Applied Environmental Science and Engineering for a Sustainable Future

Ram Lakhan Singh · Rajat Pratap Singh
Editors

Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future

Springer

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Applied Environmental Science and Engineering for a Sustainable Future (AESE) series covers a variety of environmental issues and how they could be solved through innovations in science and engineering. Our societies thrive on the advancements in science and technology which pave the way for better standard of living. The adverse effect of such improvements is the deterioration of the environment. Thus, better catchment management in order to sustainably manage all types of resources (including water, minerals and others) is of paramount importance. Water and wastewater treatment and reuse, solid and hazardous waste management, industrial waste minimisation, soil restoration and agriculture as well as myriad of other topics needs better understanding and application. This book series aims at fulfilling such a task in coming years.

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ISSN 2570-2165 ISSN 2570-2173 (electronic)
Applied Environmental Science and Engineering for a Sustainable Future
ISBN 978-981-13-1467-4 ISBN 978-981-13-1468-1 (eBook)
https://doi.org/10.1007/978-981-13-1468-1

Library of Congress Control Number: 2018954483

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

To
our families
for their abundant support, patience,
and understanding and for their love.

To
the students and researchers
who refined our knowledge of biological
sciences
by their intelligent questions, queries, and
discussions
over the years.

Preface

Water is a scarce natural resource on our planet. Due to rapid industrialization, water pollution problem increased worldwide. These industries use large quantities of potable water for various industrial purposes and release them in the form of wastewater as a by-product. The wastewater generated by different industries has major environmental concern because it contains various hazardous pollutants, and release of wastewater into ecosystem leads to several harmful effects on both flora and fauna. In the present scenario, although it is not possible to stop the release of wastewater in the environment, it is feasible to overcome its harmful effects by its treatment using various methods. The conventional treatment processes have been successfully applied till sometime before, but these methods have many limitations. As viable alternatives, biological treatment methods are becoming more popular day by day; they are cost-effective, eco-friendly, and energy-saving solutions for treatment of industrial wastewater. The aim of biological wastewater treatment is to remove the major pollutants from different industrial wastewater and enable them to be disposed of safely without posing potential danger to the environment and public health as well as to recycle them for various purposes. Wastewater treatment is a very important and interesting area as far as the environmental protection and public safety are concerned because water is one of the basic natural resources for the survival and existence of all living beings.

This book has been developed with the intention of providing an updated source of information on the characteristics and environmental concern of wastewater from various industries and efficient treatment as well as its recycling by biological methods in an environment-friendly and cost-effective manner. The text of this book includes all the dimensions of wastewater treatment methods with detailed account of the biological treatment methods and factors affecting the treatment of wastewater and their recycling. This book is a valuable resource for graduate and undergraduate students, environmental engineers, and others who are concerned with industrial wastewater treatment.

All chapters have been designed and prepared by the authors in such a way that present the subject in depth following a reader-friendly approach. A systematic reading of the text from the beginning will allow the readers to gain technical concepts of wastewater treatments. The book is easy to follow with simple explanation and a good framework for understanding the complex nature of biological wastewater treatment processes. Overall, this book is certainly a timely addition since the interest in emerging contaminants and wastewater treatment has been growing considerably during the last few years, related to the availability of novel treatment options together with the advanced and highly sensitive analytical techniques.

Key Features

The text of the book includes certain important features to facilitate better understanding of the topics discussed in the chapters.

Abstract at the beginning of each chapter highlights the important concepts discussed and enables recapitulation.

Tables and figures interspersed throughout the chapters enable easy understanding the concepts discussed.

Bibliography at the end of each chapter familiarizes the readers with important texts and articles cited in the text.

Organization of the Book

The book is organized into 11 chapters.

Chapter 1 covers the brief introduction about wastewater released from different industries and their biological treatment.

Chapters 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11 include the characteristics of wastewater released by different industries, harmful effects of wastewater, and their effective treatment to remove the various pollutants present in different industrial wastewater as well as recycling of wastewater for various purposes. These chapters focus on the biological treatment of industrial wastewaters by means of microorganisms and plants.

Faizabad, Uttar Pradesh, India

Ram Lakhan Singh
Rajat Pratap Singh

Acknowledgments

It is a pleasure to acknowledge our enormous debt to contributors who assisted materially in the preparation of this book. We believe that the contributors of this book provide the perfect blend of knowledge and skills that went into authoring this book. We thank each of the contributors for devoting their time and effort toward this book. We would like to express our gratitude to all those who helped directly or indirectly in the accomplishment of this work with their support, valuable guidance, and innumerable suggestions. We are grateful to both of our families who cheerfully tolerated and supported many hours of absence for finishing the book project. We wish to express special appreciation to the editorial and production staffs of Springer Nature for their excellent work. The team of Springer Nature publishing group has played a great role throughout, always helpful and supportive. Special thanks are due to Aakanksha Tyagi, Editor, Life Sciences, Springer Nature India, Raman Shuka, Senior Editorial Assistant for quality control and coordination and to Ms. RaagaiPriya ChandraSekaran, Project Coordinator for book production, with whom we started the project at the proposal level and got constant critical advice throughout the project. We acknowledge the generosity of Jega V. Jegatheesan, Li Shu, Piet Lens, and Chart Chiemchaisri, the series editors of *Applied Environmental Science and Engineering for a Sustainable Future*, for accepting this book in the series.

