.75\left(1 - 2.075\right) 2.075^{-1}\left(1 - 1.75\right)\right] \\ &/\left[\left(0.984/2 \times 2\right)\left(2.075 - 1.75\right)\right] = 2.37\,\text{mi}, \end{aligned} \tag{7.22}$$

D from NPS,
$w = 2160$ lb/day/mi from Step 1,

D at $X \leqq -2$

$$\begin{aligned} D = &\frac{2160 \times 0.25}{300 \times 5.4\left(0.4 - 0.25\right)} \left\{ \frac{\exp\left[0.677\left(X+2\right)\right] - \exp\left[0.677\left(X-2\right)\right]}{1.75 \times 0.677} \right. \\ &\left. - \frac{\exp\left[0.756\left(X+2\right)\right] - \exp\left[0.756\left(X-2\right)\right]}{2.075 \times 0.756} \right\}, \end{aligned} \tag{7.29a}$$

D at $-2 \leqq X \leqq 2$

Table 7.15 Dissolved oxygen deficit analysis of an estuary with multiple waste sources under summer average flow condition[a]

	PS		NPS		Total D, mg/L
MP	X_p	D	X	D	
60	−8	0.02	−6	0.05	0.07
58	−6	0.08	−4	0.15	0.23
56	−4	0.26	−2	0.40	0.66
55	−3	0.45	−1	0.58	1.03
54	−2	0.73	0	0.75	1.48
53	−1	1.59	2	0.95	2.54
51.34	0.66	1.80	2.66	0.96[b]	2.76
51	1	1.87	3	0.95	2.82
50	2	1.97	4	0.92	2.89
49.63	2.37	1.98[b]	4.37	0.90	2.88
49	3	1.96	5	0.87	2.83
48	4	1.88	6	0.80	2.68
46	6	1.60	8	0.64	2.24
44	8	1.29	10	0.50	1.79
37	15	0.47	17	0.17	0.64
32	20	0.21	22	0.01	0.22
27	25	0.09	27	0.00	0.09
Column: (1)	(2)	(3)	(4)	(5)	(6)

[a] Example 7.3

[b] Maximum concentration

$$D = \frac{2160\times 0.25}{300\times 5.4(0.4-0.25)}\left\{\left[\frac{\exp\left[-0.1845(X+2)\right]-1}{1.75(-0.1845)} - \frac{\exp\left[0.677(X-2)\right]-1}{1.75(0.677)}\right] - \left[\frac{\exp\left[-0.264(X+2)\right]-1}{2.075\times(-0.264)} - \frac{\exp\left[0.756(X-2)\right]-1}{2.075(0.756)}\right]\right\}, \quad (7.26a)$$

D at $X \geqq 2$

$$D = \frac{2160\times 0.25}{300\times 5.4(0.4-0.25)}\left\{\frac{\exp\left[-0.1845(X+2)\right]-\exp\left[-0.1845(X-2)\right]}{1.75(-0.1845)} - \frac{\exp\left[-0.264(X+2)\right]-\exp\left[-0.264(X-2)\right]}{2.075(-0.264)}\right\}. \quad (7.32a)$$

Table 7.15 is established using Eqs. (7.29a), (7.26a), and (7.32a).

5. *Determination of Maximum Dissolved Oxygen Deficit and Critical Distance*

For PS,

$X_c = 2.37$ mi from Step 4,

$D_c = 1.98$ mg/L at $X_p = X_c$ using Eq. (7.20a).

For NPS, Table 7.8 lists four important equations for determining the location of maximum concentration for distributed sequentially reacting waste, such as DO deficit. Initially, the slope of the DO deficit curve(s) must be determined by Eq. (7.65),

$$s = \left[\exp\left(2aj_1\right) - 1\right] / m_1 \; - \; \left[\exp\left(2aj_2\right) - 1\right] / m_2 \tag{7.65}$$

$$s = \left[\exp\left(-2 \times 2 \times 0.1845\right) - 1\right] / 1.75 \; - \; \left[\exp\left(-2 \times 2 \times 0.264\right) - 1\right] / 2.075.$$

$$s = +0.016$$

Since the slope is positive, the location of D_c is

$$X_c > 2$$

and the numerical value of X_c can be determined by Eq. (7.66),

$$\frac{\exp\left[j_1\left(X_c + a\right)\right] - \exp\left[j_1\left(X_c - a\right)\right]}{m_1} \tag{7.66}$$

$$= \frac{\exp\left[j_2\left(X_c + a\right)\right] - \exp\left[j_2\left(X_c - a\right)\right]}{m_2}$$

or

$$\frac{\exp\left[-0.1845\left(X_c + 2\right)\right] - \exp\left[-0.1845\left(X_c - 2\right)\right]}{1.750}$$

$$= \frac{\exp\left[-0.264\left(X_c + 2\right)\right] - \exp\left[-0.264\left(X_c - 2\right)\right]}{2.075},$$

from which $X_c = 2.66$ mi. Then, $D_c = 0.96$ mg/L by substituting $X = X_c = 2.66$ into Eq. (7.32a).

The maximum DO deficit (D_c) caused by both PS and NPS is estimated to be 2.89 mg/L at MP-50 according to Table 7.15.

Glossary [46, 48–54]

Biochemical Refers to chemical processes that occur inside or are mediated by living organisms.

Biochemical oxygen demand (BOD) The amount of oxygen, measured in milligrams per liter, that is removed from aquatic environments by the life processes of microorganisms.

Constituent A chemical or biological substance in water, sediment, or biota that can be measured by an analytical method.

Contaminant Biological or chemical substances or entities, not normally present in a system, which may be capable of producing an adverse effect in a biological system, seriously injuring structure or function.

Contamination Degradation of water quality compared to original or natural conditions due to human activity.

Denitrification A process by which oxidized forms of nitrogen such as nitrate (NO_3^-) are reduced to form nitrites, nitrogen oxides, ammonia, or free nitrogen: commonly brought about by the action of denitrifying bacteria and usually resulting in the escape of nitrogen to the air.

Discharge Rate of fluid flow passing a given point at a given moment in time, expressed as volume per unit of time.

Dissolved constituent Operationally defined as a constituent that passes through a 0.45-μm filter.

Dissolved solids Amount of minerals, such as salt, that are dissolved in water; amount of dissolved solids is an indicator of salinity or hardness.

Drainage area The drainage area of a stream at a specified location is that area, measured in a horizontal plane, which is enclosed by a drainage divide.

Drainage basin The portion of the surface of the Earth that contributes water to a stream through overland runoff, including tributaries and impoundments.

Ecosystem A system that is made up of a community of animals, plants, and bacteria and its interrelated physical and chemical environment.

Eutrophication enrichment of waters with nutrients, primarily phosphorus, causing abundant aquatic plant growth, and often leading to seasonal deficiencies in dissolved oxygen.

Fecal bacteria Microscopic single-celled organisms (primarily fecal coliforms and fecal streptococci) found in the wastes of warm-blooded animals. Their presence in water is used to assess the sanitary quality of water for body-contact recreation or for consumption. Their presence indicates contamination by the wastes of warm-blooded animals and the possible presence of pathogenic (disease producing) organisms.

Fecal coliform Fecal bacteria.

Load General term that refers to a material or constituent in solution, in suspension, or in transport; usually expressed in terms of mass or volume.

Mean discharge The arithmetic mean of individual daily mean discharges during a specific period, usually daily, monthly, or annually.

Nitrate An ion consisting of nitrogen and oxygen (NO_3^-). Nitrate is a plant nutrient and is very mobile in soils.

Nonpoint source contaminant A substance that pollutes or degrades water that comes from lawn or cropland runoff; the Nonpoint-source Water pollution: Water contamination that originates from a broad area (such as leaching of agricultural chemicals from crop land) and enters the water resource diffusely over a large area.

Nonselective herbicide Kills or significantly retards growth of most higher plant species.

Not detectable Below the limit of detection of a specified method of analysis.

Nutrient Element or compound essential for animal and plant growth. Common nutrients in fertilizer include nitrogen, phosphorus, and potassium.

Overland flow The part of surface runoff flowing over land surfaces toward stream channels.

Oxidation The combination of oxygen with a substance, or the removal of hydrogen from it or, more generally, any reaction in which an atom loses electrons.

Oxygenation The process of adding dissolved oxygen to a solution

Phosphorus A nutrient essential for growth that can play a key role in stimulating aquatic growth in lakes and streams.

Photodegradation Breakdown of a substance by exposure to light; the process whereby ultraviolet radiation in sunlight attacks a chemical bond or link in a chemical structure.

Photolysis The decomposition of a compound into simpler units as a result of the absorption of one or more quanta of radiation.

Photosynthesis Synthesis of chemical compounds by organisms with the aid of light. Carbon dioxide is used as raw material for photosynthesis, and oxygen is a product.

Point source A source at a discrete location such as a discharge pipe, drainage ditch, tunnel, well, concentrated livestock operation, or floating craft.

Point-source contaminant Any substance that degrades water quality and originates from discrete locations such as discharge pipes, drainage ditches, wells, concentrated livestock operations, or floating craft.

Point-source pollution Pollution discharged through a pipe or some other discrete source from municipal water-treatment plants, factories, confined animal feedlots, or combined sewers.

Pollutant Any substance that, when present in a hydrologic system at sufficient concentration, degrades water quality in ways that are or could become harmful to human and/or ecological health or that impair the use of water for recreation, agriculture, industry, commerce, or domestic purposes.

Pollution The introduction of unwanted components into waters, air, or soil, usually as a result of human activity, e.g., hot water in rivers, sewage in the sea, and oil on land.

Salinity The presence of soluble salts in or on soils or in water.

Streamflow A type of channel flow, applied to that part of surface runoff in a stream whether or not it is affected by diversion or regulation.

Surface water An open body of water, such as a lake, river, or stream.

Suspended sediment Particles of rock, sand, soil, and organic detritus carried in suspension in the water column, in contrast to sediment that moves on or near the streambed.

Suspended solids Different from suspended sediment only in the way that the sample is collected and analyzed.

Suspended-sediment concentration The velocity-weighted concentration of suspended sediment in the sampled zone (from the water surface to a point approximately 0.3 ft above the bed) expressed as milligrams of dry sediment per liter of water-sediment mixture (mg/L).

Tributary A river or stream flowing into a larger river, stream, or lake.

Water quality The physical, chemical, and biological characteristics of water and the measure of its condition relative to the requirements for one or more biotic species and/or to any human need or purpose.

Water-quality criteria Criteria that comprise numerical and narrative *criteria*. Numerical criteria are scientifically derived ambient concentrations developed by the US Environmental Protection Agency (USEPA) or the States for various pollutants of concern so that human health and aquatic life can be protected. Narrative criteria are statements that describe the desired water-quality goal.

Water-quality data Chemical, biological, and physical measurements or observations of the characteristics of surface and ground waters, atmospheric deposition, potable water, treated effluents, and waste water and of the immediate environment in which the water exists.

Water-quality guidelines Specific levels of water quality, which, if reached, may adversely affect human health or aquatic life. These are nonenforceable guidelines issued by a governmental agency or other institution.

Appendix

A practical method of determining reaeration coefficients would greatly aid design engineers in determining the degree of wastewater treatment required for a proposed effluent discharge. The reaeration coefficient in saline water, K_{2s} (day^{-1}, base *e*) at any chloride concentration CL (g/L) and at 20 °C, can be expressed by

$$K_{2s} = K_{2f} \exp\left(0.0127\text{CL}\right),$$

in which K_{2f} is the reaeration coefficient in fresh water at 20 °C [17].

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Chapter 8

First Wave of Flotation Technology Evolution: Once the World's Largest DAF-Filtration Plant and Its Hydroelectric Facility

Lawrence K. Wang and Mu-Hao Sung Wang

Contents

Abstract Dissolved air flotation (DAF) was previously only used for sludge thickening in industrial and municipal biological wastewater treatment plants. There are two waves DAF technology developments. The first wave of DAF technology development elevates DAF for drinking water treatment, and a second wave of DAF

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technology development elevates DAF further for primary DAF clarification, secondary DAF clarification, and independent physicochemical wastewater treatment. This book chapter introduces the two new waves DAF technology evolutions, with special emphasis on the development once the world's largest drinking water flotation-filtration (DAFF) plant and its hydroelectric power generation facility in Pittsfield, Massachusetts, USA. The heart of the Pittsfield Water Supply Facilities (PWSF) system is 6 DAFF package plants, commercially known as Krofta Sandfloat (Type 49, each diameter = 49 ft.; depth = 6 ft.; each design capacity = 6.25 MGD). The authors describe the DAFF package plant, the overall PWSF system, its chemical treatment, water disinfection, flow control, 5-MG concrete water storage tank, high pressure zones control system and management, innovative hydroelectric plant for energy generation, its supervisory control and data acquisition (SCADA) system, innovative direct filter backwash wastewater recycle, innovative elimination of water distribution lift pumps for energy saving, and innovative direct alum sludge reuse in the nearby Pittsfield Wastewater Treatment Plant for phosphate removal. The total project success was due to a collaborative team work involving our leader, Dr. Milos Krofta, the Lenox Institute of Water Technology (LIWT), Krofta Engineering Corporation (KEC), O'Brien & Gere Engineers, the Commonwealth of Massachusetts, and the City of Pittsfield. The authors also discuss other DAF process equipments (Supracell, AquaDAF, Clari-DAF), and the flotation's future in America and the entire world.

Keywords Milos Krofta · Lenox Institute of Water Technology · Krofta Engineering Corporation · O'Brien & Gere Engineers · Pittsfield · Massachusetts · USA · Dissolved air flotation · Potable water filtration · DAF · DAFF · Sandfloat · Supracell · AquaDAF · Clari-DAF · Innovations · Filter backwash wastewater recycle · Reuse alum sludge for phosphate removal · Hydroelectric plant for energy generation · Elimination of lift pumps

Abbreviations

DAF	Dissolved air flotation
DAFF	Dissolved air flotation-filtration package plant
KEC	Krofta Engineering Corporation
LIWT	Lenox Institute of Water Technology
PWSF	Pittsfield Water Supply Facilities
SCADA	Supervisory control and data acquisition
USEPA	US Environmental Protection Agency

1 Introduction

1.1 New Waves of Flotation Technology Development

Dissolved air flotation (DAF) is a process involving pressurization of air at 25 to 95 psig for dissolving air into water, and subsequent release of the pressure from 25–95 psig to 1 atm under laminar flow hydraulic conditions for generating extremely fine air bubbles (20–80 μm) which become attached to the impurities to be removed. The air bubbles and the attached impurities rise to the water surface together. The impurities or pollutants which are removed on the water surface are called float or scum. They are scooped off by sludge collection means. The clarified water is discharged from the flotation clarifier's bottom. The air flow rate is about 1% of influent water flow rate. The attachment of air bubbles to the impurities can be a result of physical entrapment, electrochemical attraction, surface adsorption, and/or air stripping. The specific gravity of the bubble-impurity agglomerate is less than one, resulting in buoyancy or non-selective flotation (i.e. Save-All). If other gas instead of air is used, the process is called dissolved gas flotation (DGF) processes when another gas is used for generation of gas bubbles. DGF then is one of adsorptive bubble separation processes and has been used for various applications for decades [1–242].

In the field of environmental engineering, however, DAF was previously only used for sludge thickening in industrial and municipal biological wastewater treatment plants [1–3, 157]. There are two waves DAF technology developments. The first wave of DAF technology development elevates DAF for drinking water treatment [71–74, 76–79, 93–100, 105–110, 112–114, 122–128, 170, 194–197, 224–226, 241–251], and a second wave of technology development elevates DAF further for primary DAF clarification, secondary DAF clarification, and independent physicochemical wastewater treatment [68–70, 83–92, 104, 108–111, 120, 129–142, 144–159, 166–183, 191, 192, 225–229]. This book chapter introduces the two new waves DAF technology evolutions, with emphasis on the development once the world's largest drinking water flotation-filtration (DAFF) plant in the City of Pittsfield, Massachusetts, USA.

1.2 First Wave of Flotation Technology Development in Potable Water Applications

The first wave of flotation technology development in potable water application in the continents of America begun from the Town of Lenox, Massachusetts, USA, where the Lenox Institute of Water Technology (formerly Lenox Institute for Research) and Krofta Engineering Corporation jointly designed and installed an 1.1-MGD potable water DAF-filtration (DAFF) for the Town in 1981 [74, 76, 79, 93–100, 105, 106, 112–114, 139, 170, 197, 218, 219, 224, 247].

The heart of the innovative Lenox Water Treatment Plant is a DAFF package plant commercially known as Krofta Sandfloat, which is a combination of a DAF clarifier and an automatic backwash filter (ABF). An ABF system is divided into many identical-shape filtration sections for automatic filtration operation and backwash. There is a moving carriage having a backwash hood and a backwash pump and traveling back and forth on top of the filtration sections. When the backwash hood covers one filtration section for automatic backwash (controlled by a timer), the rest filtration sections are in filtration mode. One filtration section is backwashed at a time, until all filtration sections are backwashed and restored to filtration mode again.

A combination of DAF and filtration has been proven to be highly applicable to removal of extremely high color and turbidity [76, 117, 184, 185], powdered activated carbon [247], arsenic [137, 140], volatile organics [247, 251], algae [40, 41, 110, 154], odor [185], coliform bacteria [247, 249], surfactant [71, 130], hardness [234, 247], iron and manganese [45, 244, 251], particle counts and THM formation potential [114, 117, 160, 184, 200], and heavy metals [118, 137, 140, 250]. The DAF and filtration combination is feasible for treatment of river water [248], groundwater [142, 187, 188, 210], lake water [101, 243], or storm run-off water [182, 183], and are adequate for serving large communities [221, 245–247], small communities [105, 106, 112, 113, 224], institutions or even single families [247].

The small full-scale Lenox Water Treatment Plant which consists of one DAFF package plant (Krofta Sandfloat, 22-ft diameter; 5-ft depth; 1.1 MGD) was considered to be a pilot plant for the much larger Pittsfield Water Supply Facilities (PWSF) system. Since the operation and performance of the Lenox Water Treatment Plant were very successful [95, 96, 98–100, 105, 106, 112, 113, 170, 218, 219], the design of the PWSF system using 6 DAFF package plants was approved, and additional pilot plant demonstration using actual Pittsfield raw water was required by both the Commonwealth of Massachusetts, and the US Environmental Protection Agency (USEPA).

2 Development of Dissolved Air Flotation and Filtration (DAFF) Plants for the City of Pittsfield, Massachusetts, USA

2.1 Process Design and Further Pittsfield Pilot Plant Demonstration

The designed PWSF system requires six Krofta Sandfloat package plant (DAFF), Type 49. Each DAFF package plant's dimensions are: diameter = 49 ft.; and depth = 6 ft. Each DAFF's design capacity is 6.25 MGD. The estimated total construction costs and O&M costs were one-third of an equivalent conventional water treatment plant consisting of rapid mixing, flocculation, coagulation, sedimentation clarification, and sand filtration.

The results of Pittsfield pilot study using actual Pittsfield raw water and DAFF pilot plant were also excellent [72, 74, 77, 122–124]. The rest was a successful history. The City of Pittsfield, Massachusetts, USA, has built and has been successfully operating the following two innovative water plants since 1986: (a) Cleveland Water Treatment Plant and (b) Ashley Water Treatment Plant (Fig. 8.1). The first wave of DAF technology evolution has created the largest potable water DAF-filtration in the world.

Cleveland Plant is equipped with four Krofta Sandfloat units (Type SAF-49; Diameter = 49 ft.; Depth = 6 ft.; Design Capacity = 6.25 MGD per unit) and treats raw Cleveland Reservoir water containing high alkalinity, moderate color, and moderate turbidity.

Ashley Plant is equipped with two identical Krofta Sandfloat units (Type SAF-49) and treats mainly raw Farnham Reservoir water containing extremely low alkalinity, extremely high color and moderate turbidity (Fig. 8.2). Ashley Reservoir water, containing sufficient alkalinity, high color and moderate turbidity, is a supplemental source of water supply to Ashley Plant with only limited availability.

Both Cleveland Plant and Ashley Plant serve the same Pittsfield water supply facilities system as shown in Fig. 8.1 for 55,000 residents and many City's industries. The entire Pittsfield water treatment facilities include the following: (a) four major reservoirs, (b) chemical feed equipment, (c) six Sandfloat water treatment units, (d) two chlorination stations, (e) two flow control stations and distribution pipes, (f) one hydroelectric plant, (g) one 5-MG concrete water storage tank, (h) one standpipe, (i) two pumping stations, and (j) one central/data acquisition system, which are described in Sect. 3 in detail.

Two Sandfloat units at Ashley Plant (Fig. 8.2) were started up in October 1986, while all four Sandfloat units at Cleveland Plant were started up in January 1987 for

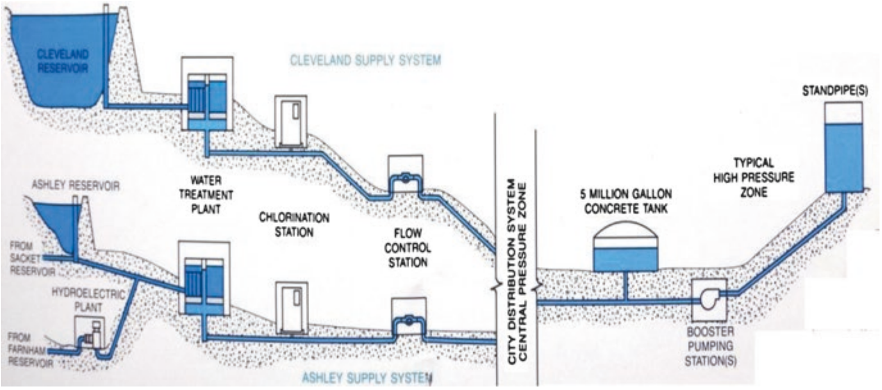


Fig. 8.1 Pittsfield Water Treatment Plant System: (**a**) Cleveland Plant: 4 DAFF (Sandfloat SAF49); and (**b**) Ashley Plant: 2 DAFF (Sandfloat SAF49)

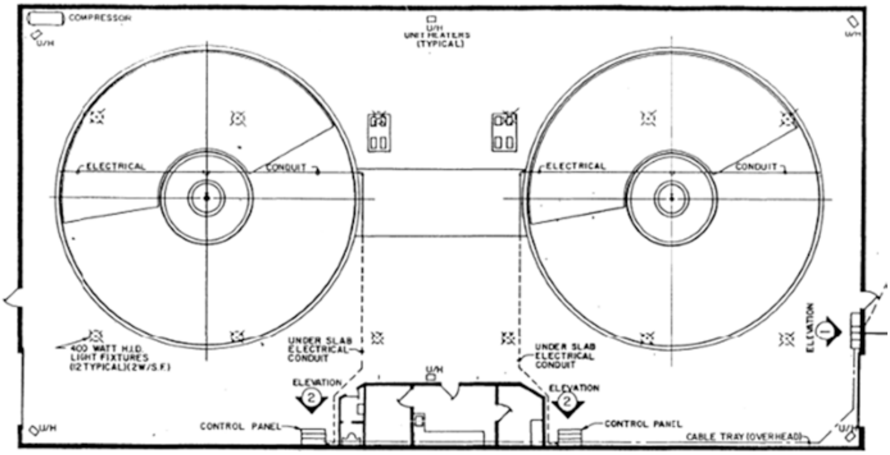


Fig. 8.2 Two DAFF clarifiers (Model Sand Flotat SAF-49; 49 Ft. diameter each) Pittsfield's Ashley Water Treatment Plant (Source: Lenox instituteof Water Technology)

on-line service. The top view of Cleveland Plant is similar to Ashley Plant except Cleveland has four Sandfloat units and is two times bigger.

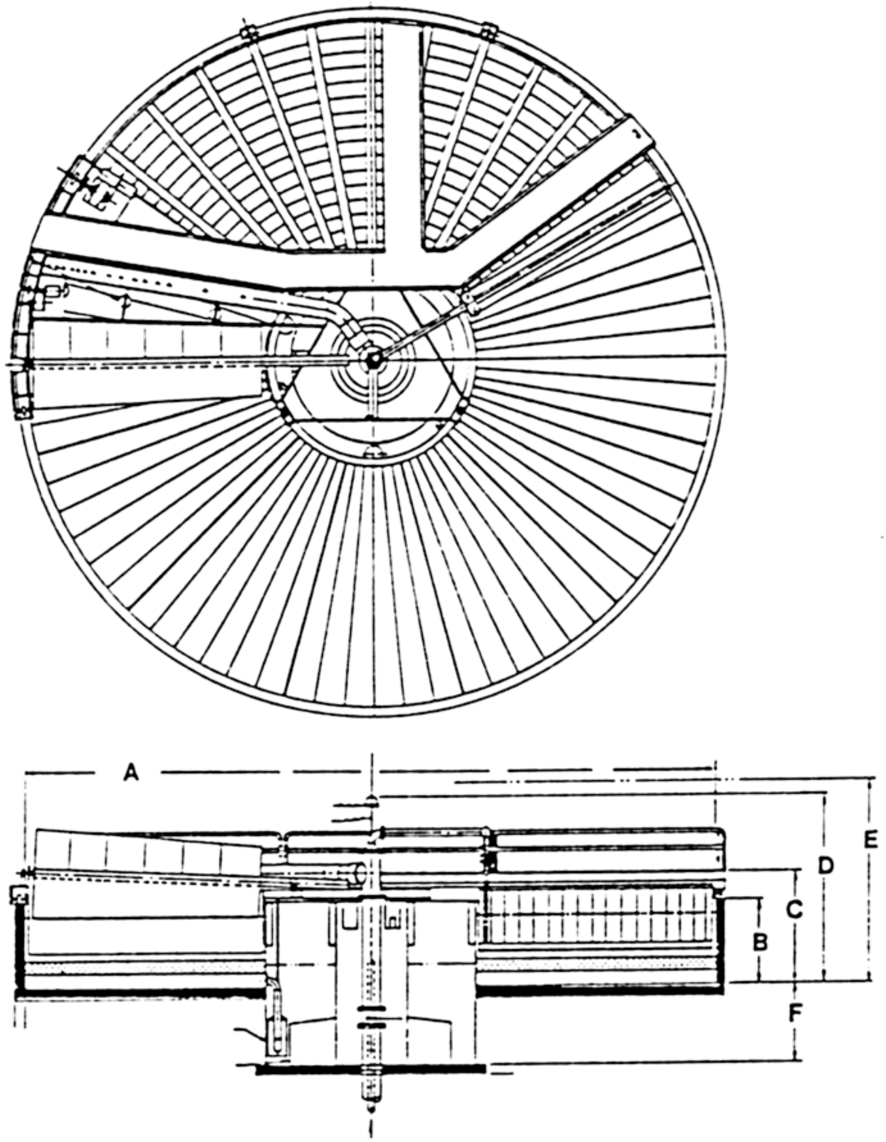
Each of the Pittsfield's Sandfloat units (Fig. 8.3) is a DAFF package water treatment clarifier consisting of chemical feeders, mixing chamber, flocculation chamber, dissolved air flotation tank, automatic backwash filters and clearwell. It is mainly a combination of dissolved air flotation (DAF) and sand filtration, therefore, it is the reason why it is technically called a DAFF plant.

In normal water treatment operation, one Sandfloat unit at each plant is the standby unit. The flow distribution of Cleveland Plant and Ashley Plant is as follows shown in Table 8.1. The description of the selected Sandfloat Type 49 is shown in Table 8.2 and Fig. 8.3.

The maximum daily flow is the design flow of each Sandfloat (i.e. 6.25 MGD per Sandfloat Type SAF-49; Diameter = 49 ft.). Figure 8.3 shows the top view and side view of Sandfloat Type SAF-49. Referring to the notations in Fig. 8.3, the dimensions of Sandfloat are presented above.

At the manufacturer's design flow, each operating Sandfloat's physical operational parameters can be predicted as

Maximum Influent Flow = 6.25 MGD
Range of Filter Backwash Rate = 12–20 gpm/ft^2
Diameter of Sandfloat Type SAF-49 = 49 ft. I.D.
Diameter of Clearwell = 15 ft
Area of Flotation Chamber = 996.43 ft^2
Area of Sand Filter = 1709.03 ft^2



A	– INSIDE TANK DIAMETER	(varies with TYPE)	
B	– HEIGHT of TANK	6'-0"	– 1830 mm
C	– " of CARRIAGE WALKWAY	8'-0"	– 2440 mm
D	– " MAX. of EQUIPMENT	13'-4"	– 4060 mm
E	– " MIN. of HEAD CLEARANCE	14'-6"	– 4420 mm
F	– TANK DEPTH	5'-0"	– 1520 mm

Fig. 8.3 Top view and side view of a 6.25-MGD Sandfloat SAF-49 clarifier

Table 8.1 The Design Flow Distribution of Cleveland Plant and Ashley Plant

Sandfloat (DAFF) and flow distribution	Cleveland plant	Ashley plant
Total Sandfloats	4	2
Standby Sandfloat	1	1
Operating Sandfloats	3	1
Average daily flow, MGD	10	5
Average flow/Sandfloat, MGD	3.33	5
Maximum daily flow, MGD	18.75	6.25
Maximum flow/Sandfloat, MGD	6.25	6.25

Note: 1 MGD = 3.785 million liters per day; 1 MG = 1,000,000 gallons

Table 8.2 Description of Sandfloat Package Plant (DAFF)

Sandfloat (DAFF) description	Notation in Fig. 8.3	Dimensions	
		ft (in.)	mm
Inside tank diameter	A	49′-0″	14,935
Height of tank	B	6′-2″	1880
Height of Carriage Walkway	C	8′-2″	2489
Height of maximum of equipment	D	13′-6″	4115
Height of minimum of head clearance	E	14′-6″	4420
Tank depth	F	3′-6″	1067

Note: 1 ft. = 0.3048 m; 1 in. = 2.54 cm

Effective Filter Area During Backwash = 1662.81 ft^2
No. of Filter Compartments = 37
No. of Compartments Being Backwashed = 1 Maximum Backwash Wastewater Flow = 854.52 gpm
Total Flow to Sandfloat During Backwash = 5194.80 gpm
Maximum Filtration Rate Between Backwash = 2.54 gpm/ft^2
Maximum Filtration Rate During Backwash = 3.04 gpm/ft^2
Maximum Flotation Overflow Between Backwash = 4.06 gpm/ft^2
Max. Flotation Overflow During Backwash = 4.86 gpm/ft^2

It should be noted that only with the success of the 1.1-MGD Lenox Water Treatment Plant assured, the Commonwealth of Massachusetts, USA, then approved a much larger DAF water filtration plant in the nearby City of Pittsfield. When the 37.5-MGD (142 million liters per day) Pittsfield water treatment plant was installed in 1986, it was then the world's largest water treatment plant using dissolved air flotation (DAF). This status has since been eclipsed by other plants in the U.S. and abroad [122–124, 163–165, 214, 220, 226].

The decision to build such a large Pittsfield plant was driven by concern that the DAF process may not work as advertised, despite the example of the small Lenox full-scale DAF water filtration plant. As a result, the Commonwealth of Massachusetts wanted a new Pittsfield flotation-filtration plant to be planned to handle double the amount needed by the City of Pittsfield.

Even the Lenox DAF-filtration (DAFF) plant came fully on line in July of 1982 and operated successfully, the Commonwealth of Massachusetts reluctantly gave final approval of the much larger plant in the 50,000-resident City of Pittsfield, Massachusetts. It was lucky that finally a waiver from the state was issued because DAF was not a standard process; DAF was not included as a form of treatment for drinking water in the "10 State Standards" guideline publication. Anyway it was not easy for developing an innovative flotation-filtration system for potable water treatment.

2.2 Summary of Initial Design, Cost Estimation and Pittsfield Plant Operation

Cleveland raw water having sufficient alkalinity can be treated satisfactorily using alum, sodium aluminate and polymer, at a cost of $0.02458 per 1000 gallons of water treated (1986 cost). Ashley raw water having low alkalinity requires alkalinity supplement at a slightly higher cost. Effluent turbidity from both plants ranges 0.3 to 0.5 NTU under optimum operational conditions [122–124, 165].

Pittsfield Water Treatment Facilities including both Cleveland Plant and Ashley Plant have a peak capacity of 37.5 MGD. At the same hydraulic capacity and treatment efficiency, the capital cost of a potable flotation plant such as Sandfloat is only about one-third of comparable conventional water treatment plants. Water conservation and chemical cost saving are its added advantages [122–124, 165].

Pittsfield Water Treatment System has been faithfully serving the City of Pittsfield, MA USA, since its startup in December 1986. The two Sandfloat plants passed the most stringent operating tests under severe winter conditions using only common cheap chemicals.

Since each Sandfloat flotation unit with 49 ft. of diameter is capable of treating 6.25 MGD water, its flotation clarification rate (gpm/ft.^{2}) and filtration rate (gpm/ft.^{2}) are both very satisfactory.

3 Complete Pittsfield Water Supply Facilities (PWSF) System: Once the Largest Potable Water Flotation-Filtration Plant in the World

Previous Sect. 2 has introduced that the heart of the Pittsfield Water Supply Facilities System is two potable DAF–filtration plants, Ashley Plant and Cleveland Plant: (a) the Ashley Plant has two DAF-filtration clarifiers, and (b) the Cleveland Plant has four DAF-filtration clarifiers. Each DAF-filtration clarifier has a capacity of 6.25 MGD, for a total capacity of 37.5 MGD. Each DAF-filtration clarifier is 49 ft. in diameter and 6 ft. in depth, and is a Krofta Sandfloat Model SAF49 package clarifier consisting of mainly dissolved air flotation (DAF) and automatic backwash filtration (ABF), shown in Fig. 8.3.

3.1 City of Pittsfield's Poor Water Quality and Water Pressure Balance Problems

Chlorination was the only water treatment process during the 1970s and early 1980s. The City of Pittsfield was confronted with taste, odor, discoloration, high color, high turbidity, high trihalomethanes and low residual chlorine problems. In addition to the water quality problems, adequate water pressure was not always available in the areas west and north of the Pittsfield water system. In the lower elevation (downtown) areas of the City, water pressure was at times excessive.

3.2 Overall Pittsfield Water Supply Facilities System

Since the Lenox Water Treatment Plant (LWTP) was on line for successful water supply service in 1982, Krofta Engineering Corporation (KEC) and O'Brien & Gere were retained by the City to evaluate the planning and design a new Pittsfield water supply system shown in Figs. 8.1 and 8.4. KEC invited the Lenox Institute of Water Technology (LIWT; formerly Lenox Institute for Research) was KEC's planning and design partner. The planned new Pittsfield water supply facilities system

Fig. 8.4 Pittsfield WTP's water treatment buildings are next to the raw water reservoir

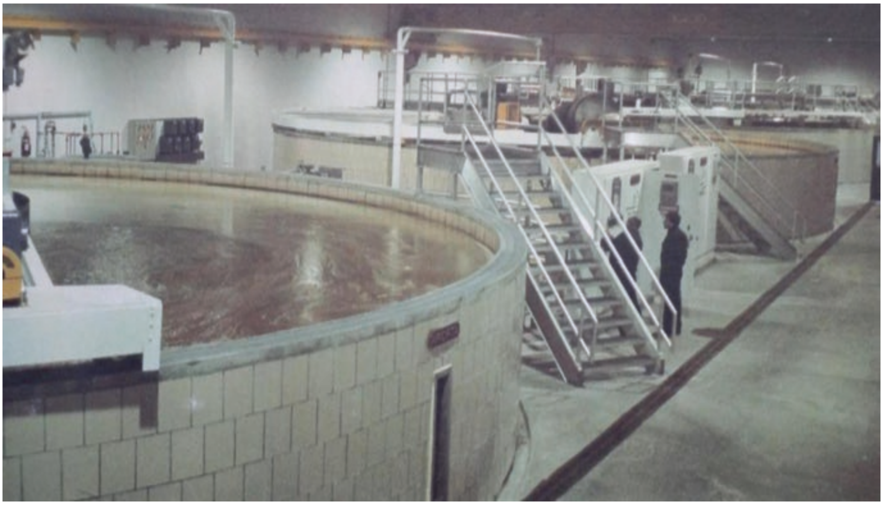


Fig. 8.5 The Heart of the Pittsfield WTP is 6 DAF-filtration clarifiers (DAFF, Krofta Sandfloat SAF49), each being 49-ft in diameter, 6-ft in death, treating 6.25 MGD

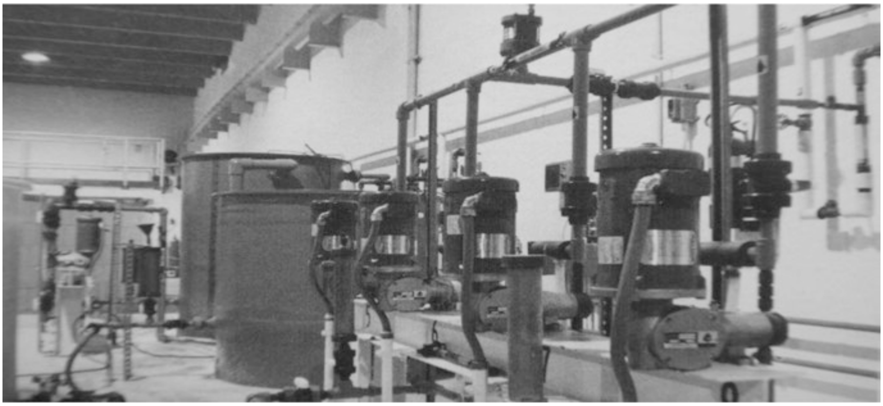


Fig. 8.6 Pittsfield WTP's Chemical feed equipment

included the following facilities illustrated by Figs. 8.1, 8.2, 8.3, 8.4, 8.5, 8.6, 8.7, 8.8, 8.9 and 8.10:

(a) Two water treatment plants: Cleveland Plant (Figs. 8.1 and 8.5; four Sandfloat SAF49 clarifiers) and Ashley Plant (two Sandfloat SAF49 clarifiers; Fig. 8.2);
(b) Cleveland Plant to treat Cleveland Reservoir raw water about 10 MGD safe yield;
(c) A raw water transmission pipeline to consolidate the three smaller water sources for treatment (Ashley Reservoir, Sackett Reservoir, and Farnham Reservoir together having 4.7 MGD safe yield) at Ashley Plant (Fig. 8.1);

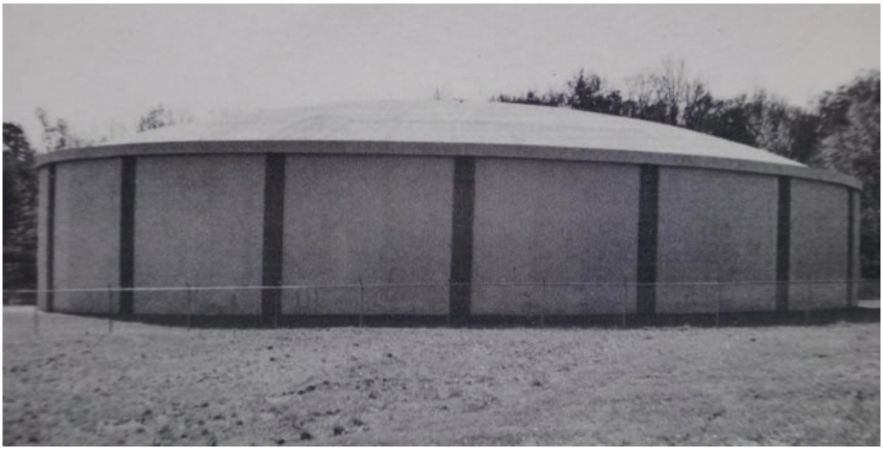


Fig. 8.7 Pittsfield WTP's five-million-gallon concrete tank

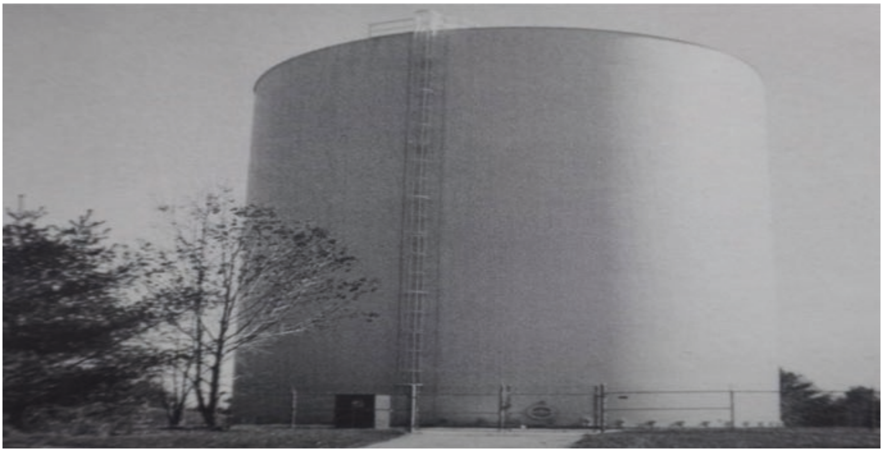


Fig. 8.8 Pittsfield WTP's Lebanon Avenue standpipe

(d) Two flow control stations (one for Cleveland Plant, and another one for Ashley Plant);
(e) A five million gallon concrete tank (Figs. 8.1 and 8.7) to function as clearwell/distribution storage;
(f) Distribution booster stations (Fig. 8.1) and associated standpipe storage (Fig. 8.8) to service high pressure areas in the northern, western, and southern parts of the City;
(g) A supervisory control and data acquisition (SCADA) system to monitor and control and water flow, pressure and quality (Fig. 8.9);

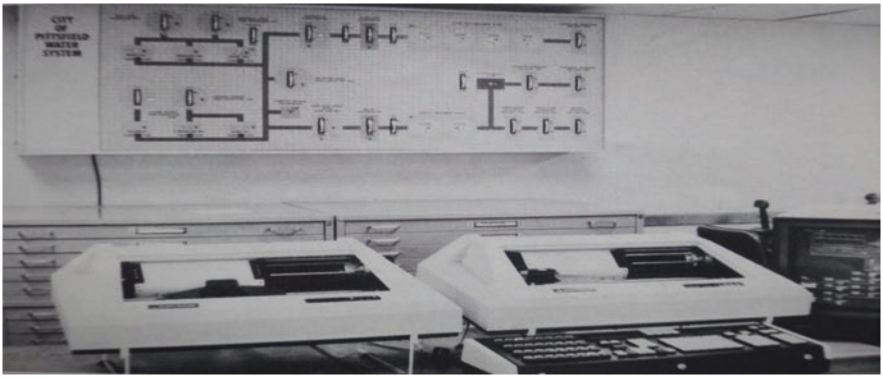


Fig. 8.9 Pittsfield WTP's supervisory control and data acquisition (SCADA) system

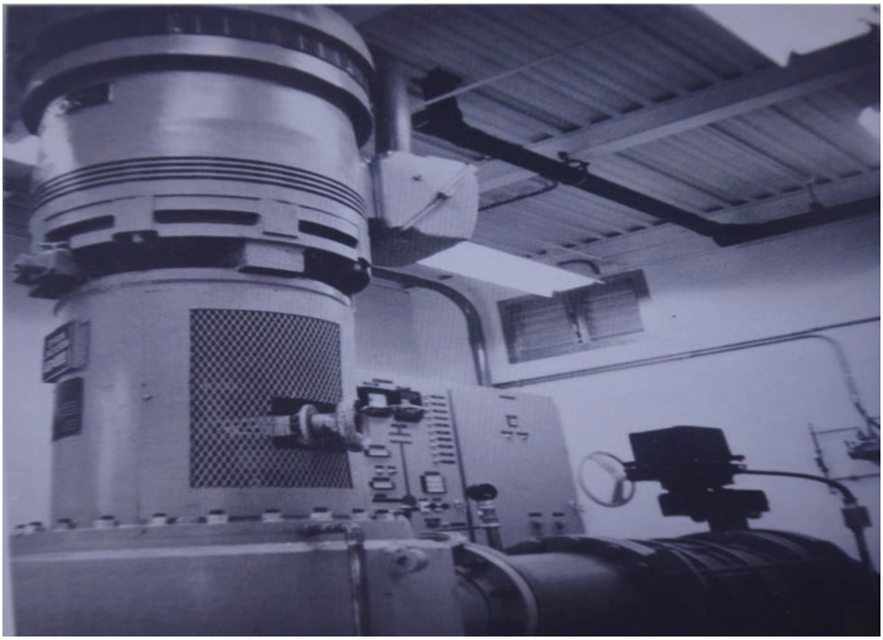


Fig. 8.10 Pittsfield WTP's hydroelectric plant

(h) A hydroelectric generation plant (Figs. 8.1 and 8.10) on the raw water transmission pipeline to recover energy that otherwise would be wasted by throttling valves.

3.3 Water Treatment Plants and Chemical Treatment

Cleveland Plant (4 Sandfloat or DAFF units) treats the Cleveland Reservoir water supply with average daily flows of 10 to 15 MGD, and maximum daily flows of 18 MGD. Ashley Plant (2 Sandfloat or DAFF units) treats the combined Ashley, Sackett, and Farnham water supplies with average daily flows of 4 to 6 MGD and an 8 MGD maximum daily flow. The plant facility, system flow diagram, and plant operation can be found from the literature [247].

Liquid alum, sodium aluminate, polyelectrolytes, and pH adjustment chemicals are added to the raw water pipeline ahead of each pair of Sandfloat (DAFF) units. Figure 8.6 shows the chemical treatment system of each plant. The raw water is transported to the center of the DAFF unit and flows through a rotary joint to the rapid mix section of the slowly moving carriage. An inlet distributor spreads the flow of water across the flocculation section to build up particles. At the outlet of the flocculation section, pressurized return water, saturated with air, is injected. As the pressure drops, finely divided air bubbles escape and raise floc particles to the surface. The sludge accumulation o the surface is then scooped off and discharged into a center sludge well. Ultimately, the plant waste flows to a sewer pipeline which takes the waste product to the City's sewage system and waste treatment plant mainly for phosphate removal.

The bottom of the DAFF (Sandfloat; Fig. 8.3) unit consists of individual sand filtering sections for the ultimate polishing of the clarified water. Each filter section is backwashed in a near-continuous backwashing cycle. Filtered water is pumped under the sand filter and a separate pump removes the backwash solids from the top of each filter section. This backwash water can either be recycled to the inlet of the DAFF (Sandfloat) unit or be washed to the sewer system.

3.4 Filtered Water Disinfection and Flow Control

The treated water from Cleveland Plant or Ashley Plant flows by gravity from the plant sites to the City. The filtered water is disinfected at chlorination stations, which existed prior to construction of the new Pittsfield water supply system, just downstream of each plant. The rate of flow from the treatment plants is controlled by throttling valves on each of the main supply lines just within the City limits (Fig. 8.1).

3.5 Five Million Gallon Concrete Tank

The filtered and disinfected water (plant effluent) entering the City of Pittsfield is delivered to the customers through an extensive water distribution piping network. The pressure gradient for the zone with the highest water demand is established by a new five million gallon concrete tank (Fig. 8.7). This concrete tank supplements the flow delivered through the flow control stations and permits the maintenance of relatively constant rate through each treatment plant. The tank effectively serves as a clearwell for the plants, thereby eliminating the need for significant storage at the plant sites.

3.6 High Pressure Zones Management and Operation

The northern, western, and southern parts of the City of Pittsfield are at higher elevations and require water pressure gradients greater than those created by the five-million-gallon tank. In each of these areas, separate high-pressure zones have been established for servicing customers at higher elevations. Six booster pumping stations service these areas in conjunction with three new standpipes (Figs. 8.1 and 8.8).

3.7 Innovative Hydroelectric Plant

The newly improved Pittsfield water supply system includes a raw water pipeline from the Farnham Reservoir to the Ashley Plant (Fig. 8.1). Because the Farnham Reservoir is considerably higher than the Ashley Reservoir, a hydroelectric power plant was constructed on this raw water line at the Ashley Plant site. The hydroelectric plant (Fig. 8.10) utilizes the available flow and head to generate power for operation of the Ashley Plant. The turbine generator operates between 5 cfs and 12 cfs to generate up to 225 kilowatts of power. It is extremely important to note that the footprint of a chemical coagulation DAF-filtration water treatment plant is much smaller than the footprint of a conventional coagulation-sedimentation-filtration water treatment plant. Accordingly the DAF-filtration water plant can be installed at high elevation near a raw water reservoir, resulting two great advantages: (a) the treated water may be discharged to the water distribution system by gravity, in turn, a high lift pump is not needed for energy saving; and (b) a hydroelectric plant may be installed for energy generation by utilization of the elevation difference between the DAF-filtration water plant up near the reservoir and the water distribution system in the down town Pittsfield City (Fig. 8.1).