August 2018

Ram Lakhan Singh
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About the Editors

Dr. Ram Lakhan Singh (Editor) is presently holding the positions of Professor of Biochemistry and Coordinator of Biotechnology Programme at Dr. Rammanohar Lohia Avadh University, Faizabad, India. He has also held the positions of Dean, Faculty of Science; Head, Departments of Biochemistry and Environmental Sciences; and Director, Institute of Engineering and Technology in the same university. He completed his master's degree in biochemistry from Lucknow University and joined Indian Institute of Toxicology Research, Lucknow, India, in 1980. He worked extensively on the toxicity of synthetic dyes and their metabolites and has been awarded Ph.D. degree in 1987. Professor Singh worked in UP Pollution Control Board as Junior Scientific Officer and studied the effects of effluents discharged from various industries on air and water qualities. He moved to G.B. Pant University of Agriculture and Technology, Pantnagar, India, in 1988 as Assistant Professor of Biochemistry and worked on the toxicity of pulp and paper mill effluents on plant and animal systems. He acquired special training in rapeseed-mustard quality analysis at Agriculture Canada Research Station, Saskatoon, in the year 1991 under IDRC, Canada sponsored programme.

He joined Dr. Rammanohar Lohia Avadh University, Faizabad, as Associate Professor of Biochemistry in 1994 and became full Professor in 2002. He has been instrumental in developing the undergraduate and postgraduate programmes in biochemistry, environmental sciences and biotechnology. He led and completed various projects funded by DST, UGC, DOE, UPCAR, UPCST, etc. and guided 25 Ph.D. students. His main area of research is environmental biochemistry and toxicology. Professor Singh has published more than 81 research papers in peer-reviewed journals and participated in various national and international scientific conferences, meetings, symposia and workshops, chaired scientific and technical sessions and presented more than 73 research papers.

Professor Singh has been awarded IUTOX Senior Fellowship by International Union of Toxicology during XI International Congress of Toxicology at Montreal, Canada, in 2007. He has been admitted to the Fellowship of the Society of Toxicology, India, in 2011, and the Fellowship of Academy of Environmental Biology, India, in 2015. He also received "Shikshak Shri Samman" from Government of Uttar Pradesh, India, in the year 2012. Recently, Professor Singh has published two books entitled *Biotechnology for Sustainable Agriculture: Emerging Approaches and Strategies* (Elsevier: Woodhead Publishing) and *Principles and Applications of Environmental Biotechnology for a Sustainable Future* (Springer Nature Publishing).

Dr. Rajat Pratap Singh (Co-editor) is presently working as Guest Faculty in Biotechnology Programme at Dr. Rammanohar Lohia Avadh University, Faizabad, since 2008. He completed his master's degree in biochemistry from Dr. Rammanohar Lohia Avadh University, Faizabad, in 2005, and worked as Junior Research Fellow in DBT-sponsored project entitled "Development of sustainable management strategies for the control of *Parthenium* weeds using biotechnological approaches in U.P." at ICAR – National Bureau of Agriculturally Important Microorganisms, Mau, India, from 2005 to 2008. He joined the Department of Biochemistry at Dr. Rammanohar Lohia Avadh University, Faizabad, in 2010, and worked extensively on microbial decolourization of textile effluents and has been awarded Ph.D. degree in 2015. Dr. Singh qualified several national exams such as CSIR UGC NET, ASRB ICAR NET and GATE. He published six research papers in peer-reviewed journals and four book chapters published by international publishers such as Springer Nature and Elsevier. He participated in various national and international scientific conferences and symposia and presented 14 research papers. Dr. Singh also participated in three national training programmes related to microbial diversity analysis and identification of agriculturally important microorganisms. He has guided 11 postgraduate students for their dissertation work.

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Abbreviations

%	Percent
$(SO_4)^{2-}$	Sulfate
°C	Degree Celsius
μm	Micrometer
2,4,6-TCP	2,4,6-Trichlorophenol
2,6-DiCH	2,6-Dichloro-*p*-hydroquinone
6-CHQ	6-Chloro-1,2,4-trihydroxybenzene
ABA	American Beverage Association
ABR	Anaerobic baffled reactor
AC(LB)	Activated carbon (Luria-Bertani)
AC(ME)	Activated carbon (molasses effluent)
Acesulfame K	Acesulfame potassium
AD	Anaerobic digester
ADMI	American Dye Manufacturers Institute
ADP	Alkaline degradation products
AF	Anaerobic filter
AFB	Anaerobic fluidized bed reactor
$AlCl_3$	Aluminum chloride
AMBBR	Anaerobic moving bed biofilm reactor
AMBR	Anaerobic migrating blanket reactor
AOP	Advance oxidation process
AOX	Adsorbable organic halides
API	Active pharmaceutical ingredient
API	American Petroleum Institute
AS	Activated sludge
ASBR	Anaerobic sequencing batch reactors
ASP	Activated sludge process
ASR	Active sludge reactor
BAF	Biological aerated filter
BE	Bioreactor effluent

BFA	Bagasse fly ash
BMV	Beet molasses vinasse
BOD	Biochemical/biological oxygen demand
BOD_5	Biochemical oxygen demand, 5-day test
BTEX	Benzene, toluene, ethylbenzene, and xylene
C:N	Carbon and nitrogen
$Ca(OH)_2$	Calcium hydroxide
CAGR	Compound annual growth rate
CaO	Calcium oxide
CD	Corona discharge
CE	Columbic efficiency
CETP	Common Effluent Treatment Plant
CFU	Colony-forming unit
CHPTAC	3-Chloro-2-hydroxypropyltrimethylammonium chloride
Cl_2	Chlorine gas
ClO_2	Chlorine dioxide
CMC	Carboxymethyl cellulose
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CPCB	Central Pollution Control Board
CPI	Corrugated plate interceptor
CP-MAS NMR	Cross polarization/magic-angle spinning nuclear magnetic resonance
Cr (III)	Trivalent chromium
Cr (VI)	Hexavalent chromium
$Cr(OH)_3$	Chromium hydroxide
CRB	Chromium-reducing bacteria
CSTR	Continuous stirred tank reactors
CuCl	Cuprous chloride
CuO	Copper oxide
$CuSO_4$	Copper sulfate
CWs	Constructed wetlands
Da	Dalton
DAF	Dissolved air flotation
DCE	Dichloroethylene
DCIP reductase	2,6-Dichloroindophenol *reductase*
DE	Dairy effluent
DEA	Drug Enforcement Administration
DEAE	Diethylaminoethyl cellulose
DF	Drain field
DGGE	Denaturing gradient gel electrophoresis
DO	Dissolved oxygen
DW	Drain well
EC	Electrocoagulation
EC	European Community

Ecb	Electrons from conduction band
EGSB	Expanded granular sludge bed
EO	Electro-oxidation
EPA	Environmental Protection Agency
EU	European Union
$Fe_2(SO)_3$	Ferric sulfate
Fe^{2+}	Ferrous
Fe^{3+}	Ferric
$FeCl_3$	Ferric chloride
FMN	Flavin mononucleotide
FOG	Fat, oil, and grease
FT-ICR	Fourier transform ion cyclotron resonance
FTIR	Fourier transform infrared spectroscopy
g	Gram
g/l	Gram per liter
GAA	Glucose-aspartic-acid
GACs	Granular-activated carbons
GFD	Gallons per square foot per day
GGA	Glucose-glutamate-acid
GMO	Genetically modified
H	Hour
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2S	Hydrogen sulfide
HACCP	Hazard analysis for critical control points
HDPE	High-density polyethylene
HORW	Heavy oil-refining wastewater
HPLC	High-performance liquid chromatography
HRT	Hydraulic retention times
HTL	Heat-treatment liquor
$h\nu$	Photon (light)
ICR	Internal circulation reactor
ID	Indirect discharge
IGF	Induced gas floatation
IPPC	Integrated pollution prevention and control
ISI	Indian Standard Institution
JLMBR	Jet loop membrane bioreactor
JLR	Jet loop reactors
K	Kelvin
K_2FeO_4	Potassium iron oxide
kDa	Kilodalton
kg	Kilogram
kg m^{-3}	Kilogram per meter cube
KH_2PO_4	Potassium dihydrogen phosphate
KL	Kiloliter

$KMnO_4$	Potassium permanganate
L	Liter
l/kg	Liter per kilogram
LB	Lactose broth
LD_{50}	Lethal dose
LiP	Lignin peroxidase
LME	Lignin-modifying enzymes
LPG	Liquefied petroleum gas
LTAS	Long-term aerated storage
m	Meter
m/s	Meter per second
m^2	Meter square
m^2/g	Meter square per gram
$m^{-3}\ d^{-1}$	Meter cube per day
$m^3\ ha^{-1}$	Meter cube per hectare
MAVF	Macrophyte-assisted vermifilter
MBBR	Moving bed biofilm reactor
mbpd	Million barrels per day
MBR	Membrane bioreactor
MCL	Maximum contaminant level
MDW	Model dairy wastewater
MEC	Microbial electrolysis cell
MF	Microfiltration
MFCs	Microbial fuel cells
mg	Milligram
mg/l	Milligram per liter
MgO	Magnesium oxide
$MgSO_4$	Magnesium sulfate
MICs	Minimum inhibitory concentrations
ml	Milliliter
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
mmol/L	Millimole per liter
Mn	Manganese
MnO_2	Manganese oxide
MnP	Manganese peroxidase
MS	Mass spectroscopy
MSW	Molasses spent wash
MTCC	Microbial Type Culture Collection
mV	Millivolt
NaCl	Sodium chloride
NADH	Nicotinamide adenine dinucleotide
NADPH	Nicotinamide adenine dinucleotide phosphate
NaOH	Sodium hydroxide
NF	Nanofiltration

nm	Nanometer
NMR	Nuclear magnetic resonance
NOx	Nitrogen oxides
NPK	Nitrogen phosphorus potassium
NR	Not reported
NTU	Nephelometric turbidity unit
NZVI	Nanoscale zerovalent iron
O_2	Oxygen
O_2/L	Oxygen per liter
O_3	Ozone
OF	Overland inflow
OLR	Organic loading rate
PAC	Powdered activated carbon
PAHs	Polycyclic aromatic hydrocarbons
PBDEs	Polybrominated diphenyl ethers
PBSS	Porous biomass support system
PCBs	Polychlorinated biphenyls
PCP	Pentachlorophenol
PET	Poly ethylene terephthalate
PFS	Polyferric hydroxysulfate
pH	Potential of hydrogen
PMDE	Post-methanated *distillery* effluent
PPCPs	Pharmaceuticals and personal care products
ppm	Parts per million
PRE	Petroleum refinery effluents
PUF	Polyurethane foam
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
RBC	Rotating biological contactor
RCRA	Resource Conservation and Recovery Act
RI	Rapid infiltration
RM_{oxi}	Redox mediator oxidized
RM_{red}	Redox mediator reduced
RNA	Ribonucleic acid
RO	Reverse osmosis
RPM	Refiner mechanical pulp
RS	Reactive separation
SAA	Sucrose-aspartic-acid
SBI	Sludge biotic index
SBR	Sequential batch reactor
SCADA	Supervisory control and data acquisition system
SCP	Single cell protein
SGA	Sucrose-glutamate-acid
SO_2	Sulfur dioxide
SOC	Soluble organic substances

sp.	Species
SR	Slow rate
SRT	Solids retention time
SS	Suspended solids
STE	Secondary treated effluent
STPs	Sewage treatment plants
SW	Spent wash
SW	Scouring web
TAN	Total ammoniacal nitrogen
TBA	Tert-butyl alcohol
TCE	Trichloroethylene
TCE	Trichloroethanol
TDS	Total dissolved solids
TDW	Treated distillery wastewater
TeCH	Tetrachloro-*p*-hydroquinone
TiO_2	Titanium oxide
TKN	Total Kjeldahl nitrogen
TMP	Thermomechanical pulp
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TPH	Total petroleum hydrocarbon
TS	Total solids
TSS	Total suspended solids
TVS	Total volatile solid
UAF	Upflow anaerobic filter reactor
UASB	Upflow anaerobic sludge blanket
UF	Ultrafiltration
U-MWW	Untreated molasses wastewater
USBF	Upflow sludge bed-filter
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
v/v	Volume by volume
VF	Vermifilter
VFAs	Volatile fatty acids
VP	Versatile peroxidases
w/v	Weight by volume
WAS	Waste activated sludge
WHO	World Health Organization
WQT	Water quality trading
WSC	Water Supply Corporation
XRD	X-ray diffraction
ZLD	Zero liquid discharge