3.8 Supervisory Control and Data Acquisition System

The City of Pittsfield's Cleveland Plant and Ashley Plant have their own internal controls for automatic operation of the DAFF (Sandfloat) units during normal water quality and flow fluctuations. Plant operators visit each plant daily to perform necessary operating procedures and record plant data. As part of the overall Pittsfield new water supply system improvement, a Supervisory Control and Data Acquisition (SCADA) System as shown in Fig. 8.9 was provided to allow for the remote observation and control of the two treatment plants, flow control stations, storage tanks and booster pumping stations throughout the water supply system, which alerts the remote operator of problems occurring in the water supply system and reduces the staff required for continuous operation of the entire water supply system.

3.9 Innovative Wastewater and Waste Alum Sludge Management

The Pittsfield DAF-filtration potable water treatment plant has introduced too many innovative ideas to environmental water engineers. A DAF-filtration water plant significantly reduces the water treatment detention time (DT), footprint, water treatment facility volume, construction costs, and energy saving when it is compared with a conventional sedimentation-filtration water plant. Due to a DAF-filtration's small footprint, it can be installed up in the mountain near the raw water reservoir. So not only the treated water may be distributed to the Pittsfield downtown by gravity for eliminating the need of water lift pumps, but also a hydroelectric power plant can be installed for energy generation.

Additional important innovations of the Pittsfield DAF-filtration water plant include the following (a) direct filter backwash wastewater recycle for reproduction of potable water within the DAF-filtration plant, and (b) direct discharge of the water plant's waste alum sludge to the Pittsfield Wastewater Treatment Plant for phosphate removal.

4 Team Work to Build the New Pittsfield Water Supply Facilities (PWSF) System

Dr. Milos Krofta, President of both Lenox Institute of Water Technology (LIWT) and Krofta Engineering Corporation (KEC), passed away soon after he celebrated his 90th birthday with the authors. In the normal course of any important life events, Dr. Krofta would have been with the authors in writing this book chapter together. In Dr. Krofta's memory, the authors are reporting all new potable water systems that LIWT and KEC developed side-by-side together instead, as the authors' own memoir.

Sincere thanks are extended to (a) LIWT Laboratory Supervisor Betty C. Wu [251] and all LIWT faculty, administration staff, laboratory staff, students, technicians who worked tirelessly for conceiving new flotation process ideas, conducting initial laboratory test, conducting subsequent pilot plant demonstrations, filing patent applications, raising funds, preparing proposals, publishing academic papers, teaching education, etc.; (b) KEC Vice President Daniel B. Guss, Marketing Manager Craig C. Gaetaini and all KEC engineers, designers, computer operators, sales managers who accepted LIWT's proposals for innovative process commercialization, marketing, sales, process design, equipment installation, and process operation and monitoring; (c) City of Pittsfield Mayor Charles L. Smith, City Council President Angelo C. Stracuzzi, Water Committee Chairperson JANE Pellish, Public Utilities Commissioner William L. Forestell, and Public Works Commissioner Gerald S. Doyle, Sr., for their continued assistance, and encouragement during the course of entire Pittsfield water supply system improvement project; and (d) the municipal engineering team of O'Brien & Gere Engineers, Inc., who was willing to work with KEC/LIWT for this innovative, and almost unbelievable new water engineering project.

The authors, along with late Dr. Milos Krofta, are very much indebted to the Commonwealth of Massachusetts Commissioner Russell Sylva of the Massachusetts Department of Environmental Quality Engineering (MDEQE), and the MDEQE Regional Environmental Engineer John Higgins, and Sanitary Engineer Angelo Iantosca, for their trust in the LIWT/KEC innovative potable water DAF-filtration (DAFF, Sandfloat) process, their continued advice, encouragement, and final approval for the water system construction.

5 Flotation's Future in America and the Entire World

More than a dozen drinking water treatment plants using DAF have been completed [245, 246] using Sandfloat, AquaDAF or Clari-DAF, or are in the planning stages in the United States. This includes the world's largest DAF plant, located in New York City, with a capacity of 290 MGD. The City of Boston has also discussed the concept of a 450 MGD DAF drinking water plant.

Though DAF was launched by KEC/LIWT as a drinking water treatment option in the U.S. in early 1980', their specific designs were limited to Lenox-MA water treatment plant (1982), Pittsfield-MA water treatment plant (1986), Coxsackie-NY water treatment plant (1985), Nanty Glo-PA water treatment plant (1986), Howell-NJ water treatment plant (1988), Lee-MA water treatment plant (1998) in the USA and a few others in foreign countries in which the KEC/LIWT team successfully worked. This is because the man leading the charge, Dr. Krofta, passed away in 2002. Dr. Krofta was a mechanical engineer whose company was primarily in business to manufacture mechanical products. As a result, the Lenox and Pittsfield package plant designs included modular, reproducible components—such as the ABF system—that newer DAF plants by other manufacturers are not employing ABF [221].

Dr. Krofta's death was also the beginning of the end of the LIWT as a breeding ground for experts in the use of DAF for drinking water production. Though LIWT still exists as a research institute, publishes many new engineering books and scientific papers every year, and holds many patents, it no longer produces graduates as it once did. However, from its inception in 1981 until 2002, the institute produced hundreds of graduates who attended tuition-free. Many of these graduates are involved in the expansion of DAF as a drinking water treatment method as well as wastewater treatment methods in the United States and many foreign countries.

It is important to note that although the KEC/LIWT team did not design and build many "municipal" DAF drinking water plants in the USA, their team did design and install over 3000 DAF wastewater treatment plants around the world (including this country) for various industries mainly because the industrial owners are interested in adopting high efficiency, low cost and small foot-print processing units, such as DAF.

It is also noted that Dongshin in South Korea and a few DAF companies in America, Asia and Europe are continuously manufacturing the circular flotation clarifiers mainly for industries [145, 200]. Municipalities have sufficient land space, and construction funds prefer to adopt flotation systems with individual units (i.e. not package plants). The drinking water process systems developed by LIWT/KEC and introduced in this book chapter can be applied to both package-plant systems and individual-units systems.

Other DAF-related systems which can be used for potable water treatment include, but will not be limited to:

(a) **DAF-DAF:** A two-stage water or wastewater treatment process system consisting of double dissolved air flotation clarifiers (2 DAF clarifiers) connected in series, usually one DAF is on the top of another DAF.
(b) **DAF-DAFF:** A two-stage water or wastewater treatment process system consisting of a dissolved air flotation clarifier (DAF) and a dissolved air flotation-filtration clarifier (DAFF) connected in series, usually DAF is on the top of a DAFF.
(c) **Dissolved carbon dioxide flotation (DCDF):** One of dissolved gas flotation (DGF) processes when carbon dioxide is used for generation of gas bubbles.
(d) **Dissolved ozone flotation (DOF):** One of dissolved gas flotation (DGF) processes when ozone is used for generation of gas bubbles, with or without UV.
(e) **Sedimentation-flotation (SediFloat):** A combined sedimentation and dissolved air flotation clarifier, with sedimentation at the bottom and dissolved air flotation on the top. A typical example is SediFloat manufactured by Krofta Engineering Corporation.

Glossary [239, 240, 243, 247]

Automatic backwash filtration (ABF) A filtration system that is divided into many identical-shape filtration sections for automatic filtration operation and backwash. There is a moving carriage having a backwash hood and a backwash pump and traveling back and forth on top of the filtration sections. When the backwash hood covers one filtration section for automatic backwash (controlled by a timer), the rest filtration sections are in filtration mode. One filtration section is backwashed at a time, until all filtration sections are backwashed and restored to filtration mode again.

DAF-DAF A two-stage water or wastewater treatment process system consisting of double dissolved air flotation clarifiers (2 DAF clarifiers) connected in series, usually one DAF is on the top of another DAF.

DAF-DAFF A two-stage water or wastewater treatment process system consisting of a dissolved air flotation clarifier (DAF) and a dissolved air flotation-filtration clarifier (DAFF) connected in series, usually DAF is on the top of a DAFF.

Dissolved air flotation (DAF) It is a process involving pressurization of air at 25 to 95 psig for dissolving air into water, and subsequent release of pressure (to 1 atm) under laminar flow hydraulic conditions for generating extremely fine air bubbles (20–80 μm) which become attached to the impurities to be removed and rise to the water surface together. The impurities or pollutants to be removed are on the water surface are called float or scum which scooped off by sludge collection means. The clarified water is discharged from the flotation clarifier's bottom. The air flow rate is about 1% of influent water flow rate. The attachment of air bubbles to the impurities can be a result of physical entrapment, electrochemical attraction, surface adsorption, and/or air stripping. The specific gravity of the bubble-impurity agglomerate is less than one, resulting in buoyancy or non-selective flotation (i.e. Save-All). If other gas instead of air is used, the process is called dissolved gas flotation (DGF) processes when another gas is used for generation of gas bubbles.

Dissolved air flotation-filtration (DAFF) A package plant which consists of both dissolved air flotation and filtration. A typical example is Krofta Engineering Corporation's Sandfloat clarifier.

Dissolved carbon dioxide flotation (DCDF) One of dissolved gas flotation (DGF) processes when carbon dioxide is used for generation of gas bubbles. See dissolved gas flotation (DGF).

Dissolved gas flotation (DGF) It is a process involving pressurization of gas at 25 to 95 psig for dissolving gas into water, and subsequent release of pressure (to 1 atm) under laminar flow hydraulic conditions for generating extremely fine gas bubbles (20–80 μm) which become attached to the impurities to be removed and rise to the water surface together. The impurities or pollutants to be removed are on the water surface are called float or scum which scooped off by sludge collection means. The clarified water is discharged from the flotation clarifier's bottom. The gas flow rate is about 1% of influent liquid flow rate. The attachment of gas bubbles to the impurities can be a result of physical entrapment, electrochemical attraction, surface adsorption, and/or gas stripping. The specific gravity of the bubble-impurity agglomerate is less than one, resulting in buoyancy or non-selective flotation (i.e. Save-All).

Dissolved ozone flotation (DOF) One of dissolved gas flotation (DGF) processes when ozone is used for generation of gas bubbles with or without UV. See dissolved gas flotation (DGF).

Krofta Engineering Corporation (KEC) It is an equipment manufacturer and engineering design company in Lenox, Massachusetts, USA, working closely with the Lenox Institute of Water Technology (LIWT) for develop, production, sales, installation and operation of innovative water and wastewater treatment processes, monitoring devices and analytical methods.

Lenox Institute of Water Technology (LIWT) It is a non-profit humanitarian environmental engineering college in Massachusetts, USA, with expertise in environmental STEAM (science, technology, engineering, arts and mathematics) education, R&D, invention, process and monitoring system development, patent application, licensing, fund raising, engineering design and project management. LIWT teams up with Krofta Engineering Corporation (KEC), for technology transfer, equipment design, and voluntary humanitarian global service through free education, training, and academic publications.

Sedimentation-flotation (SediFloat) A combined sedimentation and dissolved air flotation clarifier, with sedimentation at the bottom and dissolved air flotation on the top. A typical example is SediFloat manufactured by Krofta Engineering Corporation.

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Chapter 9

Cationic Surfactant Analysis with Good Laboratory Practice and Waste Management

Lawrence K. Wang, Mu-Hao Sung Wang, Nazih K. Shammas, Valerie Renak, Yung-Tse Hung, and Omotayo Sarafadeen Amuda

Contents

Abstract The objectives of this research are to (a) demonstrate how to select an organic solvent (such as 1,1,1-trichloroethane) for spectrophotometric determination of cationic surfactant in water and wastewater; (b) investigate and recommend possible better organic solvents for surfactant analysis; and (c) introduce good laboratory practice for personal protection, laboratory protection, and hazardous waste management. Specifically, this research involves selection of alternate less toxic and

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greener organic solvent for use in a methyl orange method for colorimetric determination of cationic surfactants in the 0.2 to 2.0 mg/L range. The principles, steps and management of the methyl orange method include the following (a) complexation of cationic surfactant with methyl orange at acidic pH condition forming a methyl orange-surfactant complex; (b) organic solvent extraction; (c) water-solvent phase separation; (d) spectrophotometric measurement; and (e) good laboratory practice and laboratory hazardous waste management.

Initially, the water sample to be analyzed is treated with 50 mL of organic solvent and an excess amount of methyl orange dye reagent in the presence of a pH-3 buffered solution. The methyl orange reagent reacts with the cationic surfactant forming an organic solvent-soluble complex (i.e., a methyl orange-surfactant complex). The complex is dissolved in the organic solvent phase by rapidly shaking the separatory funnel for a sufficient short period of time. Since the organic solvent is heavier than water, the organic solvent phase can be separated from the water phase simply by gravity separation. The intensity of yellow color in the organic solvent layer is directly proportional to the methyl orange-surfactant complex concentration. Thus, the intensity of the yellow color can be subsequently measured by the use of a spectrophotometer (light path = 10 cm). The absorbance curves for the treated surfactant (cetyldimethylbenzylammonium chloride; or any target cationic surfactant in an industrial water) show an absorbance maximum of 415 nm. The preliminarily selected organic solvent in this initial demonstration research is 1,1,1-trichloroethane, which is less toxic than the commonly used chloroform. Chloroform is one type of toxic trihalomethanes (THM). The even greener organic solvents recommended by the authors for further replacing 1,1,1-trichloroethane are D-limonene ($C_{10}H_{16}$) and alkyl bromide. The readers are encouraged to investigate the feasibility of using even better, greener organic solvents for various analytical methods involving the use organic solvents. Laboratory personal protection, laboratory protection, and waste management are introduced in detail.

Keywords Analytical method · Cationic surfactant · Methyl Orange method · Spectrophotometric measurement · Good laboratory practice · Personal protection · Laboratory protection · Hazardous waste management · Glossary

Nomenclature

AR	Analytical reagent
$C_{10}H_{16}$	D-limonene
CDBAC	Cetyldimethylbenzylammonium Chloride
CFR	Code of Federal Regulations
$CHCl_3$	Chloroform
CWA	Clean Water Act
DOT	US Department of Transportation
GLP	Good laboratory practices
HMIS	Health Management Information System

MSDS	Material Safety Data Sheet
$Na_2HPO_4{\bullet}7H_2O$	Disodium hydrogen orthophosphate
NFPA	National Fire Protection Association
PPE	Personal Protective Equipment
TCLP	Toxicity Characteristic Leaching Procedure
THM	Trihalomethanes
USEPA	US Environmental Protection Agency
VSQG	Very small quantity generator

1 Introduction

A methyl orange method for the colorimetric determination of cationic surface-active agents was introduced by Wang and Langley in 1975 [1]. Their method determines these cationic surface-active agents in the 0.10 to 1.25 mg/L range. It involves (a) complexation of cationic surfactant with methyl orange at acidic pH condition, (b) chloroform extraction, (c) water-chloroform phase separation, and (d) spectrophotometric measurement of the color intensity of chloroform extract containing the methyl orange-surfactant complex. Wang and Langley's method [1] has the advantage of being quick and easy to perform the surfactant determination task, but has the disadvantage of using chloroform, a toxic cancer-causing organic solvent [2–4].

The objective of this research is to continuously find other, less toxic organic solvents that can be used in a similar methyl orange method. Two organic solvents that were tested in this demonstration research were 1,1,1,-trichloroethane and trichlorotrifluoroethane. These both have chemical structures similar to chloroform. The solubility of methyl orange-surfactant complex in the two solvent was investigated experimentally.

2 Experimental Reagents for Demonstration

(a) Methyl Orange Reagent Solution: Dissolve 0.10 g methyl orange in 100 mL distilled water (0.1% concentration).
(b) Buffer Solution: Dissolve 52.5 g citric acid in 500 mL distilled water (0.5 L); 26.80 g disodium hydrogen orthophosphate ($Na_2HPO_4{\bullet}7H_2O$) in 500 mL distilled water (0.5 L); combine both to form 1000 mL (1 L) of pH 3 buffer solution.
(c) Standard Cetyldimethylbenzylammonium Chloride (CDBAC) Solution: Dissolve 50 mg CDBAC in 1000 mL distilled water (50 mg/L).
(d) Organic Solvents: Both 1,1,1-trichloroethane and trichlorotrifluoroethane were tested as possible organic solvents for dissolving the methyl orange-surfactant complex. Only 1,1,1-trichloroethane was found to be feasible for extracting the

methyl orange-surfactant complex. The recommended organic solvent, 1,1,1-trichloroethane, should be anhydrous and of reagent grade.

3 Experimental Apparatus for Demonstration

The following apparatus is needed:

(a) volumetric pipets of various sizes (1–50 mL);
(b) 500-mL separatory funnels;
(c) spectrophotometer providing a 10-cm light path, at a wavelength of 415 nm; and,
(d) two 10-cm glass spectrophotometer cells. (Note: Although the light path of 10 cm is recommended, other light paths in the 1–10 cm range can also be used.)

4 Calibration Curve Preparation

(a) Prepare a series of separatory funnels with 0, 0.10, 0.20, 0.50, 0.70, 1.00, 1.20 and 1.50 mL of a 50 mg/L standard cationic surfactant (CDBAC) solution (see Sect. 7).
(b) Add distilled water to make a total volume of 50 mL in each separatory funnel, so that the corresponding CDBAC surfactant concentrations in the series of separatory funnels are 0, 0.10, 0.20, 0.50, 0.70, 1.00, 1.20, and 1.50 mg/L, respectively.
(c) Treat each sample as described in Sect. 5 (c) through (e). Plot a calibration curve showing mg/L of cationic surfactant versus absorbance (or mg/L cationic surfactant versus percent transmittance).

5 Analytical Procedure

(a) Prepare a reference Cell A of pure 1,1,1-trichloroethane and adjust the spectrophotometer to zero absorbance, or 100% transmittance, at 415 nm. (Note: For more accurate cationic surfactant determination, 50 mL of distilled water is treated as described in Sect. 5 (c) through (d). Then drain the separated 1,l,1-trichloroethane layer into the reference Cell A and adjust the spectrophotometer to zero absorbance, or 100% transmittance.)

(b) Pipet a determined amount of the water sample into a separatory funnel, record the sample size in milliliters, and then adjust as needed to 50 mL with distilled water.
(c) Add 5 mL of buffer solution, 0.5 mL of methyl orange reagent solution, and 50.0 mL of 1,1,1-trichloroethane to the separatory funnel, stopper, and shake vigorously for 30 s to allow equilibrium to be established.
(d) Let the 1,1,1-trichloroethane and water separate completely by gravity separation for about 20 min or until the 1,1,1-trichloroethane layer is not cloudy.
(e) Drain the separated 1,1,1-trichloroethane layer into the sample Cell B and measure the absorbance (or percent transmittance).
(f) Determine the measured amount of cationic surfactant from the calibration curve described previously and calculate the cationic surfactant concentration by the following equation:

$$\begin{aligned}&\mathrm{mg/L\ of\ cationic\ surfactant\ as\ CDBAC}\\&=\mathrm{(mg/L\ of\ cationic\ surfactant\ read\ from\ calibration\ curve)}\\&\times 50/\mathrm{(mL\ of\ sample\ size)}.\end{aligned}$$

6 Experimental Results for Demonstration

Trichlorotrifluoroethane was tried first as a possible alternate organic solvent for cationic surfactant determination. It was discovered that the methyl orange-surfactant complex (i.e., cationic surfactant and methyl orange complex) remained in the water phase (i.e., not being soluble in the added trichlorotrifluoroethane). Therefore, trichlorotrifluoroethane is not a feasible alternate organic solvent for cationic surfactant determination. No results for trichlorotrifluoroethane are available for presentation.

Subsequently, another organic solvent, 1,1,1-trichloroethane, was tried, and found to be feasible. Table 9.1 indicates the maximum absorbance for a 2.0 mg/L cetydimethylbenzylammonium chloride (CDBAC) sample occurred at the wavelength of 415 nm. Based on the experimental data, Fig. 9.1 is plotted for graphical illustration.

After the feasible organic solvent (l,1,1-trichloroethane) and the optimum wavelength (415 nm) were chosen, a series of cationic surfactant (CDBAC) solutions was prepared, and treated by the recommended chemical reagents according to the procedures for calibration curve preparation. The calibration's experimental data are plotted in Fig. 9.2 which shows a linear relationship between the absorbance and CDBAC concentration in the concentration range of 0.00 to 2.00 mg/L.

Table 9.1 Toxicity characteristic constituents and regulatory levels for the TCLP test[a]

Constituent	Regulatory level (mg/L)
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresol[b]	200.0
m-Cresol[b]	200.0
p-Cresol[b]	200.0
Cresol[b]	200.0
2.4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13
Endrin	0.02
Heptachlor (and its hydroxide)	0.008
Hexachlorobenzene	0.14
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2.4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (silvex)	1.0
Vinyl chloride	0.2

[a] Procedure and levels promulgated March 29, 1990

[b] If *o*-, *m*-, *p*-cresol concentrations cannot be differentiated, the total cresol concentration is used

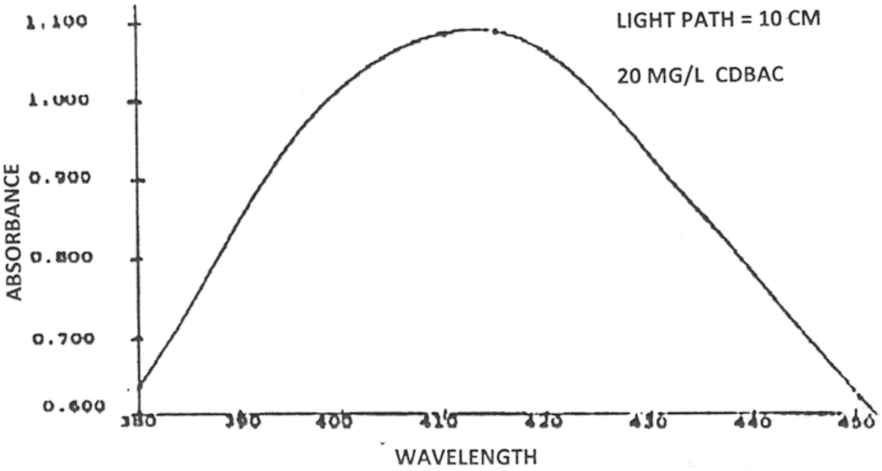


Fig. 9.1 Determination of optimum wavelength using CDBAC and selected organic solvent

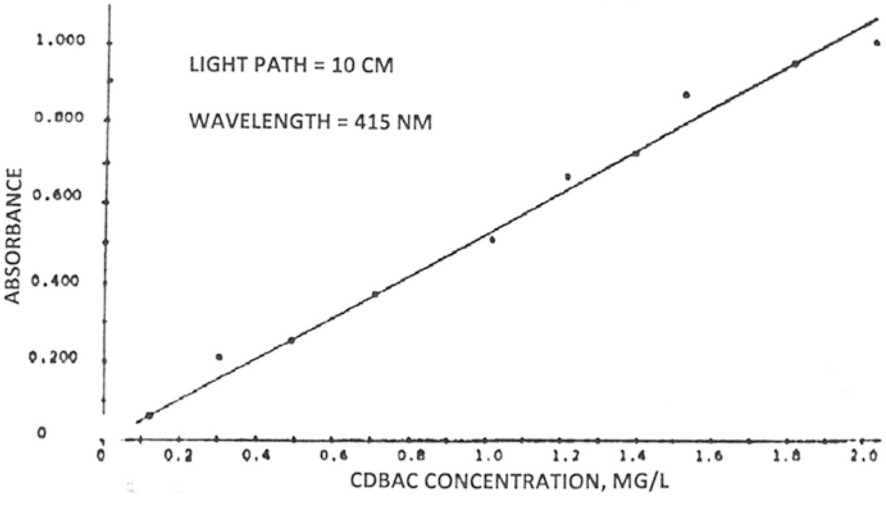


Fig. 9.2 Preparation of calibration curve using cationic surfactant (CDBAC) and selected organic solvent

7 Conclusions and Recommendations

Chloroform is one type of toxic trihalomethanes (THM) [4, 5]. The preliminarily selected organic solvent in the demonstration research is 1,1,1-trichloroethane, which is less toxic than the commonly used chloroform, and indeed can be used for cationic surfactant determination. The even greener organic solvents recommended by the authors for further replacing 1,1,1-trichloroethane are D-limonene ($C_{10}H_{16}$)

and alkyl bromide. The readers are encouraged to contact the authors for collaboration of more green research projects.

8 Good Laboratory Practice and Waste Management

8.1 Personal Protection and Laboratory Protection

An environmental scientist or engineer responsible for a laboratory analysis must follow the Good Laboratory Practice guidelines [6], and protect himself/herself and the laboratory facilities first before carrying out any intended duties.

8.1.1 Material Safety Data Sheets Review as an Example

Each laboratory chemical normally is required by the Federal government to have its Material Safety Data Sheet (MSDS) introducing the chemical's contents, characteristics and related safety issues. As a typical example, Table 9.1 presents the MSDS of organic solvent, 1,1,1-Trichloroethane, to be used in this analytical method. The MSDS shows that the organic solvent was manufactured by spectrum Laboratory produces, Gardena, CA, USA. The solvent's National Fire Protection Association (NFPA) and Health Management Information System (HMIS) designations are (a) Health Hazard = 2; (b) Fire Hazard = 1; and (c) Reactivity = 0. Its recommended Personal Protective Equipment (PPE) are as follows: safety goggles, laboratory gown, vapor respirator (Hazmat mask), and 7 mil-thickness nitrile disposal gloves. Figure 9.3 shows an approved/certified vapor respirator. Different cartridges of the vapor respirator can be used for removal of different toxic vapors. Figure 9.4 shows the recommended safety goggles and the 7-mil-thickness nitrile disposal gloves.

8.1.2 Discussion of Content and Characteristics for a Specific Chemical as an Example

While the content of the chemical is, indeed, 1,1,1-Trichloroethane based on the MSDS, it may also be commercially called methyl chloroform, methylchloroform, methyltrichloroformethane, or trichloroethane. Its chemical formula is CH_3CCl_3. The chemical's composition is 100% by weight.

The chemical's Health Hazard is rated 2, meaning medium hazard mainly related to human health. The MSDS (Table 9.1) states that 1,1,1-Trichloroethane is hazardous in case of skin contact (irritant), of eye contact (irritant), and of inhalation, and is slightly hazardous in case of ingestion. Besides, its vapor (LC50) is toxic at high concentrations (3911–18,000 ppm) if/when rat and mouse are exposed to it for

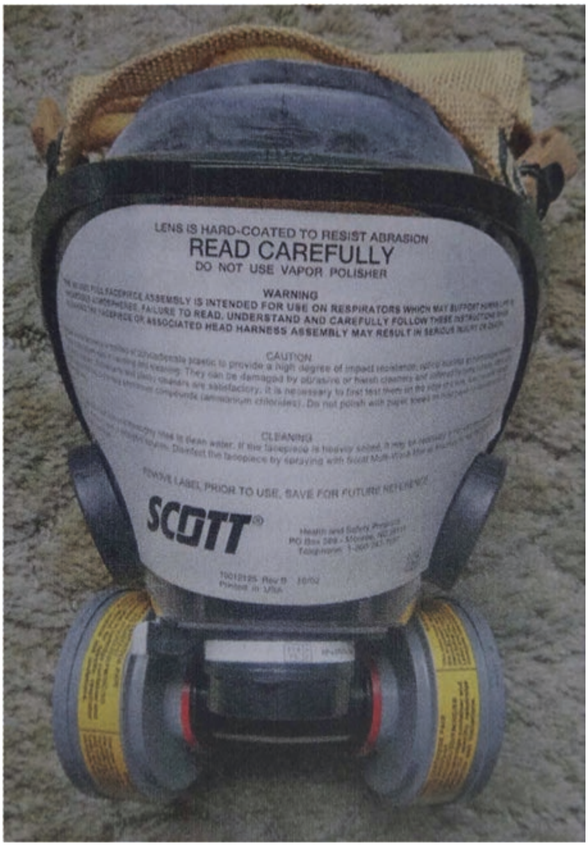


Fig. 9.3 An approved/certified vapor respirator

2–4 h. Section 4 of the MSDS recommends the first aid measures in case of eye contact, skin contact, inhalation, or ingestion. In case of emergency, the performing chemist or laboratory staff may call 800-424-9300 or 310-516-8000. Any chemical substance exhibits the characteristic of toxif, using approved methods, such as Toxicity Characteristic Leaching Procedure (TCLP), the extract from the chemical contains any of the substances listed in a concentration equal to or greater than the values listed in Table 9.2 is a legally controlled toxic hazardous substance. 1,1,1-Trichloroethane is not in the Table 9.2 list., however, it must be handled with care.

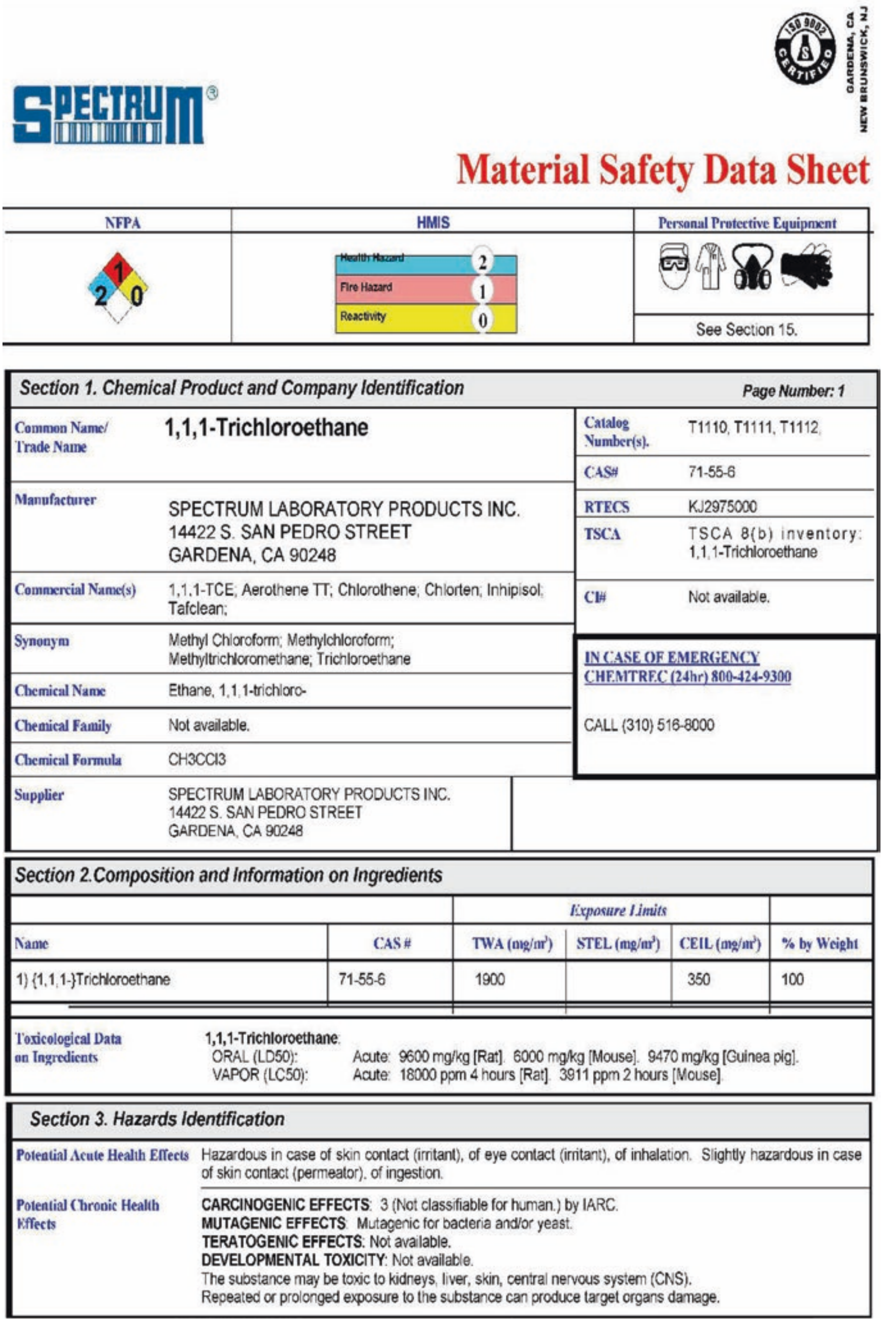
The chemical's Fire rating is 1 meaning low hazard, in accordance with National Fire Protection Association (NFPA). Any substance that exhibits any of the following properties is considered a hazardous substance due to ignitability: (a) a liquid that has a flash point less than 60 °C; (b) a non-liquid capable, under normal conditions, of spontaneous and sustained combustion; (c) an ignitable compressed gas under the US Department of Transportation (DOT) regulations; and (d) an oxidizer under DOT regulations. 1,1,1-Trichloroethane is a liquid which is considered

Fig. 9.4 Recommended splash goggles and 7-mil nitrile disposal gloves

slightly hazardous substance due to ignitability. Accordingly, a fire extinguisher is needed on-site during the chemical analysis.

The Reactivity Rating of 1,1,1-Trichloroethane is zero meaning the chemical is safe due to reactivity. Any substance exhibits the characteristic of reactivity if it has any of the following properties: (a) it is normally unstable and readily undergoes violent change without detonation; (b) it reacts violently with water; (c) it forms potentially explosive mixtures with water; (d) when mixed with water, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment; (e) it is a cyanide- or sulfide- bearing substance which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment; (f) it is capable of detonation or explosive reaction if subjected to a strong initiating source or if heated under confinement; (g) it is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure; (h) it is forbidden explosive as defined in 49 CFR 173.51, or a Class A explosive as defined in 49 CFR 173.53 or Class B explosive as defined in 49 CFR 173.88. Although 1,1,1-Trichloroethane is not one of the hazardous substances defined

Table 9.2 Spectrum's Material Safety Data Sheet (MSDS) for 1,1,1-Trichloroethane (MSDS Page 1 of 7)



SPECTRUM®

ISO 9002 CERTIFIED

GARDENA, CA
NEW BRUNSWICK, NJ

Material Safety Data Sheet

NFPA	HMIS	Personal Protective Equipment
1 2 0	Health Hazard 2 Fire Hazard 1 Reactivity 0	See Section 15.

Section 1. Chemical Product and Company Identification

Page Number: 1

Common Name/ Trade Name	1,1,1-Trichloroethane	**Catalog Number(s).**	T1110, T1111, T1112
		CAS#	71-55-6
Manufacturer	SPECTRUM LABORATORY PRODUCTS INC. 14422 S. SAN PEDRO STREET GARDENA, CA 90248	**RTECS**	KJ2975000
		TSCA	TSCA 8(b) inventory: 1,1,1-Trichloroethane
Commercial Name(s)	1,1,1-TCE; Aerothene TT; Chlorothene; Chlorten; Inhipisol; Tafclean;	**CI#**	Not available.
Synonym	Methyl Chloroform; Methylchloroform; Methyltrichloromethane; Trichloroethane	**IN CASE OF EMERGENCY CHEMTREC (24hr) 800-424-9300**	
Chemical Name	Ethane, 1,1,1-trichloro-		
Chemical Family	Not available.	CALL (310) 516-8000	
Chemical Formula	$CH3CCl3$		
Supplier	SPECTRUM LABORATORY PRODUCTS INC. 14422 S. SAN PEDRO STREET GARDENA, CA 90248		

Section 2. Composition and Information on Ingredients

		Exposure Limits			
Name	**CAS #**	**TWA (mg/m^3)**	**STEL (mg/m^3)**	**CEIL (mg/m^3)**	**% by Weight**
1) {1,1,1-}Trichloroethane	71-55-6	1900		350	100

Toxicological Data on Ingredients

1,1,1-Trichloroethane:
ORAL (LD50): Acute: 9600 mg/kg [Rat]. 6000 mg/kg [Mouse]. 9470 mg/kg [Guinea pig].
VAPOR (LC50): Acute: 18000 ppm 4 hours [Rat]. 3911 ppm 2 hours [Mouse].

Section 3. Hazards Identification

Potential Acute Health Effects

Hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation. Slightly hazardous in case of skin contact (permeator), of ingestion.

Potential Chronic Health Effects

CARCINOGENIC EFFECTS: 3 (Not classifiable for human.) by IARC.
MUTAGENIC EFFECTS: Mutagenic for bacteria and/or yeast.
TERATOGENIC EFFECTS: Not available.
DEVELOPMENTAL TOXICITY: Not available.
The substance may be toxic to kidneys, liver, skin, central nervous system (CNS).
Repeated or prolonged exposure to the substance can produce target organs damage.

above, other chemicals to be used in this chemical analysis may be. So a responsible chemist should review and evaluate each chemical.

Finally, the corrosivity of a chemical to be used in a chemical test must also be investigated. Any substance which exhibits any of the following properties is considered a hazardous waste due to corrosivity: (a) an aqueous material with pH less than or equal to 2 or greater than or equal to 12.5; and (b) a liquid that corrodes steel at a rate greater than 1/4 in. per year at a temperature of 55 °C. The organic solvent, 1,1,1-Trichloroethane, is not corrosive against glass. However, according to its MSDS, it is corrosive in presence of zinc metal and is extremely corrosive in presence of aluminum metal. A chemist must be very careful. Other chemicals to be used in a chemical analysis must also be investigated in terms of its corrosivity.

8.1.3 Conclusions of Personal Protection and Laboratory Protection as an Example

Only 1,1,1-Trichloroethane is chosen for evaluation as a typical example. All other chemicals to be used in this chemical analysis should be evaluated in a similar manner. Do not use any aluminum container to hold or store 1,1,1-Trichloroethane.

If 1,1,1-Trichloroethane is used as a solvent for extraction of surfactant in this analysis, splash goggles, gloves, laboratory coats, vapor respirators are recommended for laboratory personal protection, It must be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Perform a test under a fume hood if it is available to assure adequate ventilation. The laboratory should be equipped at least with a water sink, eye shower, and fire extinguisher for both personal and facility protection.

8.2 Hazardous Laboratory Waste Management

The authors of this article further suggest that every chemical and/or biological laboratory analysis include a section on Good Laboratory Practice (GLP), recommending some specific GLP requirements, procedures and equipment for the laboratory analysis [7, 8]. The purposes are for protection of persons, laboratory and environment, and hazardous waste management. All wastes generated from this chemical analysis are considered to be hazardous laboratory wastes.

8.2.1 Waste Definitions and Classifications

Solid Wastes

In order for a waste to be considered a hazardous waste, it must first be classified as a solid waste. A solid waste is defined by the US Environmental Protection Agency (USEPA) as the following: Any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant or air pollution control facility and other discarded material including solid, liquid, semisolid or contained gaseous material resulting from industrial, commercial, mining and agricultural operations and from community activities Section6903(27). The regulatory definition is found at 40CFR261.2(a)(1). A solid waste is defined by the US regulation as any "discarded material" not expressly excluded by the US regulations. A material is considered "discarded" if it is "abandoned" "recycled," or "considered inherently waste-like.". Accordingly, the discarded, abandoned, recycled, or waste-like materials generated from a laboratory facility are all considered to be solid wastes.

Hazardous Wastes

A hazardous waste is defined in the US statutes as: " a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, of infections characteristics may: (a) cause, or significantly contribute to, an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or (b) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed." A material may be classified as a hazardous waste if meets the criteria of any of the following four categories: (a) the government listed wastes; (b) characteristic wastes; (c) mixed wastes; and (d) "derived from" wastes.

Government Listed Wastes

In the USA, the government listed wastes are wastes specifically regulated by the USEPA and appear on one of four lists found in 40CFR 261.3. The four USEPA lists, however, fall into three categories of wastes: (a) nonspecific source wastes, such as generic wastes, commonly produced wastes by CFR 261.32; (c) commercial chemical products, such as wastes including specific commercial chemical products or manufacturing chemical intermediates—creosote and kepone, etc., under 40 CFR 261.33 (e) and (f).

Hazardous Characteristic Wastes

In the USA, characteristic wastes may be regulated to exhibit one of the four characteristics (ignitability, corrosivity, reactivity, and toxicity) of the waste as determined by the USEPA.

Hazardous Mixed Wastes

The entire volume of any waste mixture containing a listed hazardous waste, regardless of concentration, is considered a hazardous waste with the following exceptions: (a) the listed waste in the mixture was listed solely because it exhibits a hazardous waste characteristic and the mixture no longer exhibits that characteristic; (b) a wastewater discharge subject to regulation by the Clean Water Act (CWA) and the hazardous waste mixed with the mixtures of non-hazardous wastes and characteristic hazardous wastes if the mixture no longer exhibits any of the characteristics (ignitability, corrosivity, reactivity, and toxicity); (c) a wastewater discharge subject to regulation by the Clean Water Act (CWA) and the hazardous waste mixed with the waste water which concentration of carcinogenic and non-carcinogenic spent solvents listed in 40 CFR Part 261.31 in the wastewater, provided the concentration does not exceed 1 ppm and 25 ppm, respectively; (d) a wastewater discharge subject to regulation by the Clean Water Act (CWA) and the hazardous waste mixed with the small loss of discarded commercial chemical products or intermediaries used as raw materials in manufacturing or produced as by-products; (e) a wastewater discharge subject to regulation by the Clean Water Act (CWA) and the hazardous waste mixed with a laboratory wastewater containing small amounts of listed toxic wastes; (f) a wastewater discharge subject to regulation by the Clean Water Act (CWA) and the hazardous waste mixed with the heat exchanger bundle cleaning sludge (petroleum refining industry).

“Derived from” Wastes

USEPA’s “derived from” rule regulates any solid waste generated from the treatment, storage, or disposal of a hazardous waste, including any sludge, spill residue, ash, emission control dust or leachate (but not including precipitation run-off). The aforementioned solid waste is considered to be one of hazardous wastes under 40 CFR 261.4(c)(2)(i), with some specified exclusions.

8.2.2 Conclusions of Hazardous Waste Management as an Example

1,1,1-Trichloroethane is chosen in this section as an example. The wastes generated from other chemical substances can be evaluated in a similar manner.

Laboratory wastes generated from a very small amount of used 1,1,1-Trichloroethane are not considered to be a hazardous laboratory waste under this publication’s Sect. 8.2.1.5, *“The entire volume of any waste mixture containing a listed hazardous waste, regardless of concentration, is considered a hazardous waste with the following exceptions.............. (e) a wastewater discharge subject to regulation by the Clean Water Act (CWA) and the hazardous waste mixed with a laboratory wastewater containing small amounts of listed toxic wastes”* .

If large amount of the laboratory wastewater containing 1,1,1-Trichloroethane and/or other chemicals is generated, a different approach should be adopted. Unfortunately, the amount of the laboratory waster which is considered to be small amount or large amount is not decided by the USEPA. In the USA, each State's environmental protection agency will decide the legal amount. For instance, if a laboratory in the State of Massachusetts, USA, generates less than 100 kg a month of hazardous waste, and no acutely hazardous wastes, the laboratory is eligible to register as a very small quantity generator (VSQG) [9]. Then, certain Massachusetts rules and regulations concerning the generated wastes shall be followed.

In general, organic solvent (such as 1,1,1-Trichloroethane) and inorganic chemical wastes should be separated for good waste management. Some wastes are legally allowable to discharge into a laboratory drain. Some inorganic chemical wastes are allowed to recycle or on-site process before a drain discharge. The organic solvents are usually stored and hauled away for the off-site or off-site disposal by a certified waste management company.

Selection of the solvent (such as 1,1,1-Trichloroethane) has an advantage because many of industries use the solvent, as shown in Table 9.3. It is very common and the target plant may already have a waste management plan for the solvent. Table 9.4 shows that many physicochemical processes may treat a laboratory wastewater stream containing 1,1,1-Trichloroethane. Granular activated carbon appears to be the best, although its cost is high. In case discharge of the laboratory wastewater into a municipal sewer system for biological treatment is intended, there is a good news that the low-cost activated sludge system can properly remove 1,1,1-Trichloroethane over 99% (see Table 9.4).

Glossary of Spectrophotometric Analysis and Laboratory Hazardous Waste Management [9–17]

Analysis (chemical) The determination of the qualitative and/or quantitative composition of a substance.

Analytical reagent (AR) The American Chemical Society's designation for the highest purity of certain chemical reagents and solvents.

Blank sample A clean sample or a sample of matrix processed so as to measure artifacts in the measurement (sampling and analysis) process.

Buffer solution It is either called pH buffer or hydrogen ion buffer, which is an aqueous solution consisting of a mixture of a weak acid and its conjugate base, or vice versa. Its pH changes very little when a small amount of strong acid or base is added to it.

Calibrate To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device, or the correct value for each setting of a control knob. The levels of the calibration standards should bracket the range of planned measurements.

Table 9.3 Industrial occurrence of 1,1,1-trichloroethane

Industry	Treated wastewater					
	Number of samples	Number of detections	Concentration (µg/L)			Loading (kg/d), mean
			Minimum	Maximum	Mean	
Auto and other laundries[a]	2	1		14		0.0013
Coal mining[b]	51	11	1	3	2	0.0074
Iron and steel manufacturing[a]	12	7	<10	200	<46	<0.69
Aluminum forming	1	1		3		0.003
Battery manufacturing	9	9	<10	270	<39	<0.0031
Coi1 coating	15	5	10	21	14	0.0015
Electrical/electronic components[c]	1	1		<10		<0.0016
Foundries	12	11	10	2100	210	0.71
Photographic equipment/supplies[d]	4	3	10	12	11	0.0020
Explosive manufacture	NA	NA	NA	NA	NA	NA
Nonferrous metal manufacturing	36	1[e]	ND	10	1.5	0.012
Ore mining and dressing[b]	2	2	0.62	0.62	0.62	0.0068
Organic chemicals manufacturing/plastics	NA	30	NA	NA	5.7	NA
Paint and ink formulation[a]	24	14	NA	560	89	0.00036
Petroleum refining[b]	17	ND				
Pulp and paperboard mills	72	12	ND	17	2.2[f]	0.066
Rubber processing	1	1		7100		17
Soap and detergent manufacturing	NA	NA	NA	NA	NA	NA
Steam electric power plants[g]	11	ND				
Textile Mills[b]	50	1		<5		<0.0035

NA not available, *ND* not detected

Information contained in this table was obtained from Volume II of the Treatability Manual and represents verification data except as noted. The pollutant was not detected during screening analyses for the following industries: leather tanning and finishing, porcelain enameling, gum and wood chemicals, pharmaceutical manufacturing, timber products processing

Pollutant loadings determined by multiplying mean pollutant concentration by industry wastewater discharges; where mean is not available, one-half the reported maximum was utilized

[a] Screening data

[b] Screening and verification data

[c] Data set unspecified

[d] Screening plus additional data

[e] Detections >10 µg/L

[f] Mean calculated using medians

[g] Verification data plus surveillance and analyses

Table 9.4 Pollutant removal/treatability wastewater treatment alternative for 1,1,1-trichloroethane

Treatment process	Number of data points		Range of removal (%)	Range of effluent concentration (μg/L)	*V*
	Pilot scale	Full scale			
Activated carbon adsorption					
– Granular	2	1	99 to >99	ND to 1.9	
Chemical oxidation					
Chemical precipitation with sedimentation					
– Lime		6	NM	ND to 51	
– Alum		3	>55	10 to <170	
– Polymer/unspecified		1	NM	0.1	
– Sodium hydroxide		2	0 to >99	ND to 1	
– Combined precipitants		4	NM	28–120	
Chemical precipitation with filtration		2	75	0.3–1.0	
Filtration		9	86 to >99	ND to 4.400	
Flotation		4	22 to >99	ND to 860	
Oil separation		1	NM	190	
Sedimentation		6	19–96	2–2500	
Stripping					
– Steam	1		9	42,000	
Activated sludge		7	99 to >99	ND to 3.3	
Lagoons					
– Aerated		1	96	22	

BDL below detection limit, *ND* not detected, *NM* not meaningful

Calibration curve The graphical relationship between the known values for a series of calibration standards and instrument responses.