Chapter 1
Introduction

Ram Lakhan Singh and Rajat Pratap Singh

Abstract Freshwater is an imperative normal asset that will keep on being sustainable as long as it is well managed. In many parts of the world, rapid industrial development have prompted to an intensive and still increasing utilization of water resources. Industries are one of the most important pollution sources around the world. The discharge of untreated or improperly treated wastewaters from industries into water bodies may contain very diverse groups of hazardous pollutants depending on the nature of industry. The industrial waste waters may have undesirable color, odour, acids, alkalies, organic matters, toxic chemical contents, heavy metals, pesticides, oils, high biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS) etc. These pollutants may pose a serious threat to all life forms. It is, therefore, necessary to treat the industrial waste water prior to their disposal into water bodies. The conventional industrial waste water treatment processes such as precipitation, adsorption, oxidation, filtration etc. have long been established in removing many hazardous pollutants but these methods have their own limitations. These methods are expensive, and require complex processes and maintenance. Biological treatment process is an important and integral part of any wastewater treatment plant. Different taxonomic group of microorganisms (bacteria, fungi and algae) and plants play a major role in the biological treatment of industrial wastewater. The fresh water demand in current and future prospects could be met by improving the efficiency of water usage and demand management. The recycling and reuse of industrial wastewater is emerging as potential source for demand management and water shortage after essential treatment.

Keywords Industrial wastewater · Pollution · Pollutants · Biological treatment · Recycling

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R. L. Singh, R. P. Singh (eds.), *Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future*, Applied Environmental Science and Engineering for a Sustainable Future,
https://doi.org/10.1007/978-981-13-1468-1_1

Rapid industrial growth, urbanization and population explosion are the major contributor of environmental pollution throughout the world. Environmental pollution is a vital concomitant of the activities of man. Wherever we find man, we fundamentally find wastes. These wastes have got to be disposed off and when they are inadequately dumped into the ocean or a river, water resources are contaminated which may pose risk to the aquatic animals and human life. Water has a broad impact on all forms of life. It is a vital natural resource for agriculture, manufacturing and many other human activities. Despite its importance, water is the most poorly managed resource in the world. The accessibility and quality of water always have played an important role in determining the quality of life. There is restricted possibility of an expansion in the supply of fresh water because of competing demands of expanding populations all over the world. Lack of fresh water supply is likewise an aftereffect of the misuse of water resources for domestic, industrial, and irrigation purposes in many parts of the world. Water has certain physical, chemical and biological properties in its natural state. Industrial wastewater may be altering the properties of water which may become unfit for consumption. During the past few decades rapid industrial development has become an important contributor of a country high economic growth. With the development of different industries a large amount of fresh water is used as a raw material. These industries produce a large quantity of wastewater as an essential by-product of modern industry which contributes to water pollution. The surface water is the main source of industries for waste disposal. Water pollution due to improper disposal of untreated industrial effluents into water bodies is a noteworthy issue in the worldwide context. The pollution caused by the release of industrial effluents into the rivers and streams has created the issue of general wellbeing as well as a social issue.

Industrial wastewaters are effluents released from industries which are associated with raw-material processing and manufacturing. Most of the wastewater generating industries include pulp and paper mill, tannery, dairy industry, distillery, winery, sugar mill, textile industry, pharmaceutical industry, oil refinery/petroleum industry, beverages/soft drink bottling industry etc. The wastewaters from these industries may not be safely treated due to the lack of highly efficient and economic treatment technology. Untreated or improper disposal of wastewater have increased the level of surface water pollution resulting in adverse effects on the quality of all forms of life.

1.1 Characteristics of Industrial Wastewater

The wastewaters released by the industries are variable in their composition depending on nature of industry and contaminants. Each industry produces its own particular combination of pollutants. The industrial wastewaters are characterized in terms of their physical (total solids, suspended solids, dissolved solids, color, odour and temperature), chemical (inorganic and organic), and biological characteristics (Table 1.1).

There are various contaminants in industrial wastewater, with organic pollutants constituting the critical part. Numerous organic compounds such as aliphatic and hetercyclic compounds, polycyclic aromatic hydrocarbons (PAHs), polychlorinated

Table 1.1 General characteristics of industrial wastewater

Physical properties	**Inorganic constituents**
Color	Alkalinity
Odor	Chlorides
Solids	Heavy metals
pH	Nitrogen
Temperature	PH
Chemical properties:	Phosphorus
Organic constituents	
Carbohydrates	Sulfur
Fats, oils, and grease	Gases
Pesticides	Hydrogen sulfide
Phenols	Methane
Proteins	Oxygen
Priority pollutants	**Biological constituents**
Surfactants	Animals
Volatile organic compounds	Plants
Other pollutants	Eubacteria
	Archaebacteria