Calibration standard A substance or reference material used to calibrate an instrument.

Calibration The checking, adjusting, or systematic standardizing of the graduations of a quantitative measuring instrument.

Cationic surfactant An organic quaternary ammonia compound with positively charged surface-active moieties.

Characteristic Wastes In the USA, characteristic wastes may be regulated to exhibit one of the four characteristics (ignitability, corrosivity, reactivity, and toxicity) of the waste as determined by the US Environmental Protection Agency (USEPA).

Chemical analysis The use of standard chemical analytical procedures to determine the concentration of a specific analyte in a sample, or qualitatively or quantitatively measure a specific parameter of a sample.

Chloroform It is a colorless, volatile, sweet-smelling liquid ($CHCl_3$) used as an organic solvent in an analytical procedure and formerly as a general anesthetic in a medical procedure.

Clean sample A sample of a natural or synthetic matrix containing no detectable amount of the analyte of interest and no interfering material.

Complex A substance consisting of many different and connected parts

Concentration In solutions, the mass, volume, or number of moles of solute present in proportion to the amount of solvent or total solution Common measures are: molarity, normality, percent, molality, and by specific gravity scales.

Contamination A general term signifying the introduction into water of microorganisms, chemicals, wastes or sewage which renders the water unfit for its intended use.

Corrosivity Any substance which exhibits any of the following properties is considered a hazardous waste due to corrosivity: (a) an aqueous material with pH less than or equal to 2 or greater than or equal to 12.5; and (b) a liquid that corrodes steel at a rate greater than 1/4 in. per year at a temperature of 55 °C.

Data Facts or figures from which conclusions can be inferred.

"Derived From" Wastes USEPA's "derived from" rule regulates any solid waste generated from the treatment, storage, or disposal of a hazardous waste, including any sludge, spill residue, ash, emission control dust, or leachate (but not including precipitation run-off). The aforementioned solid waste is considered to be one of hazardous wastes under 40 CFR 261.4(c)(2)(i), with some specified exclusions.

Distilled water Water that has been purified by distillation (boiling the water off as steam and condensing it back to a liquid, leaving the impurities behind). Having been boiled, it is also sterile.

Good laboratory practices (GLP) Either general guidelines or formal regulations for performing basic laboratory operations or activities that are known or believed to influence the quality and integrity of the results. The purpose of GLP is for personal protection, laboratory protection, proper chemical storage and proper waste management.

Grab sample A single sample which is collected at one point in time and place.

Green solvent An environmentally friendly solvent, or biosolvents, which may be derived from the processing of agricultural crops, such as corn.

Hazardous wastes A hazardous waste is a material that is subject to special consideration by the US Environmental Protection Agency (USEPA), under 40CFR261. State or local authorities may also designate additional materials as hazardous waste in their areas. The definition given by 40 CFR 261 defines a hazardous waste as a solid waste that is not excluded from regulation and meets one or more of the following criteria: (a) it is a discarded commercial chemical product, off-specification species, container residue, or spill residue of materials specifically listed in 40CFR261.33 (P- and U-codes); (b) it is a waste from a specific source listed in 40CFR261.32 (K-code); (c) it is a waste from a nonspecific source listed in 40CFR261.31 (F-code); and/or (d) it displays any of the following characteristics of hazardous wastes: ignitability (such as flash point is below 60 °C or 140 °F, it it is classified by the US Department of Transportation, DOT, as an oxidizer D001), corrosivity (such as the pH of the waste material is less than or equal to 2, or greater than or equal to 12.5, or classified by DOT as D002), reactivity (such as the waste material is unstable, reacts violently with water, may generate toxic gases when mixed with water, or classified by DOT as D003), or toxicity (such as it is classified by DOT ad D004-D043).

Ignitability Any substance that exhibits any of the following properties is considered a hazardous substance due to ignitability: (a) a liquid that has a flash point less than 60 °C; (b) a non-liquid capable, under normal conditions, of spontaneous and sustained combustion; (c) an ignitable compressed gas under the US Department of Transportation (DOT) regulations; and (d) an oxidizer under DOT regulations.

Listed wastes In the USA, the government listed wastes are wastes specifically regulated by the US Environmental Protection Agency (USEPA) and appear on one of four lists found in 40CFR 261.3. The four USEPA lists, however, fall into three categories of wastes: (a) nonspecific source wastes, such as generic wastes, commonly produced wastes by CFR 261.32; (c) commercial chemical products, such as wastes including specific commercial chemical products or manufacturing chemical intermediates—creosote and kepone, etc. under 40 CFR 261.33 (e) and (f).

Mixed wastes The entire volume of any waste mixture containing a listed hazardous waste, regardless of concentration, is considered a hazardous waste with the following exceptions: (a) the listed waste in the mixture was listed solely because it exhibits a hazardous waste characteristic and the mixture no longer exhibits that characteristics; (b) a wastewater discharge subject to regulation by the Clean Water Act (CWA) and the hazardous waste mixed with the mixtures of non-hazardous wastes and characteristic hazardous wastes if the mixture no longer exhibits any of the characteristics (ignitability, corrosivity, reactivity, and toxicity); (c) a wastewater discharge subject to regulation by the Clean Water Act (CWA) and the hazardous waste mixed with the waste water which concentration of carcinogenic and non-carcinogenic spent solvents listed in 40 CFR Part 261.31 in the wastewater, provided the concentration does not exceed 1 ppm and 25 ppm, respectively; (d) a wastewater discharge subject to regulation by the Clean Water Act (CWA) and the hazardous waste mixed with the small loss of discarded commercial chemical products or intermediaries used as raw materials in manufacturing or produced as by-products; (e) a wastewater discharge subject to regulation by the Clean Water Act (CWA) and the hazardous waste mixed with a laboratory wastewater containing small amounts of listed toxic wastes; (f) a wastewater discharge subject to regulation by the Clean Water Act (CWA) and the hazardous waste mixed with the heat exchanger bundle cleaning sludge (petroleum refining industry).

Organic solvent A carbon-based solvent that is capable of dissolving other substances.

pH The negative logarithm of the hydrogen ion concentration ($-\log10[H^+]$) where H^+ is the hydrogen-ion concentration in moles per liter. Neutral water has a pH value of 7.

pH adjustment A means of maintaining the optimum pH through the use of chemical additives.

Precision The degree to which a set of observations or measurements of the same property, usually obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative terms.

Procedure A set of systematic instructions for performing an operation.

Reactivity Any substance exhibits the characteristic of reactivity if it has any of the following properties: (a) it is normally unstable and readily undergoes violent change without detonation; (b) it reacts violently with water; (c) it forms potentially explosive mixtures with water; (d) when mixed with water, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment; (e) it is a cyanide- or sulfide- bearing substance which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment; (f) it is capable of detonation or explosive reaction if subjected to a strong initiating source or if heated under confinement; (g) it is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure; (h) it is forbidden explosive as defined in 49 CFR 173.51, or a Class A explosive as defined in 49 CFR 173.53 or Class B explosive as defined in 49 CFR 173.88.

Reagent A chemical substance used to cause a reaction for the purpose of chemical analysis.

Reagent blank A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps to error in the observed value.

Reagent grade The second highest purity designation for reagents which conform to the current specifications of the American Chemical Society Committee on Analytical Reagents.

Reagent solution A distilled water containing a chemical substance used to cause a reaction for the purpose of chemical analysis.

Sample A part of a larger whole or a single item of a group; a finite part or subset of a statistical population. A sample serves to provide data or information concerning the properties of the whole group or population.

Sampling The process of obtaining a representative portion of the material of concern.

Solid wastes A solid waste is defined by the US Environmental Protection Agency (USEPA) as the following: Any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant, or air pollution control facility and other discarded material including solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining and agricultural operations and from community activities Section6903(27). The regulatory definition is found at 40CFR261.2(a)(1). A solid waste is defined by the US regulation as any "discarded material" not expressly excluded by the US regulations. A material is considered "discarded" if it is "abandoned," "recycled," or "considered inherently waste-like". Accordingly, the discarded, abandoned, recycled, or waste-like materials generated from a laboratory facility are all considered to be solid wastes.

Solution A liquid (solvent) that contains a dissolved substance (solute).

Solvent A liquid used to dissolve another substance.

Spectrophotometers A spectrophotometer is an instrument designed for physical sample analysis via full spectrum color measurement. By providing wavelength-by-wavelength spectral analysis of a sample's reflectance, absorbance, or transmittance properties, it produces precise data beyond that observable by the human eye. Spectrophotometers offer a higher level of flexibility and versatility than colorimeters due in part to the fact that they offer multiple illuminant/observer combinations and are capable of measuring metamerism, identifying colorant strength, analyzing a comprehensive range of sample types, and giving users a choice between including or excluding specular reflectance to account for geometric attributes. Full spectrum analysis also provides for greater specificity, potentially identifying color differences missed by colorimeters.

Standard solution A solution containing a known concentration of analytes, prepared and verified by a prescribed method or procedure and used routinely in an analytical method.

Surfactant A surface active compound that lowers the surface tension (or interfacial tension) between two liquids, between a gas and a liquid, or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, etc.

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Chapter 10
Treatment of Laundry Wastewater by Physicochemical and Flotation Processes

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Abstract Laboratory and field studies were conducted to evaluate the capabilities of two commercially available laundromat waste treatment systems to treat laundromat wastes with the possibility of recycling the treated effluent: (a) The Winfair Water Reclamation System (WWRS) involves the addition of alum to a pH of 4, sedimentation, sand filtration, carbon absorption, and passage through ion exchange resins and (b) The American Laundry Machinery Industries (ALMI) system employs chemical precipitation prior to filtration through diatomaceous earth. Lenox Institute of Water Technology (LIWT) designed a physicochemical process system involving mainly the use of dissolved air flotation (DAF) for treating the same laundry wastewater.

The WWRS achieved a 56% BOD reduction, 62% COD reduction, and 94% ABS reduction, but suffered from a buildup of total solids in the effluent. The system produced an effluent suitable for discharge into many streams. For effluent recycling, a functioning demineralizer would be required.

The ALMI system achieved a 63% BOD reduction, 69% COD reduction, 87% ABS reduction, 94% P04 reduction, and complete coliform removal. The increase in effluent alkalinity and hardness render very questionable the suitability of the effluent for reuse without softening and pH adjustment.

A LIWT system has been specifically designed for small operations, such as small laundromats, prewash laundries, car washers, although large laundry plants may also adopt. It is a rectangular DAF-sedimentation system without moving parts. According to the investigation of the US Environmental Protection Agency (USEPA), a DAF unit can: (a) remove 50% COD, 59% TOC, 75% TSS, 80% O&G, and 96% TP from a laundry wastewater, if 1800 mg/L calcium chloride and 2 mg/L of polymer are dosed or (b) remove only 8% COD, 38% TOC, 36% TSS, 59% O&G, and 9% TP from a laundry wastewater, if only 60 mg/L polymer is dosed. Many heavy metals and organic pollutants may also be removed by DAF at the same time. There are over thousands of commercial Supracell DAF and Sandfloat DAFF, and KAMET-DAF-DAFF systems installed and operated for treating various industrial wastewaters around the world. They (Supracell, Sandfloat, and KAMET) are suitable for use by large auto and laundry industries, but may not be suitable to small laundromats because there are many moving parts. Other commercial DAF units, such as Clari-DAF and AquaDAF, have been applied to only drinking water treatment. It is the authors' professional judgment that either Clari-DAF or AquaDAF should be able to adequately treat the wastewater from a laundry plant, if adequate chemicals are used. A consulting engineer has successfully treated a prewash laundry wastewater using DAF. Construction of the LIWT rectangular DAF-sedimentation plant for treatment of laundry and car wash wastewaters using the optimized chemicals is recommended. This laundry wastewater treatment research was started by late Dr. Donald B. Aulenbach. Researchers around the world are invited to continue his research in order to find the best solution to treating the large-scale auto and laundry wastewater, and the small laundromat, prewash laundry, and car wash wastewaters. This was Dr. Aulenbach's final wish conveyed to his coauthors in 2019.

Keywords Winfair Water Reclamation System (WWRS) · American Laundry Machinery Industries System (ALMI) · Innovation · Lenox Institute of Water Technology Wastewater Treatment System (LIWT) · Dissolved air flotation · Supracell · DAF · Sandfloat · DAFF · KAMET · DAF-DAFF · Clari-DAF · AquaDAF · Pretreatment · Municipal sewer discharge · Rectangular DAF-sedimentation system · Car wash wastewater treatment · Prewash laundry wastewater · USEPA investigations

Abbreviations

ABS	Alkylbenzene sulfonate
ALMI	American Laundry Machinery Industries
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
DAF	Dissolved air flotation
DAF-DAFF	Primary dissolved air flotation, secondary dissolved air flotation and filtration
DAFF	Dissolved air flotation and filtration
DE	Diatomaceous earth
LIWT	Lenox Institute of Water Technology
TOC	Total organic carbon
TP	Total phosphorus
USEPA	US Environmental Protection Agency
WWRS	Winfair Wastewater Reclamation System
WWTS	Wastewater Treatment System

1 Introduction

There are many diverse types of wastes which produce problems today. One of these is the wastes from coin-operated laundromats, particularly those located in areas where sewer systems are not accessible. Numerous treatment systems have been devised for treating these wastes. Two, such systems became available and formed the conception of this study. It is the purpose of this study to evaluate these two systems for the treatment of laundromat wastes.

The post-World War II era gave rise to three developments which complicated the laundry waste problem. First, was the mass production of automatic home laundry equipment. Second, the building boom in suburban areas placed much of this equipment in unsewered areas. Finally, the appearance of coin-operated laundromats in these new suburban centers meant that millions of gallons of detergent, germ, and soil-laden waste water was being discharged into streams, estuaries, ponds, and groundwater supplies.

Since most of the early laundry detergents were not biodegradable; conventional septic tank systems were ineffective in treating these wastes. With the advent of biodegradable laundry detergents, some of the problems were ameliorated, but only if the coin-operated laundromats were located in areas where there was a sufficient quantity of suitable land for the construction of leaching fields. This was seldom the case since most of these installations were in densely populated new suburbs where land was at a premium. Therefore, waste treatment facilities for coin-operated laundromats in unsewered areas had to fulfill the following requirements:

1. Provide an effluent acceptable to health regulations.
2. Handle peak loads as well as normal demands.
3. Require a minimum of service and operational maintenance skills and time.
4. Be able to be easily dismantled, transported, and reassembled at a new site.
5. Occupy a minimum of space.
6. Be economically feasible in terms of cost per load of wash.
7. Whenever possible, recycle the water for further use.

The first part of this chapter evaluates the Winfair Wastewater Reclamation System (WWRS) which claims to fulfill all of the above requirements.

This second part of the chapter describes the operation of the American Laundry Machinery Industries (ALMI) wastewater treatment system, which claims to fulfill all but the recycle requirement of laundromat waste treatment system in unsewered areas and evaluates the actual function of that system.

2 Basic Laundry Waste Treatment System

Wastes from both individual home laundries and multiple-unit coin-operated laundromats can present problems where they cannot be discharged into sewerage systems provided with adequate treatment facilities. The spread of population into unsewered areas is followed by the establishment of coin-operated laundromats in these unsewered areas. An indication of the magnitude of the problem may be given by the estimate that there are over 120 laundromats in Suffolk County, Long Island, New York, USA, alone [1]. An illustration of laundry waste production from washers is shown in Fig. 10.1 and typical preliminary treatment of laundry wastewater using a screen is shown in Fig. 10.2. Nearly all of these ultimately discharge their effluent into the ground.

The switch to the use of synthetic detergents (syndets) has also contributed considerably to the problem. The conversion to linear alkyl benzene sulfonates (LAS) (Fig. 10.3) has reduced this problem where aerobic biological treatment is provided. However, under anaerobic conditions, such as in septic tanks and saturated soil, there is little breakdown of the LAS. In saturated soils, these syndets may travel considerable distances without being decomposed thereby entering water supplies. In addition, studies on Long Island [1] have shown that the synthetic detergents seem to cause other pollutional material, specifically coliforms, to be carried greater distances than conventional soap do. This is in partial disagreement with the work done by Robeck et al. [2] who showed that increased concentrations of alkylbenzene sulfonate (ABS) had no effect upon the travel distance of coliforms in water-saturated, sandy soils under laboratory conditions.

The problems created by laundromat wastes have led to many studies of methods for treatment, and to the creation of numerous waste treatment systems. A large volume of work was done at Manhattan College for the State of New York, USA [3]. Work was done to determine the amount of alum needed to improve the quality of the waste (with no consideration of ABS removal), and further, the amount of powdered activated carbon needed to remove the ABS. An alum dose of 100 grains/gal (1700 mg/L) and an activated carbon concentration 7 times the ABS concentration

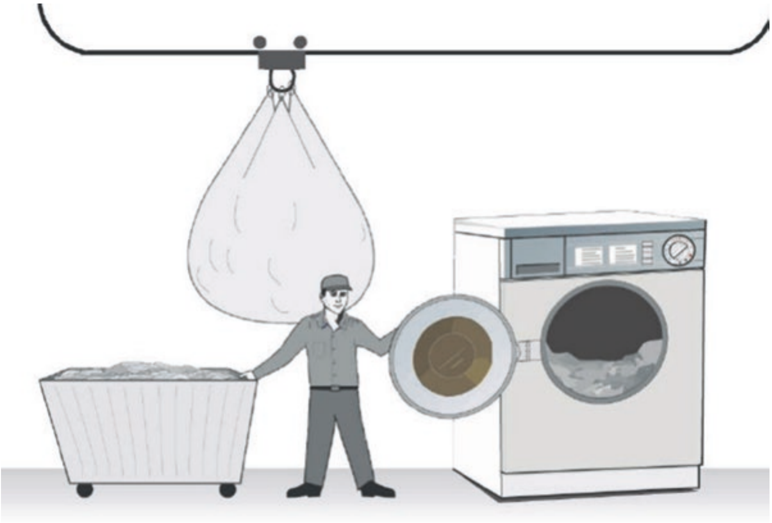


Fig. 10.1 Laundry wastewater from washers (Source: USEPA)

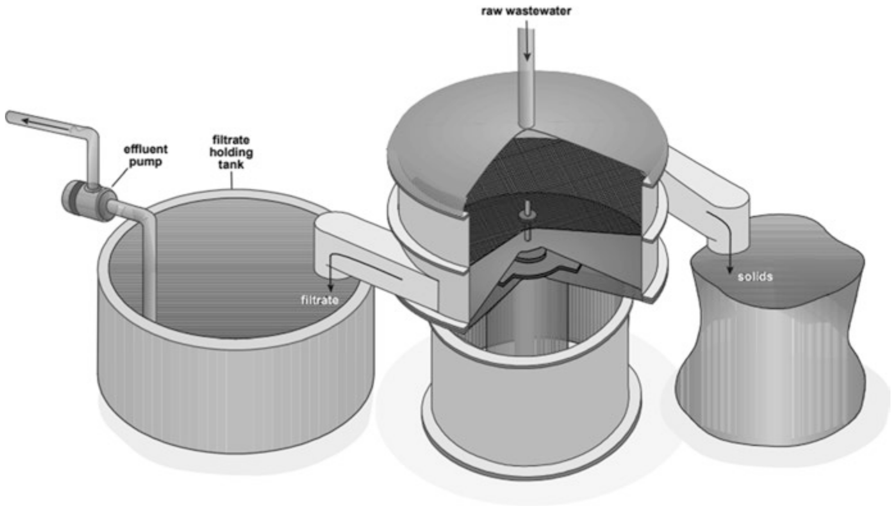


Fig. 10.2 Typical laundry waste's preliminary treatment using a screen (Source: USEPA)

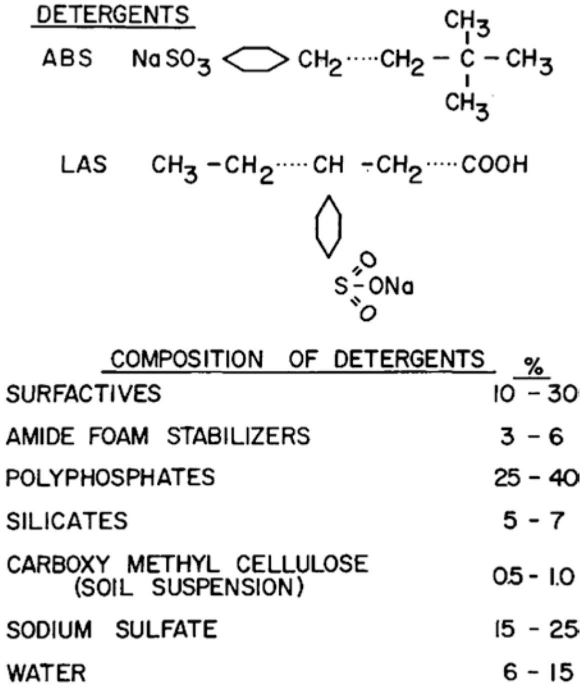


Fig. 10.3 Typical composition of detergents (USEPA)

COMPOSITION OF DETERGENTS	%
SURFACTIVES	10 – 30
AMIDE FOAM STABILIZERS	3 – 6
POLYPHOSPHATES	25 – 40
SILICATES	5 – 7
CARBOXY METHYL CELLULOSE (SOIL SUSPENSION)	0.5 – 1.0
SODIUM SULFATE	15 – 25
WATER	6 – 15

are recommended to remove substantially all anionic syndets. Close scrutiny of the data reveals that the optimum conditions for clarification of the waste without regard to ABS removal are 1530 mg/L of alum at pH 5.7, with the ranges being 850–2210 mg/L alum and pH 5.1–6.0. A dose of 1360 mg/L of alum and 340 mg/L powdered activated carbon at pH 6.0 produced an effluent containing 1.8 mg/L ABS. No studies were made to determine the removal of ABS by alum alone.

Flynn and Andres [4] recommended treatment with alum at pH 4.0 and powdered activated carbon to be effective in treating laundromat wastes. Rosenthal et al. [5] conducted a more thorough study of laundromat waste treatment using alum and activated carbon. They found that 800 mg/L of alum alone at pH 4.5 removed 77% of the ABS. The acceptable pH range was 4.3–4.6. In the laboratory, 2000 mg/L powdered activated carbon (Nuchar) increased the ABS removal to 97%. In an actual laundromat, alum plus 400 mg/L powdered activated carbon resulted in 83% removal of the ABS. The use of granular carbon in a series of three filters instead of powdered carbon increased the ABS removal to 99% in the laboratory and 93% in the plant. Further studies showed that alum coagulation at pH 11.4 with lime produced a clearer effluent which settled more rapidly and used less alum to achieve the same ABS reduction. Passing the alum-lime effluent through a 10 ft. deep granular activated carbon pressure filter produced a 99.8% reduction in ABS in the laundromat waste treatment plant. Paulson [6] used granular activated carbon to remove syndets from filtered sewage plant effluents. He applied the effluent to 4–5 ft. units in series at 10 gpm/ft.^{2} and regenerated the first unit when the ABS in the effluent reached 0.5 mg/L. Weber [7] determined that the ABS uptake by granular activated carbon increased with decreasing pH.

The basic types of laundry waste treatment systems have been studied by Flynn and Andres [4]. Their conclusion is that those employing alum at a pH of about 4.0 and powdered activated carbon produce the greatest reduction of ABS at the most reasonable cost in operation time, equipment, and chemicals.

3 The Winfair Water Reclamation System

A proprietary treatment plant utilizing the basic treatment principles of Flynn and Andres, that for employing alum at a pH of about 4.0 and powdered activated carbon [4], is manufactured by the Winfair Corporation, Green Lake, Wisconsin (now a subsidiary of the Os hko sh Filter Company, Oshkosh, Wisconsin). A complete Winfair Water Reclamation System was installed at the Coin-Op Laundry at Burnt Hills, New York. This is a small community north of Schenectady, where individual wells and waste treatment systems are the only means available to obtain water and dispose of liquid wastes, respectively. The ground water table in the immediate area surrounding the laundromat is near the surface and is used as a water supply by some neighbors. Water about 70 ft. below the surface is highly sulfurous and has a total dissolved solid content of around 700 mg/L. Permission could not be granted to dispose of the untreated laundromat waste in a septic tank system. The problems of water supply and disposal were both overcome by the installation of this complete water reclamation system.

In this system (Fig. 10.4), the washer effluents are first screened and then stored in a holding tank. From here a 15 gpm pump conveys the waste through the alum coagulation system. Alum is added to pH 4.2–4.5 and then the waste enters a 45-gal upflow tank for floc formation (3 min. Contact time). The effluent from this tank is treated with lye so that the pH after settling is 7.0 (pH slightly higher than 7.0 at the test point). The waste now travels through ¾ in. copper tubing to the mid-depth of a large settling tank. The sludge is disposed of periodically and the clear supernatant is pumped through l of 5 pressure sand filters in parallel (3 gpm through each). The sand filter effluent passes up through a bed containing Duolite (Diamond Alkali Company, Redwood City, California) anion exchange resin A 102 D for detergent removal. After removal of the detergent, the waste passes up through a bed of granular activated carbon for taste, odor, and color removal. From there, 1/3 of the flow passes through a cation and an anion exchange resin for complete deionization. After recombination, the waste is chlorinated and the pH neutralized before it enters the clean water tank prior to reuse.

It appears that such a system should provide satisfactory water for reuse in a laundromat. It is claimed that the cost of the additional treatment is offset by the saving of fresh water and reheating of the water, since it is normally still warm after passing through this treatment system. However, some difficulty was encountered after the system had been operating for several months. The detergent removal resin

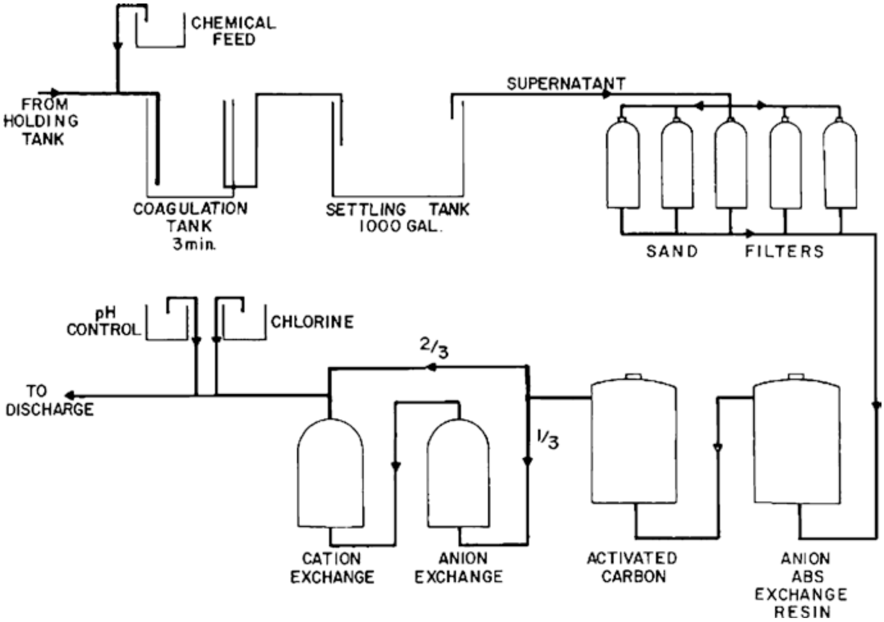


Fig. 10.4 Winfair Water Reclamation System (USEPA)

became saturated, and no longer functioned in its capacity to remove detergents. This resin cannot be regenerated by ordinary means and must be returned to the manufacturer for regeneration. Also, the two deionizer resins were entirely ineffective, causing the total solids in the recirculating water to increase constantly. These resins are normally regenerated weekly by conventional acid and alkali techniques. Efforts to rejuvenate them proved fruitless, and the total solids continued to increase.

The reason for the failure of the detergent removal resin was quite apparent. This resin was designed to function on the basis of an effluent from the alum coagulation system containing 5 mg/L of ABS or less. By test, the alum treatment effluent contained approximately 15 mg/L ABS. Thus, the resin became saturated in 1/3 the expected time. Replacement of this resin produced an effluent containing only 2 mg/L ABS after complete treatment. Further, the anion exchange resin in the deionizer would attempt to remove a portion of the residual detergent not removed by the other portions of the system. During the period when the detergent removal resin was saturated, a high detergent concentration reached the anion demineralizer where it was exchanged into the resin. Since the detergent cannot be removed from the resin by conventional means, this resin became saturated with the detergent and no longer functioned as an anion remover. No similar analogy can be made for the reason the cation exchange resin failed.

The major portion of the problem appeared to be the failure to achieve the expected ABS removal in the alum coagulation system. Whereas it was expected that this system should produce an effluent containing 5 mg/L of ABS or less, the actual effluent contained around 15 mg/L ABS, or a removal in the order of 50%. Since the work done at Manhattan College [3] did not include an evaluation of the removal of ABS by alum alone, and the work done by Rosenthal et al. [5] showed 77% removal of ABS by alum alone at pH 4.5, it was felt that further studies to determine the removal of detergent by alum coagulation alone were needed to evaluate the problem.

4 Laboratory Studies of Detergent Removal

Three series of experiments were performed to study the removal of detergents by the use of various concentrations of alum at various pH values. All mixing and coagulation were done using a typical 6-place multiple laboratory stirrer. Inasmuch as possible, an attempt was made to have the laboratory procedures reproduce the treatment provided by the Winfair Water Reclamation System. After adding alum, the samples were mixed at 50 rpm for 3 min. Then the pH was adjusted to the appropriate value, and coagulation was produced by stirring at 30 rpm for 10 min, after which the samples were allowed to settle for 30 min. Determinations were made for ABS to determine the detergent removal, and for chemical oxygen demand and turbidity to determine the quality improvement. The sludge volume after settling was also determined in order to provide some additional information on the amount of sludge storage capacity needed. ABS was determined by the methylene blue extraction technique, using 2 mL of sample. This volume of sample did not tend to produce emulsions during the extraction. All other analyses were made according to Standard Methods [8].

The waste samples were secured from the holding tank containing the mixed laundromat wastes. The only pretreatment it received was screening to remove lint and other large particles. The temperature of the waste at the time of sampling was 40 °C.

In the first test, sufficient alum was added to a portion of the waste sample to lower the pH to 4.5. This same amount of alum was then added to four other samples; a control containing no alum was given the same physical treatment. After mixing for 3 min, the pH of the samples containing alum was adjusted with acid or sodium carbonate as needed to values of 3.5, 4.5, 5.5, 6.5, and 7.5. No pH adjustment was made in the control. The results are summarized in Table 10.1, and the reductions in ABS, COD, and turbidity are shown in Fig. 10.5.

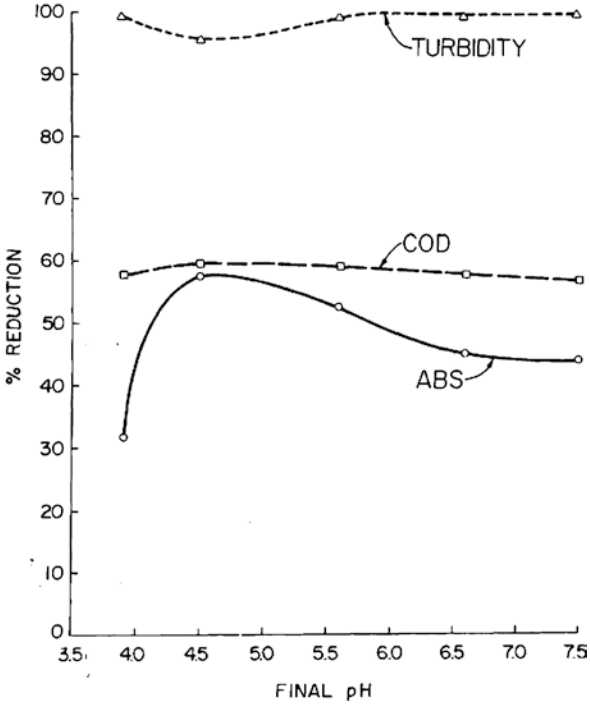
The best reductions in ABS and COD occurred at pH 4.5, whereas the best turbidity reduction occurred at pH 7.5. Actually, the turbidity reduction was good throughout the entire pH range. The lowest sludge volume occurred at pH 3.5, although the amount of sludge produced at pH 4.5 was still quite low. The high total solid content of the waste reflects the failure of the deionizer in the treatment system. Also, to be noted is that the alum treatment resulted in an increase in the total solid content of about 1000 mg/L. The results from the control containing no added alum showed no ABS removal, and a slight increase in turbidity. The reduction in the COD of the control is likely due to sedimentation of larger particles. There was some sediment on the bottom of this container, but it was insufficient to measure on the % scale. It is apparent that all the ABS reduction in the test samples was due to the added alum, and not due to plain sedimentation.

In an attempt to determine if satisfactory results could be obtained at any lower alum dosages, a second experiment was run adding 1000, 1250, and 1500 mg/L alum. Further, in order to evaluate the recommended operation of the Winfair treat-

Table 10.1 Effect of pH on alum treatment of laundromat waste

Sample	Waste	1	2	3	4	5	6
Alum concentration, mg/L	–	1500	1500	1500	1500	1500	0
pH	7.25	4.5	4.6	4.6	4.6	4.6	7.25
H_2SO_4 concentration, mg/L	–	0.13	0	0	0	0	0
Na_2CO_3 concentration, mg/L	–	0	0	455	740	1150	0
pH before settling	–	3.5	4.5	5.5	6.5	7.5	–
Final pH	–	3.9	4.5	5.6	6.6	7.5	7.3
ABS, mg/L	32.1	22	13.6	15.2	17.6	17.9	32.9
COD, mg/L	699	296	285	285	293	300	551
Turbidity, mg/L	125	1	5.5	1	0.8	0.5	140
Sludge volume, %	–	3.7	8	40	24	28	0
Temperature, °C	22	–	–	–	–	–	–
Total solids, mg/L	9076	13,364	10,176	10,046	10,116	10,376	9392

Fig. 10.5 Efficiency of alum treatment of Laundromat wastes as a function of pH



ment system in which the alum-treated mixture is neutralized to pH 7.0 before sedimentation, duplicate samples were run: 1 with no pH adjustment, and the other adjusted to pH. 7.0 with sodium carbonate after 3 min mixing at 50 rpm and before 10 min coagulation at 30 rpm. The results are summarized in Table 10.2, and the reduction in ABS, COD, and turbidity for the unnaturalized and the neutralized samples are compared in Fig. 10.6. The pH was similar with all 3 alum dosages. The ABS removal without pH adjustment was consistently near 60% over the range of alum additions, whereas in the samples adjusted to pH 7.0, the greatest ABS reduction was about 50% with 1000 mg/L alum, and this reduction dropped to 40% with 1500 mg/L alum. Neither the alum concentration nor the pH in the ranges covered had any significant effect upon the COD removal. The turbidity removal was poor with 1250 and 1500 mg/L of alum without pH control, but at pH 7.0, the turbidity removal was nearly constant at 90%. At all alum dosages used, the sludge volume without pH adjustment was about 1/3 that at pH 7.0.

Since the previous experiments indicated better ABS removal with no pH neutralization, but covered only a narrow range of alum dosages, the next logical step seemed to be to study the effects of a wide range of alum dosages with no pH neutralization. Alum was added to samples of the waste in 250 mg/L increments from 500 to 1750 mg/L. No attempt was made to maintain the pH near 4.5. Mixing and coagulation were maintained as in the previous experiments. The results are summarized in Table 10.3, and the efficiencies of removal of the ABS, COD, and turbid-

Table 10.2 Effect of alum concentration at different pH values on the treatment of laundromat wastes

Sample	Raw waste	1	2	3	4	5	6
Alum concentration, mg/L	–	1000	1000	1250	1250	1500	1500
Na_2CO_3 concentration, mg/L	–	0	560	0	780	0	925
pH before settling	7.1	4.7	7.0	4.6	7.0	4.6	7.0
Final pH	–	4.6	6.9	4.6	7.1	4.5	7.0
ABS, mg/L	38.7	16.8	19.6	15.6	21.6	15.9	23.5
COD, mg/L	625	382	400	382	385	385	389
Turbidity, mg/L	128	15	3.9	52	4. 6	76	5.4
Sludge volume, %	–	9.5	22.2	8.7	28.5	8.2	26
Temperature, °C	20	–	–	–	–	–	–

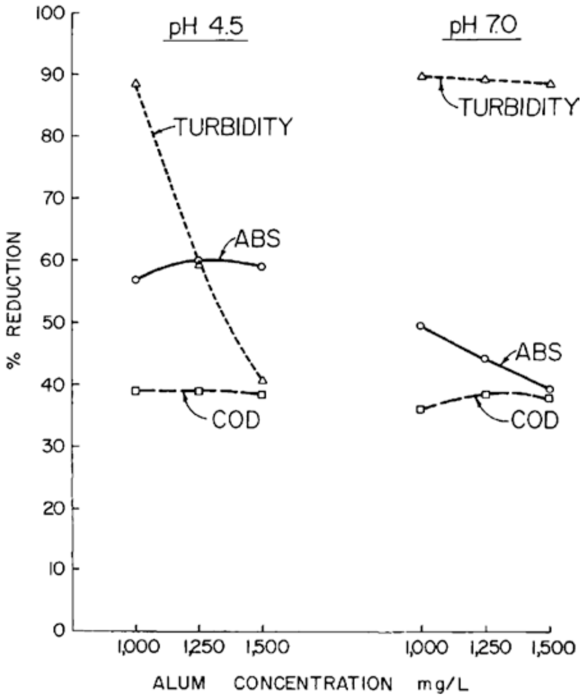


Fig. 10.6 Efficiency of alum dosage for treatment of laundromat wastes at different pH values

ity are shown in Fig. 10.7. The addition of 500 mg/L alum lowered the pH to only 5.5 whereas the addition of 750 mg/L and greater lowered the pH to nearly 4.5 and even slightly below this level with 1750 mg/ L alum. ‘The maximum ABS removal of 67% occurred with the addition of 1000 mg/L alum, and only slightly less removal occurred in the range of 750 to 1250 mg/L alum. Poor ABS removal occurred with only 500 mg/L of alum, and again with 1500 mg/L, but increased removal again occurred with 1750 mg/L alum. The COD removal was fairly consistent above 750 mg/L alum, but was somewhat less with only 500 mg/L. The best turbidity removals occurred between 750 and 1250 mg/L alum. There was no

Table 10.3 Effect of alum concentration on the treatment of laundromat wastes

Sample	Raw waste	1	2	3	4	5	6
Alum concentration, mg/L	–	500	750	1000	1250	1500	1750
Final pH	7.2	5.5	4.8	4.7	4.5	4.5	4.4
ABS, mg/L	33.2	23.5	12.3	10.8	14.9	18.3	14.4
COD, mg/L	585	358	314	307	307	314	314
Turbidity, mg/L	135	65	7	8	15	60	90
Sludge volume, %	–	9	13.2	12	10	10	7.5
Temperature, °C	21	–	–	–	–	–	–
Total solids, mg/L	9334	9118	9132	9316	9478	9670	9862

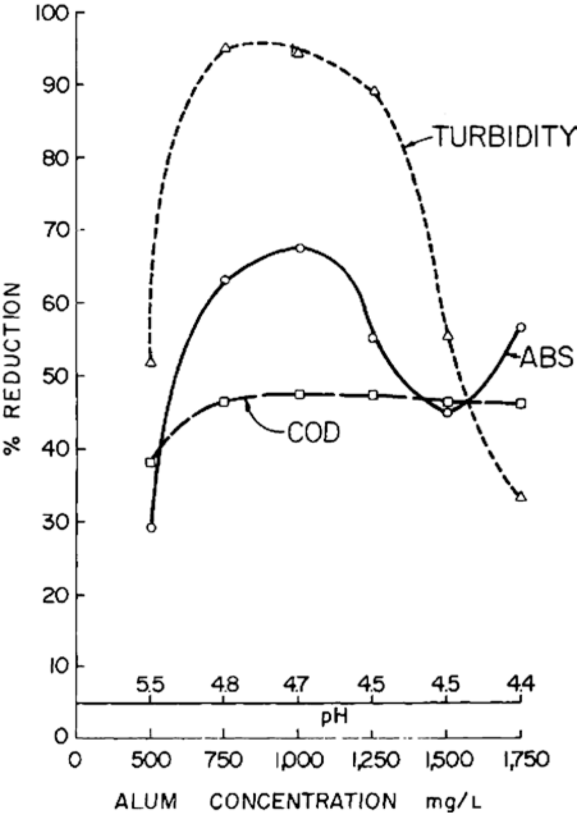


Fig. 10.7 Efficiency of alum dosage in treatment of laundromat wastes

significant difference in the sludge volumes produced with the various alum additions. The total solids generally show the effect of the added alum, but there appeared to be a slight reduction in total solids with the addition of 500 and 750 mg/L alum. Generally, it appears that optimum conditions for ABS, COD, and turbidity removal are 750 to 1250 mg/L alum in the pH range of 4.5 to 4.8.

An important observation of these lab studies is that the lowest ABS concentration achieved for any procedure was in the order of 10 mg/L. This is twice the value claimed by the manufacturer, and upon which the ABS removal resin is based. This means simply that the resin will be saturated in half the predicted time, or to put it another way, the cost for the ABS removal by the resin will be twice that predicted by the manufacturer.

5 Treatment System Operation

The above studies were performed under the auspices of the New York State Health Department and showed the need for a more thorough study of the system. Meanwhile, the laundromat operator had to discontinue use of the Winfair system

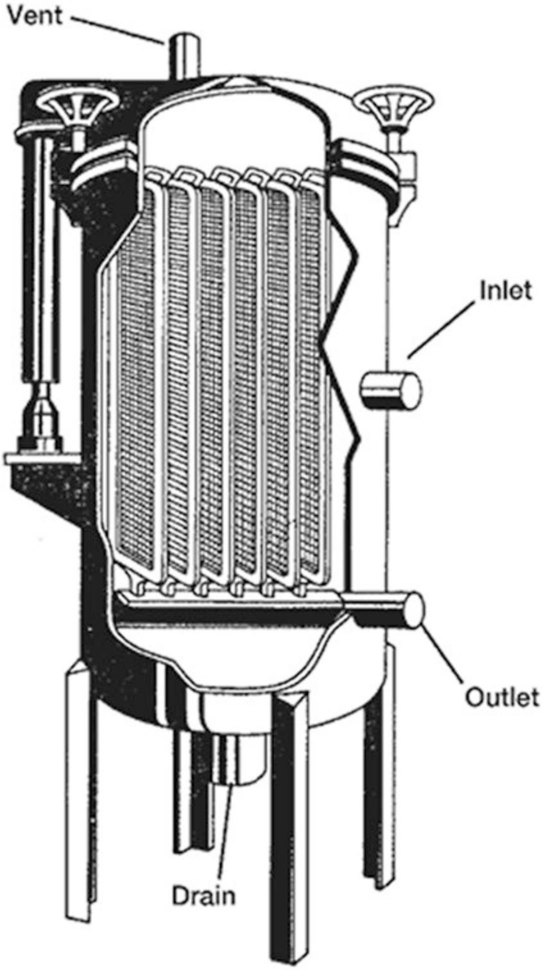


Fig. 10.8 American Laundry Machinery Industry diatomaceous earth filtration equipment

due to complaints by customers of odors and foaming in the recycled water. In an effort to alleviate the problem, he purchased and put into use a treatment system designed by American Laundry Machinery Industries. This system is based upon the precipitation of the anionic syndets by means of a cationic syndet, the precipitation of phosphates and other materials with $CaCl_2$, and separating the solids by means of a pressure diatomaceous earth filter (Fig. 10.8).

Whereas this provided satisfactory treatment of the waste, it did not solve the problem of water supply nor the hydraulic discharge of the treated effluent. Thus, the operator was forced to discontinue his laundromat operation at Burnt Hills.

However, the operator retained the 2 treatment systems and offered their use for research purposes. When a Federal Water Pollution Control Administration Grant became available, he graciously offered their use at another laundromat. They were set up in a shed which was somewhat remodeled and electrified. The flow diagram is shown in Fig. 10.9. A 4000 gal. Holding tank was installed and four 1000 gal. Tanks were provided for settling, sludge holding, and treated water. Chlorination was applied in the treated water storage tank. The system was designed so that the waste would flow into the holding tank, and when it was full, it would overflow into the existing distribution boxes and tile drainage field. Physical problems were encountered with these last two appurtenances, in that trucks delivering to the adjacent food market would drive over them, crushing them and blocking them. This resulted in the overflow of raw wastes from our holding tank.

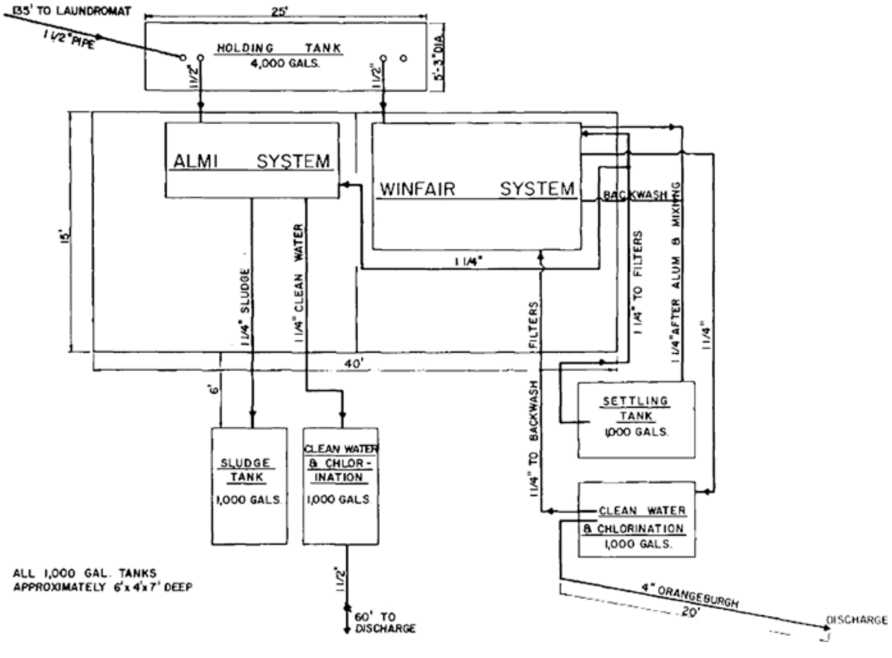


Fig. 10.9 Laundromat Treatment Plant (USEPA)

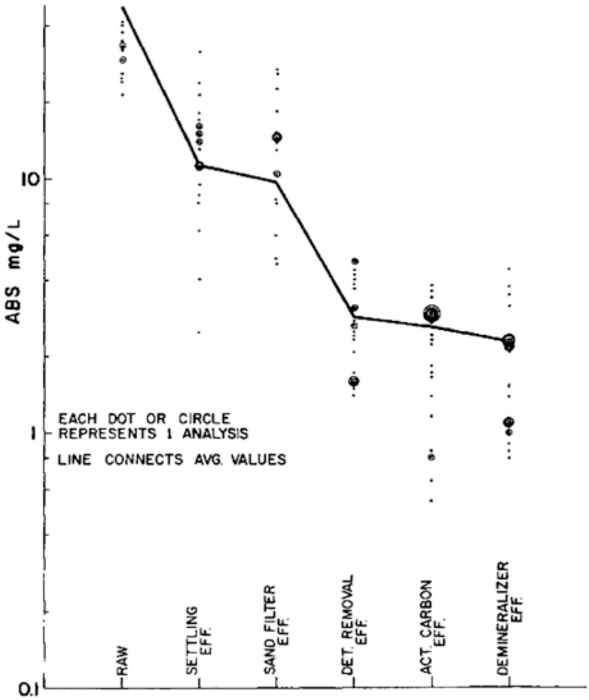


Fig. 10.10 Detergent concentrations through Winfair System

Table 10.4 Summary of ABS removal in the Winfair system

		ABS, mg/L			Average reduction	
Unit	Number of samples	Maximum	Minimum	Average	% of original	% of remaining
Raw waste	75	144.0	21.5	47.15	–	–
Settling tank	67	31.5	2.5	11.25	76	76
Sand filter	67	27.0	4.6	9.69	3	13
Detergent removal	68	4.7	1.4	2.86	14	70
Activated carbon	68	3.8	0.54	2.61	0.5	8
Demineralizer	74	4.4	0.08	2.31	0.6	11
Overall					94.1	

The Winfair system was set up and put into operation first while replacements were awaited for the filtering elements of the ALMI system which were found to be rusted beyond use upon receipt of the units. The Winfair system was operated for a period of 9 months. Analyses were performed for ABS, COD, BOD, pH, and total dissolved solids.