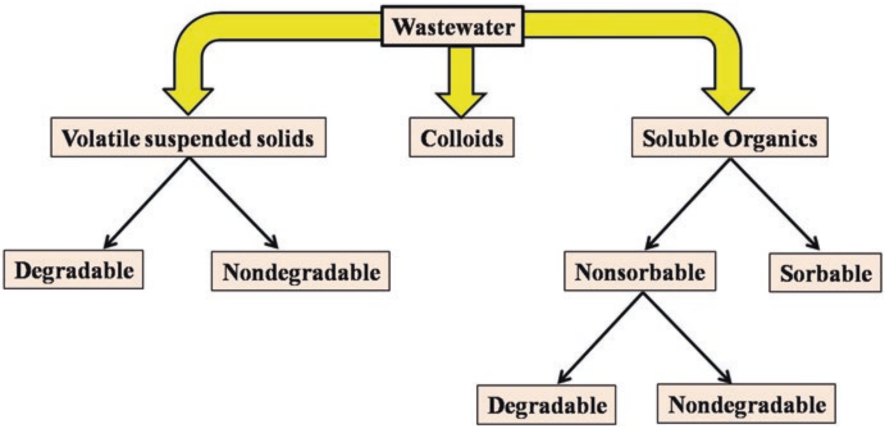

Fig. 1.1 Organic constituents of wastewater

biphenyls (PCBs), pesticides, herbicides, phenols are incorporated in the industrial wastewater. Many inorganic compounds (phosphates, nitrates, sulphates) and heavy metals (Cd, Cr, Ni, Pb) are also present in the industrial wastewater. Large amount of pollutants in water bodies cause an increase in biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS) and total suspended solids (TSS). BOD and COD represent the gross amounts of organic matter and their constituents in wastewater (Fig. 1.1). The pollutants from the discharge are directly related to the nature of the industry. For instance, the wastewater released from textile industry have high COD, BOD and color whereas wastewater released from tannery industry have high concentration of metal such as chromium and cadmium (Table 1.2).

Table 1.2 Characteristics of various industrial wastewaters

Industry	Characteristics of wastewater
Pulp and paper mill	High concentration of suspended solids, BOD, COD, inorganic dyes, chlorinated organic compounds, sodium hydroxide, sodium carbonate, sodium sulphide and bisulfites and wooden compounds such as lignin, cellulose, hemicelluloses
Tannery industry	High concentrations of chlorides, tannins, chromium, sulphate, sulphides, synthetic chemicals such as pesticides, dyes and finishing agents, heavy metals, toxic chemicals, lime with high dissolved and suspended salts, BOD, COD, and other pollutants
Dairy industry	High concentrations of organic material such as proteins (casein), carbohydrates, and lipids, concentrations of suspended solids, BOD and COD, high nitrogen, chlorides and sulphate concentrations, suspended oil and grease contents, inorganic salts, high sodium content from the use of caustic soda, detergents and sanitizers and large variations in pH
Distillery	Color, odour, high concentrations of total solids (TS), TDS, TSS, BOD, COD, ammonical nitrogen, phosphorus, potassium, calcium, magnesium, alkalinity, chloride, melanoidin and large variations in pH
Winery	Organic acids, lees, ethanol, sugars, aldehydes, phenolic compounds, detergents, high BOD, COD, TSS and slightly acidic to basic
Sugar mill	Brown color, burnt sugar like odor, high ash or solid residue, oil and grease, high percentage of dissolved organic and inorganic matter of which 50% may be present as reducing sugars with high BOD, COD, TS, TDS and TSS
Textile industry	High color content with COD and BOD, wide variety of dyes, natural impurities extracted from the fibers and other products such as acids, alkalis, salts, sulfide, formaldehyde, phenolic compounds, surfactants and heavy metals
Pharmaceutical industry	Pharmaceutically active compounds, high BOD, COD, TSS, TDS, TS and high concentrations of acids, phenol, chlorides, nitrogen, sulphate, oil and grease
Oil refinery/ petroleum industry	Oil, grease, polyaromatic hydrocarbons (PAH), benzene, toluene, ethylbenzene, xylene, phenols, ammonia, hydrogen sulfide and suspended solids with high BOD and COD
Beverages/soft drink bottling industry	Suspended solids (sac material, juice, pulp and waxes), soluble organics (sugar, and acids), inorganics (caustic soda) and volatile organics (d-limonene from peel oils) with a high BOD:COD ratio, salts of chlorides, phosphate, sulfates, sodium, potassium and calcium, large amount of nitrogen and phosphorous

1.2 Environmental Hazards of Industrial Wastewater

Industrial wastewater is one of the important sources of water pollution. The discharge of industrial wastewater into rivers, lakes and coastal areas resulted in serious water pollution problems and caused negative impacts on the ecosystem and human beings. The industrial discharge carries various types of pollutants such as organic matter, suspended solids, inorganic dissolved salts, petroleum hydrocarbons, heavy metals, surfactants and detergents. These pollutants may pollute receiving water bodies rendering them unsuitable for drinking and irrigation as well as they adversely affects the humans, animals, plants and aquatic life (Table 1.3).

Table 1.3 Adverse effects of pollutants of industrial wastewater

Pollutants	Adverse effects
Alkalinity and acidity	If the permissible range of pH value is violated by the pollutants, it may affect the aquatic life, cause health problems to human and animals and loss of productivity in agriculture
Heavy metals	The accumulation of heavy metals may have adverse effect on aquatic flora and fauna and may constitute a public health problem. Allergic reactions, skin rashes, respiratory tract irritation, gastro-intestinal disorders, renal failure and neurotoxicity are some examples of human health problems caused by heavy metals. Examples of some disease caused by heavy metals: Minamata disease caused by mercury, fluorosis caused by fluoride
Inorganic dissolved salts	Inorganic dissolved salts increase the total dissolved solids (TDS) which may interfere with the use of water in industries, water supplies and for irrigation purposes. Phosphorus and nitrogen are inducing algal growth and create eutrophic condition. The depletion of oxygen by excess algal production giving bad odour and taste of water. They are detrimental to aquatic life and toxic for human and animal life if concentration is beyond permissible limits
Polycyclic aromatic hydrocarbons (PAHs)	PAHs are problematic pollutants of industrial wastewater. They could accumulate in environment and affect the living organisms due of their acute toxicity, mutagenicity or carcinogenity
Pathogens	Pathogenic bacteria, viruses, etc. are health hazards. Number of water borne diseases may be transmitted by these pathogens such as typhoid, cholera, polio, dysentery, and infectious hepatitis in human beings
Polychlorinated biphenyls (PCBs)	PCBs are carcinogenic and mutagenic in nature and could accumulate in adipose tissue. They may cause internal organs, brain and skin disease. PCBs affect the immune system, nervous system and reproductive system
Pesticides/ insecticides	The discharge of pesticides/insecticides containing wastewater could cause serious environmental problem. They are highly poisonous and have acute toxicity on the human beings and livestock. They can damage the liver and affect the respiratory and nervous system. They also play a role in development of Parkinson's disease in humans. In agriculture, they affect the germination of seeds
Petroleum products (oil/grease/oil sludge)	Petroleum products are harmful for soils, aquatic life, animal, human and plant life. Oil spreads over the surface of water resulting in reduction of light transmission which obstructs the photosynthetic activity of the aquatic plants. Accumulation of oily waste affects the aeration and fertility of agricultural land
Phenols	Phenols are toxic to living organisms and impart unpleasant odour. Some phenols such as nitrophenyl are human carcinogens. It also affects plant growth and has potential to decrease the growth and reproductive capacity of the aquatic organisms
Sulphide	It gives bad odour and toxic to animals and aquatic life
Surfactants and detergents	They inhibit the self-purification of water and are harmful for aquatic organisms, animals and humans

Industries produce and utilize a large number of synthetic substances. Many of these substances are recalcitrant in nature which are non-biodegradable or degrade very slowly. Such substances persist in the environment for prolonged periods of time and may, therefore, become progressively more concentrated. These recalcitrant substances are toxic, mutagenic or carcinogenic and may accumulate in the tissues of organisms. These pollutants enter the food chain through bio-magnification and ultimately affect the human beings and other living organisms.

1.3 Treatment of Industrial Wastewater

The treatment of industrial wastewater is classified according to following levels (Fig. 1.2):

Preliminary treatment

It is a separation process and involves the removal of debris and coarse solids.

Primary Treatment

Primary treatment includes the removal of settleable solids (a portion of suspended solids) and part of the organic matter from the wastewater.

Secondary Treatment

The aim of secondary treatment is the further treatment of wastewater from primary treatment to remove the residual biodegradable organic matter, suspended solids and possibly nutrients (Phosphorus and nitrogen) by means of biological process.

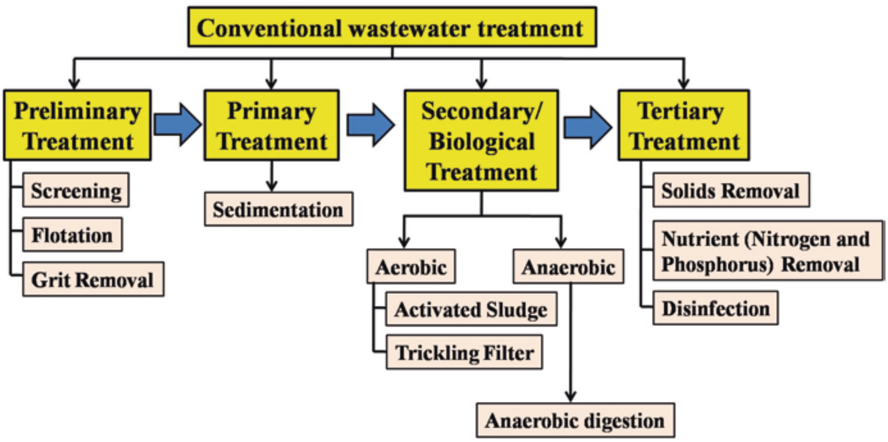

Fig. 1.2 Treatment of industrial wastewater

Tertiary Treatment

Tertiary treatment or advanced treatment is employed for the removal of specific pollutants of wastewater which cannot be sufficiently removed in secondary treatment.

1.3.1 Wastewater Treatment Operations

The wastewater treatment methods are composed of unit operations (Fig. 1.3):

Physical unit operations (**Physical treatment**)

The wastewater treatment methods in which physical forces are predominant such as screening, aeration, filtration, floating.

Chemical unit operations (**Chemical treatment**)

The treatment methods in which removal of pollutant occurs by addition of chemical products or due to chemical reactions such as ozonation, coagulation, advanced oxidation processes.