The ABS concentration throughout the system is shown in Fig. 10.10. The actual values are summarized in Table 10.4. The greatest removal of ABS was accom-

Table 10.5 Summary of overall BOD and COD removal in the Winfair Water Reclamation System

Parameter	No. of samples	Influent, mg/L			Effluent, mg/L			Average % reduction
		Maximum	Minimum	Average	Maximum	Minimum	Average	
BOD	101	105	80	119.2	118	20.5	52.2	56.4
COD	70	438	136	293.4	244	38	113.8	62.1

Table 10.6 Summary of pH values in the Winfair system

Unit	No. of samples	Maximum	Minimum	Average
Raw waste	134	7.6	5.0	7.13
Flocculation tank	136	6.0	3.9	4.45
Settling tank	117	6.7	4.2	5.58
Sand filter	117	6.7	4. 5	5.76
Detergent removal	117	7.0	5.0	5.95
Activated carbon	117	6.9	5.2	5.99
Demineralizer	134	6.8	5.1	6.07

plished by the alum addition followed by sedimentation. This was in the order of 76% of the initial ABS, and resulted in an average ABS, after settling, of slightly over 11 mg/L. This is in the same order as the laboratory experiments. The sand filter removed a little more ABS, but the detergent removal resin lowered the ABS to an average of less than 3 mg/L. This resin actually removed in the order of 70% of the remaining ABS. The activated carbon and the demineralizer system removed little additional ABS. The average overall ABS removal was 94%.

The BOD and COD results are summarized in Table 10.5. These parameters were determined to show the effectiveness of this system as a treatment system. If the effluent is to be recycled, these parameters must be followed in order to be alerted to an undesirable buildup. If the effluent is to be discharged, their concentrations must be known in order to determine if the effluent will be acceptable in the receiving body of water. The average BOD of the effluent was 52 mg/L and the average BOD reduction was in the order of 56%. The average COD of the effluent was 114 mg/L and the average COD reduction was 62%.

The pH (Table 10.6) of the raw waste was generally near neutral to slightly alkaline. On only two occasions was the pH below 6.8. These are considered due to the production of septic conditions in the holding tank. The pH adjustment in the flocculating tank was maintained between 3.9 and 5.1 with one value at 6.0. The pH increased more than one unit on an average as it passed through the settling tank. By the time it reached the end of the treatment system, it reached an average value greater than 6.0.

The total dissolved solids pose a problem if the effluent is to be reused in a laundromat. The dissolved solids through each unit of the system are summarized in Table 10.7. The variation was greatest in the raw waste which had a minimum value of 625 mg/L and a maximum of 1450 mg/L. The primary concern is that the overall system resulted in an increase of total dissolved solids, rather than the desired reduction. This is shown in Fig. 10.11. The greatest increase was due to the alum addition and was in the order of 20 mg/L. The demineralizer, which was designed

Table 10.7 Summary of total dissolved solids in the Winfair system

Unit	Number of samples	Total dissolved solids, mg/L		
		Maximum	Minimum	Average
Raw waste	81	1450	625	931
Settling tank effluent	79	1425	750	952
Sand filter effluent	79	1400	700	953
Detergent removal effluent	79	1375	690	956
Activated carbon effluent	79	1410	700	968
Demineralizer effluent	81	1325	750	974

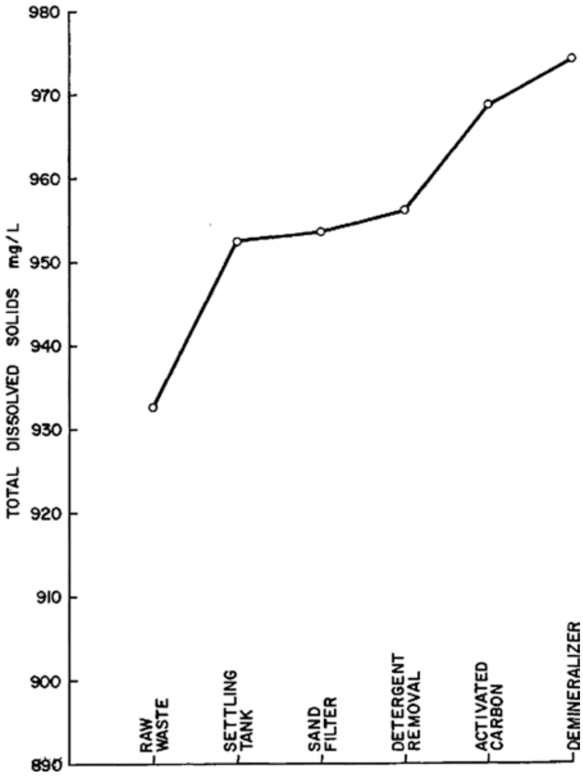


Fig. 10.11 Summary of total dissolved solids in Winfair System, mg/L

to reduce the dissolved solids, resulted in an average increase of 6 mg/L, or essentially no effective reduction.

The effluent from the system was chlorinated in the final holding tank before being discharged to a swampy area of a slow-running stream. This stream was little more than a drainage ditch which helped to drain the high-water table of the surrounding area. All the houses in the area are provided with septic tank and tile field systems. The overflow from the holding tank (as described previously) also reached this swampy area. During warm weather an offensive odor arose from the stagnant stream, causing complaints by the neighbors. An injunction was brought against the laundromat operator to prevent the overflow of wastes from the holding tank. It was decided to install a float valve on the holding tank so that the system would operate automatically when the holding tank was full. Even with the promise to have the float valve operative within a week's time, the judge closed the laundromat. This also resulted in the land owner's filling in the swamp and digging a channel to carry off the water, thereby eliminating the problem created by the stagnant water. Whereas the injunction closed the laundromat, there was no claim against the operation of the treatment system. Arrangements were made to transfer 2000 gal/day of laundromat waste from another laundromat about 3 miles away. This allowed operation of the treatment system without moving the equipment. However, no further studies were performed using the Winfair system.

6 Discussion of the Winfair System

The Winfair Water Reclamation System was operated for a period of 9 months adjusting the pH of the raw waste with alum in the range of 4.0 to 5.0, but with no neutralization prior to sedimentation. The average ABS content after settling was 11 mg/L, which correlates well with the results of the lab studies. The value is double that which the manufacturer claims can be expected from this portion of the system. However, it is less than the 15 mg/L obtained by the original operator. It does confirm that the anion ABS exchange resin will be depleted in half the time predicted by the manufacturer. So long as consideration is made for this, it will not create a serious problem except for an increase in cost for the operation. The overall ABS reduction was 94%, resulting in a residual ABS of 2.3 mg/L. This is greater than the recommended drinking water standards but should be satisfactory for reuse in a laundromat.

The BOD and COD removals are intermediate between primary and secondary treatment. The residual may or may not be acceptable for discharge depending upon the receiving stream. This would also depend on the volume of the waste from each individual laundromat under consideration. Generally speaking, the average BOD of 52 mg/L and the average COD of 114 mg/L in the effluent are considered rather high for recycling of the effluent. Chlorination may reduce these slightly and also prevent septic conditions in the recycle holding tank.

pH was to have been an important key in this study. Since the initial pH adjustment was difficult to establish, it was expected that a wide range of pH values would be obtained allowing for an evaluation of the degree of treatment over a wide pH range. Instead, the lab assistants went to extreme pains to maintain the pH between 4.0 and 5.0 in order to obtain what the laboratory studies had shown to be the pH for the greatest purification. An attempt was made to correlate the pH treatment, but the results showed no conclusive trend. It is interesting to note that when the system was first set up and operated to get the bugs out, on one occasion the pH in the flocculation tank was 6.0, and the ABS in the effluent was recorded as 0.0. Since this was a break-in period both from the standpoint of operating the system and perfecting lab techniques, no great value can be placed on this single result.

One of the greatest disappointments was the operation of the demineralizer system for removal of the total dissolved solids. The increase in the total dissolved solids due to the addition of the alum of about 20 mg/L was less than that of up to 1000 mg/L experienced in the lab studies. This indicates better control and separation in the system than in the lab. The increases in passing through the remaining units of the system are insignificant. However, when it comes to the demineralization, this is supposed to reduce the total solids, not result in an insignificant increase. When the system was started up, fresh resins were placed in the units. Some difficulty was found in balancing the valves so that approximately one-third of the flow passed through the demineralizers. After this was established, samples were secured for the dissolved solids test which showed no reduction. It is possible that in establishing the flow, the resins became exhausted. Therefore, they were regenerated as per specifications, but with no change in results. Numerous efforts were made to regenerate the resin and they were completely replaced later in the study. The flow was regulated to all extremes including passing all the liquid through the resins. All of these efforts proved fruitless. It can only be concluded that the demineralizer system provided by the company was not capable of performing the job for which it was designed. This is the same conclusion reached with the initial evaluation of the failure of the system in its first location.

Although the possibility of reuse of the treated effluent was considered, it was not attempted in any of these studies. The water supply for the laundromat was adequate, and it was felt that the existing good-quality water would be preferred to reused water. The only advantage that could have been gained by reuse would have been a saving in waste water that would have had to be discharged. The quality of the effluent is considered to be adequate for reuse in a laundromat, but certainly not for drinking. No consideration could be made of the number of reuse cycles that could have been made before the buildup of non-removed materials would reach an undesirable level. It is also considered that this treatment would result in an effluent which could be discharged into a subsurface disposal system with a minimum of problems.

7 The Alum Filtration System

As early as 1944, the U.S. Army Corps of Engineers developed a diatomite filtration unit for use in supplying safe and potable water for field troops [9]. These units had to (a) be portable and (b) operate at a high rate of output. Since the nation was then involved in a global war, the economic factor was not of great importance in evaluating the overall success of the system. In addition to the conventional health and aesthetic requirements, the system had to remove the cysts of Endamoeba histolytica and the cercaria of schistosomes. This was particularly crucial in both the South Pacific and the Mediterranean Theatres of war. At flow rates of 6 to 12 gpm, many cysts passed through conventional sand-type filtration units. On the other hand, the diatomite filters affected virtually complete removal of cysts under the most severe tests.

These findings were again utilized as the post-World War II boom of home laundries and public laundromats spread into unsewered areas, increasing the need for effective treatment units. The American Laundry Machinery Industries (ALMI) Diatomaceous Earth Filtration System was developed for such laundry waste treatment.

Structurally, the ALMI wastewater treatment system (WWTS) used is a continual water filtration system consisting of a mixing tank, 2 chemical feed tanks, 2 pressure filter units operated in parallel, and the appropriate pumps, valves, and connecting piping. Additional appurtenances include a 4000-gal raw wastewater holding tank to provide flow equalization, a 1000 gal treated water tank which served as a chlorine contact tank, and a 1000 gal. Sludge holding tank which retained the filtered materials plus the spent diatomaceous earth (DE) until hauled away by a scavenger. Each filter unit contains 45 vertical mesh screen tubular elements (total of 90 elements) which serve as a septum for the diatomaceous earth (DE) precoat. Figures 10.8 and 10.12 together show an 8000 gal/day single diatomaceous earth filtration system. A schematic flow diagram of a double diatomaceous earth filtration system is shown in Fig. 10.13. The principal characteristics of this unit are listed in Table 10.8.

System operation consists of applying a precoat on the filter elements by recirculating a water suspension of DE from the mixing tank through the filters with return to the mixing tank. The precoat operation usually requires 3–6 min using a 45 lb. change of diatomaceous earth. Following precoating, the waste purification cycle is

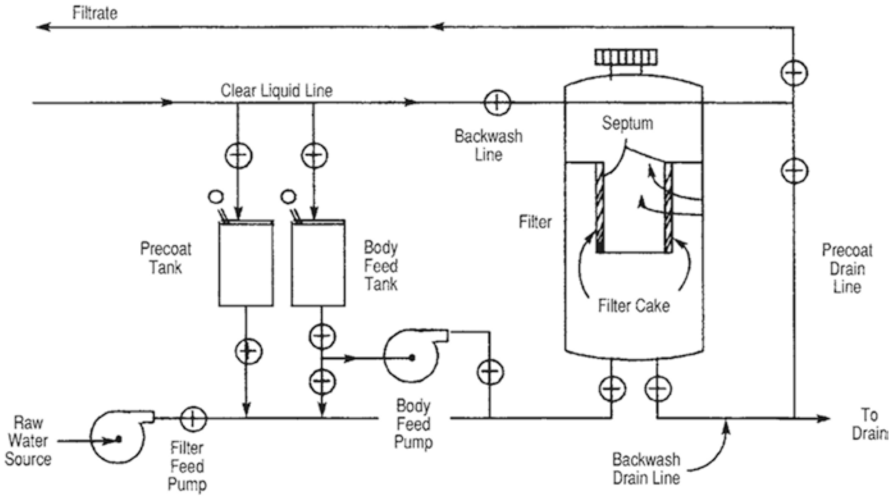
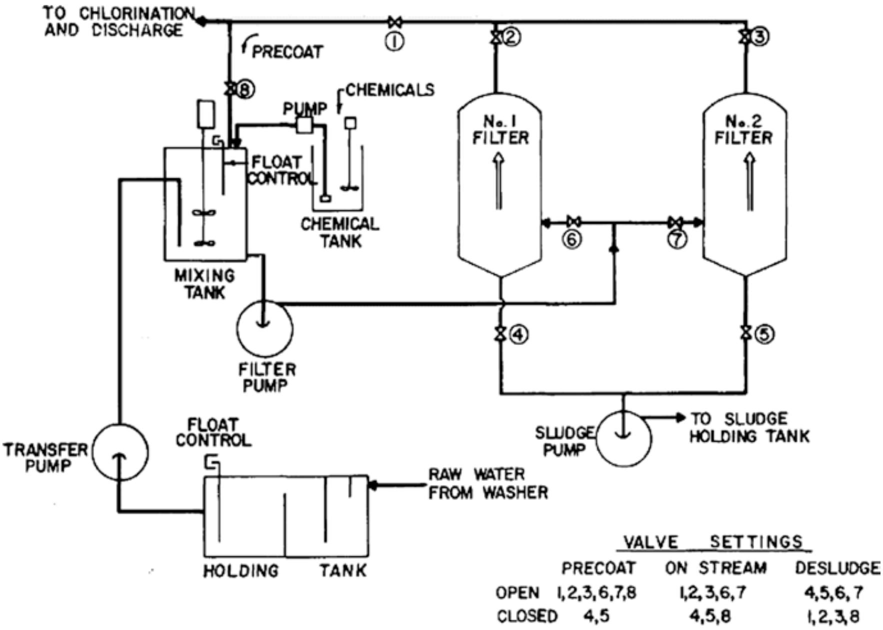


Fig. 10.12 Simplified schematic flow diagram of American Laundry Machinery Industry (ALMI) single diatomaceous earth filtration system



VALVE SETTINGS

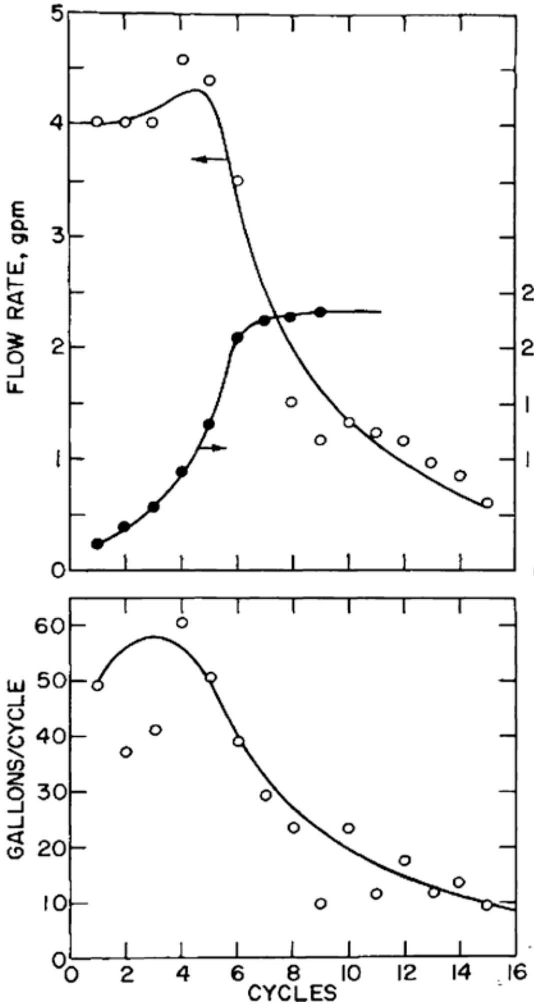
	PRECOAT	ON STREAM	DESLUDGE
OPEN	1,2,3,6,7,8	1,2,3,6,7	4,5,6,7
CLOSED	4,5	4,5,8	1,2,3,8

Fig. 10.13 Simplified schematic Flow Diagram American Laundry Machinery Industry double diatomaceous earth filtration system

Table 10.8 American Laundry Machinery Industries (ALMI) Diatomaceous Earth Filtration System

Overall size	
Base	5′–3″ × 5′–5″
Height	7′–2″
No. filter elements	90
Size	25.5″ long × 1″ diameter
Mesh	60
Filter element area	0.564 ft.^{2}/element
Total	50.76 ft.^{2}
Normal flow	
In	25–26 gpm
Out	14–15 gpm
Flow loading	~ 0.5 gpm/ft.^{2} filter area
Diatomite charge	45 pounds (0.89 lb/ft.^{2})
Normal total daily flow	6300–8500 gals
Chemical feed solution rate	60–70 mL/min

Fig. 10.14 ALMI System Pressure Drop–Flow Changes



initiated by pumping wastewater from the holding tank to the mixing tank, through the filters and to the treated water tank. A purification cycle normally lasts 15 min during which 400 gallons of wastewater are processed at a flow rate of 25 gpm. Following each 15 min filtration cycle, a timer switch shuts off the filter pumps and activates a mechanical shaker mechanism which "bumps" off the precoat from the filter elements. The precoat and filtration cycles are then repeated following completion of the bump phase. The periodic bump to remove and re-precoat the filter elements restores pressure drop loss which occurs as solids accumulate on the filter elements. Figure 10.14 illustrates the rate of pressure drop increase (and flow decrease) as a function of number of filtration cycles [10, 11]. Usually, it is possible to achieve 10–15 filtration cycles with one DE charge, which allows processing of 4000–6000 gal of wastewater.

The recommended chemical operation of the ALMI system consists of the addition of $CaCl_2$ and Roccal (commercial name for a quaternary ammonium compound, which is in effect both a cationic detergent to remove residual anionic detergents and a germicide to kill bacteria) to the raw waste in the mixing tank. In addition, NaOH, alum and ferric chloride were added in tests to study the removal of phosphates. Finally, sodium hypochlorite (Clorox) was added to the effluent to reduce bacteria. The entire chemical reactions of the ALMI Wastewater Treatment System take place in the mixing tank. They are designed to neutralize and/or precipitate phosphates, spent detergents, nitrates, organic matter, and suspended particulates in the wastes. To the degree that the chemical process is effective, these substances are then trapped upon the filter medium, theoretically leaving a clear, odorless, and non-pathogenic effluent low in organic matter.

This entire phase of this study was conducted under less than ideal conditions. Just prior to commencing of this project, an injunction was obtained against the laundromat operator, forcing him to shut down his operation. This was due to an overflow of wastes from the holding tank at the treatment plant. The system was designed so that when the holding tank was full, the waste would spill over into a septic tank and leaching system. However, delivery trucks had crushed the pipes leading to the septic tanks and tile fields, so that the waste overflowed at the holding tank. Fortunately, the injunction which closed the laundromat said nothing about the treatment plant, so arrangements were made with the operator of a laundromat about 3 miles away to truck 2000 gal. Per day from his septic tank to our holding tank. This waste was septic and not fresh as the local waste was. This probably made the waste more difficult to treat. It was assumed that if this system could treat this septic waste satisfactorily, it could do an even better job of normal fresh laundromat wastes.

8 Laboratory Analysis

Discussion of the information available from the data is expanded for each of the parameters measured, and then the most nearly optimum operating conditions are evaluated.

8.1 ABS Removal

With one exception, 97% or better ABS removal was achieved with Roccal dosages of 26 mg/L and greater as summarized in Table 10.9. With one exception, the ratio of $CaCl_2$ to Roccal ranged between 4.78 and 5.1 on these occasions. Poorer ABS removals occurred when the Roccal addition dropped below 26 mg/L and the $CaCl_2$:

Table 10.9 Summary of ABS reduction with $CaCl_2$ and Roccal additions on various dates

Roccal dosage (mg/L)	Ratio $CaCl_2$ to Roccal	Average reduction %
110.0	4.8	100
105.0	4.8	No data
88.5	4.6	97.77
84.0	4.8	100
64.0	4.9	97.76
63.2	11.5	99.04
63.0	4.8	91.59
56.0	4.8	100.00
55.6	4.8	99.31
48.5	5.1	98.10
45.0	4.9	97.78
32.0	4.8	98.25
29.2	4.8	99.37
26.2	9.9	97.93
24.0	6.75	38.33[a]
23.8 (NaOH added)	24.0	97.96
20.2	9.7	88.45
20.0 (alum + $FeCl_3$ added)	No data	No data
19.8 (NaOH added)	23.8	81.02
18.3 (NaOH added)	23 0.8	80.48
15.4 (NaOH added)	22.7	72.43
15.2	10.1	75.98
12.0	4.7	77.58
9.2 (NaOH added on 9/3 only—results not typical)	23.7	46.34

[a] 1500 mg/L alum added, settled in WWRS before ALMI treatment

Roccal ratio was greater than 10. The summary of the removal of ABS is shown in Table 10.10. The concentration of ABS in the raw waste was fairly constant with a variation only from 16 to 26 mg/L and an avg. of 20 mg/L. The highest value in the effluent was 5.2 mg/L and on numerous occasions the ABS was removed completely. The avg. ABS in the effluent was 2.5 mg/L, representing an avg. reduction or 87%.

8.2 BOD Reduction

The values of the BOD reduction are summarized in Table 10.11. The highest BOD recorded in the influent was 371 mg/L, but the next highest value was 168 mg/L. The avg. BOD of the waste was 126 mg/L. The avg. BOD of the effluent was 47 mg/L. The avg. reduction was 63%; the maximum. Was 82% and the minimum 7%. The 82%

Table 10.10 Summary of removal of alkyl benzene sulfonate in the ALMI System

Influent					Effluent					Reduction				
High		Low		Average	High		Low		Average	High		Low		Average
Date	mg/L	Date	mg/L	mg/L	Date	mg/L	Date	mg/L	mg/L	Date	%	Date	%	%
8/26	25.7	8/8	15.7	20	9/3	15.3	8/2, 7, 8, 11, 27	0	2.5	8/2, 7, 8, 11, 27	100	9/3	18	87

Table 10.11 Summary of removal of BOD in the ALMI System

Influent					Effluent					Reduction				
High		Low		Average	High		Low		Average	High		Low		Average
Date	mg/L	Date	mg/L	mg/L	Date	mg/L	Date	mg/L	mg/L	Date	%	Date	%	%
8/14	371	8/21	80	126	8/16	102	9/4	15	47	8/21	82	8/16	7.3	63

reduction was achieved using a 46 lb. charge of Pitcher Celatom and resulted in an actual reduction of BOD from 109 mg/L to 20 mg/L.

8.3 COD Reduction

Table 10.12 shows the summary of the COD reduction. The COD of the influent ranged from 200 to 455 mg/L with an avg. value of 340 mg/L. The values in the effluent ranged from 42 to 196 mg/L with an avg. of 104 mg/L. The greatest reduction of 84% occurred on two occasions and the poorest reduction was 1%. The avg. reduction in COD was 69%. The best COD reduction was achieved using Diatomitein in a 44 lb. charge resulting in actual reductions of 258 and 285 mg/L to 42 and 45 mg/L, respectively.

8.4 Turbidity Reduction

The turbidity of the effluent varied appreciably with the pH as shown in Fig. 10.15 (% transmittance is plotted instead of actual turbidity; a high transmittance indicates a low turbidity). It may be seen that the best turbidity removal occurs when the pH is adjusted to values greater than 8. Table 10.13 shows the variation of the effluent turbidity with various dosages of each of the diatomaceous earths used. The best reduction of turbidity was achieved using Pitcher Celatom at a SO lb. charge resulting in an effluent which manifested 96% transmittance.

8.5 Organic Nitrogen

The small number of results for Kjeldahl nitrogen available is summarized in Table 10.14. Although the data are not statistically significant, on one occasion there was an increase in the organic nitrogen of 146% from the influent to the effluent; on the other two occasions there was a reduction.

8.6 Total Dissolved Solids Increase

In all cases, due to the chemicals added for the treatment, there was an increase in the total dissolved solids as shown in Table 10.15. The average increase was 61%. The greatest increase was 144% from 450 mg/L to 1100 mg/L. The least increase, 3%, from 390 and 400 mg/L to 400 and 410 mg/L, respectively, occurred using Diatomite in a 44 lb. charge combined with 56 mg/L of $CaCl_2$ and 12 mg/L of active

Table 10.12 Summary of removal of COD in the ALMI System

Influent					Effluent					Reduction				
High		Low		Average	High		Low		Average	High		Low		Average
Date	mg/L	Date	mg/L	mg/L	Date	mg/L	Date	mg/L	mg/L	Date	%	Date	%	%
8/19	455	8/8	200	340	8/6, 19	196	8/26	42	104	8/26, 29	84	8/19	31	69

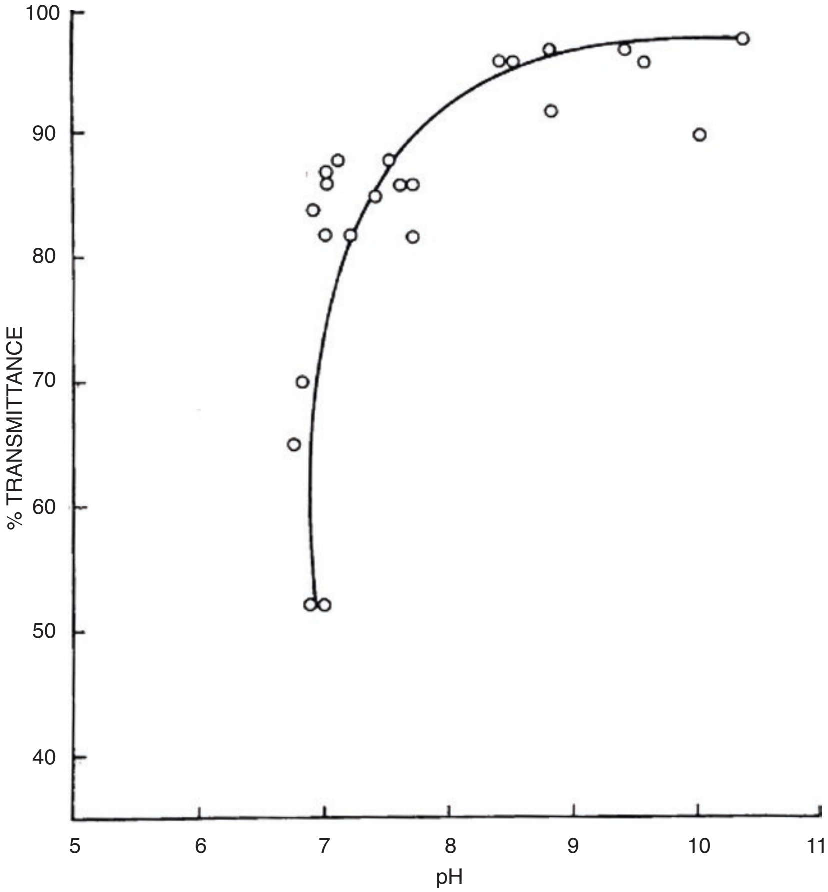


Fig. 10.15 Effluent turbidity vs. pH of the ALMI System

Table 10.13 Effluent turbidity vs. filter aid

Filter aid	Dosage, lb	Average pH	Average transmittance, %
Diatomite	24	7.1	87
Diatomite	42	7.4	85
Diatomite	44	7.4	81
Pitcher Celatom	46	ND	61
Pitcher Celatom	43	ND	No data
Pitcher Celatom (NaOH added)	50	9.1	96
Diatomite (NaOH added)	43	ND	91
Diatomite (NaOH added)	37	ND	No data
Diatomite (NaOH added)	43	ND	No data[a]
Diatomite (NaOH added)	43	ND	59.5
Johns Manville Hyflo-Supercel	44	ND	No quantitative data (poor)
Celite 545	44.5	7.6	79.5

[a] Six (6) minute precoat hereafter

Table 10.14 Summary of changes in the organic nitrogen in the ALMI System

Influent					Effluent					Change				
High		Low		Average	High		Low		Average	High		Low		Average
Date	mg/L	Date	mg/L	mg/L	Date	mg/L	Date	mg/L	mg/L	Date	%	Date	%	%
8/6	10.1	8/7	5.6	7.8	8/7	13.8	8/8	7.5	11.25	8/8	−24	8/7	+146	+44

Table 10.15 Summary of the increase in total dissolved solids in the ALMI System

Influent					Effluent					Increase				
High		Low		Avg.	High		Low		Avg.	High		Low		Avg.
Date	mg/L	Date	mg/L	mg/L	Date	mg/L	Date	mg/L	mg/L	Date	%	Date	%	%
8/19	690	8/15	390	442	8/21	1100	8/15	400	713	8/21	144	8/15	2.5	61

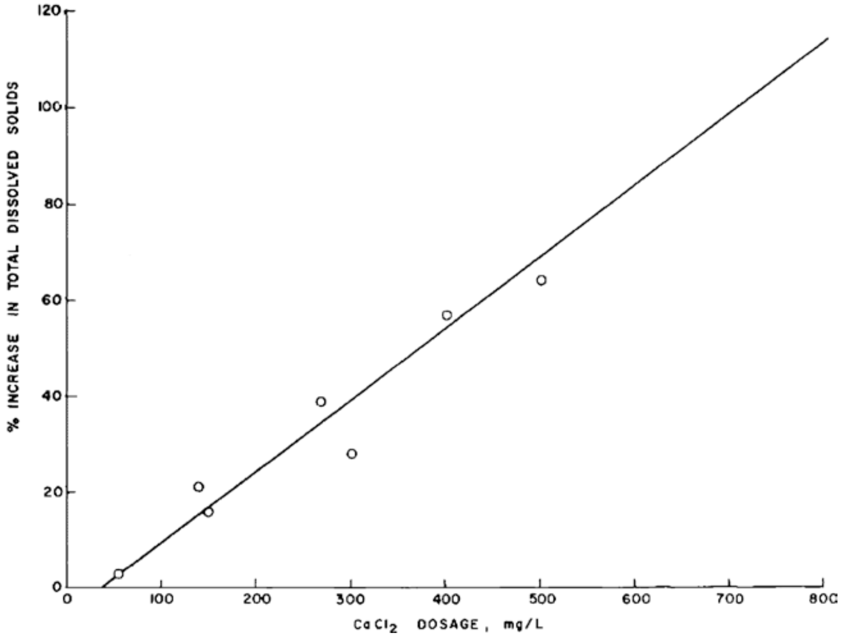


Fig. 10.16 Effect of $CaCl_2$ dosage on total dissolved solids in effluent from the ALMI system

Roccal. That the increase in total dissolved solids is directly related to the $CaCl_2$ added is shown visually in Fig. 10.16.

8.7 Hardness

The scant hardness data do not lend themselves to statistical evaluation. It would be useful to correlate hardness in the effluent with $CaCl_2$ dosage, but this is not possible. A summary of the existing data is shown in Table 10.16. The hardness in the influent varied only between 172 and 248 mg/L with an average of 209 mg/L. On two occasions on the same day there was an extreme increase in hardness in the effluent to 620 and 668 mg/L. Including these two values, the average hardness in

Table 10.16 Summary of the changes in hardness in the ALMI System

Influent					Effluent					Change				
High		Low		Average	High		Low		Average	High		Low		Average
Date	mg/L	Date	mg/L	mg/L	Date	mg/L	Date	mg/L	mg/L	Date	%	Date	%	%
8/19	248	9/3	172	209	8/21	668	8/19	96	284	8/19	−56	8/21	+660	+36
					8/19[a]	218[a]			166[a]					−20[a]

[a] Excluding two (2) extremely high values on 8/21

the effluent was 284 mg/L showing an average increase of 36%. Excluding these two abnormal values there was an average reduction of 20% to 166 mg/L.

8.8 Phosphate Removal

It is well known that phosphate removal is directly related to the pH of the solution. This is shown clearly in Fig. 10.17. Below pH 7.5 the phosphate removal was in the order of 25%, whereas above pH 8.5, it was above 90%. To show any effect of $CaCl_2$ dose on phosphate removal, Fig. 10.18 was constructed. It may be seen that increased CaCl2 dosage does result in a greater removal of phosphate, but this removal approaches only 50% with $CaCl_2$ dosages up to 700 mg/L. On the other hand, $CaCl_2$ dosages in the range of 400 to 600 mg/L removed over 90% of the phosphate when NaOH was added. When alum was added and the waste settled in the Winfair system prior to treatment in the ALMI system, an 85% reduction of phosphate was achieved using only 150 mg/L $CaCl_2$. For these reasons, the summary of the phosphate removal results (Table 10.17) is divided into sections showing the removals with CaCl2 alone, with addition of NaOH, and with alum and settling. The maximum phosphate removal, from 169 mg/L to 3 mg/L representing a 98% reduction, was obtained using Pitcher Celatom in a 50 lb. charge with the addition of NaOH to a pH of 9.55, and 435 mg/L of CaCl2 with 18.3 mg/L of Roccal (23.77 to 1 ratio).

8.9 Alkalinity

The results of the alkalinity are summarized in Table 10.18. The average alkalinity in the raw waste was 368 mg/L with a range of 340 to 420 mg/L. With no addition of NaOH, there was an average slight reduction in alkalinity to 329 mg/L With the addition of NaOH, the alkalinity increased to an average of 475 mg/L.

8.10 Acidity

The results of the acidity are summarized in Table 10.19. The average acidity in the raw waste was 91 mg/L with a range of 73 to 124 mg/L. With no NaOH added, the average acidity showed a slight increase to 112 mg/L during treatment. Upon addition of NaOH, the acidity was lowered to an average value of 31 mg/L, with occasional instances of completely removing the acidity (pH > 8.3).

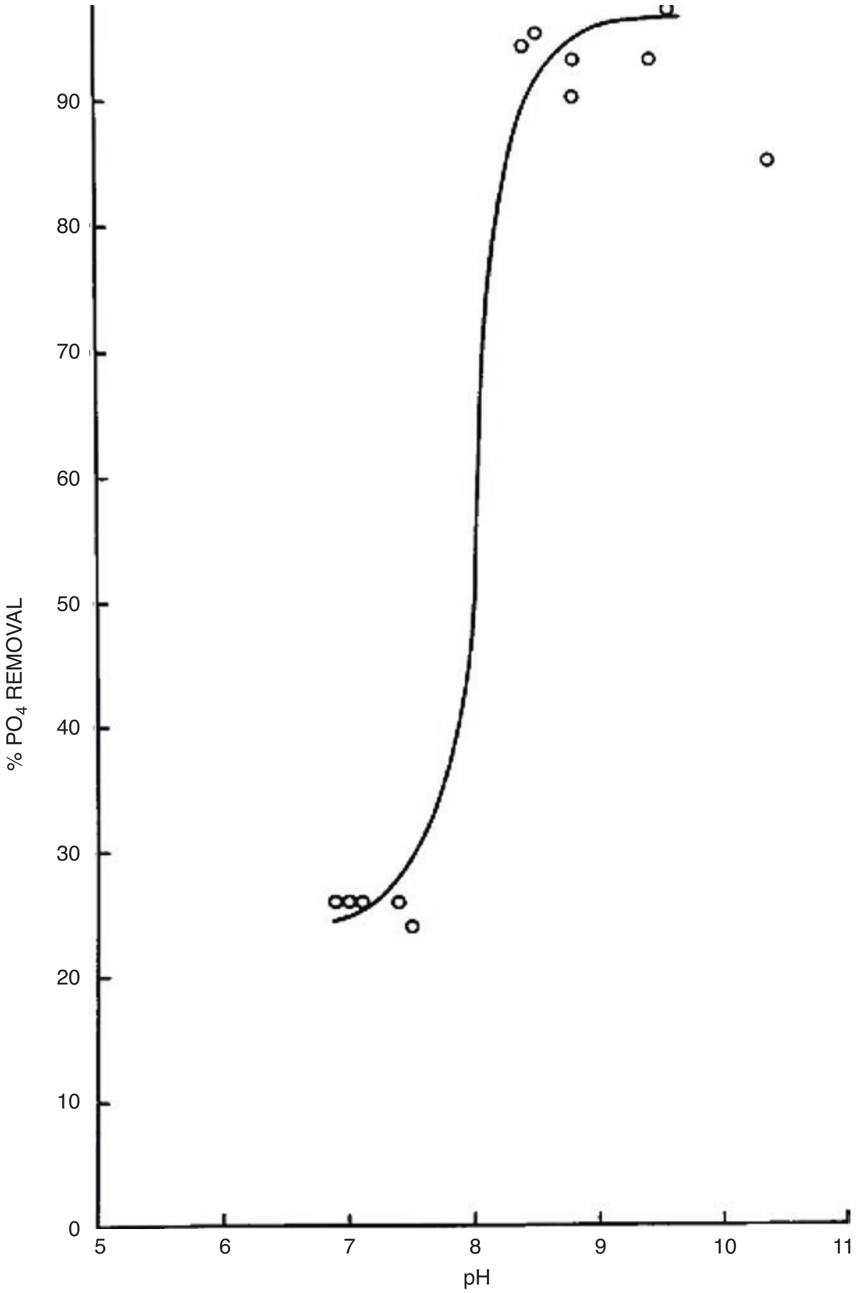


Fig. 10.17 Effect of pH on PO_4 removal in the ALMI system

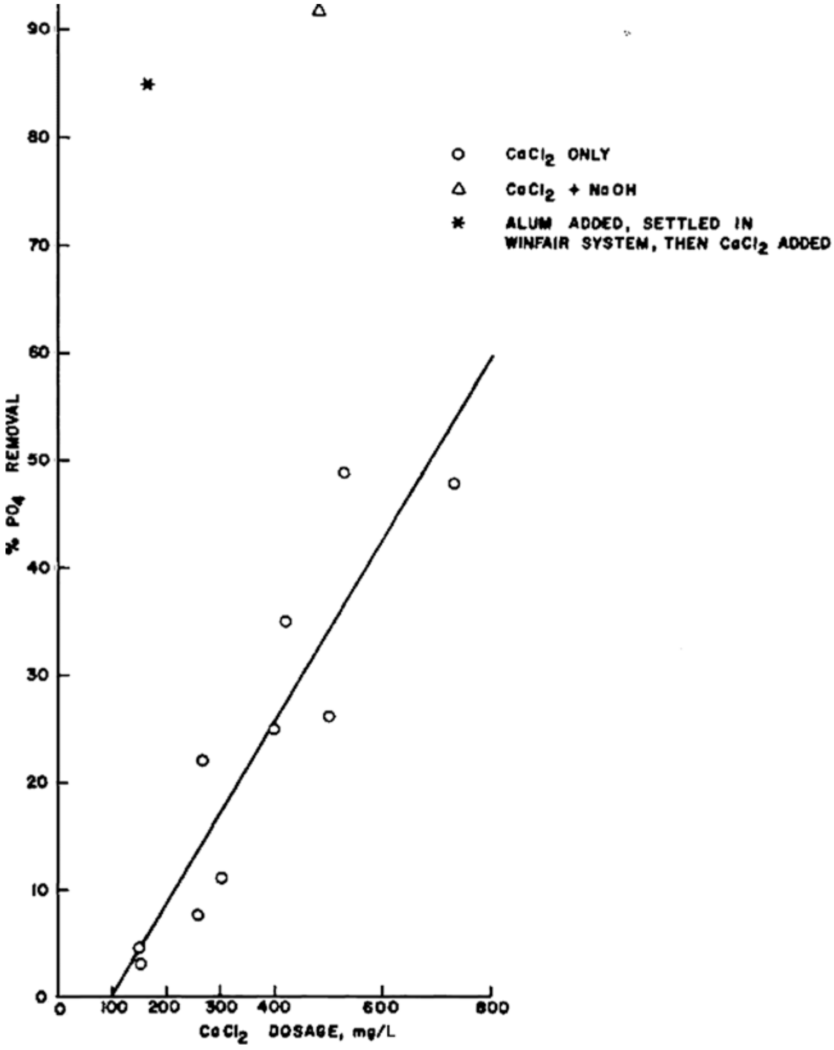


Fig. 10.18 Effect of $CaCl_2$ dosage on PO_4 removal in the ALMI system

8.11 Optimum Operating Conditions

There was no one set of operating conditions which produced the maximum reduction of all parameters of pollution. However, the best overall results, as shown in Table 10.20, were produced under the following conditions: (1) 50 lbs of Pitcher Celatom as filter aid; (2) a 3 min pre-coat time; (3) 567 mg/L of $CaCl_2$; (4) 23.8 mg/L of active Roccal during a 7530-gal run; and (5) with the addition of NaOH. This combination of treatment resulted in: (1) 98% reduction of ABS from 21.6 mg/L to 0.20 mg/L, satisfactory for USPHS Drinking Water Standards; (2) a 73% reduction

Table 10.17 Summary of PO_4 removal in the ALMI System

Influent						Effluent						Reduction				
High		Low		Average		High		Low		Average		High		Low		Average
Date	mg/L	Date	mg/L	mg/L		Date	mg/L	Date	mg/L	mg/L		Date	%	Date	%	%
9/11	199	8/12	84	146	$CaCl_2$ only	9/11	199	8/21	55	113	$CaCl_2$ only	8/21	50	9/11 9/20	0 0	22.6
				–	$CaCl_2$+NaOH	8/28	28	8/29	3	11.7	$CaCl_2$+NaOH	8/29	98	8/28	86	94
					Alum; settled in Winfair; then $CaCl_2$	9/22	36	9/22	9	24	Alum; settled in Winfair; then $CaCl_2$	9/22	95	9/22	80	87

Table 10.18 Summary of the alkalinity in raw and treated waste

					Effluent					Effluent				
Influent					No NaOH added					NaOH added				
High		Low		Average	High		Low		Average	High		Low		Average
Date	mg/L	Date	mg/L	mg/L	Date	mg/L	Date	mg/L	mg/L	Date	mg/L	Date	mg/L	mg/L
9/3	420	8/21	340	368	8/19	350	8/21	288	329	9/3	500	9/3	452	475

Table 10.19 Summary of the acidity in raw and treated waste

					Effluent					Effluent				
Influent					No NaOH added					NaOH added				
High		Low		Average	High		Low		Average	High		Low		Average
Date	mg/L	Date	mg/L	mg/L	Date	mg/L	Date	mg/L	mg/L	Date	mg/L	Date	mg/L	mg/L
9/3	124	8/19	73	91	8/19	158	8/19	87	112	9/3	68	9/3	0	31

Table 10.20 Optimum combination of chemical and mechanical factors in the removal of pollutants and pathogens from laundromat wastewater in the ALMI Wastewater Treatment System

		Active		ABS			BOD		
Filter aid dosage	$CaCl_2$ dosage	Roccal dosage	NaOH	Influent, mg/L	Effluent, mg/L	Reduction, %	Influent, mg/L	Effluent, mg/L	Reduction, %
50 lb	567 (mg/L)	23.8 (mg/L)	Yes	21.6	0.20	98	133	34	73

COD			TDS			Turbidity	PO_4			pH	
Influent, mg/L	Effluent, mg/L	Reduction, %	Influent, mg/L	Effluent, mg/L	Increase, %	% Transmittance, effluent.	Influent, mg/L	Effluent, mg/L	Reduction, %	Influent	Effluent
285	45	85	488	715	44	97	169	6	94	7.2	8.5

Acidity			Alkalinity			Hardness			Coliform/100 mL	
Influent, mg/L	Effluent, mg/L	Reduction, %	Influent, mg/L	Effluent, mg/L	Increase, %	Influent, mg/L	Effluent, mg/L	Increase, %	Influent	Effluent
91	89	2	368	372	1	208	266	8	>2000	<10

Filter aid Pitcher Celatom using a 3 min pre-coat

Time results based upon 7530 gallons of treated waste of BOD from 133 to 34 mg/L; (3) an 85% reduction of COD from 285 mg/L to 45 mg/L; (4) a 94% reduction of PO_4 from 169 mg/L to 6 mg/L; (5) a 97% transmittance for turbidity of the effluent; (6) no significant change in acidity; (7) raising the pH from an influent value of 7.2 to 8.5; (8) increasing the total dissolved solids (TDS) 44% from 488 mg/L to 715 mg/L; (9) little change in the alkalinity; (10) an 8% increase in the hardness from 208 mg/L to 266 mg/L; and (11) <10 coliform/100 mL when chlorinating the effluent.

9 Discussion of the ALMI System

The first criterion for a satisfactory effluent is that it meets health department standards. In New York, this demands (l) an effluent which manifests a coliform count of zero after chlorination based upon a 1 mL sample and (2) a reduction of 75% in biochemical oxygen demand (BOD). The ALMI system meets the requirement with respect to the elimination of coliform organisms and at optimum conditions achieves a 73% reduction of BOD. The ABS and total solids (TS) in the effluent meet the US Environmental Protection Agency (USEPA) drinking water standards.

The second requirement of a wastewater treatment system is the ability to handle peak loads as well as normal demands. The ALMI System proved able to treat a maximum of 25–26 gpm and also produce a satisfactory effluent at a regular flow of 14–15 gpm resulting in a total daily flow of 6300–8500 gpd. At two runs per day, this unit can treat a total of 7530 gpd. At a maximum average flow of 587 gpd per washing machine as shown in Fig. 10.1, the maximum average daily effluent from 12 to 13 machines could be treated in these two runs. It required 252 min or 4.2 h to treat the average daily effluent from approximately seven machines. Based upon a 12 h/day, the ALMI system could treat the average daily flow from approximately 20 machines. The holding tank of 4000 gallons capacity provided storage during peak flows.

The third requirement is that it requires a minimum of service, operational and maintenance skills, and operator time. After the optimum combination of chemical and mechanical aids was determined, it required very little time to add the DE charge and refill the chemical solution reservoirs. However, with two runs a day, the operator would have to return to add the second DE charge. All the other operations were such that the system could be activated automatically by a float valve in the holding tank. It would be possible to install an automatic DE charging setup so that the system could operate unattended during the weekend which is usually the peak usage period of the laundromat. Also, the sludge holding tank must be pumped out periodically, approximately on a weekly basis. This is best handled by a conventional septic tank service.

The fourth criterion is easily met be the ALMI system which was dismantled and removed to the RPI (Rensselaer Polytechnic Institute) laboratories with a minimum use of labor and transport facilities. It should be noted, however, that removal of the

4000 lb. holding tank, 1000 gal. Clean water tank, and 1000-gal sludge tank was not included, as these are fairly permanently installed in the ground.

As for the space requirement, the fifth criterion, the ALMI system, exclusive of holding and storage tanks, required no more than 80 ft.^{2}, including storage of filter aids and chemicals, with a normal ceiling height.

The goal of recycling water for further use should be an ultimate aim of any waste water treatment system. In terms of reduction of spent detergents, phosphates, coliform organisms, turbidity, organic nitrogen, BOD, and COD, the effluent could be reused for uses other than drinking. However, the increases in TDS, and pH, while within the upper limits of USEPA drinking water standards, might not be suitable for certain agricultural and industrial uses. Furthermore, the increase in alkalinity and hardness, due to the addition of NaOH, and the high ratio of $CaCl_2$ to Roccal (22.3:1) in order to increase PO_4 removal render very questionable the suitability of the effluent for reuse without softening and pH adjustment.

The American Laundry Machinery Industries Diatomaceous Earth Filtration System can thus be an effective system for the treatment of laundromat wastes. Whereas there was no single optimum operating condition under which all waste parameters were removed to the greatest extent, there can be reached an optimum chemical addition and operation which will effectively treat the waste and render it safe for certain reuse or discharge into a receiving water.