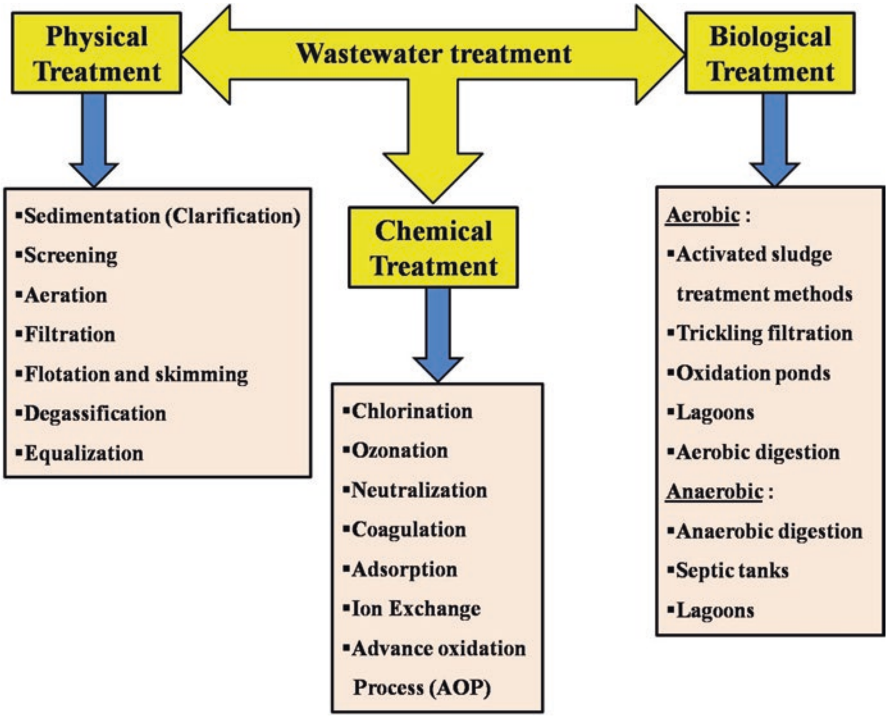

Fig. 1.3 Wastewater treatment operations

Biological unit operations (Biological treatment)

The treatment methods in which removal of pollutant occurs by means of biological activity under aerobic and anaerobic conditions such as activated sludge, trickling filtration and anaerobic digestion.

1.4 Role of Microorganisms and Plants in Biological Treatment of Industrial Wastewater

The wastewater released from various industries contains different pollutants. The discharge of untreated wastewater to natural ecosystems poses a serious threat to all life forms hence affordable and effective methods have become a necessity for the treatment of pollutants present in industrial wastewater. The conventional wastewater treatment system usually involves complicated procedures and is economically unfeasible. The biological treatment processes by means of microorganisms (bacteria, fungi, yeast, algae) and plants may present a relatively inexpensive and environment friendly way to remove different pollutants from various industrial wastewater. The use of biological system to treat the pollutants of industrial wastewater is largely dependent on source and characteristics of wastewater. Microorganisms can break down the pollutants/xenobiotics of industrial wastewater for their growth and/or energy needs. The biological systems have capabilities to remove the pollutants from wastewater by absorption, adsorption and enzymatic degradation processes. A large number of enzymes such as peroxidases, oxidoreductases, laccases, cellulolytic enzymes, proteases and amylases from a variety of different biological sources play an important role in the treatment of industrial wastewater.

1.4.1 Bacteria

The existence of diverse bacterial populations makes it possible to degrade most of the pollutant of industrial wastewater. The bacterial treatment of wastewater involves the conversion of complex organic matter to harmless simple compounds by aerobic or anaerobic process. The bacteria are frequently applied for the treatment of industrial wastewater because they are easy to cultivate, grow rapidly and suited fine for degradation and even complete mineralization of pollutants. Generally, bacteria obtain their energy from the carbonaceous organic matter (pollutant) of industrial wastewater. Some bacteria used the pollutants of industrial wastewater as their sole carbon and energy source. Several bacteria have been reported in the treatment of various industrial wastewaters (Table 1.4). These bacteria play a major role in phenol degradation, heavy metal removal (chromium reduction from leather industry), dye decolorization from textile industry, decolorization of distillery mill effluent and removal of pollutants of other industrial wastewater such as aliphatic and aromatic hydrocarbons, heavy metals, insecticides and other pollutants by biosorption or enzymatic degradation processes. Few examples of bacteria involved in

Table 1.4 List of some bacteria, fungi, algae and plants involved in biological treatment of industrial wastewater

Bacteria	**Algae**
Bacillus sp.	*Chlamydomonas reinhardtii*
Citrobacter sp.	*Chlorella vulgaris*
Enterobacter sp.	*Dictysphaerium pulchellum*
Flavobacterium sp.	*Gracilaria* sp.
Micrococcus sp.	*Lyngbya* sp.
Pseudomonas sp.	*Oscillatoria* sp.
Rhodobacter sphaeroides	*Scenedesmus dimorphus*
Serratia marcescens	*Scenedesmus obliquus*
Sphingomonas sp.	*Scenedesmus quadricauda*
Xanthomonas sp.	*Spirogyra* sp.
Fungi	**Plant**
Aspergillus sp.	*Acorus calamus*
Ganoderma lucidum	*Eichhornia crassipes*
Geotrichum candidum	*Cynodon dactylon*
Gliocladium roseum	*Euphorbia Prostrata*
Penicillium sp.	*Helianthus annuus*
Phaerochaete chrysosporium	*Lemna minor*
Trametes versicolor	*Phragmites karka*
Trichoderma sp.	*Pistia stratiotes*
Trichophyton rubrum	*Ralstonia eutropha*
Trichosporon domesticum	*Typha latifolia*

treatment of pollutants of various industrial wastewaters are as follows: *Aeromonas hydrophila* and *Bacillus* sp. are capable of dye decolorization, *Pseudomonas putida* has potential application for bioremediation of heavy metals, *Sphingomonas chlorophenolica* is capable of complete mineralization of pentachlorophenol (PCP) and *Pseudomonas fluorescence* has capability to decolorize the distillery wastewater.