10 Feasibility of Treating Laundry Wastewater by Dissolved Air Flotation

10.1 Treatment of Prewashed Denim Laundry Wastewater by Dissolved Air Flotation

The recent consumer demand for fashions made from prewashed denim has created a booming prewash industry and an unexpected wastewater problem of significant proportion [12]. Since the demand for prewashed fashion has outpaced the major denim apparel companies' prewash capabilities and a satellite industry of contract small washers has emerged. Due to the tremendous consumer demand for prewashed denim fashions, prewashing has become highly profitable. Many small contract laundries which do not recognize the impact of prewashing on local municipal wastewater treatment plants are formed. They are similar to the small laundromats that the authors are studying. A consulting engineer has successfully treated a prewash laundry wastewater using DAF [12]. Specifically, DAF preceded by pH adjustment, polymer addition, and flocculation using over-and-under baffles did remove all apparent dye-related color. All wetted parts should be 304 stainless steel, and provisions for draining and cleaning grit from the interior of units should be made. A 250 gpm DAF unit was operated under recycle flow conditions to treat approximately 240,000 gpd of equalized prewash denim wastewater flow. DAF was followed by 80 mesh shaker screens for further TSS removal at a major corporate jeans manufacturing facility. The DAF operation requires approximately 40 gallons of 50% liquid caustic and approximately 30 gallons of liquid polymer per day for successful color removal. The float produced is a foamy blue gel and is dewatered using a precoat rotary drum vacuum filter unit coated with a cake layer of diatomaceous earth (DE). The dewatered sludge cake is 20 to 30% solids. Between on-half and one pickup truck bed load of dewatered sludge is produced per day.

Table 10.21 Treatment of auto and laundry wastewater by chemical coagulation/precipitation and sedimentation using 2800 mg/L alum and 200 mg/L polymer (Source: USEPA, Reference No. 13)

Sampling: Composite and grab	Analysis: Data set I (V. 7. 3. 1)			
	Concentration			
Pollutant/parameter	Influent	Effluent	Percent removal	Detection limit
Classical pollutants (mg/L)				
BOD(5)	160	57	64	
COD	240	130	46	
TOC	63	40	37	
TSS	40	46	NM	
OiI and grease	15	4	73	
Total phenol	0.038	0.026	26	
Total phosphorus	7.0	1.6	77	
Toxic pollutants (μg/L)				
Cadmium	51	12	76	2
Chromium	39	34	13	4
Copper	140	31	78	4
Lead	71	66	7	22
Nickel	55	50	9	36
Silver	14	11	21	5
Zinc	610	240	61	1
Phenol	ND	2	NM	0.07
Toluene	5	3	40	0. 1
Tetrachloroethylene	2	100	NM	
Trichloroethylene	0.5	12	NM	0.5
Cyanide	<2	<2	NM	
Chloroform	ND	70	NM	5
Methyl chloride	ND	38	NM	0.4
Chlorodibromomethane	BDL	ND	NM	0.9
Bis(2-ethylhexyl) phthalate	ND	67	NM	0.04
Butyl benzyl phthalate	ND	36	NM	0.03
Di-n-butyl phthalate	ND	7	NM	0.02
Di-n-octyl phthalate	ND	5	NM	0.89

Blanks indicate data not available

BDL below detection limit, *ND* not detected, *NM* not meaningful

10.2 US Environmental Protection Agency Data for Treating Auto and Laundry Wastewater by Dissolved Air Flotation or Sedimentation

According to the investigation of the US Environmental Protection Agency (USEPA) shown in Table 10.21, a conventional chemical coagulation/precipitation and sedi-

Table 10.22 Treatment of auto and laundry wastewater by chemical coagulation/precipitation and dissolved air flotation using 1800 mg/L calcium chloride and 2 mg/L polymer (Source: USEPA, Reference No. 14)

Sampling: 2-day composite and grab	Analysis: Data set 1			
	Concentration			
Pollutant/parameter	Influent	Effluent	Percent removal	Detection limit
Classical pollutants (mg/L)				
COD	6400	3200	50	
TOC	1700	690	59	
TSS	390	98	75	
Oil and grease[a]	700	140	80	
Total phosphorus	42	1.7	96	
Toxic pollutants (μg/L)				
Antimony	94	BDL	95[b]	10
Arsenic	10	2	80	1
Cadmium	110	BDL	>99[b]	2
Chromium	480	270	44	4
Copper	1500	500	67	4
Cyanide	57	54	5	
Lead	4800	130	97	22
Nickel	350	250	29	36
Zinc	3700	230	94	1
Bis(2-ethylhexyl) phthalate	1200	220	82	0.04
Butyl benzyl phthalate	310	ND	>99	0.03
Di-n-butyl phthalate	92	19	79	0.02
Di-n-octyl phthalate	150	33	78	0.89
2,4-Dimethylphenol	460	ND	>99	
Phenol	98	42	57	0.4
Dichlorobenzene	1100	260	76	
Anthracene/phenanthrene	380	66	83	0.01
Naphthalene	4800	840	83	0.007
Methylene chloride	2	2	0	0.4
1,1,1-Trichloroethane	18	14	22	2

Blanks indicate data not available

BDL below detection limit, *ND* not detected

[a] Average of four samples

Chemical dosages = 1800 mg/L $CaCl_2$ and 2 mg/L polymer

[b] Approximate value

Table 10.23 Treatment of auto and laundry wastewater by chemical coagulation/precipitation and dissolved air flotation using 60 mg/L polymer (Source: USEPA, Reference No. 14)

Sampling: 2-day composite and grab	Analysis: Data set 1			
	Concentration			
Pollutant/parameter	Influent	Effluent	Percent removal	Detection limit
Classical pollutants (mg/L)				
COD	500	460	8	
TOC	140	87	38	
TSS	50	32	36	
Oil and grease[a]	39	16	59	
Total phenol	0.43	0.39	9	
Toxic pollutants (μg/L)				
Copper	55	50	9	4
Cyanide	29	25	14	
Zinc	290	240	17	1
Bis(2-ethylhexyl) phthalate	82	74	10	
Butyl benzyl phthalate	17	ND	<99	0.03
Di-n-butyl phthalate	2	ND	<99	0.02
Di-n-octyl phthalate	28	11	61	0.89
Anthracene/phenanthrene	0.9	0.2	78	0.01
Naphthalene	0.9	0.6	33	0.007
Pyrene	0.3	0.3	0	0.01
Chloroform	41	24	41	5
Methylene chloride	57	22	61	0.40
Tetrachloroethylene	2	2	0	
1,1,1-Trichloroethane	2	ND	>99	2

Blanks indicate data not available
ND not detected
[a] Average of four samples
Chemical dosage = 60 mg/L polymer

mentation process using 2800 mg/L alum and 200 mg/L polymer can remove 64% BOD, 46% COD, 37% TOC, 26% total phenol, 73% O&G, 0% TSS, and 77% TP from an auto and laundry wastewater. Apparently there was a chemical sludge rising problem which might have caused a poor zero percent TSS removal. BOD, COD, and TOC removals are acceptable, but its high chemical dosages (2800 mg/L alum and 200 mg/L polymer) would be expensive [13].

USEPA has also supported research for treating the auto and laundry wastewater using chemical coagulation/precipitation and dissolved air flotation (DAF). The data in Tables 10.22 and 10.23 show that a DAF unit can: (a) remove 50% COD, 59% TOC, 75% TSS, 80% O&G, and 96% TP from an auto and laundry wastewater, if 1800 mg/L calcium chloride and 2 mg/L of polymer are dosed; or (b) remove only 8% COD, 38% TOC, 36% TSS, 59% O&G, and 9% TP from an auto and laundry wastewater, if only 60 mg/L polymer is dosed. Many heavy metals and organic pollutants may also be removed by DAF at the same time [14].

LIWT Wastewater Treatment System process description: (1) influent to the LIWT Wastewater Treatment System; (2) influent distributor; (3) primary clarification (gravity flotation) for floating O&G; (4) double primary clarification (sedimentation) for settling TSS; (5) settled sludge in primary sedimentation clarifier; (6) chemical feeding system; (7) mixer and rapid mixing chamber; (8) baffle flocculator; (9) water distributor; (10) optional lamella settling device; (11) secondary clarification (sedimentation); (12) sludge collection hopper; (13) settled sludge in secondary sedimentation clarifier; (14) DAF fine bubble distributor; (15) DAF air dissolving tube; (16) float collector and float collection trough; (17) double secondary clarification (DAF); (18) recycle flow for DAF; (19) LIWT Wastewater Treatment System outlet; (20) LIWT Wastewater Treatment System effluent; (21) air addition to DAF recycle flow; (22) water surface.

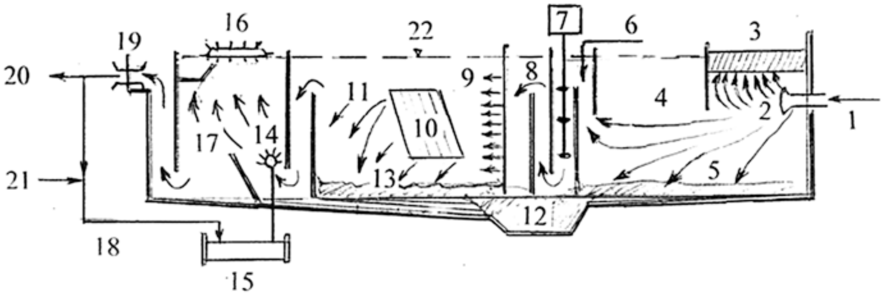


Fig. 10.19 A rectangular combined DAF-sedimentation wastewater treatment unit for treating either auto and laundry wastewater or car wash wastewater (Source: Lenox Institute of Water Tecgnlogy)

10.3 A Rectangular Dissolved Air Flotation System Designed by Lenox Institute of Water Technology

A LIWT Wastewater Treatment System (shown in Fig. 10.19) has been specifically designed for small operations, such as small laundromats, prewash laundries, car washers, etc., although large laundry plants may also adopt. It is a rectangular DAF-sedimentation system almost without moving parts. The description of Fig. 10.19 is listed below:

1. Influent to the LIWT wastewater treatment system inlet.
2. Influent distributor.
3. Primary clarification (gravity flotation) for floating O&G.
4. Double primary clarification (sedimentation) for settling TSS.
5. Settled sludge in primary sedimentation clarifier.
6. Chemical feeding system.
7. Mixer and rapid mixing chamber.
8. Baffle flocculator.
9. Water distributor.
10. Optional Lamella settling device.
11. Secondary clarification (sedimentation).
12. Sludge collection hopper.
13. Settled sludge in secondary sedimentation clarifier.

14. DAF fine bubble distributor.
15. DAF air dissolving tube.
16. Float collector and float collection trough.
17. Double secondary clarification (DAF).
18. Recycle flow for DAF.
19. LIWT wastewater treatment system outlet.
20. LIWT wastewater treatment system effluent.
21. Air addition to DAF recycle flow.
22. Water surface.

The raw wastewater enters the LIWT wastewater system's combined primary flotation-sedimentation chamber through a water distributor after that the light-weight oil flows to the water surface by gravity flotation, and the heavy-weight suspended solid settles to the primary sedimentation chamber's bottom also by gravity. In the center of the LIWT system, there is a chemical feeding device and chemical coagulation-precipitation mixing chamber, where the optimized chemicals are added to the primary effluent, and pH is adjusted. The thoroughly mixed/coagulated primary effluent goes through a few up-and-down baffles for flocculation. The mixing/flocculation effluent then flows through a vertical water distributor, entering a secondary sedimentation chamber for settling of TSS. There is an optional laminar settling module installed inside of the secondary sedimentation chamber for enhancing sedimentation action. The secondary sedimentation effluent finally enters a secondary flotation chamber where the extremely fine air bubbles carry the remaining TSS to the water surface. The float (scum on the top) can be mechanically or manually removed from the water surface, while the purified flotation effluent (subnatant) is discharged as the final LIWT system effluent.

All wetted parts should be 304 stainless steel, and provisions for draining and cleaning grit from the interior of units should be made. The LIWT system may be an excellent pretreatment unit meaning the LIWT system effluent is ready to be discharged into a municipal sewer system for further biological treatment. In order to meet the National Pollution Discharge Elimination System (NPDES) or the State Pollution Discharge Elimination System (SPDES) requirements for direct effluent to a receiving water, tertiary filtration and tertiary granular activated carbon (GAC) may be needed. The readers are referred to another publication for the details of an Independent Physicochemical Wastewater Treatment System [17].

11 Conclusions

11.1 The Winfair Water Reclamation System (WWRS)

WWRS was evaluated for its ability to treat a laundromat waste for possible reuse. Alum added to achieve a pH of 4–5 resulted in an effluent containing an average of 11 mg/L ABS. This is twice the level recommended for the detergent removal ion exchange resin. This will require replacing the resin twice as often as specified.

The BOD reduction was in the order of 61%, and the COD reduction 71%. This may be sufficient for discharge to many streams, and certainly satisfactory for discharge to a subsurface disposal system. The demineralizer system was absolutely nonfunctional. This will result in a buildup of total solids if the effluent is reused. If the effluent is to be discharged to waste, the demineralizer system is not needed. The system appears to operate satisfactorily without neutralization before sedimentation. The average ABS reduction was 94%, having an average residual of 2.3 mg/L.

With satisfactory operation of a demineralizer system, this effluent could be reused at least once in a laundromat. Consideration of the amount of makeup water to control the buildup of non-removed materials would have to be made. The system produces an effluent which should be suitable for discharge into many streams.

11.2 The American Laundry Machinery Industries (ALMI) Diatomaceous Earth Filtration System

ALMI system can be an effective system for laundromat waste treatment. Under optimum operating conditions, the System can achieve better than 98% ABS reduction, 94% PO_4 reduction, 70% BOD reduction, and 84% COD reduction. Coliforms can also be effectively removed.

A 98% or better removal of the ABS can be achieved with the addition of 24 mg/L or greater of Roccal (a combination of cationic detergent and germicide). No apparent relation was observed between calcium chloride addition and ABS removal, or between chemical addition and BOD or COD reduction. In most cases the COD exceeded the BOD.

The total dissolved solids in the effluent was directly related to the calcium chloride dose added. Thus, to minimize the increase in total dissolved solids, a minimum amount of calcium chloride should be used to effect treatment. The increase in total organic nitrogen due to treatment was not significant.

The turbidity of the effluent was directly related to the pH. At pH values above 8 with the addition of NaOH, the transmittance was always greater than 95%. The transmittance dropped off sharply at pH values below 7.

There was a general slight reduction in the hardness due to the treatment; however, there are insufficient data to achieve a statistical significance to this conclusion. Several data suggest that an excess of $CaCl_2$ increases the hardness in the effluent.

Increased $CaCl_2$ dosage can result in an increased removal of phosphate. However, more significantly an increase in pH results in a marked increase in phosphate reduction with lower $CaCl_2$ dosages. Pretreatment with alum followed by settling in the Winfair Water Reclamation System (WWRS) prior to treatment in the ALMI system resulted in a high phosphate removal at a low $CaCl_2$ dose. The ALMI System meets most of the requirements for treatment of wastes from coin-operated laundromats.

11.3 Dissolved Air Flotation (DAF) System

Krofta Engineering Corporation (KEC) has been a manufacturer partner of the Lenox Institute of Water Technology (LIWT) for quick technology transfer from idea to commercial products. There are over thousands of commercial Supracell DAF and Sandfloat DAFF, and KAMET-DAF-DAFF systems installed by LIWT/KEC and their related companies for treating various industrial wastewaters around the world. These process equipment (Supracell, Sandfloat, and KAMET) are suitable for use by large auto and laundry industries, but may not suitable to small laundromats, prewash laundries, or car washers, because there are many moving parts.

Other commercial DAF units, such as Clari-DAF and AquaDAF, have been applied to only drinking water treatment. It is the authors' professional judgment that all DAF commercially available (including Supracell, Sandfloat, KAMET, Clari-DAF, AquaDAF, etc.) should all be able to adequately treat the wastewater from a laundry plant, if adequate chemicals are used [15, 16, 18, 19].

12 Recomendations

Individual recommendations must be made on the basis of specific existing and potential uses of these treatment systems.

1. Treatment of laundromat wastes for discharge into the ground or to a surface water.
   Either system could be used for this degree of treatment. The ALMI system is recommended due to ease of operation and greater reliability. Additional studies could be made into the reason for the failure of the demineralizer system in the WWRS.
2. Reuse of the treated effluent in the laundromat.
   The WWRS was designed for reuse, whereas the ALMI system was not. Due to the malfunction of the demineralizer system of the Winfair Water Reclamation System (WWRS), the effluent from this system cannot be recommended for continuous reuse. Due to adverse conditions during operation of the American Laundry Machinery Industries (ALMI) system, no determination of the buildup in total solids could be made. In order to determine potential reuse, it is recommended that additional studies be made at a location where at least partial reuse of the effluent could be practiced.
3. Potential for phosphate removal.
   In view of the use of alum, the WWRS and of calcium and potentially ferric chloride or alum in the ALMI system, both these systems have a potential for use in phosphate removal. It is recommended that additional studies be made of the use of these treatment systems for phosphate removal.
4. Application to treatment of other types of liquid wastes.

Since both treatment systems' have been shown to be reasonably effective in treating laundry wastes, they should also be effective in treating normal domestic sewage, especially for phosphate removal. The systems used in these studies could be used for small housing developments or shopping centers. The principles could be expanded to serve larger facilities. It is, therefore, recommended that studies be made to determine the applicability of these systems to treat domestic sewage, particularly for phosphate removal.

5. This laundry wastewater treatment research was started by late Dr. Donald B. Aulenbach. Researchers around the world are invited to continue his research in order to find the best solution to treating the large-scale auto and laundry wastewater, and the small laundromat, prewash laundry, and car wash wastewaters. This was Dr. Aulenbach's final wish conveyed to his coauthors in 2019.

Dedication This book chapter is dedicated to two coauthors, Dr. Nazih K. Shammas and Dr. Donald B. Aulenbach, who both worked closely with Professors Lawrence K. Wang, Mu-Hao Sung Wang, William A. Selke, Milos Krofta, and Daniel Guss of the Lenox Institute of Water Technology, Massachusetts, USA, from 1981 to 2019 for developing a humanitarian engineering program at the Lenox Institute of Water Technology (LIWT), teaching/researching there as an Adjunct Professor for almost two decades [14, 15, 17, 18, 20–30], and publishing many research papers and textbooks for academic contribution to the humanity.

Glossary

Sandfloat A circular combined dissolved air flotation and sand filtration package plant (DAFF) manufactured by and commercially available from Krofta-related companies worldwide.

Supracell A circular dissolved air flotation clarifier (DAF) manufactured by and commercially available from Krofta-related companies worldwide.

KAMET (Krofta Advanced Municipal Effluent Treatment) A circular combined Supracell-Sandfloat (DAF-DAFF) package plant manufactured by and commercially available from Krofta-related companies worldwide.

Clari-DAF A rectangular dissolved air flotation clarifier (DAF), manufactured by and commercially available from Xylem Water & Wastewater, 227 S. Division St, Zelienople, PA 16063, USA.

AquaDAF A rectangular dissolved air flotation clarifier (DAF) manufactured by and commercially available from SUEZ Water Technologies and Solutions, 8007 Discovery Drive, Richmond, VA 23229, USA.

LIWT Lenox Institute of Water Technology, which is a nonprofit humanitarian environmental engineering college with a goal of scientific development and world peace.

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Chapter 11
Book Reviews: Natural Resources

Lawrence K. Wang and Mu-Hao Sung Wang

Contents

Abstract The authors have reviewed seven technical books published by WIT Press, Ashurst, Southampton, UK; CRC Press, Taylor & Francis Group, Boca Raton, Florida, USA; and ASCE Press, American Society of Civil Engineers, Reston, Virginia 20,191, USA. These seven books are: (1) Flood Risk Assessment and Management, WIT Press, 2012; (2) Groundwater Assessment, Modeling, and

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Management. CRC Press, Taylor & Francis Group, 2016; (3) Natural Decadal Climate Variability: Societal Impacts. CRC Press, Taylor & Francis Group, 2017; (4) Sustainable Water Management and Technologies: Volume I, Sustainable Water Management; Volume II, Sustainable Water Technologies; CRC Press, Taylor & Francis Group, 2017; (5) Underground Aqueducts Handbook. CRC Press, Taylor & Francis Group, 2017; (6) Urban Storm Water Management, Second Edition, CRC Press, Taylor & Francis Group, 2016; and (7) Water Engineering with the Spreadsheet, ASCE Press, 2016. All seven reviewed books are in the professional areas of natural resources, management, treatment, and resources recovery. In each book review, the authors introduce the publisher, authors, editors, and previous old editions of the book, if they exist. Each book is reviewed and discussed in terms of its technical coverage, professional level, area of applications, affordability to readers, advantages, disadvantages, suitability for international distribution, recommended readership, possible improvements, etc.

Keywords Book review · WIT Press · CRC Press · ASCE Press · Lenox Institute of Water Technology · Flood · Risk assessment · Risk management · Groundwater assessment · Modeling · Groundwater management · Natural decadal climate variability · Societal impacts · Sustainable water management · Sustainability technologies · Sustainable water technologies · Underground aqueducts · Urban storm water management · Water engineering · Spreadsheet

Abbreviations

ASCE	American Society of Civil Engineers
CRCES	Center for Research on the Changing Earth System
DCV	Decadal climate variability
FE	Fundamentals of engineering
GIS	Geographical information systems
LIWT	Lenox Institute of Water Technology
PE	Professional engineering
RMP	Risk management plan
WIT	Wessex Institute of Technology

1 Flood Risk Assessment and Management. S. Mambretti (editor). (2012). WIT Press, Ashurst, Southampton, SO40 7AA, UK (Headquarters), Billerica, MA 01821, USA (North American Office). 137 pp., ISBN: 978-1-84564-646-2

WIT Press is a book publisher of the Wessex Institute of Technology (WIT), which publishes high-end scientific books and journals, available both electronically and in print. With over 30 years of experience in science and technology publishing, WIT Press produces a series of books enabling researchers, engineers, scientists, graduate students, and managers within industry to remain up-to-date with the latest developments in the field of safety and security engineering.

Since one-third of the annual natural disasters and economic losses, and more than half of the respective victims and flood-related, this book is devoted to flood control engineering, being the first book in the Safety and Security Engineering series. The book contains selected technical papers presented at the Conferences organized by the WIT.

Editor S. Mambretti (Politecnico di Milano, Italy) is an experienced scholar who has published many other related books in the field of environmental engineering, such as *Urban Water* (2012), *Landsides* (2012), *Tsunami: From Fundamentals to Damage Mitigation* (2013), *Water Hammer Simulations* (2013), *Dam-Break Problems Solutions and Case Studies* (2009), *Urban Water II* (2014), etc.

This book has 12 chapters all written by the experienced professionals: (1) flood risk assessment; (2) mathematical models in flood management; (3) effects of topographic data resolution and spatial model resolution on hydraulic and hydromorphological models for flood risk assessment; (4) an investigation of the relationship between perceptions of social responsibility and community resilience to flood; (5) decision-making methods for operational flood management; (6) European and Chinese integrated river basin management: experiences and perspectives; (7) advantage of using risk curves to assess flood protection measures; (8) real-time environmental information for the public and public safety organizations in case of flood events; (9) alternatives in flood protection; (10) psychological factors affecting flood coping strategies; (11) a model for simulating event scenarios and estimating expected economic losses for residential buildings; (12) flooding tendencies for the City of Ensenada, Baja, California, Mexico, 1948–2004. The technical presentation style by the different chapter authors is same and smooth throughout the entire book.

The reviewers appreciate the high quality of the technical materials in this fine book which is one of the most valuable tools for flood control engineers and managers.

Flood risk assessment focuses on the likelihood of adverse effects of floods as a basic philosophy for making environmental decisions related to flood measurements in the watershed. Making good watershed management decisions requires some science-based information presented in this book that can be evaluated and priority ranked in terms of the risks to the watershed. Modern flood risk management is affected by global population growth wealth growth, climate change predictions, and urban development. The book may be further improved by adding more technical information on the effects of these factors, individually and in various combinations, on the flood risk assessment and control.

A minor deficiency of this 2012-book is that the references are slightly outdated. The most recent references cited by the chapter authors are: 2006 (1 chapter), 2007 (1 chapter), 2008 (3 chapters), 2009 (4 chapters), 2010 (2 chapters), and 2011 (1 chapter). Editor Mambretti should have asked the chapter authors to update their chapter manuscripts all to 2011 before publishing the book.

2 Groundwater Assessment, Modeling, and Management. M. Thangarajan and Vijay P. Singh (2016). CRC Press, Taylor & Francis Group; 6000 Broken Sound Parkway NW, Suite 300, Boca Raton, FL 33487-2742, USA. www.crcpress.com; 511 pp., ISBN: 978-1-4987-4284-9

The ever-increasing water demand, global warming, and water pollution have a significant, negative impact on groundwater quantity and quality, leading to the problems of continuous groundwater depletion and contamination.

Under the leadership of two award-wining editors, M. Thangarajan (PhD in Geophysics) and Vijay P. Singh (PhD in Engineering), 14 American experts and 70 international experts have contributed to this timely engineering book mainly for water resource managers, decision makers, professors, and researchers.

In general, this new book has contributed the following in the field of water resources engineering: (1) providing an international perspective on effective groundwater assessment, modeling, and management; (2) addressing best available water resources management methods, groundwater decontamination technologies, and environmental impact analyses of climate change on groundwater availability in arid and semiarid regions; (3) describing remote sensing applications, geographical information systems (GIS), and electrical resistivity methods to delineate groundwater potential zones; (4) introducing 30 case studies and six hypothetical studies to reflect a wide range of groundwater management themes including groundwater basics/flow, resources exploration & assessment, aquifer parameterization, aquifer augmentation, water environment, and agricultural utilization; (5) introducing the inverse models, simulation optimization models, mass transport models, mapping groundwater potential models, and vertical 2-D and 3-D groundwater flow models; and (6) catering to the needs of water engineers, managers, and scientists to enhance their knowledge of both theory and theory's applications under real-life situations.

Specifically, the book is divided into six sections and 32 chapters: (1) Section I has 3 chapters discussing groundwater resources and assessment; (2) Section II has 4 chapters discussing groundwater exploration; (3) Section III has 7 chapters presenting groundwater flow modeling methods and applications; (4) Section IV has 5 chapters presenting groundwater transport modeling methods and applications; (5) Section V has 6 chapters discussing groundwater pollution and remediation; and (6) Section VI has 7 chapters covering the topics of water resources management and climate change's impact on groundwater.

The book has been written and edited very well because all chapters are uniform in presentation format/style, share the same groundwater theme, and are updated to the publication year. Each chapter is independent with its own chapter title, author(s), table of contents, text, related tables/figures, summary/conclusions, and references. It is very interesting that the same new book can be mail-ordered from India with about one-half of the publisher's cost.

It is the reviewers' conclusion that this is an outstanding reference book for practicing engineers/scientists as well as a very useful supplemental textbook for water resources engineering courses. The reviewers offer the following recommendations for further improvement when it is time to publish a second edition: (1) inclusion of each chapter author's email address and affiliation on the first page of each chapter, so the readers may contact the author directly for enhancing their academic communications; (2) inclusion of an abstract (with key words) for each chapter immediately below the chapter's table of contents; (3) inclusion of the publisher's name, publication year, editors' names, book title, etc., at the bottom of each chapter's first page because each chapter is independent and available to be downloaded online; (4) inclusion of a Nomenclature section (with dimensional units, or metric units, or a note of dimensions) for each chapter having many equations or mathematical models; and (5) inclusion of a Glossary section in any chapter whenever new methods, technologies, definitions, or laws are introduced.

3 Natural Decadal Climate Variability: Societal Impacts. Vikram M. Mehta. (2017), CRC Press/Taylor & Francis Group, Boca Raton, FL, USA. 33487-2742; 326 pp.; ISBN: 978-1-46655-4528; CAT #K15322

This is a beautiful book with 42 color and 47 black-and-white illustrations, detailed text, glossary terms, and updated references. It is one of five books in a book series entitled, *"Drought and Water Crises: Science, Technology and Management Issues",* which is managed by Series Editor Donald A. Wilhite, and published by CRC Press. Dr. Wilhite is a Professor Emeritus of Applied Climate Science at the University of Nebraska-Lincoln, and has been managing this series since 2005. The author, Dr. Vikram Mehta, earned his MS in Physics from Gujarat University, India, and his MS and PhD in Meteorology from Florida State University, USA. Dr. Mehta is the founder and the President of the Center for Research on the Changing Earth System (CRCES) which specializes in research on natural decadal climate variability (DCV), and its impacts on water, food, energy, and water-borne transportation.

This exceptionally well-written book has eight chapters covering the following important but largely overlooked academic subjects: (1) a prologue with stories of devastating droughts in the US, France, and India several centuries ago; and an introduction to water, food, water-borne transportation, natural DCV, caveats, etc.; (2) an introduction to DCV phenomena; (3) ancient observers riding decadal hydrologic cycles; (4) modern observers riding decadal hydrologic cycles; (5) worldwide river flow variability and its impacts on water-borne transportation and hydroelectricity generation; (6) land's bounty, climate-related stresses on agriculture, climate variability on agriculture, irrigation, DCV impacts on production variability in over 100 crops, DCV consistency with variability in high winds, precipitation, dryness/wetness in 10 countries; (7) ocean's bounty, ocean science, DCV impacts on fish and crustacean capture in Pacific, Atlantic, and Indian Oceans; and (8) an epilogue with stories of such droughts and wet epochs in the current decade of twenty-first century.

Dr. Mehta has adopted a scientist's way to write his memoir which summarizes his lifelong professional experience and accomplishment in climate science, and climate information applications for water resources management.

The book is useful for (1) understanding and prediction of DCV, (2) assessment and prediction of DCV impacts on regional and global water-food-energy-public health securities, and (3) development of international climate and public policy. The reviewers (LK Wang and MHS Wang) highly recommend this 5-star reference book to environmental and water resources engineers, scientists, managers, and researchers.

4 Sustainable Water Management and Technologies: Volume I, Sustainable Water Management; Volume II, Sustainable Water Technologies. Daniel H. Chen (Editor), (2017). CRC Press, Taylor & Francis Group, 6000 Broken Sound Parkway, NW, Suite 300, Boca Raton, Fl. 33487, USA. Volume I: 429 pp., ISBN 978-1-4822-1518-2. Volume II: 391 pp., ISBN 978-1-4822-1510-6

This two-volume book set, *Sustainable Water Management and Technologies,* is a part of *Green Chemistry and Chemical Engineering* book series, managed by CRC Press Series Editor Sunggyu Lee. The book set has been contributed by 40 experts for Volume I and 35 experts for Volume II, and successfully edited by Dr. Daniel H. Chen, who is an experienced chemical engineering professor of Lamar University, TX, USA.

Volume I of the book set has 15 chapters covering the sustainable water management subjects of: water quality management; water monitoring and diagnosis; sustainable monitoring of algal blooms; groundwater management of aquifer storage, recovery, and overdraft; reservoir system management; sustainable urban water management; water management for shale oil and gas development; outreach programs for awareness of water resources sustainability and adoption of best management practices; water scarcity in developing regions; perspectives on managing freshwater systems; climate change and future water supply; adapting water infrastructure to nonstationary climate changes; integration of water and energy sustainability; water, energy, and ecosystem sustainability; and optimum, sustainable, and integrated water management.

Volume II of the book set has 12 chapters covering the sustainable water technology subjects of: water transport; groundwater contaminant transport mechanisms; groundwater protection and remediation; GIS, GPS, and satellite data; nanotechnology applications; industrial water usage and wastewater treatment/reuse; wastewater treatment, reuse and disposal; wastewater treatment and disposal for unconventional oil and gas development; membrane technology for water purification and desalination; biotechnology for water sustainability; biodegradation-bioremediation for soil and water; and sustainable manufacturing and water sustainability.

Both Volumes I and II discuss the current most pressing issues of water, energy, and climate interactions and are very uniform in chapter format, style, and length. Each chapter includes the chapter title, author(s), table of contents, text, and a list of useful references. Most of the chapter authors adopt both the US customary units and the metric units for international academic references.

Overall, this two-volume book set is an excellent technical reference for civil, environmental, chemical, and water resources engineers/managers/scientists/professors. The book set meets Editor Daniel H. Chen's expectation for educating young science and engineering students the basics of water technology and management and in turn developing the aspiration and skill set to contribute to an optimized solution of water sustainability.

Even the best-seller books will have room for further improvements. The following are simply some reviewers' humble recommendations for possible consideration by the publisher (CRC Press) and the editors (Daniel H. Chen and Sunggyu Lee) when the excellent book set is ready to have its new edition:

(1) Practical design examples be added to some chapters that have many design equations, so these design equations may be easily understood by the intended young readers; (2) A Nomenclature section (including both the US customary units and international metric units) be added to some chapters that have many theoretical and design equations; (3) A Glossary section be added to some chapters that introduce new sustainability theories, technologies, and/or managerial skills; (4) An Abstract (including appropriate keywords) be added to each chapter immediately after the chapter Contents because each chapter is an independent publication; (5) The authors' affiliations and email addresses be added on the first pages of all chapters, so the readers may contact the authors directly for academic discussions and/or

possible collaborations; (6) The book title, book editor's name, chapter page range, publisher's name/address, publication year, etc., be printed at the bottom of each chapter's first page, because each chapter is an independent publication. With this important information, each chapter can be marketed by the publisher separately, and purchased/downloaded by the readers from the Internet individually. A reader may also properly quote the chapter as his/her reference in another publication; and (7) Current water sustainability regulatory requirements, professional association's certification program, case histories of water treatment plants, wastewater treatment plants, industrial plants, resources recovery facilities, Leadership in Energy and Environmental Design (LEED), etc., be included in the new edition.

5 Underground Aqueducts Handbook. Andreas N. Angelakis, Eustathios D. Chiotis, Saeid Eslamian, and Herbert Weingartner (2017). CRC Press, Taylor & Francis Group; 6000 Broken Sound Parkway NW, Suite 300, Boca Raton, FL 33487-2742, USA. www.crcpress.com; 522 pp., ISBN: 978-1-4987-4830-8

International collaboration for detailed introduction of various underground hydraulic works around the world has been successfully done and documented in this water resources engineering book. Editors AN Angelakes, Chiotis, S Eslamian, and H Weingartner are famous water resources experts in Greece, Greece, Iran, and Austria, respectively. Sixty-six contributors from nine disciplines (archaeology, hydrology, history, engineering, life sciences, public health, environment, biology, and geotechnology), four continents (Europe, Africa, Asia, and Americas), and 26 countries have collaborated together on this academic contribution.

This 2017 new handbook focuses on the technological development and management practices related to worldwide underground aqueduct technologies throughout the millennia. After a comparison of the water technological developments in several civilizations has been made and discussed, the future trends and technology advancement are predicted. Entire handbook is divided into eight sections and 29 chapters. Although all chapters share the same central theme "underground aqueducts", each chapter is independent consisting of chapter title, chapter author(s), table of contents, text, discussion, conclusions/summary, and updated references. Many useful and modern photos, maps, flow diagrams, and system design drawings are inserted in the text for detailed illustration. Only international metric units are adopted throughout the entire handbook.

The contents of this handbook are impressive. Section I introduces and concludes various types and definitions of underground aqueducts. Underground aqueduct history is reviewed, and its selection and classification scheme are proposed.

Section II has four chapters covering mainly the following topics in Europe: Roman underground hydraulic structures in Croatia; Roman underground aqueducts in Germany; updated appraisal of ancient underground aqueducts in Greece; and the aqueduct of Eupalinos on Samos, Greece and its restoration.

Section III has three chapters covering some topics in Africa: the past and present of underground aqueducts in Algeria; the water supply history of underground aqueducts in Egypt; and qanat evolution and use in Libya.

Section IV has nine chapters covering many topics in Middle East: an ancient and sustainable water resources utilization in Iran; spring tunnels in Israel: the Jerusalem Hills perspective; an underground Roman water system in Syria and Jordan; the aqueducts of the Sultanate of Oman and sustainable water-supplying system irrigating Oases cities; aqueducts in Saudi Arabia; qanats of Syria; groundwater structures throughout Turkish history; history and factors affecting recharge, discharge, and water quality in the United Arab Emirates; and polycentric and multi-period innovation case studies in Iran and the United Arab Emirates.

Section V has three chapters covering ancient and historical topics in Eurasia: ancient aqueducts and the irrigation system in Armenia; evolution of the qanat systems in the arid countries of the Caucasus and Central Asia; and ancient water mining in tunnels and wells in West Central Asia.

Section VI has six chapters covering several Asian topics: underground aqueducts in Japan; managing drought through qanat and water conservation in Afghanistan; utilization and contribution of underground aqueducts in the Turpan Oasis of China; traditional methods of groundwater abstraction and recharge along the windward side of the foothills of the Western Ghats of India; historical development of qanats and underground aqueducts in Pakistan; and underground aqueduct and water tunneling development in Thailand.

Section VII has two chapters briefly covering the topics in Americas: puquios and aqueducts in the Central Andes of South America; and the ancient hydraulic catchment systems of the Tepeaca-Acatzingo archaeological zone in Puebla, Mexico. Finally, Section VIII with one chapter concludes the past, present, and future trends of underground aqueducts. The book emphasizes that the future trends of underground aqueducts should consider the possibility and practicality of integrating older, proven technologies into modern infrastructure.

Overall, this is a very unique engineering book introducing the underground aqueduct technologies and practices which are not widely known among civil, environmental, and water resources engineers. It does help address the current issues of groundwater sustainability, construction cost-effectiveness, environment adaption, water resources management, water supply system decentralization or centralization. It also helps engineers understand the underground aqueduct-related history, hydrology, geotechnology, and environmental sciences.

The reviewers highly recommend this handbook to practicing civil, environmental, and water resources engineers, government managers/planners, and university professors/researchers. The reviewers further suggest that the big underground aqueduct systems in the USA (such as the City of New York system, the City of Boston system, etc.) be introduced, analyzed, and discussed in the new edition of this book due to their engineering significance, and due to the fact that CRC Press is an American book company.

6 Urban Storm Water Management, Second Edition, Hormoz Pazwash (2016) CRC Press, Taylor & Francis Group, Boca Raton, FL 33487, USA. 684 pp., ISBN: 978-1-4822-9895-6

An older edition with identical book title (978-1-4398-1035-4) was published in 2011. The timing for publishing this second edition (978-1-4822-9895-6) in 2016 is very appropriate.

Dr. Pazwash, the author of both editions, is a municipal engineer as well as a professor. He has been involved in the field of storm water management since 1985. His extensive experience has included practical design of over one hundred of drainage and storm water management systems. He has summarized his lifelong experience in this very concise book. Since the book contains many case studies that illustrate methods and procedures for designing detention basins, infiltration basins, and underground retention/infiltration basins, it is an excellent reference book for guiding practicing engineers and planners in designing such storm water management elements. Since there are numerous engineering examples in the book to provide detailed hydrologic and hydraulic calculations for storm water system design and management, it may also serve as a very good water engineering textbook for university/college students.

The book has 10 chapters. Specific coverage of this book includes urbanization impact on runoff; pipe and open-channel flows; hydrologic calculations; storm drainage systems design; storm water management regulations; manufactured water treatment devices; structural storm water management systems; new trends in storm water management; hydraulic structure installation, inspection, and maintenance; storm water management systems; storm water conservation; and water reuse. Also included in the book are useful glossary terms and some technical information on the unified soil-classification system and nominal sizes of coarse and fine aggregates.

Although the chapter numbers and the chapter titles of the two editions are almost identical, there are many new elements in this second edition: (1) it provides an updated presentation of urbanization's impact on storm water; (2) it presents further analysis of the universal runoff model and the applications; (3) it offers a more detailed presentation of storm water management systems; (4) it includes a comparative analysis of the effectiveness and costs of best management practices; (5) it adds more than twice as many problems as before; and (6) it contains an in-depth discussion of the means of collecting storm water.

Overall, this is one of the best books in the field of civil and water resources engineering. The reviewers highly recommend this book to all water engineers, planners, and professors.

7 Water Engineering with the Spreadsheet. Ashok Pandit (2016). ASCE Press, American Society of Civil Engineers, 1801 Alexander Bell Drive, Reston, Virginia 20191, USA. 214 pp., ISBN: 978-0-7844-1404-0

This is one of the ASCE Press books helping civil engineering students use spreadsheets for various engineering calculations. ASCE is commended for publishing these books with spreadsheets for serving its members and general professional readers.

Dr. Pandit, the author, is currently head of the civil engineering department at the Florida Institute of Technology. He has 30+ years of professional experience in the areas of fluid mechanics, hydraulics, hydrology, groundwater modeling, and storm water drainage and management, and has been employing spreadsheets in the classroom and in practice for more than 20 years. The book is intended for use as a supplement to undergraduate and graduate texts and lectures. The print edition of this book contains a CD-ROM with unlocked Excel files. The e-book edition is accompanied by a downloadable ZIP file for the Excel files. Microsoft Excel software is not included. Only Microsoft Excel 2003 or above can be used. It is important to note that the book contains only the spreadsheets for organized water engineering calculations, but does not contain any computer programs for rapid calculations.

The book contains four chapters which are (1) fluid mechanics: force calculations under static and dynamic conditions, and flow in pressure pipes; (2) hydraulics: open channel flow, gradually varying flows, rapidly varying flows, and open channel design; (3) hydrology: lake evaporation, direct runoff hydrographs, and reservoir and channel routing; and (4) storm water management: system components for land development, and system design for land development.

Both students and professionals may find the book useful for the following reasons: (1) it provides a large spectrum of examples, from easy to difficult, to explain key fundamentals, analyses, and water engineering design; updated presentation of urbanization's impact on storm water; (2) its examples are solved with the help of spreadsheets; (3) it provides background information before each section to discuss the theory and equations covered in the examples; (4) it provides background information within each problem to emphasize some key points regarding the example; (5) it provides key assumptions, where needed, within each example; (6) it provides key equations to solve the problem when needed; (7) it provides a solution procedure within each example; (8) it provides the "what-if" analysis associated with every problem; (9) it adopts the trial-and-error solution procedures when necessary and such solution procedures are iterative by nature; (10) it uses the trendline equations to avoid the tedious task of interpolation while maintaining accuracy; and (11) it provides "assigned problems" to let readers create their own new spreadsheets.

Overall, this book is an excellent "supplemental"water engineering textbook for students, or a preparation tool for engineers to take the fundamentals of engineering (FE) and professional engineering (PE) examinations, if it is used correctly.

However, it is not a university/college's "main" water engineering textbook covering the subjects of fluid mechanics, hydraulics, hydrology, or storm water management. Since the book is entitled "Water Engineering with the Spreadsheet", and intended for both the US and worldwide distributions, its future edition may be improved by: (1) expansion of the book to include other important water engineering subjects, such as water distribution and drinking water treatment; and (2) adoption of both the US customary units and the metric units, side-by-side throughout the entire book.

Glossary [1–15]

Above ground aqueduct It is a conduit, at or above ground level, usually of considerable size and open to the air, used to convey water or other liquid by gravity flow.

Flood It is a relatively high water flow as measured by either gauge height or discharge quantity, or any water flow equal to or greater than a designated basic water flow.

Groundwater It is the water contained in interconnected pores located either below the land's water table in an unconfined aquifer or in a confined aquifer.

Modeling It is an act of developing a mathematical or physical representation of a real-world system, in order to study and understand the behavior of that system.

Natural resources They include all natural products, energy, forces, lights, biological lives, of the universe that support life and satisfy people's needs. Air, land, and water are natural resources, as are biological and physical resources in the air, on the land and in the water, such as solar heat, rains, birds, bees, flowers, bacteria, wild animals, and fish, as well as minerals, oil, coal, metals, stone, sand, lights, winds, magnetic forces, radioactivity, even elements, DNA, etc.

Nonrenewable or unsustainable natural resources They are natural resources that are not renewable, such as mineral and fossil fuels. Some renewable resources may become nonrenewable if they are destroyed or lost by bad resource management, e.g. farmland losing topsoil or denuding of watersheds.

Renewable or sustainable natural resources They are natural resources that are renewable, such as solar, wind, tidal energy, farmland, forests, fisheries, surface water, etc.

Risk assessment It is either a utility's assessment in the workplace of dangers or harm to employees, equipment, or both, or an individual's assessment of possible events that could lead to harm and danger or exposure to uncomfortable situations.

Risk management plan (RMP) It is a managerial plan intended to prevent and minimize the impact of accidental release of hazardous, infectious, or any other undesirable substances.

Risk management It is a managerial process of weighing policy alternatives, selecting the most appropriate regulatory action, and integrating the results of risk assessment with scientific data and related social, economic, and political concerns to reach a low-risk decision.

Storm water runoff That portion of the rainfall over a given area that finds its way to natural or artificial drainage channels.

Storm water It is water that is collected as runoff from a rainfall event.

Underground aqueduct It is a conduit, below ground level, usually of considerable size and not open to the air, used to convey water or other liquid by gravity flow.

Water engineering It is an academic branch of engineering that studies, researches, or implements, or builds anything involving water.

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Chapter 12
Glossary of Water Quality, Treatment, and Recovery

Mu-Hao Sung Wang and Lawrence K. Wang

Contents

Abstract Technical and legal terms commonly used by environmental water and wastewater engineers in the professional areas of environmental STEAM (science, technology, engineering, arts, and mathematics), water quality control, resources management, wastewater treatment, water purification, and resources recovery are introduced.

Keywords STEAM · Science · Technology · Engineering · Arts · Mathematics · Natural resources · Analysis · Management · Flotation · Water quality · Wastewater treatment · Water treatment · Resources recovery facilities · Glossary

Abbreviations and Acronyms

ABF	Automatic backwash filtration
ADT	Air dissolving tube
AL	Action level
APWC	Average population weighted concentration
ATP	Advanced treatment plant
BAT	Best available technology
BOD	Biochemical oxygen demand
Bq	Becquerel
COD	Chemical oxygen demand
DAF	Dissolved air flotation

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DAF-DAF	Two-stage process system consisting of one dissolved air flotation (DAF) and another dissolved air flotation (DAF) connected in series
DAF-DAFF	Two-stage process system consisting of one dissolved air flotation clarifier (DAF) and a dissolved air flotation–filtration clarifier (DAFF) connected in series
DBP	Disinfection by-products
DE	Diatomaceous earth
DO	Dissolved oxygen
EC	Electrical conductivity
GAC	Granular activated carbon
GLP	Good laboratory practices
GV	Guideline value
HAA5	Haloacetic acids; the sum of the concentrations in milligrams per liter of five haloacetic acid compounds (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid)
HPC	Heterotrophic plate count
IAF	Induced air flotation
IE	Industrial ecology
IGF	Induced gas flotation
IPCWWTS	Independent physicochemical wastewater treatment system
KAMET	Krofta Advanced Municipal Effluent Treatment, which is a circular package plant consisting of both Supracell and Sandfloat with Supracell on the top. KAMET can be used for either water treatment or wastewater treatment, but is advertised for wastewater treatment
KAMWT	Krofta Advanced Municipal Water Treatment
KEC	Krofta Engineering Corporation
LIWT	Lenox Institute of Water Technology
MAL	Maximum allowable limit (MAL) of Mexico
MCL	Maximum contaminant level
MCLG	Maximum contaminant level goal
MF	Microfiltration
MRDL	Maximum residual disinfectant level
MRDLG	Maximum residual disinfectant level goal
NF	Nanofiltration
NH_3	Free ammonia
NOM	Natural organic matter
NPDWR	National Primary Drinking Water Regulations
NSDWR	National Secondary Drinking Water Regulations
ORSG	Office of Research and Standards Guideline
PAC	Powdered activated carbons
PC	Physicochemical process
PRT	Pressure retention tank
PWS	Public water systems
QA	Quality assurance

R&D	Research and development
RAA	Running annual average
RMP	Risk management plan
RO	Reverse osmosis
Sandfloat	Dissolved air flotation–filtration clarifier manufactured by Krofta Engineering Corporation and its related companies
SMCL	Secondary maximum contaminant level
STEAM	Science, technology, engineering, arts, and mathematics
STEM	Science, technology, engineering, and mathematics
Supracell	Dissolved air flotation clarifier manufactured by Krofta Engineering Corporation and its related companies
TDS	Total dissolved solids
TOC	Total organic carbon
TS	Total solids
TSS	Total suspended solids
TT	Treatment technique
TTHM	Total trihalomathanes
TTHMFP	Total trihalomathanes formation potential
TVSS	Total volatile suspended solids
UF	Ultrafiltration
USEPA	US Environmental Protection Agency
UV	Ultraviolet
VOC	Volatile organic compounds
WHO	World Health Organization
WL	Working level

Glossary of Water Quality, Treatment, and Recovery [1–15]

90th percentile level It means that out of 10 sites sampled, 9 out of 10 were at or below this level. This number is compared to the action level to determine lead and copper compliance and many others.

Above ground aqueduct It is a conduit, at or above ground level, usually of considerable size and open to the air, used to convey water or other liquid by gravity flow.

Absolute A degree of filtration or other process that guarantees 100% removal of suspended solids over a specified particle size.

Absolute method A body of procedures and techniques for which measurement is based entirely on physically defined, fundamental quantities.

Absorb To take up a liquid, like a sponge takes up water.

Accuracy The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. US Environmental Protection Agency

(USEPA) recommends that this term not be used and that precision and bias be used to convey the information usually associated with accuracy.

Acid Any substance capable of giving up a proton; a substance that ionizes in solution to give the positive ion of the solvent; a solution with a pH measurement less than 7.

Acidity The quantitative capacity of aqueous solutions to react with hydroxyl ions. It is measured by titration with a standard solution of base to a specified end point.

Action level (AL) The concentration of a contaminant which, if exceeded, triggers water treatment or other requirements which a water system must follow.

Activated alumina A charged form of aluminum substance which is commonly used in combination with a synthetic, porous media in an ion exchange process, for removing charged impurities (such as fluoride) from water.

Activated carbon (a) An adsorbent carbon which removes dissolved color, odor, taste, metals, etc., from liquids or gases; (b) a carbon activated by high temperature steam or carbon dioxide to form a material of high adsorptive capacity.

Activated clay An adsorbent clay that removes color, odor, free fatty acids, etc., from oils and tallows.

Admix A substance that is added directly into the batch tank of prefilt to create a permeable filter cake. Usually used in place of body feed.

Adsorb (a) The act of selectively attracting and holding a gas, vapor, liquid or colloid onto the surface of a solid; (b) The act of selectively attracting and holding surface active substances onto the surface of a gas bubble.

Adsorbate The materials, such as color bodies, taste and odor compounds, volatile organic compounds, soluble lead, etc., which are adsorbed on the surface of an adsorbent (activated carbon or polymeric adsorbent).

Adsorbent A solid material which adsorbs such as clay, carbon, polymeric adsorbent.

Adsorption It is a chemical reaction or a physical-chemical that the attraction and adhesion of molecules of a gas, liquid, or dissolved substances to a surface. Adsorption is a passive and reversible reaction or process.

Adsorption-destabilization It is chemical mechanism for the coagulation of particles in which counterions are adsorbed on the surface of stable particles; thus, the particles can approach one another close enough to stick together and lose their stability in water.

Adsorption flotation The powdered activated carbons (PAC) may be dosed into a dissolved air flotation system for taste and odor control and/or toxic substances removal. A flotation process involving the use of PAC is adsorption flotation.

Adsorptive bubble separation Any water, wastewater, or sludge treatment system that involves the use of gas bubbles for water–solids separation.

Advanced oxidation process A disinfection and oxidation process that involves the use of (a) ozone plus hydrogen peroxide; (b) ozone plus UV; (c) hydrogen peroxide plus UV; (d) calcium peroxide plus UV; (e) magnesium peroxide plus UV; (f) potassium permanganate plus UV; and (g) any other strong oxidizing agent (such as chlorine, chlorine dioxide, etc.) plus UV, or another oxidation agent.

Advanced treatment plant (ATP) (a) A treatment facility using treatment processes that provide treatment to a higher level than that considered conventional; (b) an advanced water treatment plant may include processes such as granular activated carbon adsorption, ion exchange, ozonation, etc., in addition to a conventional surface water treatment plant consisting of mixing, coagulation/precipitation, flocculation, clarification (either sedimentation or flotation), and filtration; (c) an advanced wastewater treatment plant may include processes such as tertiary filtration, denitrification, granular activated carbon adsorption, ion exchange, ozonation, advanced oxidation process, post-aeration, etc., in addition to a conventional biological wastewater treatment consisting of preliminary treatment, primary clarification (sedimentation or flotation), biological oxidation, and secondary clarification (sedimentation or flotation).

Air dissolving tube (ADT) or pressure retention tank (PRT) It is a metal tank in which the water flow and compressed air are mixed and held under high pressure for several minutes to allow sufficient time for dissolving air into water.

Algae They are organisms containing chlorophyll. They are frequently found in surface waters exposed to sunlight and during the summer months. They become so numerous as to produce “blooms” which appear to completely cover whole sections of a reservoir or lake. Under the influence of sunlight chlorophyll enables the organism to combine water and carbon dioxide to form complex chemicals and produce oxygen as a by-product. Although the production of oxygen by the photosynthesis process is beneficial in that it promotes oxidation of organic debris, supports life, algae are the chief cause of bad tastes and odors in a water supply. Algae are normally controlled at the raw water source, such as a lake or reservoir using an algacide.

Aliquot A subsample derived by a divisor that divides a sample into a number of equal parts and leaves no remainder; a subsample resulting from such a division. In analytical chemistry the term aliquot is generally used to define any representative portion of the sample.

Alkalinity The capacity of water to neutralize acids, a property imparted by the water’s content of carbonate, bicarbonate, hydroxide, and on occasion borate, silicate, and phosphate. It is expressed in milligrams per liter of equivalent calcium carbonate (mg/L $CaCO_3$).

Alkalinity and pH Alkalinity is a normal characteristic of natural waters. It provides buffering capacity to water for maintaining an optimum pH, and also is needed in chemical precipitation and coagulation process for water treatment. Alkalinity is imparted to water by bicarbonate, carbonate, or hydroxide components. The presence of these compounds is determined by standard methods involving titration with various indicator solutions. Knowledge of the alkalinity components is useful in the treatment of water supplies. pH is a measure of the hydrogen ion concentration in water. It is also a measure of the acid or alkaline content. pH values range from 0 to 14, where 7 indicates neutral water; values less than 7, increasing acidity; and values greater than 7, increasing alkalinity. The pH of water in its natural state often varies from 5.5 to 9.0. Determination of the pH value assists in the control of corrosion, the determination of proper chemical dosages, and adequate control of disinfection. pH of the drinking water should be maintained within the range from 6.5 to 8.5. For healthy fresh water aquatic habitat, the desirable bicarbonate alkalinity ranges from 30 to 135 mg/L. Legally the recommended pH range is 6.5–8.5 in the USA and Canada, and the required pH range is 6.5–8.5 in Mexico.

Ammonia stripping It is a physicochemical desorption process for removing ammonia content from a wastewater by a gas stripping operation. In the process, wastewater at elevated pH is pumped to the top of a packed tower with a countercurrent flow of air drawn through the bottom openings.

Amorphous Noncrystalline. Having no ordered molecular structure of its own.

Analysis (chemical) The determination of the qualitative and/or quantitative composition of a substance.

Analyte The substance, a property of which is to be measured by chemical analysis.

Analytical batch A group of samples, including quality control samples, which are processed together using the same method, the same lots of reagents, and at the same time or in continuous, sequential time periods. Samples in each batch should be of similar composition and share common internal quality control standards.

Analytical reagent (AR) The American Chemical Society's designation for the highest purity of certain chemical reagents and solvents.

Anhydrous A term meaning without water.

Anion exchange An ion exchange process involving the use of anion exchanger (anionic ion exchange resin), mainly for removal of negatively charged ions, such as sulfate, phosphate, chloride, etc., from water.

Anions Substances that are negatively charged, such as chlorides, fluorides, nitrates, nitrites, sulfates, phosphates, etc.

AquaDAF It is a rectangular dissolved air flotation (DAF) clarifier commercially available from SUEZ Water Technologies and Solutions, Richmond, VA 23229, USA.

Area, filter The surface available in a filter for the passage of liquid and formation of a filter cake. Usually measured in square feet.

Arsenic (As) (a) It is an element with an atomic weight of 74.9216; (b) it is a toxic substance which occurs naturally and is also used in insecticides. It is found in tobacco, shellfish, drinking water, and in the air in some locations. The maximum allowable concentrations of arsenic in drinking water by the standards are: 0.01 mg/L (WHO, USA, and Canada) and 0.05 mg/L (Mexico). If persons drink water that continuously exceeds the standard by a substantial amount over an extended period of time, they may suffer from fatigue and loss of energy. Extremely high levels can cause toxicity.

Asbestos Asbestos is an airborne contaminant, and also a waterborne contaminant, regulated by many State governments in the USA. The health effect of asbestos in water, however, is not totally known. According to the U.S. Primary Drinking Water Standards, the maximum contaminant level (MCL) of asbestos in drinking water is seven million fibers per liter (MF/L).

Atm. Atmosphere. A measurement of pressure. The air pressure at sea level: 14.7 psi.

Attrition Breaking down or wearing away by friction. Usually as particle to particle degradation in a diatomite slurry.

Automatic backwash filtration (ABF) An automatic filtration system that its filter bed is divided into multiple identical cells for continuous filtration and backwash without shutdowns. A traveling bridge with a hood moves to the top of one filter cell when it is due for backwash. The hood which is identical to the filter cell in shape can move up when the backwash is not needed, or move down to cover the filter cell for backwash, one cell at a time. An ABF can be a single medium filter, such as sand filter, or GAC filter, or a dual-media filter, such as anthracite over sand bed. The shape of ABF can be circular or rectangular. When the backwash hood covers one filtration section for automatic backwash (controlled by a timer), the rest filtration sections are in filtration mode. One filtration section is backwashed at a time, until all filtration sections are backwashed and restored to filtration mode again.

Average population weighted concentration (APWC) A value representing the occurrence of natural radionuclides in drinking water supplies (average of surface water and groundwater supplies) which can be calculated by the equation of: $\text{APWC} = C\ (P_{\text{exp}}/P_{\text{total}})$, where APWC is the population weighted average, pCi/L; C is the radioactivity concentration, pCi/L; P_{exp} is the number of people exposed to that concentration, #; and P_{total} is the total number of people, #.

Background level (environmental) The concentration of substance in a defined control area during a fixed period of time before, during, or after a data gathering operation.

Backwash The process of reversing the flow of water back through the filter media to remove the entrapped solids.

Backwash, filter A reverse flow of liquid to remove solids from the filter.

Bacteria The principal bacterial waterborne diseases of the middle latitudes, typhoid fever and cholera, are two highly specific infections that exacted their awful toll of sickness and death in the cities emerging from the industrial revolution. *Paratyphoid (salmonellosis)* and *bacillary dysentery (shigellosis)* as well as *hemorrhagic jaundice (leptospirosis)* are waterborne diseases in a less direct sense.

Baffle, precoat filter A plate or deflector to provide flow distribution in a filter. Primary functions are to prevent erosion of precoat and setting of body feed in the filter tank.

Barium (Ba) (a) It is an element with an atomic weight of 137.327; (b) barium is a heavy metal which occurs naturally in the environment in some areas. It can also enter water supplies through hazardous industrial waste discharges or releases. Small doses of barium are not harmful. However, it is quite dangerous when consumed in large quantities. The maximum allowable concentrations of barium in drinking water by the standards are: 2 mg/L (USA), 1 mg/L (Canada), and 0.7 mg/L (WHO and Mexico).

Bar screens There are two types of bar screens (or racks). The most commonly used, and oldest technology, consists of hand-cleaned bar racks. These are generally used in smaller wastewater treatment plants (WWP). The second type of bar screen is the type that is mechanically cleaned, which is commonly used in larger facilities.

Base Any substance which contains hydroxyl (OH) groups and furnishes hydroxide ions in solution; a molecular or ionic substance capable of combining with a proton to form a new substance; a substance that provides a pair of electrons for a covalent bond with an acid; a solution with a pH of greater than 7.

Batch A quantity of material produced or processed in one operation, considered to be a uniform discrete unit.

Batch-flow sedimentation One or more basins sized to receive a volume of flow, such as spent filter backwash water, in a specific period of time. The flow is detained for a specific period of time to allow sedimentation, and then the tank is emptied.

Becquerel (Bq) An international unit of radioactivity representing the rate at which nuclear radiations are emitted. The Becquerel is the activity of a radionuclide decaying at the rate of one disintegration (one spontaneous nuclear transition) per second.

Best available technology (BAT) The best technology, treatment techniques, or other means which the U.S. EPA Administrator finds, after examination for efficacy under field conditions and not solely under laboratory conditions, are available (taking cost into consideration).

Biochemical Refers to chemical processes that occur inside or are mediated by living organisms.

Biochemical oxygen demand (BOD) (a) The amount of oxygen, measured in milligrams per liter, that is removed from aquatic environments by the life processes of microorganisms; (b) The BOD test measures the oxygen utilized during a specified incubation period for the biochemical degradation of organic material, and the oxygen used to oxidize inorganic materials, such as sulfides and ferrous iron.

Biological flotation In a biological flotation system, fermentations take place in the presence of anaerobic bacteria, nitrates and substrates under anaerobic environment, anaerobic bacteria in waste sludge convert nitrate and the substrate with carbon source (such as methanol or residual BOD) to nitrite, water and carbon dioxide fine bubbles. Nitrite further reacts with a substrate (such as methanol or residual BOD) in the same waste sludge, producing fine nitrogen bubbles, more fine carbon dioxide bubbles, water and hydroxide ions. The biological waste sludge, such as activated sludge, can then be floated to the surface by the fine nitrogen and carbon dioxide bubbles and be thickened (i.e., concentrated). The thickened sludge which are the final products of the biological flotation thickening process are skimmed or scooped off from the liquid sludge surface, while the subnatant clarified water is discharged from the biological flotation thickener's bottom. The energy consumption of this process is low. Its detention time is long. More research is needed for this newly developed sludge thickening process.

Blank sample A clean sample or a sample of matrix processed so as to measure artifacts in the measurement (sampling and analysis) process.

Blinding, filter Plugging or sealing of any portion of a filter septum by solids that are not removed during the normal cleaning cycle.

Blind spots Any place on a filter septum where liquid cannot flow through due to blinding.

Blowdown, filter cake The use of air or inert gas pressure to displace a liquid out of a filter. Usually through the filter cake. Continued blowdown is used to dry a filter cake in situ.

Body feed, precoat filter A filter aid product, such as CELITE that is continuously added to the filter while it is on-stream. Its purpose is to create a permeable filter cake.

Breakthrough A condition whereby filter effluent water quality deteriorates (as measured by an increase in turbidity, particle count, or other contaminant). This may occur due to excessive filter run time or hydraulic surge.

Bridging, precoat filter (a) The act of particles forming an arch over the openings on a septum; and (b) filter cakes that have grown to a size where they actually touch each other in the filter.

Cadmium (Cd) (a) It is an element with an atomic weight of 112.411; (b) it is a heavy metal frequently found in the natural waters and the hazardous waste discharges from the electroplating, photography, insecticide, and metallurgy industries. A common source of cadmium in drinking water is from galvanized pipes and fixtures if the pH of a water supply is not properly controlled. The sources of cadmium exposure are the foods we eat and cigarette smoking. The maximum allowable concentrations of cadmium in drinking water by the standards are: 0.005 mg/L (USA, Canada, and Mexico) and 0.003 mg/L (WHO).

Cake, filter The accumulation of solids (and the filter aid, such as CELITE) on the surface of a precoat or septum.

Cake space, precoat filter The volumetric space available in a filter to support the formation of a cake.

Calibrate To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device, or the correct value for each setting of a control knob. The levels of the calibration standards should bracket the range of planned measurements.

Calibration The checking, adjusting, or systematic standardizing of the graduations of a quantitative measuring instrument.

Calibration curve The graphical relationship between the known values for a series of calibration standards and instrument responses.

Calibration standard A substance or reference material used to calibrate an instrument.

Candidate method A body of procedures and techniques of sample collection and/or analysis that is submitted for approval as a reference method, an equivalent method, or an alternative method.

Cartridge filtration A filtration process that has a pressure vessel containing one or more filter cartridges of a specified nominal (or absolute) pore size rating used for removal of particles from water.

Catenary grid aeration A unit process designed to transfer impurities (such as volatile organic compounds, color, taste, and odor-causing substances) from the liquid phase to the gaseous phase, or to provide air (oxygen) to the liquid for oxidation. The process equipment consists of multiple, porous catenary grids in a column. There are fluidized zones between the catenary grids. Inside of the process unit, the forced air flows upward through the centenary grids, but the liquid to be treated flows downward through the catenary grids and fluidized zones forming mists. The countercurrent flow mechanism promotes the mass transfer and/or oxidation.

Cathodic protection A corrosion control method that involves reduction or elimination of corrosion by making the metal a cathode by means of an impressed direct current or attachment to a sacrificial anode (such as magnesium, aluminum, zinc, etc.).

Cation exchange An ion exchange process involving the use of cation exchanger (cationic ion exchange resin), mainly for removal of calcium, magnesium, iron, and other positively charged metal ions.

Caustic Capable of destroying or eating away by chemical action; a hydroxide of a light metal.

Caustic soda Sodium hydroxide, NaOH.

CELITE Manville's registered trade name for its line of diatomaceous earth filter aids and fillers.

Cellulose A fibrous material of vegetable origin.

Centrate Water separated from the solids by a centrifuge.

Check sample An uncontaminated sample matrix spiked with known amounts of analytes usually from the same source as the calibration standards. It is generally used to establish the stability of the analytical system but may also be used to assess the performance of all or a portion of the measurement system.

Check standard A substance or reference material obtained from a source independent from the source of the calibration standard; used to prepare check samples.

Chemical It is substance produced or used in a chemical reaction.

Chemical analysis The use of a standard chemical analytical procedures to determine the concentration of a specific analyte in a sample, or qualitatively or quantitatively measure a specific parameter of a sample.

Chemical coagulation It is a chemical reaction or unit process in which colloidal and finely divided suspended matter are destabilized and aggregated together due to addition of inorganic coagulant or polyelectrolyte.

Chemical oxygen demand (COD) The amount of oxygen, measured in milligrams per liter, that is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant.

Chemical precipitation (a) A chemical process in which one chemical agent precipitates another soluble chemical; (b) it is a chemical reaction or unit process in which insoluble solids are generated from the soluble matters by changing the equilibrium conditions of a solution, or by adding chemicals that react with the soluble matters.

Chloramination A disinfection process that involves the mixing of chlorine and ammonia for production of mainly monochloramine and a small amount of dichloramine, in turn, for disinfection of water storage tank and distribution system.

Chlorides (Cl^-) Most waters contain some chloride ions. The amount of chloride present can be caused by the leaching of marine sedimentary deposits, by pollution from sea water, brine, or wastewaters. Chloride concentrations in excess of about 250 mg/L usually produce a noticeable taste in drinking water. In areas where the chloride content is higher than 250 mg/L and all other criteria are met, it may be necessary to use a water source that exceeds this limit. An increase in chloride content in water may indicate possible pollution from waste sources, particularly if the normal chloride content is known to be low. Accordingly 250 mg/L is the maximum allowable limit in Mexico, and also the recommended limit in the USA and Canada.

Chlorination A disinfection or oxidation process involving the use of chlorine.

Chlorine (Cl_2) A disinfectant and oxidizing agent widely used in chlorination/oxidation process for water and wastewater treatment.

Chlorine dioxide (ClO_2) A red yellow gas that is a very strong oxidizing agent and disinfectant.

Chromium (Cr) (a) It is an element with an atomic weight of 51.996; (b) chromium is a heavy metal commonly released to the environment from the electroplating industry and is extremely hazardous. Some studies suggest that in minute amounts, chromium may be essential to human beings. The maximum allowable concentrations of total chromium in drinking water by the standards are: 0.05 mg/L (WHO, Mexico, and Canada) and 0.1 mg/L (USA).

Clari-DAF It is rectangular dissolved air flotation (DAF) clarifier commercially available from Xylem Water and Wastewater, Zelienople, PA 16063, USA.

Clarification It is water–solids separation process by either sedimentation (sedimentation clarification) or flotation (flotation clarification).

Clarifier, flotation A large circular or rectangular tank or basin in which water is held for a period of time, during which the air bubbles with suspended solids attached float to the top by flotation. Flotation clarifiers are also called flotation basins or dissolved air flotation basins.

Clarifier, sedimentation A large circular or rectangular tank or basin in which water is held for a period of time, during which the heavier suspended solids settle to the bottom by gravity. Sedimentation clarifiers are also called settling basins and sedimentation basins.

Clarity Clearness of a liquid as measured by a variety of methods.

Clean sample A sample of a natural or synthetic matrix containing no detectable amount of the analyte of interest and no interfering material.

Cloth, filter A type of woven filter septum made from natural or synthetic yarns.

Coagulant A chemical (alum or iron salts) added to water to destabilize particles, allowing subsequent floc formation and removal by clarification (flotation or sedimentation) and/or filtration.

Coagulation A process of destabilizing charges of suspended and colloidal particles in water by adding chemicals (coagulants). In coagulation process, positively charged chemicals are added to neutralize or destabilize these negative charges and allow the neutralized particles to accumulate and be removed by clarification (flotation or sedimentation) and/or filtration.

Coliform A group of related bacteria whose presence in drinking water may indicate contamination by disease-causing microorganisms.

Coliform bacteria Since there are several thousand species of bacteria, it is difficult to control pathogenic bacteria in drinking water individually and effectively. Coliform bacteria are naturally present in the environment. Total coliforms (including fecal coliform and *E. coli*) which cause no health threat in themselves are used to indicate whether other potentially harmful bacteria may be present in drinking water. No MCL/MAC/MAL is specified for heterotrophic plate count (HPC) bacteria in drinking water, however. Instead, increases in HPC concentrations above baseline levels are considered undesirable. Coliform bacteria are regulated by both the U.S. Environmental Protection Agency (USEPA) and the State governments—-are only indicators showing whether or not the water has been properly disinfected. For a disinfected water, a zero count of coliform bacteria indicates that the water is properly disinfected, and other microorganisms are assumed to be sterilized. The U.S. Drinking Water Standards have established limits for the mean concentration of coliform bacteria in a series of water samples and the frequency at which concentrations may exceed the mean. The results are expressed either in terms of a direct count of bacteria per unit volume—if the *membrane filter* (MF) procedure is used—or in terms of the "*most probable number*" (MPN)—if the multiple tube fermentation method is used. This latter term (MPN) is an estimate based on mathematical formulas of probability. The recommended standards for drinking water are roughly equivalent to restricting the coliform concentration to not more than one organism for each 100 milliliters of water. Application of the U.S. Drinking Water Standards to individual water supplies is difficult due to the low frequency with which samples can be properly collected and examined. Bacteriological examinations indicate the presence or absence of contamination in the collected sample only, and are indicative of quality only at the time of collection. A sample positive for coliforms is a good indication that the source may have been contaminated by surface washings or fecal material. On the other hand, a negative result cannot be considered assurance of a continuously safe supply unless the results of a thorough sanitary survey of the surrounding area, together with subsequent negative samples, support this position. In the USA, the maximum contaminant level goal (MCLG) of total coliforms in drinking water is set at "zero," but the MCL is more complicated. For water systems that collect 40 or more routine water samples per month, no more than 5% samples *total coliform-positive* (TC-positive) in a month should be detected. For water systems that collect fewer than 40 routine samples per month, no more than one sample can be TC-positive per month. Every sample that has total coliform must be analyzed for either fecal coliforms or *E. coli*. If two consecutive TC-positive samples, and one is also positive for *E. coli* fecal coliform, the water system has an acute MCL violation.

Coliform indicator parameter Pathogenic microorganisms from the biotechnology industry, agricultural industry, hospitals, and so on may cause waterborne diseases. Coliforms are naturally present in the environment; as well as feces; fecal coliforms and *E. coli* only come from human and animal fecal waste. Coliform bacteria are also called enteric bacteria. The terms "coliform" and "enteric" are simply labels that describe bacteria that are found in the digestive tract and, as a result, in fecal material. The term "fecal coliforms" are considered to be those coliform group bacteria that are present specifically in the gut and feces of warm-blooded animals. The major species in the fecal coliform group is *Escherichia coli* (*E. coli*). Of the five genera of coliform bacteria, only *E. coli* is generally not found growing and reproducing in the environment. As a result, *E. coli* is considered to be the coliform bacteria species that is most indicative of fecal pollution and the possible presence of enteric pathogens. The term "total coliform" refers to the sum of the coliform bacteria present in a given water sample. All coliform bacteria tests begin by placing water in or on a growth medium for reproduction of all species of coliforms. If a sample is identified as positive, it means that one or more of the coliform bacteria are present. Fecal coliforms are the subgroup of the total coliforms that can ferment lactose in 24 ± 2 h at 44.5 ± 0.2 °C. *E. coli* are those fecal coliforms that can hydrolyze beta glucuronides. Fecal coliform and *E. coli* are bacteria whose presence indicates that the water may be contaminated with human or animal wastes. Disease-causing microbes (pathogens) in these waters can cause diarrhea, cramps, nausea, headaches, or other symptoms. These pathogens may pose a special health risk for infants, young children, and people with severely compromised immune systems.

Collector A device or system designed to collect filter backwash water, or other treatment unit.

Colloid Very small, insoluble non-diffusable solid or liquid particles that remain in suspension in a surrounding liquid. Solids usually on the order of 0.2 μm or less.

Colorimeters A colorimeter is designed to perform a type of psychophysical sample analysis by mimicking human eye–brain perception, or designed to see color the way we do. If desired, this data may be compared to a standard or reference to determine acceptability. Colorimeters are accurate for straightforward color measurement and ideally suited for determination of color difference, fastness, and strength as well as routine comparisons of similar colors. They can be invaluable for color quality control and are primarily used in the production and inspection phases of manufacturing. While colorimeters can produce highly accurate color measurements, they also have several shortcomings; they are not able to identify metamerism or colorant strength, are not ideally suited for color formulation, and cannot be used under variable illuminant/observer conditions.

Comminuting It is a grinding or shredding operation for reducing the particle size of objects or debris in the influent wastewater. They are installed with a screen directly in the influent wastewater flow's channel, with the shredded particles returned to the flow downstream of the screen. The influent flow is channeled to and through these units. The debris is collected against the screen, or outside drum, and the teeth which penetrate this screen cut up the solids. When the solids are reduced to the size of the screen or drum openings, they pass through and on for additional downstream wastewater treatment. The barminutor is a comminuting device that incorporates revolving cutters that move up and down the upstream face of a bar screen, shredding and cutting whatever debris has accumulated against the screen. The screenings are transported to the cutting device, shredded and then allowed to fall back into the influent channel downstream of the bar screen.

Community water system (there are approximately 54,000) A public water system that serves the same people year-round. Most residences including homes, apartments, and condominiums in cities, small towns, and mobile home parks are served by community water systems.

Completely mixed continuous flow It is a hydraulic flow regime in which a heterogeneous mixture of constituents exists throughout the liquid stream.

Completely mixed continuous flow reactor It is a chemical engineering reactor in which hydraulic behavior is such that the liquid in the reactor is completely mixed.

Compliance The act of meeting all state and federal drinking water regulations.

Composite sample A sample prepared by physically combining two or more samples having some specific relationship and processed to ensure homogeneity.

Compressibility Degree of physical change in suspended solids (or filter cake) when subjected to pressure.

Concentration In solutions, the mass, volume, or number of moles of solute present in proportion to the amount of solvent or total solution. Common measures are: molarity, normality, percent, molality, and by specific gravity scales.

Constituent A chemical or biological substance in water, sediment, or biota that can be measured by an analytical method.

Contact clarification A water treatment process in which flocculation and clarification (and often the rapid mix) are combined in one unit, such as an upflow solids contactor or contact clarifier.

Contact time, adsorbent The length of time an adsorbent is in contact with a liquid prior to being removed by the filter.

Contaminant (a) Anything found in water (including microorganisms, minerals, chemicals, radionuclides, etc.) which may be harmful to human health; (b) Biological or chemical substances or entities, not normally present in a system, which may be capable of producing an adverse effect in a biological system, seriously injuring structure or function.

Contamination (a) A general term signifying the introduction into water of microorganisms, chemicals, wastes, or sewage which renders the water unfit for its intended use; (b) degradation of water quality compared to original or natural conditions due to human activity.

Continuous flow sedimentation A process by which flow is received on a continuous basis at its normal flow rate and solids are allowed to settle.

Conventional biological wastewater treatment system It normally includes (a) preliminary treatment units (i.e., screen, comminutor, grit chamber, etc., for removal of sand, gravel, cinders, coffee grounds, small stones, cigarette filter tips, logs, cans, and other large-sized unwanted materials from raw wastewater), (b) primary sedimentation clarification for removing mainly total suspended solids from preliminary effluent, (c) secondary biological treatment units (such as activated sludge aeration or equivalent plus secondary sedimentation clarification) for removing dissolved organic/inorganic pollutants from primary effluent, and (d) tertiary treatment plant units (i.e., filtration, granular activated carbon adsorption, ion exchange, oxidation, nitrification, denitrification, and/or disinfection) for final polishing the secondary effluent in order to meet the effluent discharge standards.

Conventional filtration treatment plant A series of processes including coagulation, flocculation, sedimentation, and filtration resulting in substantial particulate removal.

Conventional physicochemical wastewater treatment system It normally includes (a) preliminary treatment units (i.e., screen, comminutor, grit chamber, etc., for removal of sand, gravel, cinders, coffee grounds, small stones, cigarette filter tips, logs, cans, and other large-sized unwanted materials from raw wastewater), (b) primary sedimentation clarification for removing mainly total suspended solids from preliminary effluent, (c) secondary physicochemical treatment units (such as chemical precipitation/coagulation or equivalent plus secondary sedimentation clarification) for removing dissolved organic/inorganic pollutants from primary effluent, and (d) tertiary treatment plant units (i.e., filtration, granular activated carbon adsorption, ion exchange, oxidation, nitrification, denitrification, and/or disinfection) for final polishing the secondary effluent in order to meet the effluent discharge standards. In the nitrification and denitrification steps, only tertiary sedimentation clarification will be used for solid–water separation.

Conventional water treatment plant (conventional water filtration plant) It includes at least the unit operations and unit processes of screening, pumping, rapid mixing for chemical feeding, coagulation–flocculation, sedimentation, filtration, post-disinfection, corrosion control, storage and water distribution, and waste disposal.

Copper (Cu) (a) It is an element with an atomic weight of 63.546; (b) it is toxic heavy metal found in some natural waters, particularly in areas where these ore deposits have been mined. Excessive amounts of copper ions can occur in corrosive water that passes through copper pipes. Copper in small amounts is not considered detrimental to health, but will impart an undesirable taste to the drinking water. For this reason, the limits for copper by the standards are: 1.0 mg/L (recommended; USA and Canada) and 2.0 mg/L (MAL; Mexico). In the USA, lead and copper are also regulated by a treatment technique (TT) that requires water systems to control the corrosiveness of their water. If more than 10% of tap water samples exceed the action level, water systems must take additional steps. For copper, the action level is 1.3 mg/L, and for lead is 0.015 mg/L. (c) Soluble copper is an essential nutrient to human health, but some people who drink water containing copper in excess of the action level of 1.3 ppm over a relatively short period of time could experience gastrointestinal distress. Some people who drink water containing copper in excess of the copper's action level over many years could suffer liver and/or kidney damage. People with Wilson's disease should consult their personal doctor.

Coprecipitation A chemical precipitation process in which two chemical agents precipitate each other producing two precipitates.

Corrosion control A water treatment method that keeps the metallic ions of a material, typically a pipe or tank from going into solution. Corrosion control method includes: pH adjustment, addition of inorganic phosphates, addition of silicates, cathodic protection, and coatings and linings.

Corrosion inhibitors A substance that slows corrosion by forming a protective film on the interior surface of water tanks, pipes, and process equipment.

Cream flotation It is a new process invented by the Lenox Institute of Water Technology. The new process involves pressurization of air or other gases at 25–60 psig for dissolving air or other gas into water containing surfactant, and subsequent release of pressure (to 1 atm) under laminar hydraulic flow conditions for generation of thick cream or foam bubbles, which become attached to the suspended matter (impurities or the recoverable substances) to rise together to the water surface. The attachment of foam bubbles to the suspended matter can be a combined result of physical entrapment, electrochemical attraction, and surface adsorption. The specific gravity of foam-suspended agglomerate is less than 1, resulting in rapid buoyancy or flotation. Cream flotation can also be operated in different modes: (a) full flow pressurization; (b) partial flow pressurization, and (c) recycle flow pressurization. It is economically feasible for separation of insoluble matter from a water stream which already contains surfactant.

Cryptosporidium It is a parasite commonly found in lakes and rivers, especially when the water is contaminated with sewage and animal wastes. *Cryptosporidium* has caused several large waterborne disease outbreaks of gastrointestinal illness, with symptoms that include diarrhea, nausea, and/or stomach cramps. Despite not being identified until 1976, it is one of the most frequent causes of waterborne disease (drinking water and recreational water) among humans in the USA. In March and April 1993, an outbreak of *cryptosporidiosis* in Milwaukee resulted in diarrheal illness in an estimated 403,000 persons. In the USA, the maximum contaminant level goal (MCLG) of *Giardia* and *Cryptosporidium* in drinking water is zero. In the USA and Canada, the treatment technique (TT) in place should achieve at least a 3-log reduction and and/or inactivation of cysts and oocysts, unless source water quality requires a greater log reduction and/or inactivation. TT is a required process intended to reduce the level of a contaminant in drinking water. The U.S. Surface Water Treatment Rules require water systems using surface water or ground water under the direct influence of surface water to (a) disinfect their water and (b) filter their water or meet criteria for avoiding filtration so that the following contaminants are controlled at the following levels: 99% removal/inactivation of *Cryptosporidium*, 99.9% removal/inactivation of *Giardia lamblia* and 99.99% removal/inactivation of viruses.

Curie (Ci) A unit of radioactivity mainly used in the USA, representing the rate at which nuclear radiations are emitted. One curie equals 0.037 billion disintegrations per second or approximately the radioactivity of 1 g of radium-226. 1 Ci = 0.037×10^{12} Bq.

Cycle, filter The length of time a filter is "on-stream" before cleaning is needed. Frequently meant to include cleaning time as well.

DAF-DAF A two-stage water or wastewater treatment process system consisting of double dissolved air flotation clarifiers (2 DAF clarifiers) connected in series, usually one DAF is on the top of another DAF.

DAF-DAFF A two-stage water or wastewater treatment process system consisting of a dissolved air flotation clarifier (DAF) and a dissolved air flotation–filtration clarifier (DAFF) connected in series, usually DAF is on the top of a DAFF.

D'Arcy, filter cake A measurement of filter cake permeability. Named after the French mathematician that first developed the equation.

Data Facts or figures from which conclusions can be inferred.

DDT It is a pesticide. The maximum allowable limit (MAL) of Mexico and the guideline value (GV) of WHO for DDT are both 0.001 mg/L, but DDT is not regulated by the USEPA because DDT has been totally banned by the USEPA for its application.

DE A commonly used abbreviation for diatomaceous earth.

Decant To draw off the liquid from a basin or tank without stirring up the sediment in the bottom.

Deformable Used to describe suspended solids that extrude into the interstices of a filter cake and cause rapid filter plugging.

Degree of treatment The desired or required degree of treatment depends on objectives. It may meet the effluent discharge standards, or the requirements for water reuse, or the quantity/quality of recovered materials.

Denitrification followed by flotation clarification The process involves the reduction of nitrates and nitrites to nitrogen gas through the action of facultative heterotrophic bacteria. In suspended-growth separate stage denitrification processes, nitrified wastewater containing primarily nitrates is passed through a mixed anaerobic vessel containing denitrifying bacteria. Since the nitrified feed-water contains very little carbonaceous materials, a supplemental source of carbon (such as methanol, sugar, acetic acid, ethanol, or other compounds) is required to maintain the denitrifying biomass. This supplemental energy is provided by feeding methanol, for instance, to the biological reactor along with the nitrified wastewater. Mixing in the anaerobic denitrification reaction vessel may be accomplished using low speed paddles analogous to standard flocculation equipment. Flotation clarification follows the denitrification step with the floated sludge being either returned to the head end of the denitrification system or wasted. An intermediate aeration step for stabilization (much less than 40 minutes) may be needed to guard against carryover of carbonaceous materials. The denitrification reactor may be covered but not air tight to assure anaerobic conditions.

Denitrification followed by membrane clarification Same as "denitrification followed by flotation clarification" except that the flotation clarification is replaced by a membrane filtration reactor.

Denitrification followed by sedimentation clarification The process involves the reduction of nitrates and nitrites to nitrogen gas through the action of facultative heterotrophic bacteria. In suspended-growth separate stage denitrification processes, nitrified wastewater containing primarily nitrates is passed through a mixed anaerobic vessel containing denitrifying bacteria. Since the nitrified feed-water contains very little carbonaceous materials, a supplemental source of carbon (such as methanol, sugar, acetic acid, ethanol, or other compounds) is required to maintain the denitrifying biomass. This supplemental energy is provided by feeding methanol, for instance, to the biological reactor along with the nitrified wastewater. Mixing in the anaerobic denitrification reaction vessel may be accomplished using low speed paddles analogous to standard flocculation equipment. Following the reactor, the denitrified effluent is aerated for a short period (5 to 10 min) to strip out gaseous nitrogen formed in the previous step which might otherwise inhibit sludge settling. Sedimentation clarification follows the gas stripping step with the collected sludge being either returned to the head end of the denitrification system, or wasted. An intermediate aeration step for stabilization (about 50 minutes) between the denitrification reactor and the stripping step may be used to guard against carryover of carbonaceous materials. The denitrification reactor may be covered but not air tight to assure anaerobic conditions.

Density, filter cake The weight of a given volume of filter aid or its filter cake. Usually measured in pounds per cubic foot (PCF). Can be measured wet or dry.

Design flow It is feed or influent to be applied to the flotation unit, or a different water or waste treatment unit, for design purpose. It can be obtained by examining the existing or expected future flow data.

Detection limit (DL) The lowest concentration or amount of the target analyte that can be determined to be different from zero by a single measurement at a stated level of probability.

Determination The application of the complete analytical process of measuring the property of interest in a sample, from selecting or measuring a test portion to the reporting of results.

Dewatering processes Mechanical and nonmechanical methods used to remove excess liquids from residual solids in order to concentrate the solids. These methods include belt presses, centrifuges, filter presses, vacuum presses, lagoons, and monofill.

Diatomaceous earth filtration A process resulting in substantial particulate removal in which (a) a precoat cake of diatomaceous earth filter media is deposited on a support membrane (septum), and (b) while the water is filtered by passing through the cake on the septum, additional filter media known as body feed is continuously added to the feed water to maintain the permeability of the filter cake.

Diatomaceous earth The fossilized skeletons of minute, prehistoric aquatic plants.

Diatomite An abbreviation of diatomaceous earth.

Differential pressure, filter The difference in pressure between the upstream and downstream sides of a filter or filter cake.

Diffused aeration A process involving the dissolution of air or oxygen in water by the use of coarse bubble diffusers or bubble porous disks or tubes. Typical examples of diffused aeration are (a) removing volatile organic compounds and taste, odor and color-causing substances from water and (b) increasing the oxygen concentration in water for oxidation of iron and manganese.

Diluent A substance added to another to reduce the concentration and resulting in a homogeneous end product without chemically altering the compound of interest.

Dilution factor The numerical value obtained from dividing the new volume of a diluted substance by its original volume.

Direct filtration A series of processes including coagulation and filtration but excluding sedimentation resulting in substantial particulate removal.

Direct recycle The return of recycle flow within the treatment process without first passing the recycle flow through treatment or equalization.

Discharge Rate of fluid flow passing a given point at a given moment in time, expressed as volume per unit of time.

Disinfectant Any oxidant, including but not limited to chlorine, chlorine dioxide, chloramines, and ozone added to water in any part of the treatment or distribution process, that is intended to kill or inactivate pathogenic microorganisms. A chemical (commonly chlorine, chloramine, or ozone) or physical process (e.g., ultraviolet light) that kills microorganisms such as bacteria, viruses, and protozoa.

Disinfectant by-products (DBP) DBP are the by-products of drinking water disinfection. Different disinfectants will product different DBP. They are all cancer-causing substances. The maximum allowable concentrations (MCL of USA, MAC of Canada, MAL of Mexico, or GV of WHO) of four common DBP are: (a) bromate = 0.01 mg/L (USA, Canada, WHO); (b) chlorite = 1.0 mg/L (USA, Canada); 0.7 mg/L (WHO); (c) haloacetic acids (HAAs) = 0.06 mg/L (USA); 0.08 mg/L (Canada); and (d) total trihalomethanes (TTHMs) = 0.08 mg/L (USA); 0.1 mg/L (Canada); 0.2 mg/L (Mexico). TTHM includes bromodichloromethane, bromoform, dibromochloromethane, and chloroform. HAA5 includes five compounds—dichloroacetic acid, trichloroacetic acid, monochloroacetic acid, bromoacetic acid, and dibromoacetic acid. The guideline values (GV) established by World Health Organization (WHO) for DBP are: bromate, 0.0 1 mg/L; bromodichloromethane, 0.06 mg/L; bromoform, 0.1 mg/L; chlorate, 0.7 mg/L; chlorite, 0.7 mg/L; chloroform, 0.3 mg/L; dibromoacetonitrile, 0.07 mg/L; dibromochloromethane, 0.1 mg/L; dichloroacetate, 0.05 mg/L; dichloroacetonitrile, 0.02 mg/L; monochloroacetate, 0.02 mg/L; n-nitrosodimethylamine, 0.0001 mg/L; trichloroacetate, 0.2 mg/L; and 2,4,6-trichlorophenol, 0.2 mg/L. Although there is no collective maximum contaminant level goal (MCLG) in the USA for this contaminant group, there are individual MCLGs for some of the individual contaminants: (a) trihalomethanes: bromodichloromethane (zero); bromoform (zero); dibromochloromethane (0.06 mg/L): chloroform (0.07 mg/L); and (b) haloacetic acids: dichloroacetic acid (zero); trichloroacetic acid (0.02 mg/L); monochloroacetic acid (0.07 mg/L). Bromoacetic acid and dibromoacetic acid are regulated with this group but have no MCLGs.

Disinfectant by-products contaminants Disinfectant by-products (DBP) are organic compounds produced when chlorine and/or bromine are used as the disinfectant(s) to kill microbial contaminants, such as bacteria, in the water supply. These disinfectants react with naturally occurring organic matters forming DBP.

Disinfection A process which inactivates pathogenic organisms in water by chemical oxidants or equivalent agents.

Disinfection by-products (DBP) Organic compounds formed by the reaction of the disinfectant, natural organic matter, and the bromide ion during water disinfection process. Regulated DBP include TTHMs, HAA5s, bromate, and chlorite.

Dispersed air flotation Same as induced air flotation (IGF). It is one of induced gas flotation (IGF) processes when air is used for generation gas bubbles.

Dispersed gas flotation Same as induced gas flotation (IGF).

Dispersed nitrogen flotation Same as induced nitrogen flotation (IGF). It is one of induced gas flotation (IGF) processes when nitrogen is used for generation gas bubbles.

Dispersion A uniform and maximum separation of extremely fine particles, often of colloidal size.

Dissolved air flotation (DAF) (a) A method of solids separation, whereby a side stream is saturated with air at high pressure and then injected into the flotation tank to mix with the incoming water stream. As the air bubbles rise to the surface they attach to floc particles and create a sludge layer at the surface of the tank, which is then removed for disposal. (b) One of dissolved gas flotation (DGF) processes when air is used for generation of gas bubbles. A typical example is Krofta Engineering Corporation's Supracell clarifier; see dissolved gas flotation (DGF).

Dissolved air flotation–filtration (DAFF) A package plant which consists of both dissolved air flotation and filtration. A typical example is Krofta Engineering Corporation's Sandfloat clarifier.

Dissolved carbon dioxide flotation (DCDF) One of dissolved gas flotation (DGF) processes when carbon dioxide is used for generation of gas bubbles. See dissolved gas flotation (DGF).

Dissolved constituent Operationally defined as a constituent that passes through a 0.45-μm filter.

Dissolved gas flotation (DGF) It is a process involving pressurization of gas at 25 to 95 psig for dissolving gas into water, and subsequent release of pressure (to 1 atm) under laminar flow hydraulic conditions for generating extremely fine gas bubbles (20–80 μm) which become attached to the impurities to be removed and rise to the water surface together. The impurities or pollutants to be removed are on the water surface are called float or scum which scooped off by sludge collection means. The clarified water is discharged from the flotation clarifier's bottom. The gas flow rate is about 1% of influent liquid flow rate. The attachment of gas bubbles to the impurities can be a result of physical entrapment, electrochemical attraction, surface adsorption, and/or gas stripping. The specific gravity of the bubble-impurity agglomerate is less than 1, resulting in buoyancy or nonselective flotation (i.e., save-all).

Dissolved nitrogen flotation (DNF) One of dissolved gas flotation (DGF) processes when nitrogen is used for generation of gas bubbles. See dissolved gas flotation (DGF).

Dissolved oxygen (DO) The level of dissolved oxygen (DO) in natural surface water is an indication of extent of pollution by oxygen-demanding substances. Low DO concentrations are associated with low-quality water, aquatic animal may die if DO concentration is below certain tolerable level, and water treatment plants may face taste and odor problems. In treated water, the DO is one of the most important factors influencing the corrosion rate of metal treatment facilities and pipelines.

Dissolved ozone flotation (DOF) One of dissolved gas flotation (DGF) processes when ozone is used for generation of gas bubbles. See dissolved gas flotation (DGF).

Dissolved protein Protein substances that can dissolve in water.

Dissolved solids (a) Amount of minerals, such as salt, that are dissolved in water; amount of dissolved solids is an indicator of salinity or hardness; (b) any solid material that will dissolve in the liquid that is being filtered, such as sugar in water.

Distilled water Water that has been purified by distillation (boiling the water off as steam and condensing it back to a liquid, leaving the impurities behind). Having been boiled, it is also sterile.

Distribution system A network of pipes leading from a treatment plant to customers' plumbing systems.

Doctor blade (knife) A sharp, hard blade that cuts the cake off the surface of a filter. Usually found on rotary vacuum precoat filters.

Document control A systematic procedure for indexing documents by number, date, and revision number for archiving, storage, and retrieval.

Drainage area The drainage area of a stream at a specified location is that area, measured in a horizontal plane, which is enclosed by a drainage divide.

Drainage basin The portion of the surface of the Earth that contributes water to a stream through overland runoff, including tributaries and impoundments.

Dual-media filtration A water filtration system which is designed to operate at a filtration rate higher than conventional rapid granular filtration by using two different types of filter media, such as granulated black anthracite on the top and silica sand at the bottom.

Dual-membrane filtration A membrane filtration system, also known as integrated membrane system, is composed of two different types of membrane filtration modules in series. For instance, a surface water treatment plant may use a microfiltration (MF) or ultrafiltration (UF) membrane module for particle and microorganisms removal followed by a nanofiltration (NF) or reverse osmosis (RO) module for dissolved solids removal.

Duplicate An adjective describing the taking of a second sample or performance of a second measurement or determination. Often incorrectly used as a noun and substituted for “duplicate sample.” Replicate is to be used if there are more than two items.

Duplicate analyses or measurements The analyses or measurements of the variable of interest performed identically on two subsamples of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation, or storage internal to the laboratory.

Duplicate samples Two samples taken from and representative of the same population and carried through all steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variance of the total method including sampling and analysis.

Ecology It is the branch of biology that deals with the mutual relations between organisms and their environment. Ecology implies more the webs of natural forces and organisms, their competition and cooperation, and how they live off one another.

Ecosystem A system that is made up of a community of animals, plants, and bacteria and its interrelated physical and chemical environment (USFWS).

Effluent (a) Any liquid that is discharged from a factory, waste treatment facility, or filter; (b) it is the water being discharged from a water or wastewater treatment unit, such as a flotation unit.

Electrodialysis (ED) A nonpressure driven membrane process which is driven by an electrical potential difference between oppositely charged electrodes. Ions are transferred by direct electric current flow through cation and anion membranes depending on ion charges, from a less concentrated solution to a more concentrated one, producing demineralized water.

Electrodialysis reversal (EDR) An electrodialysis process which is not driven by pressure, but driven by an electrical potential difference between oppositely charged electrodes. In the electrodialysis reversal process, the electrical polarity of the electrodes is reversed on a set time cycle thereby reversing the direction of ions in the process system for control of membrane scaling and fouling problems.

Electroflotation It is a process involving the generation of hydrogen and oxygen bubbles in a dilute electrolytic aqueous solution by passing a direct current between two electrodes: (a) anode and (b) cathode. Anode reaction generates oxygen bubbles and hydrogen ions, while cathode reaction generates hydrogen bubbles and hydroxide ions. Either aluminum or steel sacrificial electrodes can be employed for generating the gas bubbles as well as coagulants at the same time. Non-sacrificial electrodes are employed for generating the gas bubbles only, and can be mode of titanium (as the carrier material) and lead dioxide (as the coating material). Electrical power is supplied to the electrodes at a low voltage potential of 5 to 20 volts DC by means of a transformer rectifier. Small bubbles in the range of 20–50 m microns are produced under laminar hydraulic flow conditions feasible for flotation separation of fragile flocs from water in a small system. The floats on the water surface are the impurities/pollutants removed from water. The clarified water is discharged from the flotation clarifier's bottom. There can be unexpected advantages and disadvantages when electroflotation is employed. For instance, chlorine bubbles may be generated as a water disinfectant if the water contains significant amount of chloride ions. Certain unexpected gas bubbles may be generated and may be undesirable.

Electrolytic flotation Same as electroflotation.

Element, filter Any structural member in a filter on which the septum is supported. May be round, rectangular, or cylindrical.

Enclosed flotation It is a flotation unit with airtight cover or roof on its top, so the air emission can be eliminated for odor or air pollution control. An enclosed flotation unit may also be operated as an aerobic vacuum flotation unit or an anoxic/ anaerobic biological flotation unit.

Environmentally related measurement Any assessment of environmental concern generated through or for field, laboratory, or modelling processes; the value obtained from such an assessment.

Environmental sample A sample of any material that is collected from an environmental source.

Equalization A method used to control the flow of water or residual stream by providing storage and detention time between the point of origin and the return location of the water residual stream. The water or residual stream is then removed from the storage unit at a controlled, uniform rate.

Equivalent method Any method of sampling and/or analysis demonstrated to result in data having a consistent and quantitatively known relationship to the results obtained with a reference method under specified conditions and formally recognized by the USEPA.

Error (measurement) The difference between an observed or corrected value of a variable and a specified, theoretically correct, or true value.

Eutrophication Enrichment of waters with nutrients, primarily phosphorus, causing abundant aquatic plant growth and often leading to seasonal deficiencies in dissolved oxygen.

External quality control The activities which are routinely initiated and performed by persons outside of normal operations to assess the capability and performance of a measurement process.

Fecal bacteria Microscopic single-celled organisms (primarily fecal coliforms and fecal streptococci) found in the wastes of warm-blooded animals. Their presence in water is used to assess the sanitary quality of water for body-contact recreation or for consumption. Their presence indicates contamination by the wastes of warm-blooded animals and the possible presence of pathogenic (disease producing) organisms.

Fecal coliform Fecal bacteria.

Feed, filter The mixture of solids and liquid that enters the filter. Synonyms: prefilt influent and incoming slurry.

Fiber separation It is a solid–water separation process by flotation, or cloth filtration, aiming at fiber recovery.

Field blank A clean sample (e.g., distilled water), carried to the sampling site, exposed to sampling conditions (e.g., bottle caps removed, preservatives added) and returned to the laboratory and treated as an environmental sample. Field blanks are used to check for analytical artifacts and/or background introduces by sampling and analytical procedures.

Filte (noun) A device for containing the filter media.

Filte (verb) To pass a liquid containing solids through a filter medium whereby the solids and liquid are separated from each other.

Filter aid Any material that assists in the separation of solids from liquids. Usually used on difficult filtration applications.

Filter medium The permeable material that separates particles from a fluid passing through it.

Filter system The combination of a filter and associated hardware required for the filtration process.

Filter-to-waste The practice of discarding filter effluent that is produced during the "filter ripening" period immediately after backwash due to its impaired quality.

Filtrate The water separated from the solids by a belt filter press or the liquid that has passed through a filter.

Filtration (a) A process for removing particulate matter from water by passage through porous media. (b) It is usually a granular medial filtration process which involves the passage of wastewater or water through a bed of filter media with resulting deposition of suspended solids. Eventually the pressure drop across the bed becomes excessive or the ability of the bed to remove suspended solids is impaired. Cleaning is then necessary to restore operating head and effluent quality. The time in service between cleanings is termed the filter run time or run length. The head loss at which filtration is interrupted for cleaning is called the terminal head loss, and this head loss is maximized by the judicious choice of media sizes. Dual-media filtration involves the use of both sand and anthracite as filter media, with anthracite being placed on top of the sand. Gravity filters operate either by using the available head from the previous treatment unit or by pumping to a flow split box after which the wastewater flows by gravity to the filter cells. Pressure filters utilize pumping to increase the available head. A filter unit generally consists of a containing vessel, the filter media, structures to support the media, distribution and collection devices for filter influent, effluent, and backwash water flows, supplemental cleaning devices, and necessary controls for flows, water levels and backwash sequencing. Backwash sequences can include air scour or surface wash steps. Backwash water can be stored separately or in chambers that are integral parts of the filter unit. Backwash water can be pumped through the unit or can be supplied through gravity head tanks. (c) The process by which solid particles are separated from a liquid by passing the liquid through a permeable material.

Filtration rate The volume of liquid that passes through a given area of filter in a specific time. Usually expressed as gallons per square foot per minute (or hour).

Finished water Water that has been treated and is ready to be delivered to customers.

Float detector It is a monitoring means for detecting the concentration and/or movement of floatable substances.

Float (floated sludge or floated scum) It is the concentrated matter (impurities, pollutants, or recovered useful materials) scooped or skimmed off from the top of a flotation unit. The float is generally measured in mg/L, and its flow measured in gallons per minute (gpm), million gallons per day (MGD), or cubic meters per sec (m^3/s).

Float skimmer It is a treatment process unit or a mechanical means for removal of substances that can float to the water surface.

Floc Collections of smaller particles that have agglomerated together into larger, more separable (floatable or settleable) particles as a result of the coagulation process.

Flocculating agent or flocculant, or coagulant Any chemical that can convert soluble or colloidal substances to insoluble flocs.

Flocculation A process to enhance agglomeration or collection of smaller floc particles into larger, more easily settleable particles by sedimentation (or floatable particles by flotation) through gentle stirring by hydraulic or mechanical means.

Flocculator A process device to enhance the formation of floc in a water. Mixing energy can be provided by slow turning mechanical means or head loss.

Flood It is a relatively high water flow as measured by either gauge height or discharge quantity, or any water flow equal to or greater than a designated basic water flow.

Flotation aid Any chemical that coagulates solids, breaks an oil emulsion, or assists in adsorbing solids onto air bubbles for water–solids separation.

Flotation chamber or flotation tank It is the main tank of a flotation unit where the influent water enters and the water–solids separation occurs due to flotation actions.

Flotation clarification It is flotation unit designed for clarification of water or wastewater. Therefore, the main objective of the flotation clarifier is for clarifying or cleaning the incoming water or wastewater.

Flotation-sludge press (FloatPress) A combined dissolved air flotation thickener and sludge press with the flotation thickener at the bottom and the sludge press on the top. A typical example is FloatPress manufactured by Krofta Engineering Corporation.

Flotation thickener A dissolved air flotation unit that is used for thickening (concentration) of waste sludge using air bubbles. Since the combined density of air bubbles and the attached sludge is lighter than water, the sludge floats to the water surface as scum (floats) which are collected for either further dewatering treatment or disposal.

Flow rate The unit rate at which a liquid is passed through a system. Usually expressed in gallons per minute (or hour).

Fluorides (F^-) High levels of fluoride in drinking water can cause brown spots on the teeth, or mottling, in children up to 12 years of age. Adults can tolerate ten times more than children. In the proper amounts, however, fluoride in drinking water prevents cavities during formative years. This is why many communities add fluoride in controlled amounts to their water supply. The maximum amount of fluoride allowed in drinking water by the standard ranges from 0.4 to 2.0 mg/L depending on one average maximum daily air temperature. The hotter the climate, the lower the amount allowed, for people tend to drink more in hot climates. In hot areas, the maximum allowable level for fluoride is 2.0 mg/L of water. Optimum concentrations from 0.7 to 1.2 mg/L fluoride ions are recommended. Legally the maximum allowable concentration of fluoride in drinking water by the standards is 1.5 mg/L in Canada and Mexico, but the recommended limit for fluoride is 2.0 mg/L in the USA.

Foam separation (a) A dispersed air flotation process in which mechanical aeration or diffused aeration devices are used for generation of fine air bubbles, and surfactants are separated from water or wastewater by air bubbles, producing foam/scum on the water surface. The foam separation effluent water (subnatant) is withdrawn from the bottom; (b) Same as induced gas flotation (IGF), normally air is used for generation of gas bubbles.

Frazier A test to measure the air permeability of filter septums. Expressed in c.f.m. or air at a pressure drop of 1/2″ W.C.

Free ammonia (NH_3) It is stripped from the falling water droplets into the air stream which is then discharged to the atmosphere. Lime or caustic soda is added prior to the stripping to raise the pH of the wastewater to the range of 10.8 to 11.5 converting essentially all ammonium ions to ammonia gas which can then be stripped by air. Process controls required for the operation are the proper pH adjustment of the influent wastewater, and maintenance of proper air and water flows. Ammonia removal efficiency is highly dependent on air temperature and air/water ratios. As the air temperature decreases, the efficiency drops significantly. For instance, the ammonia removal efficiency can be 75% at air temperature of 10 °C, while the ammonia removal efficiency can be 90–95% at air temperature of 20 °C. Very poor ammonia removal efficiency will be experienced in cold weather location (0 to 10 °C). The influent wastewater should always be clarified before stripping. Residual ammonia in the ammonia stripping effluent can be removed by breakpoint chlorination. The countercurrent flow ammonia stripping process is technically and economically feasible for a wastewater containing about 10–100 mg/L of ammonia.

Friable Easily crushed or crumbled.

Fungi Unlike algae, fungi have no chlorophyll in their cellular structure. Water forms of fungi include *phycomycetes*, similar to algae, and *ascomycetes*, commonly called yeasts and molds. Although parasitic fungi occur in water, they do not appear to significantly infect humans through water.

Gas dissolving tube or pressure retention tank It is a metal tank in which the water flow and compressed gas are mixed and held under high pressure for several minutes to allow sufficient time for dissolving gas into water.

Gelatinous Used to describe suspended solids that are slimy and deformable, causing rapid filter plugging, or clarifier scumming.

Giardia It is a parasite which infection can cause a variety of intestinal signs or symptoms, which include diarrhea, gas or flatulence, greasy stools that tend to float, stomach or abdominal cramps and upset stomach or nausea. These symptoms may lead to weight loss and dehydration.

Giardia lamblia Flagellated protozoan which is shed during its cyst stage with the feces of humans and animals. When water containing these cysts is ingested, the protozoan causes a severe gastrointestinal disease called giardiasis.

Good laboratory practices (GLP) Either general guidelines or formal regulations for performing basic laboratory operations or activities that are known or believed to influence the quality and integrity of the results.

G.P.H. Abbreviation for gallons per hour.

G.P.M. Abbreviation for gallons per minute.

Grab sample A single sample which is collected at one point in time and place.

Granular activated carbon An activated carbon which is porous and in granular form with many micro- and macro-channels and surface area, suitable for adsorption of many soluble organics and some inorganics.

Granular activated carbon adsorption (a) A unit process used to remove mainly dissolved organics from water, wastewater, or air. A receptacle is filled with granular carbon, and the fluid (water, wastewater, or air) is passed through either fixed or moving beds. (b) A wastewater GAC systems generally consist of vessels in which the carbon is placed, forming a "filter" bed. These systems can also include carbon storage vessels and thermal regeneration facilities. Vessels are usually circular for pressure systems or rectangular for gravity flow systems. Once the carbon adsorptive capacity has been fully utilized, it must be disposed of or regenerated. Usually multiple carbon vessels are used to allow continuous operation. Columns can be operated in series or parallel modes. All vessels must be equipped with carbon removal and loading mechanisms to allow for the removal of spent carbon and the addition of new material. Flow can be either upward or downward through the carbon bed. Vessels are backwashed periodically. Surface wash and air scour systems can also be used as part of the backwash cycle. Small systems usually dispose of spent carbon or regenerate it offsite. Systems above about 3 to 5 MGD (million gallons per day) usually provide on-site regeneration of carbon for economic reasons.

Granular activated carbon (GAC) filtration A filtration bed consists of granular activated carbon.

Gravity flotation It is a water–solids separation process by floating solids due to natural specific gravity difference of a water and the light-weight solids (specific gravity is less than 1) within water. In natural gravity flotation, oil, grease, wax, fiber, or other substances lighter than water (specific gravity is less than 1) are allowed to rise naturally to the water surface of quiescent tank, where they are skimmed off or scooped off. The bottom clean water is discharged as the treated water. The floats skimmed off or scooped off from the water surface are either the impurities/pollutants to be removed or the resources (such as fibers or oils) recovered for reuse.

Gravity sedimentation It is a water–solids separation process by settling solids due to specific gravity difference of water and solids (specific gravity is greater than 1 or greater than water) within water. In gravity sedimentation process unit, chemical flocs, biological flocs, silts, sands, or other substances having specific gravity greater than water (specific gravity is less than 1) are allowed to settle to the sedimentation tank's bottom. The top portion water body is clean or clarified water is discharged as the treated water effluent. The settled sludge is removed from the sedimentation tank's bottom as the waste sludge.

Gravity thickener A sedimentation tank that is used for thickening (concentration) of waste sludge by gravity force due to the fact that the sludge solids are heavier than water. The settled sludge solids are collected for further dewatering treatment or disposal.

Greensand A naturally occurring mineral that consists largely of greenish, granular glauconite and possesses cationic ion exchange (cation exchanger) capability. It is the base product for manufacturing manganese greensand zeolite products. Greensands are the sand media coated with manganese dioxide.

Greensand filtration A filter bed that adsorbs soluble iron and manganese through the use of granular greensands. The greensand filter bed can be regenerated with potassium permanganate or chlorine.

Grinding It is a unit operation for reducing the particle size of objects or debris in the influent wastewater, also termed shredding or comminuting. These devices may be installed with a screen directly in the wastewater flow or separately out of the wastewater flow, with the shredded particles returned to the flow downstream of the screen. Only those shredding and grinding devices that are installed directly in the influent channel are termed comminuting devices.

Grit It includes sand, gravel, cinders, coffee grounds, small stones, cigarette filter tips, and other large-sized unwanted materials in wastewater.

Grit chamber It is a grit removal device that is designed to allow the settling out of this material. Grit removal is an important process for several reasons: (1) to prevent cementing effects at the bottom of sludge digesters and primary clarification tanks; (2) to reduce the potential for clogging of pipes and sludge hoppers; (3) to protect moving mechanical equipment and pumps from unnecessary wear and abrasion; (4) to reduce accumulations of materials in aeration tanks and sludge digesters which would result in a loss of usable volume; and (5) to reduce accumulations at the bases of mechanical screens. There are two types of grit chambers. The velocity controlled grit chambers limit the velocity in the rectangular channels to a maximum of 1 foot per second (fps). This velocity is low enough to allow the grit to settle but fast enough to maintain a majority of the organic material in suspension. The aerated grit chambers are normally sized on the basis of both detention time and volume of air. Typically, the detention time is in the range of 2–5 min and the air flow is in the range of 0.04 to 0.06 cu ft./gallon of wastewater. The constant head type of system is normally designed using an overflow rate of 15,000 gallons per day per square foot and a 1 min detention time at peak day flows.

Ground water (a) The water that systems pump and treat from aquifers (natural reservoirs below the earth's surface); (b) it is the water contained in interconnected pores located either below the land's water table in an unconfined aquifer or in a confined aquifer.

Ground water under the direct influence of surface water (GWUDI) Any water beneath the surface of the ground with significant occurrence of insects or other macroorganisms, algae, or large-diameter pathogens such as *Giardia lamblia* or *Cryptosporidium*, or significant and relatively rapid shifts in water characteristics such as turbidity, temperature, conductivity, or pH which closely correlate to climatological or surface water conditions. Direct influence must be determined for individual sources in accordance with criteria established by the State. The State determination of direct influence must be based on site-specific measurements of water quality and/or documentation of well construction characteristics and geology with field evaluation.

G.S.F.M. Abbreviation for gallons per square foot per minute. Also GSFH for hour.

Haloacetic acids (HAA5) The sum of the concentrations in milligrams per liter of five haloacetic acid compounds (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid), rounded to two significant figures after addition.

Hardness, calcium and magnesium, carbonate and bicarbonate Hard water and soft water are relative terms. Hard water retards the cleaning action of soaps and detergents, causing an expense in the form of extra work and cleaning agents. Furthermore, when hard water is heated it will deposit a hard scale (as in a kettle, heating coils, or cooking utensils) with a consequent waste of fuel. Calcium and magnesium salts, which cause hardness in water supplies, are divided into two general classifications: (a) carbonate or temporary hardness and (b) noncarbonate or permanent hardness. Carbonate or temporary hardness is so called because heating the water will largely remove it. When the water is heated, bicarbonates break down into insoluble carbonates that precipitate as solid particles which adhere to a heated surface and the inside of pipes. Noncarbonate or permanent hardness is so called because it is not removed when water is heated. Noncarbonate hardness is due largely to the presence of the sulfates and chlorides of calcium and magnesium in the water. The classifications of water based on hardness are: (a) soft water, 0–40 mg/L of total hardness as $CaCO_3$; (b) moderately hard water, 40–100 mg/L of total hardness as $CaCO_3$; (c) hard water, 100–300 mg/L of total hardness as $CaCO_3$; (d) very hard water, 300–500 mg/L of total hardness as $CaCO_3$; and (e) extremely hard water, greater than 500 mg/L of total hardness as $CaCO_3$. The total hardness in drinking water is unregulated in the USA. The Mexico maximum allowable limit for total hardness and Canada recommended concentration for total hardness in drinking water are both 500 mg/L as $CaCO_3$.

Hazardous wastes A hazardous waste is a material that is subject to special consideration by the USEPA, under 40CFR261. State or local authorities may also designate additional materials as hazardous waste in their areas. The definition given by 40 CFR 261 defines a hazardous waste as a solid waste that is not excluded from regulation and meets one or more of the following criteria: (a) it is a discarded commercial chemical product, off-specification species, container residue, or spill residue of materials specifically listed in 40CFR261.33 (P- and U-codes); (b) it is a waste from a specific source listed in 40CFR261.32 (K-code); (c) it is a waste from a nonspecific source listed in 40CFR261.31 (F-code); and/or (d) it displays any of the following characteristics of hazardous wastes: ignitability (such as flash point is below 60 °C or 140 °F, it is classified by DOT as an oxidizer D001), corrosivity (such as the pH of the waste material is less than or equal to 2, or greater than or equal to 12.5, or classified by DOT as D002), reactivity (such as the waste material is unstable, reacts violently with water, may generate toxic gases when mixed with water, or classified by DOT as D003), or toxicity (such as it is classified by DOT ad D004-D043).

Heel, precoat filter (a) The liquid left in a filter shell at the end of a cycle. (b) The precoat left on an R.V.P.E. at the end of its cycle.

Heterotrophic plate count (HPC) *Heterotrophic plate count* (HPC) has no health effects; it is an analytic method used to measure the variety of bacteria that are common in water. The lower the concentration of bacteria in drinking water, the better maintained the water system is. HPC measures a range of bacteria that are naturally present in the environment. No MAC/MAL has been specified by Canada and Mexico for heterotrophic plate count (HPC) bacteria in drinking water. However, increases in HPC concentrations above baseline levels are considered undesirable. In the USA, no more than 500 bacterial colonies per milliliter are allowed in drinking water.

Higee aeration It is a commercial aeration process involving the use of an air–liquid mixing device commercially known as “Higee” through which the water and the forced air are mixed and contacted, so the impurities (such as volatile organic compounds, color substances, and taste and odor-causing substances) can be stripped from the liquid phase to the gaseous phase and/or the iron and manganese can be oxidized by the oxygen in the air. The process equipment consists of an air blower, a water pump, a water filter, and a Higee device.

Hydraulic loading rate It is the influent flow divided by the flotation surface area. The hydraulic loading rate of a flotation unit is expressed in gallons per minutes per square foot of flotation unit’s surface area (gpm/ft^2) or cubic meters per second per square meter of flotation unit’s surface area (m^3/s/m^2).

Hydrophilic Water accepting.

Hydrophobic Water rejecting.

Independent physicochemical wastewater treatment system (IPCWWTS) An independent physicochemical wastewater treatment system (IPCWWTS) utilizes physicochemical (PC) process technology other than biological process technology to obtain combined primary and secondary treatment efficiency for removals of mainly biochemical oxidation demand (BOD), chemical oxidation demand (COD), total suspended solids (TSS), and phosphate. Typically, an IPCWWTS uses combinations of preliminary treatment (flow equalization, bar screening, comminution, grit chamber, ammonia stripping), chemical precipitation/coagulation, primary clarification (primary sedimentation clarification or primary flotation clarification), secondary clarification (secondary sedimentation clarification or secondary flotation clarification, without biological treatment), tertiary wastewater treatment (filtration and/or granular activated carbon adsorption, ion exchange, PC oxidation, etc.), and disinfection. An innovative efficient primary flotation clarifier or a secondary flotation clarifier can be in any shape, circular or rectangular. In general this IPCWWTS requires much less land area than conventional biological secondary treatment systems. Phosphor removal is inherent in this physicochemical process system.

Induced gas flotation (IGF) It is a process involving introduction of gas directly into the water through a revolving impeller, a diffuser system, or an ejector, or a combination of them, at low pressure (slightly higher than 1 atm) for generating big gas bubbles (80 μm to over 1 mm) in large volume under turbulent hydraulic flow conditions. The gas flow rate is about 400% of the influent water flow rate. Physical entrapment and electrochemical attraction play minor roles in an induced gas flotation system. The attachment of gas bubbles to the impurities is mainly a result of surface adsorption, gas stripping, and oxidation. Surface active substances (inks, detergents, ores, soaps, etc.) together with impurities are selectively separated in a foam phase at the water surface. The foam containing the surfactant and the impurities are removed by suction device. Volatile substances are removed by gas stripping action. The clarified water is discharged from the flotation clarifier's bottom. Reducing agents, such as ferrous ions, can be oxidized to ferric ions for subsequent separation in ferric hydroxide form if air is used as a gas.

Industrial ecologist He/she is an expert who takes a systems view, seeking to integrate and balance the environmental, business, and economic development interests of the industrial systems, and who will treat "sustainability" as a complex, whole systems challenge. An industrial ecologist will work to create comprehensive solutions, often simply integrating separate proven components into holistic design concepts for possible implementation by the clients.

Industrial ecology (IE) It is intelligent or clever working as well as the particular branches of productive labor. It is now a branch of systems science for sustainability, or a framework for designing and operating industrial systems as sustainable and interdependent with natural systems. It seeks to balance industrial production and economic performance with an emerging understanding of local and global ecological constraints.

Industrial ecology team It includes industrial ecology partners, associates, and strategic allies qualified in the areas of industrial ecology, eco-industrial parks, economic development, real estate development, finance, urban planning, architecture, engineering, ecology, sustainable agriculture, sustainable industry systems, organizational design, and so on. The core capability of the industrial ecology team is the ability to integrate the contributions of these diverse fields into whole systems solutions for business, government agencies, communities, and nations.

Industrial effluent It is a waste stream discharged from an industrial plant.

Industrial systems They include service, agricultural, manufacturing, military, and civil operations, as well as infrastructure such as landfills, recycling facilities, energy utility plants, water transmission facilities, water treatment plants, sewer systems, wastewater treatment facilities, incinerators, nuclear waste storage facilities, and transportation systems.

Industrial wastes They are the wastes from an industry or an industrial plant.

Infections from water-related sources If infections conveyed by excrement as well as by wastewaters and their sludges are taken into account, the ways of spreading enteric disease increase in number and the list of possible infections become longer. Common modes of transmission other than through drinking water are: (a) through watercress, or shellfish harvested from or stored in sewage-polluted water (typhoid, paratyphoid, bacillary dysentery, and infectious hepatitis); (b) through vegetables and fruits contaminated by feces, sewage, or sewage sludge (typhoid, paratyphoid, the dysenteries, parasitic worms, and infectious hepatitis); (c) through exposure to soil contaminated by human dung (hookworm); (d) through all manner of food contaminated by flies and other vermin that feed also on human fecal matter (typhoid, paratyphoid, the dysenteries, and infectious hepatitis); (e) through milk and milk products contaminated by utensils that have been washed in polluted water (typhoid, paratyphoid, and bacillary dysentery); (f) through fish and crayfish from polluted waters eaten raw too soon after salting (flukes and tapeworms); and (g) through bathing or other exposure to polluted waters (*leptospirosis* and *schistosomiasis*).

Influent (feed) The liquid (water, wastewater, process water, or sludge) which is delivered to a flotation unit (flotation clarifier, or flotation thickener), or another water treatment unit or waste treatment unit. The concentration of impurities or pollutants is generally measured in mg/L, and its flow measured in gallons per minute (gpm), million gallons per day (MGD), or cubic meters per sec (m^3/s).

Influent characteristics They are the nature and solids concentration of an influent stream and other information relating to its source. They are necessary to determine what design parameters should be used.

Influent water Raw water usually but not always plus recycle streams.

Innovative biological wastewater treatment system It normally includes (a) preliminary treatment units (i.e., screen, comminutor, grit chamber, etc., for removal of sand, gravel, cinders, coffee grounds, small stones, cigarette filter tips, logs, cans, and other large-sized unwanted materials from raw wastewater), (b) primary flotation clarification for removing mainly total suspended solids from preliminary effluent, (c) secondary biological treatment units (such as activated sludge aeration or equivalent plus secondary flotation clarification) for removing dissolved organic/inorganic pollutants from primary effluent, and (d) tertiary treatment plant units (i.e., filtration, granular activated carbon adsorption, ion exchange, oxidation, nitrification, denitrification, and/or disinfection) for final polishing the secondary effluent in order to meet the effluent discharge standards.

Innovative dissolved air flotation water treatment plant (innovative dissolved air flotation water filtration plant) It includes at least the unit operations and unit processes of screening, pumping, rapid mixing for chemical feeding, coagulation–flocculation, dissolved air flotation, filtration, post-disinfection, corrosion control, storage and water distribution, and waste disposal.

Innovative physicochemical flotation-membrane wastewater treatment system It includes (a) preliminary treatment units (i.e., screen, comminutor, grit chamber, etc., for removal of sand, gravel, cinders, coffee grounds, small stones, cigarette filter tips, logs, cans, and other large-sized unwanted materials from raw wastewater), (b) primary flotation clarification for removing mainly total suspended solids from preliminary effluent, (c) secondary physicochemical treatment units (such as chemical precipitation/coagulation or equivalent plus secondary membrane clarification) for removing dissolved organic/inorganic pollutants from primary effluent, and (d) tertiary treatment plant units (i.e., filtration, granular activated carbon adsorption, ion exchange, oxidation, nitrification, denitrification, and/or disinfection) for final polishing the secondary effluent in order to meet the effluent discharge standards. In the nitrification and denitrification steps, only tertiary membrane clarification will be used for solid–water separation.

Innovative physicochemical flotation wastewater treatment system It includes (a) preliminary treatment units (i.e., screen, comminutor, grit chamber, etc., for removal of sand, gravel, cinders, coffee grounds, small stones, cigarette filter tips, logs, cans, and other large-sized unwanted materials from raw wastewater), (b) primary flotation clarification for removing mainly total suspended solids from preliminary effluent, (c) secondary physicochemical treatment units (such as chemical precipitation/coagulation or equivalent plus secondary flotation clarification) for removing dissolved organic/inorganic pollutants from primary effluent, and (d) tertiary treatment plant units (i.e., filtration, granular activated carbon adsorption, ion exchange, oxidation, nitrification, denitrification, and/or disinfection) for final polishing the secondary effluent in order to meet the effluent discharge standards. In the nitrification and denitrification steps, only tertiary flotation clarification will be used for solid–water separation.

Inorganic contaminants They include salts and soluble metals, which can be naturally occurring or result from urban storm water runoff, industrial, or domestic wastewater discharge, oil and gas production, mining or farming.

Instrument blank A clean sample processed through the instrumental steps of the measurement process; used to determine instrument contamination. See Dynamic blank.

Interference A positive or negative effect on a measurement caused by a variable other than the one being investigated.

Interstices Any void spaces in and around solid particles that are packed together.

Ion exchange (IE or IX) A reversible physicochemical water treatment process in which ions from an ion exchanger (i.e., an insoluble permanent solid medium or a resin) are exchanged for ions in a solution or fluid mixture surrounding the ion exchanger.

Ion-exchange regenerant A chemical solution used to restore an exhausted bed of ion exchange resins to the fully ionic (regenerated) form necessary for the desired ion exchange to again take place effectively.

Iron (Fe) (a) It is an element with an atomic weight of 55.847; (b) it is an important trace metal to the human health; (c) small amounts of iron are frequently present in water because of the large amount of iron present in the soil and because corrosive water will pick up iron from pipes. The presence of iron in water is considered objectionable because it imparts a brownish color to laundered goods and affects the taste of beverages such as tea and coffee. Recent studies indicate that eggs spoil faster when washed in water containing iron in excess of 10 mg/L. The U.S. and Canada recommended limits for iron are both 0.3 mg/L, and the Mexican maximum allowable limit (MAL) is also 0.3 mg/L.

Jar test A laboratory procedure that simulates a water treatment plant's coagulation, rapid mix, flocculation, and sedimentation processes. Differing chemical doses, energy of rapid mix, energy of slow mix, and settling time can be examined. The purpose of this procedure is to estimate the minimum or optimal coagulant dose required to achieve certain water quality goals. Samples of water to be treated are commonly placed in six jars. Various amounts of a single chemical are added to each jar while holding all other chemicals at a consistent dose, and observing the formation of floc, settling of solids, and resulting water quality.

KAMET It is the abbreviation of Krofta Advanced Municipal Effluent Treatment (KAMET), and is a circular package plant consisting of both Supracell and Sandfloat with Supracell on the top. KAMET can be used for either water treatment or wastewater treatment, but is advertised for wastewater treatment.

KAMWT It is the abbreviation of Krofta Advanced Municipal Water Treatment (KAMWT), and is a circular package plant consisting of both Supracell and Sandfloat with Supracell on the top. KAMWT can be used for either water treatment or wastewater treatment, but is advertised for water treatment.

Kjeldahl method The Kjeldahl method was developed in 1883 by a brewer called Johann Kjeldahl. A food is digested with a strong acid so that it releases nitrogen which can be determined by a suitable titration technique. The amount of protein present is then calculated from the nitrogen concentration of the food. The Kjeldahl method does not measure the protein content directly a *conversion factor* (*F*) is needed to convert the measured nitrogen concentration to a protein concentration. A conversion factor of 6.25 (equivalent to 0.16 g nitrogen per gram of protein) is used for many applications; however, this is only an average value, and each protein has a different conversion factor depending on its amino-acid composition. The Kjeldahl method can conveniently be divided into three steps: digestion, neutralization, and titration.

Krofta Engineering Corporation (KEC) It is an equipment manufacturer and engineering design company in Lenox, Massachusetts, USA, working closely with the Lenox Institute of Water Technology (LIWT) for development, production, sales, installation, and operation of innovative water and wastewater treatment processes, monitoring devices, and analytical methods.

Lagooning The placement of solid or liquid material in a basin, reservoir, or artificial impoundment for purposes of storage, treatment, or disposal.

Leachate The underflow from a dewatering unit such as a sludge-drying bed or monofill.

Lead (Pb) (a) It is an element with an atomic weight of 207.2; (b) lead is a heavy metal. Its sources include lead and galvanized pipes, auto exhausts, and hazardous waste releases. The maximum allowable concentrations of lead in drinking water by the standards are: 0.01 mg/L (WHO and Canada), 0.015 mg/L (USA), and 0.025 mg/L (Mexico) of water. Excessive amounts well above this standard may result in nervous system disorders or brain or kidney damage. In the USA, lead and copper together are also regulated by a treatment technique (TT). The reader is referred to Sect. 10.5.9, Copper, for the details.

Leaf, filter Any flat filter element that has or supports the filter septum.

Legionella*, *Mycobacterium avium* complex, *Aeromonas hydrophila*, and *Helicobacter pylori They are considered as the emerging bacterial waterborne pathogens in Canada. These emerging pathogens have been linked to gastrointestinal illness in human populations. In the USA, only *Legionella* which causes a type of pneumonia (Legionnaire's disease) is being controlled by an effective treatment technique (TT), and the U.S. EPA specified MCLG is zero.

Lenox Institute of Water Technology (LIWT) It is a nonprofit humanitarian engineering college in Massachusetts, USA, with expertise in environmental STEAM (science, technology, engineering, arts, and mathematics) education, R&D, process and monitoring system development, patent application, licensing, fundraising, engineering design, and project management. LIWT teams up with Krofta Engineering Corporation (KEC), for technology transfer, equipment design, and voluntary humanitarian global service through free education, training, and academic publications.

Leptospirosis It is also known as hemorrhagic jaundice or Weil's disease, is traceable to swimming or wading in polluted canals, streams, and lakes. Rats and dogs are among the carriers of the spirochetes causing the fairly large group of associated diseases.

Lime-soda softening process A process for softening water by the addition of lime and soda ash to convert soluble calcium hardness to insoluble calcium carbonate, and convert soluble magnesium hardness to insoluble magnesium hydroxide. The hardness is removed when the insoluble calcium carbonate and magnesium hydroxide are removed by clarification and filtration.

Liquids from dewatering processes A stream containing liquids generated from a unit used to concentrate solids for disposal.

Liquor (a) Material to be filtered—as in "feed liquor"; (b) material to be mixed as "mixed liquor."

Load General term that refers to a material or constituent in solution, in suspension, or in transport; usually expressed in terms of mass or volume.

Management systems review (MSR) The qualitative assessment of a data collection operation and/or organization(s) to establish whether the prevailing quality management structure, practices, and procedures are adequate for ensuring that the type and quality of data needed and expected are obtained.

Manganese (Mn) (a) It is an element with an atomic weight of 54.938; (b) manganese is normally associated with iron. There are two reasons for limiting the concentration of manganese in drinking water: (a) to prevent esthetic and economic damage and (b) to avoid any possible physiological effects from excessive intake. The domestic user finds that manganese produces a brownish color in laundered goods, and impairs the taste of beverages, including coffee and tea. Serious surface and ground water pollution problems have developed from existing and abandoned mining operations. Among the worst are those associated with coalmine operations, where heavy concentrations of iron, manganese, sulfates, and acids have resulted from the weathering and leaching of minerals (pyrites). The U.S. and Canada recommended limits for manganese are both 0.05 mg/L, while the Mexican maximum allowable limit (MAL) is 0.15 mg/L.

Manifold, filter A pipe or assembly into which the filter elements are connected to form one common discharge for the filtrate.

Matrix A specific type of medium (e.g., surface water, drinking water) in which the analyte of interest may be contained.

Maximum contaminant level (MCL) The highest level of a contaminant that is allowed in drinking water as delineated by the National Primary Drinking Water Regulations. MCLs are set as close to the MCLGs as feasible using the best available treatment technology. MCLs ensure that drinking water does not pose either a short-term or long-term health risk. USEPA sets MCLs at levels that are economically and technologically feasible. Some states set MCLs which are stricter than USEPA's.

Maximum contaminant level goal (MCLG) The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety. This goal is not always economically or technologically feasible, and the goal is not legally enforceable.

Maximum residual disinfectant level (MRDL) The highest level of a disinfectant allowed in drinking water. There is convincing evidence that addition of a disinfectant is necessary for control of microbial contaminants (e.g., chlorine, chloramines, chlorine dioxide).

Maximum residual disinfectant level goal (MRDLG) The level of a drinking water disinfectant below which there is no known expected risk to health. The MRDLG does not reflect the benefits of the use of disinfectants to control microbial contaminants.

Mean discharge The arithmetic mean of individual daily mean discharges during a specific period, usually daily, monthly, or annually.

Measurement range The range over which the precision and/or recovery of a measurement method are regarded as acceptable.

Measurement standard A standard added to the prepared test portion of a sample (e.g., to the concentrated extract or the digestate) as a reference for calibrating and controlling measurement or instrumental precision and bias.

Mechanical aeration A process of introducing air and oxygen into a liquid (water) by the mechanical action of paddle, spray, paddle wheel, or turbine mechanism.

Media (medium), filter The material that performs the actual separation of solids from liquids. Sometimes erroneously used to mean septum.

Median The middle value for an ordered set of n values; represented by the central value when n is odd or by the mean of the two most central values when n is even.

Medium A substance (e.g., air, water, soil) which serves as a carrier of the analytes of interest.

Membrane concentrate The reject stream generated when the source water is passed through a membrane for treatment.

Membrane filtration A filtration process (e.g., reverse osmosis, nanofiltration, ultrafiltration, and microfiltration) using tubular or spiral-wound elements that exhibits the ability to mechanically separate water from other ions and solids by creating a pressure differential and flow across a membrane with an absolute pore size <1 micron.

Mercury (Hg) (a) It is an element with an atomic weight of 200.59; (b) it is a heavy metal. Large increases in mercury levels in water can be caused by industrial and agricultural use and waste releases. The health risk from mercury is greater from mercury in fish than simply from waterborne mercury. Mercury toxicity may be acute, in large doses, or chronic, from lower doses taken over an extended time period. The maximum allowable concentrations of mercury in drinking water by the standards are: 0.002 mg/L (USA), 0.001 mg/L (Mexico), and 0.006 mg/L (WHO). The U.S. level (0.002 mg/L) is 13% of the total allowable daily dietary intake of mercury.

Mesh, filter (a) Number of strands in a lineal inch of woven filter fabric. (b) A commonly used synonym for septum, as in wire mesh.

Method A body of procedures and techniques for performing a task (e.g., sampling, characterization, quantification) systematically presented in the order in which they are to be executed.

Microbial contaminants They include viruses, bacteria, etc., which may come from sewage treatment plants, septic systems, agricultural livestock operations, and wildlife. Determination of total coliforms (as an indicator) is for controlling microbial contaminants.

Microfiltration (MF) It is one of the four pressure-driven membrane filtration processes (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) that removes ions, salts, other dissolved solids, and nonvolatile organics. In potable water treatment, microfiltration (MF) is operated at low transmembrane pressure (1–30 psi) and is used for separation of bacteria, large microorganisms, fine solids, large flocs, large colloids, etc., as well as other bigger substances. MF member has a large pore size range (from 0.1 to 10 micron).

Micro-flotation In micro-flotation, the entire volume of water to be treated is subjected to the increased pressure by passing the water down and up a shaft approximately 10 meters deep. At the bottom of the shaft, on the downcomer side, air is injected by one air blower under low pressure (20 psig). Undissolved air rises up the shaft against the flow, thus increasing the saturation of the water. As the water rises in the upflow section, the hydrostatic pressure decreases. Some of the soluble air is then released out of solution in the form of fine air bubbles due to a reduction in air solubility caused by pressure reduction. Floc agglomeration and bubble generation occur simultaneously and gently, providing good attachment of the air bubbles to the flocs. The amount of air which can be dissolved is limited by the depth of shaft (e.g., hydrostatic pressure provided). The saturation of the water with air at that depth is dependent on the way the air is introduced to the system (e.g., size of air bubbles produced at point of injection). Similarly the floats collected on water surface are the impurities/pollutants removed from the water. The floats are collected by a rotating sludge collection scoop or equivalent. The bottom flotation clarified water is discharged as the treated water.

Micron (a) A unit of length equal to 1 micrometer (μm). One millionth of a m or one thousandth of a mm. One micron equals 0.00004 of an inch; (b) now it is expressed as micrometer (um). A unit of length: 10^{-6} meters.

Microorganisms Tiny living organisms that can be seen only with the aid of a microscope. Some microorganisms can cause acute health problems when consumed in drinking water. Also known as microbes.

Microsand A small-grain sand used to improve settling.

Minor streams Waste streams that result due to spills, laboratory analyses, washdown of plant facilities, leaks, and other similar streams that are small in volume.

Modeling It is an act of developing a mathematical or physical representation of a real world system, in order to study and understand the behavior of that system.

Monitoring Testing that water systems must perform to detect and measure contaminants. A water system that does not follow EPA's monitoring methodology or schedule is in violation, and may be subject to legal action.

Monochloramine (NH_2 Cl) A chloramines chemical species that is produced from the reaction of chlorine and ammonia in a chloramination process. Typically monochloramine and a small amount of dichloramine (NH Cl_2) are formed in the chloramination process as the secondary disinfectant for protection of water distribution system.

Monofilament A single synthetic fiber of continuous length; used in weaving filter cloths.

Monofill An ultimate disposal technique for water treatment plant sludge in which the sludge is applied to a landfill for sludge only.

Multifilament A number of continuous fiber strands that are twisted together to form a yarn; used in weaving filter cloths.

Multiple tray aeration A unit process designed to transfer impurities from the liquid phase to the gaseous phase and/or to provide oxygen for oxidation reaction in the liquid. The process equipment consists of multiple staggered slat or porous trays which allow liquid to be treated to flow downward through the trays as rain drops, and allow contact between a countercurrent airflow and the liquid, and thereby promoting mass transfer and/or oxidation.

Nanofiltration (NF) It is one of the four pressure-driven membrane filtration processes (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) that removes ions, salts, other dissolved solids, and nonvolatile organics. In potable water treatment, nanofiltration (NF) is operated at high transmembrane pressure (75–149 psi) and mainly used for separation of di-valence and tri-valence ions, hardness, DBP, NOM, *Giardia* cysts, *Cryptosporidium*, color, surfactants, etc., as well as bigger substances. NF member has very small pore size range (from 0.0005 to 0.005 micron).

National Primary Drinking Water Regulations (NPDWRs or primary standards) In the USA, they are legally enforceable standards that apply to public water systems. Primary standards protect public health by limiting the levels of contaminants in drinking water. These regulations cover the microorganisms, disinfection by-products, disinfectants, inorganic chemicals, organic chemicals, and radionuclides.

National Secondary Drinking Water Regulations (NSDWRs or secondary standards) In the USA, they are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. U.S. EPA recommends secondary standards to water systems but does not require systems to comply. However, states may choose to adopt them as enforceable standards.

Natural flotation Same as gravity flotation, or natural gravity flotation.

Natural resources They include all natural products, energy, forces, lights, biological lives, of the universe that support life and satisfy people's needs. Air, land, and water are natural resources, as are biological and physical resources in the air, on the land and in the water, such as solar heat, rains, birds, bees, flowers, bacteria, wild animals and fish, as well as minerals, oil, coal, metals, stone, sand, lights, winds, magnetic forces, radioactivity, even elements, DNA, etc.

Nitrates (NO_3^-) and Nitrites (NO_2^-) Nitrate (NO_3^-) in drinking water above the standard poses an immediate threat to children less than 3 months of age. In some infants, excessive levels of nitrate have been known to react with the hemoglobin in the blood to produce an anemic condition commonly known as "blue baby." If the drinking water contains an excessive amount of nitrate, it should not be given to infants under 3 months of age and should not to be used to prepare formula. Nitrate can be removed from water by ion exchange, RO, or distillation. Nitrates in excess of normal concentrations, often in shallow wells, may be an indication of seepage from livestock manure deposits. In some polluted wells, nitrite (NO_2^-) will also be present in concentrations greater than 1 mg/L and is even more hazardous to infants. When the presence of high nitrite concentration is suspected the water should not be used for infant feeding. The nitrate concentration should be determined, and if excessive, advice should be obtained from health authorities about the suitability of using the water for drinking by anyone. The maximum allowable concentrations of nitrate in drinking water by the standards are: 10 mg/L as N (USA and Mexico), 45 mg/L as NO_3^- (Canada), and 50 mg/L as NO_3^- (WHO). The maximum allowable concentrations of nitrite are: 1.0 mg/L as N (USA), 0.05 mg/L as N (Mexico), and 3 mg/L as NO_2^- (WHO).

Nitrification It is a biological process by which ammonia in wastewater is converted by Nitrosomonas and Nitrobacter to nitrite, then to nitrate in the presence of oxygen. The biological reactions involved in these conversions may take place during activated sludge treatment or as separate stage following removal of carbonaceous materials. Separate stage nitrification may be accomplished via suspended growth or attached growth unit processes. In either case, the nitrification step is preceded by a pretreatment sequence (i.e., preliminary treatment, primary treatment, and secondary treatment). Possible secondary treatment may be (a) biological secondary treatment, such as activated sludge, trickling filter, roughing filter, plus secondary clarification or (b) physicochemical secondary treatment, such as chemical precipitation/coagulation plus secondary clarification.

Low BOD (i.e., BOD_5/TKN ratio of less than 3) in the secondary effluent will assure a high concentration of nitrifiers (Nitrosomonas and Nitrobacter) in the nitrification biomass. The most common separate stage nitrification process is the plug flow suspended growth configuration with clarification. In this process, pretreatment effluent (i.e., nitrification influent) is pH adjusted as required, and aerated, in a plug flow mode. Because the carbonaceous demand is low, nitrifiers predominate. A clarifier (either sedimentation clarifier or flotation clarifier) follows aeration, and nitrification sludge is returned to the aeration tank. A possible modification is the use of pure oxygen in place of conventional aeration during the plug flow operation.

Noncommunity water system A public water system that serves the public but does not serve the same people year-round. There are two types of noncommunity systems: (a) non-transient noncommunity water system (about 20,000 people) and (b) transient noncommunity water system (about 89,000 people).

Nonpoint source contaminant A substance that pollutes or degrades water that comes from lawn or cropland runoff, the nonpoint-source water pollution—water contamination that originates from a broad area (such as leaching of agricultural chemicals from crop land) and enters the water resource diffusely over a large area.

Nonrenewable or unsustainable natural resources They are natural resources that are not renewable, such as mineral and fossil fuels. Some renewable resources may become nonrenewable if they are destroyed or lost by bad resource management, e.g., farmland losing topsoil or denuding of watersheds.

Nonselective herbicide Kills or significantly retards growth of most higher plant species.

Non-transient noncommunity water system (there are approximately 20,000) A noncommunity water system that serves the same people more than 6 months per year, but not year-round, for example, a school with its own water supply is considered a non-transient system.

Nonwoven, filter A filter cloth or paper that is formed of synthetic fibers that are randomly oriented in the media. Usually held together with a binder.

Not detectable Below the limit of detection of a specified method of analysis.

Nutrient Element or compound essential for animal and plant growth. Common nutrients in fertilizer include nitrogen, phosphorus, and potassium.

Office of Research and Standards Guideline (ORSG) This is the concentration of a chemical in drinking water at or below which adverse health effects are unlikely to occur after chronic (lifetime) exposure. If exceeded, it serves as an indicator of the potential need for further action.

On-stream, filter Describes when a filter system is producing a filtered product.

Operating capacity The maximum finished water production rate approved by the State drinking water program.

Operating cycle It is the operational time of the flotation unit, or a different water or waste treatment unit, in hours/day. In most cases for industrial waste, the operating cycle is determined by the production schedule.

Optical density It is measured in a spectrophotometer, can be used as a measure of the concentration of substances in a suspension. As visible light passes through a cell suspension the light is scattered. Greater scatter indicates that more bacteria or other material is present. Optical density measures the amount of attenuation, or intensity lost, when light passes through an optical component. It also tracks attenuation based on the scattering of light, whereas absorbance considers only the absorption of light within the optical component.

Organic chemical contaminants They include synthetic and volatile organic chemicals (VOCs), which are the by-products of industrial processes and petroleum production, and can also come from gas stations, urban storm water runoff, and septic systems.

Overland flow The part of surface runoff flowing over land surfaces toward stream channels.

Oxidation The combination of oxygen with a substance, or the removal of hydrogen from it or, more generally, any reaction in which an atom loses electrons.

Oxygenation The process of adding dissolved oxygen to a solution.

Ozonation A disinfection and oxidation process for water or waste treatment using ozone.

Ozone A gas that results from complex chemical reactions between nitrogen dioxide and volatile organic compounds; the major component of smog. Ozone at the ground level is one of the six “criteria” pollutants for which EPA has established national ambient air quality standards.

Package plant A single compact process plant that contains all required unit processes and unit operations for water or waste treatment.

Package plant filtration A single compact filtration plant that contains all supporting unit processes and unit operations for water filtration treatment.

Packed column aeration (PCA) A unit process designed to transfer impurities (such as volatile organic compounds, color substances, and taste and odor-causing substances) from the liquid phase to the gaseous phase and/or to provide air (oxygen) for oxidation reaction in the liquid. The process equipment is a hollow vertical column containing packing materials which provide surface area over which the liquid to be treated flows through. There is a contact between a countercurrent airflow and the liquid on the surface of the packing materials and the contact promotes mass transfer and/or oxidation. Also referred to as packed tower aeration.

Parameter Any quantity such as a mean or a standard deviation characterizing a population. Commonly misused for “variable,” “characteristic,” or “property.”

Parasitic organisms There are five categories of parasitic organisms infective or undesirable to humans are found in water: bacteria, protozoa, worms, viruses, fungi, and algae. Bacteria, protozoa, and worms are classified as animals, which have the following characteristics: (a) release energy and may have sensory organs and a nervous system, (b) release carbon dioxide, (c) cell walls composed principally of protein matter, a nitrogen bearing compound, (d) metabolism depends upon digestion of food within an alimentary canal, and (e) digestion process in “analytic” by which ingested materials are decomposed to supply materials for synthesis of proteins required for growth and reproduction. Algae are organisms in the plant kingdom, which have the following characteristics: (a) store energy, (b) have no sensory organs or nervous system, (c) release oxygen, (d) cell walls composed of cellulose—a carbohydrate, (e) metabolism depends upon absorption of water and gases by root hairs and natural openings called stomata, and there is no digestion of food, and (f) utilize carbon dioxide from the air and water and nitrogen salts to synthesize carbohydrates and proteins needed for growth and reproduction. Bacteria, protozoa, worms, viruses, and fungi are disease producing organisms. Some of these complete their life cycle by passage through an intermediary aquatic host; others are merely transported by water from humans to humans. Fungi and algae are responsible for taste and odor in water, therefore, are undesirable.

Particle size distribution The distribution obtained from a particle count grouped by specific micron sizes.

PCBs, CFCs, and dioxin Polychlorinated biphenyl (PCB), chlorofluorocarbon (CFC), petroleum products, and dioxin are major toxic contaminants in water, soil, and air. PCBs are a family of compounds that were used extensively in electrical equipment, such as transformers, because of their insulating and heat transferring qualities. They are suspected human carcinogens and have been linked to the liver, kidney, and other health problems. Freon is a commercial trademark for a series of fluorocarbon products used in refrigeration and air-conditioning equipment, as aerosol propellants, blowing agents, fire extinguishing agents, and cleaning fluids and solvents. Many types contain chlorine as well as fluorine, and should be called chlorofluorocarbons (CFC). Dioxins form a family of aromatic compounds known chemically as di-benzo-p-dioxins. Each of these compounds has a nucleus triple ring structure consisting of two benzene rings interconnected to each other through a pair of oxygen atoms. Most interest has been directed toward the isomer 2,3,7,8-TCDD, which is the most toxic dioxin. Humans exhibit symptoms effecting on enzyme and nervous systems, and muscle and joint pains after exposure to dioxin. When a water supply source is known to be contaminated by PCB, CFC, or dioxins, the raw water must be properly treated by the advanced water treatment technology, such as carbon adsorption, membrane filtration, etc. For instance, the water of Hudson River, New York, is a water supply source to many communities along the river, but has been contaminated by PCBs from General Electric Company. The maximum contaminant level (MCL) of PCB and dioxin (2,3,7,8-TCDD) in drinking water by the US Standards are 0.0005 mg/L for PCB and 0.00000003 mg/L for dioxin.

Permeability, filter The property of the filter medium that permits a fluid to pass through under the influence of a pressure differential.

Pesticides Millions of pounds (1 lb. = 0.454 kg) of pesticides are used on croplands, forests, lawns, and gardens in the USA each year. A large quantity of hazardous pesticides is also released by the pesticide industry to the environment. Besides, careless use of pesticides can also contaminate water sources and make the water unsuitable for drinking. Numerous cases have been reported where individual wells have been contaminated when the house was treated for termite control or the lawn was treated for weed control. The use of pesticides near wells is not recommended. Otherwise, these hazardous pesticides drain off into surface waters or seep into underground water supplies. Many pesticides pose health problems if they get into drinking water and the waters not properly treated. The maximum allowable concentrations for pesticides in drinking water are: (a) endrin, 0.002 mg/L (USA) and 0.0006 mg/L (WHO); (b) indane, 0.0002 mg/L (USA) and 0.002 mg/L (WHO); (c) methoxychlor, 0.04 mg/L (USA) and 0.02 mg/L (WHO); (d) oxaphene, 0.003 mg/L (USA); (e) 2,4-D, 0.07 mg/L (USA); 0.03 mg/L (WHO); 0.1 mg/L (Canada); 0.05 mg/L (Mexico); (f) 2,4,5-TP silvex, 0.05 mg/L (USA); 0.009 mg/L (WHO); (g) Aldrin and dieldrin pesticides, 0.00003 mg/L (WHO, Mexico); 0.0007 mg/L (Canada); unregulated (USA).

pH pH is an expression of the intensity of the basic or acid condition of a solution. Mathematically, pH is the negative logarithm (base 10) of the hydrogen ion concentration, [H+]. [pH = log (1/H+)]. The pH may range from 0 to 14, where 0 is most acidic, 14 most basic, and 7 neutral. Natural waters usually have a pH between 6.5 and 8.5.

pH adjustment A means of maintaining the optimum pH through the use of chemical additives.

Pharmaceuticals They are the emerging contaminants introduced into surface and groundwater sources by discharges from individuals using these chemicals, from uncontrolled drug disposal, and from agricultural runoff from livestock manure. Routine monitoring for pharmaceuticals in drinking water advanced drinking water treatment to reduce the pharmaceuticals may become necessary in the future.

Phosphates (PO_4^{3-}) Phosphates and nitrogen are two major nutrients causing eutrophication in natural waters. Serious water quality problems may result from uncontrolled algae and aquatic plant blooms in lakes and reservoirs when phosphorus concentration exceeds 0.05 mg/L, if phosphorus is the limiting nutrient. Suggested adult daily intake for phosphorus is 800 mg/day. A deficiency in phosphorus may result in weakness, bone pain, and rickets.

Phosphorus A nutrient essential for growth that can play a key role in stimulating aquatic growth in lakes and streams.

Photodegradation Breakdown of a substance by exposure to light; the process whereby ultraviolet radiation in sunlight attacks a chemical bond or link in a chemical structure.

Photolysis The decomposition of a compound into simpler units as a result of the absorption of one or more quanta of radiation.

Photosynthesis Synthesis of chemical compounds by organisms with the aid of light. Carbon dioxide is used as raw material for photosynthesis and oxygen is a product.

Picocurie (pCi) A unit of radioactivity mainly used in the USA representing the rate at which nuclear radiations are emitted. One picocurie (1 pCi) represents a quantity of radioactive material with an activity equal to one billionth of a curie, i.e., 10^{-12} curie.

Pilot plant A small-scale water treatment plant set up on a raw water source to determine the feasibility and impacts of a treatment scheme for a given water supply. Pilot plants are used to test alternative technologies and experiment with chemical dosages for new water treatment plants or upgrades to existing plants.

Plastic separation It is a flotation process for water–plastic separation or air–plastic separation based on the flotation actions.

Plate, filter Any flat surfaced filter element. Usually found in horizontal plate filters.

Plug flow It is a hydraulic flow regime in which no longitudinal dispersion (mixing in the direction of flow) occurs.

Plug flow reactor It is a chemical engineering reactor in which the hydraulic behavior is such that the residence time of a given input, or plug, is exactly equal to the theoretical hydraulic retention time.

Point source A source at a discrete location such as a discharge pipe, drainage ditch, tunnel, well, concentrated livestock operation, or floating craft.

Point-source contaminant Any substance that degrades water quality and originates from discrete locations such as discharge pipes, drainage ditches, wells, concentrated livestock operations, or floating craft.

Point-source pollution Pollution discharged through a pipe or some other discrete source from municipal water-treatment plants, factories, confined animal feedlots, or combined sewers.

Pollutant Any substance that, when present in a hydrologic system at sufficient concentration, degrades water quality in ways that are or could become harmful to human and/or ecological health or that impair the use of water for recreation, agriculture, industry, commerce, or domestic purposes.

Pollution The introduction of unwanted components into waters, air, or soil, usually as a result of human activity, e.g., hot water in rivers, sewage in the sea, oil on land.

Polyelectrolyte Long-chained, ionic, high-molecular-weight, synthetic, water-soluble, organic coagulants. Also referred to as polymers. Nonionic polymers are not polyelectrolytes.

Polymer (a) A synthetic organic compound with high molecular weight and composed of repeating chemical units (monomers). Polymers may be polyelectrolytes (such as water-soluble flocculants), water-insoluble ion exchange resins, or insoluble uncharged materials (such as those used for plastic or plastic-lined pipe). (b) It is high-molecular-weight organic chemical that can be used as a coagulating aid.

Porosity The ratio of the void volume to the total bulk volume.

Post-treatment An additional treatment process following a prior treatment process. For instance, granular activated carbon filtration can be a posttreatment to rapid sand filtration.

Powdered activated carbon (PAC) An activated carbon which is porous and in powdered form with many micro- and macro-channels and surface area, suitable for adsorption of many soluble organics and some soluble inorganics from a fluid.

Powdered activated carbon adsorption A unit process involving the addition of powdered activated carbon to water for removal of impurities, such as taste and odor-causing substances, color-causing substances, volatile organic compounds, etc.

Ppm Parts per million. A unit of concentration: e.g., 3 ppm would be 3 pounds of solids in 1000.000 pounds of water.

Precipitation (a) A chemical process in which one chemical agent precipitates another soluble chemical; (b) the total measurable supply of water received directly from clouds as rain, sleet, hail, snow, etc.

Precision The degree to which a set of observations or measurements of the same property, usually obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative terms.

Precoat The initial layer of CELITE that is deposited on the filter septum. Usually 1/8″ thick on pressure filters and 2″ to 6″ thick on R.V.P.F.

Precoat filtration A process that is designed to remove particulates by applying the water to be treated to a fabric or membrane module coated with very fine granular medium, such as diatomaceous earth. Precoat filtration is also called diatomaceous earth filtration.

Prefilt Material to be filtered.

Preliminary treatment It is the first treatment step or preliminary step of either a conventional wastewater treatment system or an independent physicochemical treatment system. Preliminary treatment consists of bar screen, comminutor, and grit chamber mainly for removing large objects, such as rocks, logs and cans, grit, etc., from raw wastewater. Comminutor is an option depending on the nature and characteristics of raw wastewater.

Presedimentation A water treatment process in which solid particles are settled out of the water in a clarifier or sedimentation basin prior to entering the treatment plant.

Pressate The water separated from the solids by a filter press.

Pretreatment One or more process steps occurring immediately before water enters a downstream process unit.

Primary effluent The effluent from a primary treatment system (either primary sedimentation clarification or primary flotation clarification) by which most of total suspended solids in wastewater have been removed.

Primary flotation clarification It is a unit process or unit operation for removal of mainly total suspended solids (settleable solids and floatable solids) from screened wastewater using a primary flotation clarifier.

Primary flotation clarifier A dissolved air flotation (DAF) reactor is used to float total suspended solids (TSS) from screened wastewater by decreasing their apparent density. DAF consists of saturating a portion or all of the wastewater feed, or a portion of recycled effluent with air at a pressure of 25 to 90 lb./square inch (gage). The pressurized wastewater is held at this pressure for 0.5 to 3 minutes in a retention tank and then released to atmospheric pressure to the flotation chamber. The sudden reduction in pressure results in the release of microscopic air bubbles which attach themselves to TSS and oil particles in the wastewater in the flotation chamber. This results in agglomeration which, due to the entrained air, has greatly increased vertical rise rates of about 0.5 to 2 ft./min. The floated materials rise to the surface to form a froth layer (float). Specially designed scrapers or other skimming devices continuously remove the froth (or float). The retention time in the flotation chambers is usually about 20–60 minutes for rectangular flotation clarifier, and about 3–15 minutes for circular flotation clarifier using zero-horizontal velocity design. The effectiveness of dissolved air flotation depends upon the attachment of bubbles to the suspended solids and/or oil which are to be removed from the waste stream. The attraction between the air bubble and particle is primarily a result of the particle surface charge and bubble-size distribution. The more uniform the distribution of water and micro-bubbles, the shallower the flotation clarifier can be. Generally, the depth of effective flotation units is between 3 and 9 feet.

Primary sedimentation clarification It is a unit process or unit operation for removal of mainly total suspended solids (settleable solids and floatable solids) from screened wastewater using a primary sedimentation clarifier.

Primary sedimentation clarifier It is a tank used to settle mainly total suspended solids (TSS) from screened raw wastewater by gravity. The main objectives of a primary sedimentation clarifier are removal of settleable solids by settling them to the clarifier bottom and removal of floatable solids by skimming them from the clarifier's wastewater surface. In a rectangular sedimentation clarifier, the wastewater flows from one end to the other and the settled sludge is moved to a hopper at on end, either by scrapers called "flights" set on parallel chains or by a single bottom scraper set on a traveling bridge. Floating materials, such as grease and oil, are collected by a surface skimmer and then removed from the rectangular sedimentation clarifier. In a circular sedimentation clarifier, the wastewater usually enters in the middle and flows toward the outside edge. Settled sludge is pushed to the hopper that is in the middle of the circular clarifier's tank bottom. Floating material is removed by a surface skimmer connected to the sludge collector.

Primary treatment It is an important wastewater treatment step (either primary sedimentation clarification or primary flotation clarification mainly for removing total suspended solids from preliminary treatment effluent) after the preliminary treatment (i.e., bar screen, comminutor, and grit chamber mainly for removing large objects from raw wastewater), but before secondary treatment (either biological treatment or physicochemical treatment mainly for removing dissolved organic/inorganic pollutants from primary effluent).

Procedure A set of systematic instructions for performing an operation.

Protein Proteins are polymers of amino acids. Twenty different types of amino acids occur naturally in proteins. Proteins differ from each other according to the type, number, and sequence of amino acids that make up the polypeptide backbone. As a result they have different molecular structures, nutritional attributes, and physiochemical properties. Proteins are important constituents of foods for a number of different reasons. They are a major source of *energy*, as well as containing essential amino acids, such as lysine, tryptophan, methionine, leucine, isoleucine, and valine, which are essential to human health, but which the body cannot synthesize. Proteins are also the major structural components of many natural foods, often determining their overall texture, e.g., tenderness of meat or fish products. Isolated proteins are often used in foods as ingredients because of their unique functional properties, i.e., their ability to provide desirable appearance, texture, or stability.

Protozoa (including *Cryptosporidium* and *Giardia lamblia*) Although it is estimated that between 1 and 10% of the United States population are carriers of amebic cysts, the reported incidence of waterborne amebic dysentery (*amebiasi*s) has been low. Among the probable reasons are (a) the relatively small number of cysts excreted by carriers and (b) the relatively large size and weight of the cysts, which account for their natural removal from water by sedimentation as well as by filtration. Relatively massive incursion of pollution into water distribution systems by backflow from house drainage systems and by cross-connections with unsafe water supplies has generally been associated with waterborne outbreaks.

Public water systems (PWSs) They come in all shapes and sizes, and no two are exactly the same. They may be publicly or privately owned and maintained. All *public water systems* must have at least 15 service connections or serve at least 25 people per day for 60 days of the year. Drinking water standards apply to water systems differently based on their type and size: (a) community water system (about 54,000 people); (b) noncommunity water system.

Quality The sum of features and properties/characteristics of a product or service that bear on its ability to satisfy stated needs.

Quality assurance (QA) An integrated system of activities involving planning, quality control, quality assessment, reporting, and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

Quality control (QC) The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users. The aim is to provide quality that is satisfactory, adequate, dependable, and economical.

Radioactive contaminants They can be naturally occurring or be the result of oil and gas production and mining activities.

Radiological characteristics and constituents The development and use of atomic energy as a power source and mining of radioactive materials have made it necessary to establish limiting concentrations for the intake into the body of radioactive substances, including drinking water. The effects of human exposure to radiation or radioactive materials are viewed as harmful and any unnecessary exposure should be avoided. The concentrations of radioactive materials specified in the current U.S. Drinking Water Standards are intended to limit the human intake of these substances so that the total radiation exposure of any individual will not exceed those defined in the Radiation Protection Guides recommended by the USEPA. Humans have always been exposed to natural radiation from water, food, and air. The amount of radiation to which the individual is normally exposed varies with the amount of background radioactivity. Water of high radioactivity is unusual. Nevertheless, it is known to exist in certain areas, either from natural or manmade sources. Gross alpha particle activity, gross beta particle activity, and total radium-226 and radium-228 are found from radioactive wastes, uranium deposits, and certain geological formations, and are a cancer-causing energy. The MCLs for gross alpha particle activity, gross beta particle activity, and total radium-226 and radium-228 and uranium are set by the U.S. EPA at alpha particles = 15 pCi/L; beta particles and photo emitters = 4 mrem/year; combined radium-226 and radium-228 = 5 pCi/L; and uranium = 0.03 mg/L. Again the State government may have more stringent Drinking Water Guidelines. For instance, the Commonwealth of Massachusetts Drinking Water Standards include additional photon activity, tritium, strontiurn-90, and radon-222 for the State enforcement. Radon in groundwater can be effectively removed by granular activated carbon. The health-based MAC guidelines for radiological parameters in Canada are different and listed below: cesium-137 = 10 Bq/L; iodine-131 = 6 Bq/L; lead-210 = 0.2 Bq/L; radium-226 = 0.5 Bq/L; strontium-90 = 5 Bq/L; tritium = 7000 Bq/L; and uranium = 0.02 mg/L. Becquerel (Bq) is the unit of activity of a radioactive substance or the rate at which transformations occur in the substance. One becquerel (1 Bq) is equal to one transformation per second and approximately equal to 27 picocuries (pCi).

Radionuclides Radioactive, cancer-causing substances that release radiation (i.e., alpha, beta, and gamma which are radioactive isotopes or unstable forms of elements). Radionuclides include (a) radium-226, radium-228, natural uranium, radon, gross alpha, gross beta, and photon emitters; and (b) strontium-90, lead-210, polonium-210, thorium-230, and thorium-232.

Radium (Ra) One of radionuclides regulated by the U.S. EPA. Radium is a naturally occurring radioactive element in the form of radium-226 or radium-228, which are produced in the decay of uranium and thorium series.

Radon (Rn) A gaseous radioactive element that derives from the radioactive decay of radium. Radon is one of radionuclides regulated by the USEPA.

Random Lacking a definite plan, purpose, or pattern; due to chance.

Range The difference between the minimum and the maximum of a set of values.

Rapid mixing A water or wastewater treatment unit process of quickly mixing a chemical solution uniformly through the process water.

Rapid sand filtration A type of granular filter for which the granular material is sand, and the filtration rate is at least 2 gpm/ft^2 (5 m/h).

Raw data Any original factual information from a measurement activity or study recorded in laboratory worksheets, records, memoranda, notes, or exact copies thereof and that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photographs, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated, and verified accurate by signature), the exact copy or exact transcript may be substituted.

Raw wastewater or sewage Wastewater or sewage in its natural state, prior to any wastewater treatment.

Raw water Water in its natural state, prior to any treatment for drinking.

Reagent A chemical substance used to cause a reaction for the purpose of chemical analysis.

Reagent blank A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps to error in the observed value.

Reagent grade The second highest purity designation for reagents which conform to the current specifications of the American Chemical Society Committee on Analytical Reagents.

Recycle (a) The act of returning a residual stream to a wastewater treatment plant's primary treatment process; (b) the act of returning a residual stream to one of a waste treatment plant's head treatment process, such as chemical rapid mixing tank.

Recycle notification Information on recycling practices that must be provided to the State by conventional and direct filtration water treatment plants that recycle spent filter backwash, thickener supernatant, or liquids from dewatering processes.

Recycle stream Any water, solid, or semisolid generated by a plant's treatment processes, operational processes, and residual treatment processes that is returned to the plant's primary treatment process.

Reduction Chemical reaction in which an atom or molecule gains an electron; decrease in positive valence; addition of hydrogen to a molecule.

Reduction treatment The opposite of oxidation treatment wherein a reductant is used to lower the valence state of a pollutant to a less toxic form, e.g., the use of SO_2 to reduce Cr^{6+} to Cr^{3+} in an acidic solution.

Rem A dose equivalent unit, representing the effect of ionizing radiation on tissue. Specifically rem is a unit of dose equivalent from ionizing radiation to total body or any internal organ or organ system.

Renewable or sustainable natural resources They are natural resources that are renewable, such as solar, wind, tidal energy, farmland, forests, fisheries, surface water, etc.

Residual disinfectants Chlorine, chlorine dioxide, chloramines, and ozone are common chemical disinfectants. UV is a physical disinfectant. Only the residual of chlorine, chlorine dioxide, and chloramines are regulated by the U.S. EPA. The residual chlorine or chloramines can cause eye and nose irritation and stomach discomfort if either concentration exceeds 4 mg/L (as Cl_2). If the residual chlorine dioxide concentration in drinking water is over 0.8 mg/L (as ClO_2), it will have an adverse effect on infants and young children, causing anemia or nervous system illness. In the USA, *the maximum residual disinfectant levels* (MRDL) for chloramines, chlorine, and chlorine dioxide are 4 mg/L (as Cl_2), 4 mg/L (as Cl_2), and 0.8 mg/L (as ClO_2), respectively. World Health Organization (WHO) also has established the guideline values (GV) for residual disinfectants: (a) chlorine, 5 mg/L; (b) monochloramine, 3 mg/L; (c) dichloroisocyanurate, 40 mg/L; and (d) sodium, 50 mg/L. Sodium plays an important role when sodium hypochlorite or sodium dichloroisocyanurate is dosed into water as an disinfectant. Ammonia, which is used in chloramination process, is regulated by Mexican government. The Mexico maximum allowable limit (MAL) for ammonia (as NH_3) is 0.5 mg/L.

Resin (a) An ion exchange resin product; or (b) a nonionic polymeric resin product (usually in the form of specifically manufactured organic polymer beads).

Reverse osmosis (RO) It is one of the four pressure-driven membrane filtration processes (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) that removes ions, salts, other dissolved solids, and nonvolatile organics. In potable water treatment, reverse osmosis (RO) has the highest transmembrane pressure (150–500 psi) and is used for desalination or separation of monovalence ions, such as salts, sodium, nitrate, nitrite, chloride, etc., as well as bigger substances. RO member has the smallest pore size range (from 0.0001 to 0.001 micron) in comparison with MF, UF, and NF.

Rickettsiae They are similar in some respects to viruses and in others to bacteria. They are intermediate in size between viruses and bacteria, from 0.3 to 0.5 micron for most rickettsiae cells. They multiply by fission as bacteria do, but like viruses must do so in the presence of a host. *Rickettsial* diseases are common, such as Rocky Mountain spotted fever, Q fever, and typhus which are diseases of humans.

Risk assessment It is either a utility's assessment in the workplace of dangers or harm to employees, equipment, or both, or an individual's assessment of possible events that could lead to harm and danger or exposure to uncomfortable situations.

Risk management It is a managerial process of weighing policy alternatives, selecting the most appropriate regulatory action, and integrating the results of risk assessment with scientific data and related social, economic, and political concerns to reach a low risk decision.

Risk management plan (RMP) It is a managerial plan intended to prevent and minimize the impact of accidental release of hazardous, infectious, or any other undesirable substances.

Running annual average (RAA) The average of four consecutive quarters of data.

R.V.P.F. Rotary vacuum precoat filter. A drum filter that is coated with a thick (up to 6″) precoat of filter aid, such as CELITE or equivalent.

Salinity The presence of soluble salts in or on soils or in water.

Sample A part of a larger whole or a single item of a group; a finite part or subset of a statistical population. A sample serves to provide data or information concerning the properties of the whole group or population.

Sample variance (statistical) A measure of the dispersion of a set of values. The sum of the squares of the difference between the individual values of a set and the arithmetic mean of the set, divided by one less than the number of values in the set. (The square of the sample standard deviation.)

Sampling The process of obtaining a representative portion of the material of concern.

Sandfloat It is combined circular dissolved air flotation and filtration (DAFF) clarifier designed by the Lenox Institute of Water Technology (LIWT) and manufactured by Krofta Engineering Corporation (KEC).

Scavenger A filter, or element in the bottom of a filter, that recovers the liquid heel that remains in a filter tank at the end of the cycle.

Schmutzdecke The surface dirt cake of accumulated particulates, including a variety of living and nonliving micro- and macroorganisms, on top of a slow sand filter, that assists in turbidity removal.

Screen A term commonly used for septum.

Secondary effluent The effluent from a secondary treatment step which may be either (a) biological treatment, such as activated sludge aeration or equivalent plus secondary clarification or (b) physicochemical treatment, such as chemical precipitation/coagulation plus secondary clarification. Secondary treatment step removes most of dissolved organic/inorganic pollutants from primary effluent. Since secondary clarification (either secondary sedimentation clarification or secondary flotation clarification) is the final step of secondary treatment, the secondary effluent is also the secondary clarification effluent.

Secondary flotation clarification It is a unit process or unit operation for removal of the bio-oxidation process generated activated sludge, and/or the chemical precipitation/coagulation process generated chemical sludge using a secondary flotation clarifier.

Secondary flotation clarifier A dissolved air flotation (DAF) reactor is used to float biological sludge (activated sludge) from biologically oxidized wastewater (such as aeration tank effluent) and/or chemical sludge from chemically coagulated/flocculated wastewater (such as flocculator effluent) by decreasing the sludge's apparent density. DAF consists of saturating a portion or all of the wastewater feed, or a portion of recycled effluent with air at a pressure of 25 to 90 lb./square inch (gage). The pressurized wastewater is held at this pressure for 0.5 to 3 minutes in a retention tank and then released to atmospheric pressure to the flotation chamber. The sudden reduction in pressure results in the release of microscopic air bubbles which attach themselves to suspended solids and other particles in the wastewater in the flotation chamber. This results in agglomeration which, due to the entrained air, has greatly increased vertical rise rates of about 0.5 to 2 ft./min. The floated materials rise to the surface to form a froth layer (float). Specially designed scrapers or other skimming devices continuously remove the froth (or float). The retention time in the flotation chambers is usually about 20–60 minutes for rectangular flotation clarifier and about 3–15 minutes for circular flotation clarifier using zero-horizontal velocity design. The effectiveness of dissolved air flotation depends upon the attachment of bubbles to the suspended solids which are to be removed from the waste stream. The attraction between the air bubble and particle is primarily a result of the particle surface charge and bubble-size distribution. The more uniform the distribution of water and micro-bubbles, the shallower the flotation clarifier can be. Generally, the depth of effective flotation units is between 3 and 9 feet.

Secondary maximum contaminant level (SMCL) These standards are developed to protect aesthetic qualities of drinking water and are not health based.

Secondary membrane clarification A water–solid separation/clarification process uses membrane device instead of conventional sedimentation clarification in the secondary wastewater treatment step.

Secondary sedimentation clarification It is a unit process or unit operation for removal of the bio-oxidation process generated activated sludge, and/or the chemical precipitation/coagulation process generated chemical sludge using a secondary sedimentation clarifier.

Secondary sedimentation clarifier It is a tank used to settle the chemical precipitation/coagulation process generated chemical sludge, and/or the bio-oxidation process generated activated sludge for removing dissolved organic/inorganic substances from wastewater. The main objectives of a secondary sedimentation clarifier are removal of settleable chemical and/or biological sludge solids by settling them to the clarifier bottom. In a rectangular sedimentation clarifier, the wastewater flows from one end to the other and the settled sludge is moved to a hopper at on end, either by scrapers called "flights" set on parallel chains or by a single bottom scraper set on a traveling bridge. In a circular sedimentation clarifier, the wastewater usually enters in the middle and flows toward the outside edge. Settled sludge is pushed to the hopper that is in the middle of the circular clarifier's tank bottom.

Secondary treatment It is a wastewater treatment step after primary treatment (either primary sedimentation clarification or primary flotation clarification). Secondary treatment may be either biological treatment (such as activated sludge aeration plus secondary clarification) or physicochemical treatment (such as chemical precipitation/coagulation plus secondary clarification) mainly for removing dissolved organic/inorganic pollutants from primary effluent.

Sedimentation A process for removal of solids before filtration by gravity or separation. (Note: The Federal definition refers to the sedimentation process used in the main treatment train, but sedimentation can also be used for recycle streams.)

Sedimentation–flotation (SediFloat) A combined sedimentation and dissolved air flotation clarifier, with sedimentation at the bottom and dissolved air flotation on the top. A typical example is SediFloat manufactured by Krofta Engineering Corporation.

Selenium (Se) (a) It is an element with an atomic weight of 78.96; (b) it is a toxic chemical found in meat and other foods due to water pollution. Although it is believed to be essential in the diet, there are indications that excessive amounts of selenium may be toxic. Studies are underway to determine the amount required for good nutrition and the amount that may be harmful. The maximum allowable concentrations of selenium in drinking water by the standards are: 0.01 mg/L (WHO and Canada) and 0.05 mg/L (USA). If selenium came only from drinking water, it would take an amount many times greater than the standard to produce any ill effects.

Septum, filter Any permeable material that supports the filter media. Slurry—any liquid containing suspended solids.

Shredding It is a unit operation for reducing the particle size of objects or debris in the influent wastewater, also termed grinding or comminuting. These devices may be installed with a screen directly in the wastewater flow or separately out of the wastewater flow, with the shredded particles returned to the flow downstream of the screen. Only those shredding and grinding devices that are installed directly in the influent channel are termed comminuting devices.

Sievert A dose equivalent unit, representing the effect of ionizing radiation on tissue. One sievert equals 100 rem.

Silver (Ag) (a) It is an element with an atomic weight of 107.868; (b) it is a precious metal, a toxic metal, and a disinfectant. Silver is sometimes released to the environment by the photographic industry and is considered to be toxic at high concentration. Because of the evidence that silver, once absorbed, is held indefinitely in tissues, particularly the skin. Without evident loss through usual channels of elimination or reduction by transmigration to other body sites, and because of other factors, the recommended concentration of silver in drinking water by the U.S. Secondary Drinking Water Standards is 0.1 mg/L.

Slow sand filtration A process involving passage of raw water through a bed of sand at low velocity (generally less than 0.4 m/h) resulting in substantial particulate removal by physical and biological mechanisms.

Sludge thickener A tank or other piece of equipment designed to concentrate water treatment sludges.

Sodium (Na) Sodium present in a water supply can be detected by a laboratory analysis. When home water softeners utilizing the ion-exchange method are used, the amount of sodium should be increased. For this reason, water that has been softened should be analyzed for sodium when a precise record of individual sodium intake is recommended. For healthy persons, the sodium content of water is unimportant because the intake from salt is so much greater, but for persons placed on a low-sodium diet because of heart, kidney, or circulatory ailments or complications of pregnancy, sodium in water must be considered. The usual low-sodium diets allow for 20 mg/L sodium in the drinking water. When this limit is exceeded, such persons should seek a physician's advice on diet and sodium intake. The Mexican maximum allowable limit for sodium and the Canada recommended limit for sodium are both 200 mg/L.

Solids loading rate It is the loading rate of a flotation unit in dry solids weight per effective flotation surface area per time of flotation operation (lb/ft^2/hr. or kg/m^2/s).

Solution A liquid (solvent) that contains a dissolved substance (solute).

Solvent A liquid used to dissolve another substance.

Specific gravity (Sp. G.) The weight of any substance relative to the weight of water (water Sp. G. = 1.0).

Spectrophotometers A spectrophotometer is an instrument designed for physical sample analysis via full spectrum color measurement. By providing wavelength-by-wavelength spectral analysis of a sample's reflectance, absorbance, or transmittance properties, it produces precise data beyond that observable by the human eye. Spectrophotometers offer a higher level of flexibility and versatility than colorimeters due in part to the fact that they offer multiple illuminant/observer combinations and are capable of measuring metamerism, identifying colorant strength, analyzing a comprehensive range of sample types, and giving users a choice between including or excluding specular reflectance to account for geometric attributes. Full spectrum analysis also provides for greater specificity, potentially identifying color differences missed by colorimeters.

Spent filter backwash water A stream containing particles that are dislodged from filter media when water is forced back through a filter (backwashed) to clean the filter.

Spiked reagent blank A specified amount of reagent blank fortified with a known mass of the target analyte; usually used to determine the recovery efficiency of the method.

Spiked sample A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Spiked samples are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Split samples Two or more representative portions taken from a sample or subsample and analyzed by different analysts or laboratories. Split samples are used to replicate the measurement of the variable(s) of interest.

Spray aeration An aeration process involving the use of nozzles for generation water streams similar to a water fountain. The volatile organic compounds (VOCs) in water streams can be stripped off by air, and soluble iron and manganese can be oxidized by the oxygen in air, forming insoluble iron oxides and manganese oxides.

Standard (measurement) A substance or material with a property quantified with sufficient accuracy to permit its use to evaluate the same property in a similar substance or material. Standards are generally prepared by placing a reference material in a matrix.

Standard addition The procedure of adding known increments of the analyte of interest to a sample to cause increases in detection response. The level of the analyte of interest present in the original sample is subsequently established by extrapolation of the plotted responses.

Standard deviation The most common measure of the dispersion or imprecision of observed values expressed as the positive square root of the variance.

Standard method An assemblage of techniques and procedures based on consensus or other criteria, often evaluated for its reliability by collaborative testing and receiving organizational approval.

Standard operating procedure (SOP) A written document which details the method of an operation, analysis, or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

Standard reference material (SRM) A certified reference material produced by the U.S. National Institute of Standards and Technology and characterized for absolute content independent of analytical method.

Standard solution A solution containing a known concentration of analytes, prepared and verified by a prescribed method or procedure and used routinely in an analytical method.

STEAM Science, technology, engineering, arts, and mathematics.

Storm water It is water that is collected as runoff from a rainfall event.

Storm water runoff That portion of the rainfall over a given area that finds its way to natural or artificial drainage channels.

Streamflow A type of channel flow, applied to that part of surface runoff in a stream whether or not it is affected by diversion or regulation.

Streaming current A current gradient generated when a solution or suspension containing electrolytes, polyelectrolytes, or charged particles passes through a capillary space, as influenced by adsorption and electrical double layers. This phenomenon is used in monitoring and controlling coagulation and flocculation processes.

Sulfates (SO_4^{2-}) Waters containing high concentrations of sulfate caused by the leaching of natural deposits of magnesium sulfate (Epsom salts) or sodium sulfate (Glauber's salt) may be undesirable because of their laxative effects. The limits for sulfate content in drinking water by standards are: 250 mg/L (U.S. Secondary Drinking Water Standards), 400 mg/L (Mexico maximum allowable limit), and 500 mg/L (Canada guideline value).

Supracell It is a circular dissolved air flotation (DAF) clarifier designed by the Lenox Institute of Water Technology (LIWT) and manufactured by Krofta Engineering Corporation (KEC).

Surface water The water that systems pump and treat from sources open to the atmosphere, such as rivers, lakes, and reservoirs.

Suspended sediment Particles of rock, sand, soil, and organic detritus carried in suspension in the water column, in contrast to sediment that moves on or near the streambed.

Suspended-sediment concentration The velocity-weighted concentration of suspended sediment in the sampled zone (from the water surface to a point approximately 0.3 foot above the bed) expressed as milligrams of dry sediment per liter of water-sediment mixture (mg/L).

Suspended solids (SS) Solids that do not dissolve in liquid; those solids that remain suspended and can be removed by filtration.

Suspension Any liquid containing undissolved solids, such as a filter aid (such as CELITE) slurry.

Tertiary membrane clarification A water–solid separation/clarification process uses membrane device instead of conventional sedimentation clarification in the tertiary wastewater treatment step, such as nitrification and denitrification.

Thickener supernatant A stream containing the decant from a gravity thickener, or other unit that is used to treat water, solids, or semisolids from the water or wastewater treatment processes. The clarified water that exits the units after particles have been allowed to settle out is thickener supernatant.

Total dissolved solids and conductivity Total dissolved solids (TDS) in natural water are due to soluble inorganic mineral compounds. The TDS concentration in normal surface waters is generally less than 200 mg/L. The recommended upper limit of TDS in irrigation water is 1500 mg/L. The specific conductance or the electrical conductivity (EC) of water is related to TDS linearly, or TDS = k (EC), where TDS is in mg/L, EC is in μmho/cm, and k is a constant varying from 0.5 to 0.9 (average 0.64). A maximum of 500 mg/L TDS in drinking water supplies is recommended by the U.S. Environmental Protection Agency, although TDS is not a measure of the safety or harmfulness of water. The Canada guideline value for TDS is 500 mg/L and the Mexico maximum allowable limit for TDS is 1000 mg/L.

Total organic carbon (TOC) Total organic carbon in mg/L measured using heat, oxygen, ultraviolet irradiation, chemical oxidants, or combinations of these oxidants that convert organic carbon to carbon dioxide, rounded to two significant figures.

Total trihalomethane precursors Organic materials in the raw water that promote the formation of trihalomethanes.

Total trihalomethanes (TTHM) The sum of the concentration in milligrams per liter of the trihalomethane compounds (trichloromethane [chloroform], dibromochloromethane, bromodichloromethane and tribromomethane [bromoform]), rounded to two significant figures.

Total trihalomethanes formation potential (TTHMFP) A measure of the ability of a water to create trihalomethanes.

Transient, noncommunity water system A water system which provides water in a place such as a gas station or campground where people do not remain for long periods of time. These systems do not have to test or treat their water for contaminants which pose long-term health risks because fewer than 25 people drink the water over a long period. They still must test their water for microbes and several chemicals.

Treatment technique (TT) (a) A required process intended to reduce the level of a contaminant in drinking water. Unregulated contaminants: Contaminants for which the US Environmental Protection Agency (USEPA) has not established drinking water standards. The purpose of unregulated monitoring is to assist USEPA in determining their occurrence in drinking water and whether future regulation is warranted; and (b) it is a required process intended to reduce the level of a contaminant in drinking water. 0.5 NTU must be met 95% of the time. The TT was met 100% of the time.

Tributary A river or stream flowing into a larger river, stream, or lake.

Trihalomethane (THM) One of a family of organic compounds, named as derivatives of methane, wherein three of the four hydrogen atoms in methane are each substituted by a halogen atom in the molecular structure.

Tube settlers Bundles of small-bore (2 to 3 inches or 50 to 75 mm) tubes installed on an incline as an aid to sedimentation. As water rises in the tubes, settling solids fall to the tube surface. As the sludge (from the settled solids) in the tube gains weight, it moves down the tubes and settles to the bottom of the basin for removal by conventional sludge collection means. Tube settlers are sometimes installed in sedimentation basins and clarifiers to improve settling of particles.

Turbidimeter A device that measures the amount of light scattered by suspended particles in a liquid under specified conditions.

Turbidity (a) Any insoluble particle that imparts opacity to a liquid; (b) the cloudy appearance of water caused by the presence of suspended and colloidal matter which cause the scattering and adsorption of light. In the waterworks field, a turbidity measurement is used to indicate the clarity of water. Technically, turbidity is an optical property of the water based on the amount of light reflected by suspended particles. Turbidity cannot be directly equated to suspended solids because white particles will reflect more light than dark-colored particles and many small particles will reflect more light than an equivalent large particle.

Ultrafiltration (UF) It is one of the four pressure-driven membrane filtration processes (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) that removes ions, salts, other dissolved solids and nonvolatile organics. In potable water treatment, ultrafiltration (UF) is operated at medium transmembrane pressure (30–75 psi) and is used for separation of colloids, flocs, turbidity, suspended solids, large microorganisms, etc., as well as other bigger substances. UF member has a medium pore size range (from 0.005 to 0.09 micron).

Ultraviolet (UV) UV light has a wavelength range of 10 nanometers (the longest wavelength of X-ray) to 390 nanometers (the shortest wavelength of visible light); therefore, UV is at the invisible violet end of the light spectrum. UV light may be used as a disinfectant or to create hydroxyl radicals (OH).

Ultraviolet radiation A disinfection process that involves the use of UV light.

Underground aqueduct It is a conduit, below ground level, usually of considerable size and not open to the air, used to convey water or other liquid by gravity flow.

Underground source of drinking water (USDW) An underground source of drinking water is an aquifer or part of an aquifer which: (a) supplies any public water system or contains a sufficient quantity of ground water to supply a public water system and currently supplies drinking water for human consumption or contains fewer than 10,000 milligrams/liter of total dissolved solids (TDS); and (b) is not an exempted aquifer. An "exempted aquifer" is part or all of an aquifer which meets the definition of a USDW but which has been exempted by the government that the aquifer does not currently serve as a source of drinking water, and the aquifer cannot now and will not in the future serve as a source of drinking water.

Uranium (U) A metallic element with three natural radioactive isotopes, U-234, U-235, and U-238.

UV–visible spectroscopy A number of methods have been devised to measure protein concentration, which are based on UV–visible spectroscopy. These methods use either the natural ability of proteins to absorb (or scatter) light in the UV–visible region of the electromagnetic spectrum, or they chemically or physically modify proteins to make them absorb (or scatter) light in this region. The basic principle behind each of these tests is similar. First of all a calibration curve of absorbance (or turbidity) versus protein concentration is prepared using a series of protein solutions of known concentration. The absorbance (or turbidity) of the solution being analyzed is then measured at the same wavelength, and its protein concentration determined from the calibration curve. The main difference between the tests is the chemical groups which are responsible for the absorption or scattering of radiation, e.g., peptide bonds, aromatic side groups, basic groups, and aggregated proteins.

Vacuum flotation In vacuum flotation, the influent process water to be treated is usually almost saturated with air at atmospheric pressure. There is an air-tight enclosure on the top of the flotation chamber in which partial vacuum is maintained. The fine air bubbles (20–80 microns) are generated under laminar hydraulic flow conditions by applying a vacuum (negative pressure) to the flotation chamber. The theory is that the lower the pressure, the lower the air solubility in water. The soluble air originally in water is partially released out of solution as extremely fine bubbles due to a reduction in air solubility caused by negative vacuum pressure. The bubbles and the attached solid particles rise to the water surface to form a scum blanket, which can be removed by a continuous scooping or skimming mechanism. Grit and other heavy solids that settle to the bottom are raked to a central sludge sump for removal. Auxiliary equipment includes an aeration tank for saturating the water or wastewater with air, vacuum pumps, and sludge pumps.

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Velocity gradient (G) A measure of the maximum intensity (in units of per second) in a water treatment process. Very high velocity gradients (greater than 300 per second) are used for complete mixing and dissolution of chemicals in a coagulation process, whereas lower values (less than 75 per second) are used in flocculation to bring particles together and promote agglomeration.

Vertical shaft flotation Same as deep shaft flotation.

Viruses Viruses are the smallest microorganisms known to scientists. Organisms this small will pass freely through the openings of most filters or membranes. Viral diseases are many and affect all forms of life. Aside from the virus of infectious hepatitis, members of half a dozen virus groups, constituting over 100 different strains, are known to be excreted in the feces of infected persons. Isolation of these enteric organisms is especially common during the summer months, when streams are normally low. Yet the number of waterborne outbreaks of virus diseases has been small. Moreover, only two of the six groups—the Echo and Reo groups but neither the Polio, Coxsackie A and B, and Adeno groups, nor the hepatitis virus—produce enteric symptoms in man. Why water has not played a more significant role in the spread of these infections awaits explanation. Their small size is favorable to water transport, and the relatively small numbers in which they are probably excreted—apparently of the order of 10^6 daily per infected person rather than the 10^{11} for typhoid organisms—may militate against their completing the cycle from humans to humans via the water route. Other gastrointestinal upsets, apparently waterborne, possibly of viral origin, and associated with heavy pollution of water supplies, more especially during periods of severe and prolonged drought, are on record in the USA as well as abroad.

Voids The openings or pores in a filter medium.

Volatile Organic Compounds (VOCs) Carbon-containing compounds that easily go from a solid to a gaseous form at normal temperatures. Sources include household products such as paints, paint strippers, and other solvents; wood preservatives; aerosol sprays; cleansers and disinfectants; moth repellents and air fresheners; stored fuels and automotive products; hobby supplies; dry-cleaned clothing.

Water engineering It is an academic branch of engineering that studies, researches, or implements, or builds anything involving water.

Water quality The physical, chemical, and biological characteristics of water and the measure of its condition relative to the requirements for one or more biotic species and/or to any human need or purpose.

Water-quality criteria Criteria that comprise numerical and narrative *criteria.* Numerical criteria are scientifically derived ambient concentrations developed by the US Environmental Protection Agency (USEPA) or the States for various pollutants of concern so that human health and aquatic life can be protected. Narrative criteria are statements that describe the desired water-quality goal.

Water-quality data Chemical, biological, and physical measurements or observations of the characteristics of surface and ground waters, atmospheric deposition, potable water, treated effluents, and wastewater and of the immediate environment in which the water exists.

Water-quality guidelines Specific levels of water quality which, if reached, may adversely affect human health or aquatic life. These are nonenforceable guidelines issued by a governmental agency or other institution.

Watershed The land area from which water drains into a stream, river, or reservoir.

Wellhead protection area The area surrounding a drinking water well or well field which is protected to prevent contamination of the well(s).

Working level (WL) A unit used to describe the dose of radionuclides due to progeny of radon. Organ weighting factor is a factor representing relative sensitivities of organs to ionizing radiation, and yielding effective dose equivalent that can be summed for all organs.

Worms The eggs and larvae of intestinal worms may reach water courses from humans and animal carriers either directly or in washings from the soil. The eggs or larvae involved are relatively small in number, and the organisms themselves are relatively large in size. Hence worm infections are sporadic and occur only under grossly insanitary conditions or through gross mismanagement of wastewater disposal systems. Irrigation of crops that are consumed raw may transmit any one of the common intestinal worms; irrigation of grasslands may infect cattle and, through them, humans. In some parts of the world the minute crustacean *Cyclops* ingests the larvae of the guinea worm, a nematode, or roundworm that infects man through drinking water and is released by him to water again when skin ulcers filled with larvae break while he wades or swims in freshwater. Since worms are much bigger than protozoa (including *Cryptosporidium* and *Giardia lamblia*), it is assumed that after *Giardia lamblia* and *Cryptosporidium* are removed by the required treatment technique, such as membrane filtration, all worms will also be removed.

Zero horizontal velocity concept Normally both solid's vertical downward/upward velocity (vertical settling/rising velocity, ft./min or m/s) and horizontal traveling velocity (ft/min or m/s) in a clarifier must be considered for sizing a clarifier. This is a new concept developed by the Lenox Institute of Water Technology (LIWT) and Krofta Engineering Corporation (KEC) that the clarifier's size can be significantly reduced if horizontal traveling velocity can be minimized to almost zero. Then the design of a sedimentation clarifier or a flotation clarifier can be mainly based on the solid's vertical settling velocity or vertical rising velocity, respectively.

Zeta potential The electric potential arising due to the difference in the electrical charge between the dense layer of ions surrounding a particle and the net charge of the bulk of the suspended fluid surrounding the particle. The zeta potential, also known as the electrokinetic potential, is usually measured in millivolts and provides a means of assessing particle destabilization or charge neutralization in coagulation and flocculation procedures.

Zinc (Zn) Zinc is found in some natural waters, particularly in areas where these ore deposits have been mined. Zinc is not considered detrimental to health, but it will impart an undesirable taste to drinking water. The U.S. and Canada recommended limits for zinc are both 5.0 mg/L, while the Mexican maximum allowable limit (MAL) is also 5.0 mg/L.

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