1.4.2 Fungi

Fungi are multicellular organisms. They have lower sensitivity to variations in temperature, pH, nutrients, and aeration. Fungi have capability to treat the toxic pollutants of industrial wastewater released from various industries into harmless products by biosorption or enzymatic processes. Fungi secrete several isoenzymes which play major role in the removal of pollutants. White rot fungi such as *Phanerochaete chyrosporium and Trametes versicolor* are ubiquitous in nature and their adaptability to extreme conditions makes them widely exploited microorganism in treatment of industrial wastewater. They produce various enzymes including laccases, manganese peroxidases and lignin peroxidases which are involved in the degradation of various xenobiotic compounds. White rot fungi can also remove toxic metals and other pollutants by biosorption process. Their enzyme producing and biosorption activity makes them more effective in the removal of pollutants from industrial wastewater. Many fungal species are involved in the treatment of various industrial wastewaters (Table 1.4), for example, *Trametes versicolor and Rhizopus oryzae has been involved in treatment of* paper and pulp wastewater; *Phanerochaete chyrosporium* has been found effective for color removal from textile wastewater; *Aspergillus fumigatus* has been effective for decolorization of distillery wastewater; *Fusarium oxysporum, Cadosporium cladosporioides, Gliocladium roseum,* and *Trichoderma koningii* has been involved in removal of heavy metals from industrial wastewater.

1.4.3 Algae

Algae are a diverse group of photosynthetic organisms having potential to treat the pollutant of industrial wastewater mainly by bioaccumulation and biosorption. They are able to accumulate organic and inorganic toxic substances, heavy metals, nutrients, pesticides in their cells/bodies from the wastewater. Algae can remove the excess nitrogen and phosphorus present in industrial wastewater through absorption. Nitrogen and phosphorus are commonly present in wastewaters which are essential components for the growth of algae. A wide range of algal species including *Chlamydomonas, Chlorella, Spirulina, Scenedesmus, Pediastrum, Cosmarium* and *Botryococcus* have been utilized for treatment of various industrial wastewaters (Table 1.4). These species are used to treat and remove color, odour, nitrogen, phosphorus, heavy metals, BOD, COD and other pollutants from various industrial wastewaters.

1.4.4 Plants

Removal of pollutants with the utilization of plants is known as phytoremediation. This strategy includes the use of plants that show high survivability in contaminated sites and the capacity to uptake pollutants, which prompts consequent evacuation of pollutants. Plants have been effectively used to remove heavy metal, petroleum hydrocarbons, pesticides, organic and inorganic contaminants and industrial by-products. Plant species with phytoremediation potential should have specific properties. They accumulate, extract, transform, degrade or volatilize contaminants at the levels that are toxic to ordinary plants and furthermore they have ability to remediate various pollutants at the same time. The phytoremediation process can take place by any of the following ways like phytoextraction, phytostabilization, phytovolatization, phytodegredation, rhizofiltration. The pollutants enter the plant primarily through the roots by adsorption and accumulation. These pollutants might be stored in the roots, stems, or leaves; changed into less harmful chemicals inside the plant; or changed into gases that are released into the air as the plant transpires. There are several species of plants mainly aquatic plants known for their phytoremediation abilities to treat various industrial wastewaters such as *Acorus calamus*, *Typha latifolia*, *Typha domingensis, Cynodon dactylon* and *Phragmites communis* (Table 1.4).

1.5 Recycling and Reuse of Industrial Wastewater

There is consistently increasing demand of pure water by many industries. These industries utilize pure water and release large amount of wastewater. Due to rapid urbanization, the use of treated, partially treated and untreated wastewater in agriculture has received much attention in developing countries. In developing countries these wastewaters is utilized for irrigation purposes because wastewater is nutrient rich and provides food security. The untreated or partially treated industrial wastewater shows harmful effect on all life forms and the environment. One of the approaches to diminish the effect of water shortage and pollution is recycling and reuse of industrial wastewater. Water recycling is the reuse of treated wastewater for beneficial purposes such as agricultural and industrial processes. The wastewater can be treated by various technologies utilizing various distinctive measures relying upon the quality required. The treated wastewater has the potential to be recycled in a number of sectors such as agriculture and industries. The production of pure water (recycling) from different feed water sources is a complex procedure including a large number of steps and process units (Fig. 1.4).

The recycling and reuse of industrial wastewater enable communities to become less dependent on groundwater and surface water sources and can diminish the redirection of water from delicate ecosystems. Also, water reuse may lessen the supplement loads from wastewater discharges into waterways, subsequently decreasing pollution. Suitable environment-friendly sanitization process is the first necessity for recycling of wastewater because they consume less energy and along these lines positively affect endeavors to alleviate the impacts of environmental change. This is critical because the environmental issues related to water usage and wastewater release cannot be tackled basically by recycling of wastewater if the recycling procedures consume large quantities of energy.

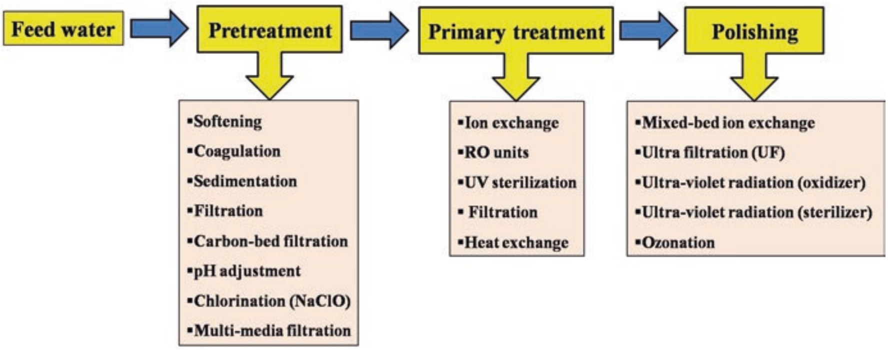

Fig. 1.4 Processes of recycling of industrial wastewater

Chapter 2
Treatment and Recycling of Wastewater from Pulp and Paper Mill

Ankit Gupta and Rasna Gupta

Abstract Paper and pulp industry is water intensive and has a greater impact on aquatic, surrounding environment and public health. Minimum fresh water usage and emphasis on waste-water recycling/management are key factors for the growth of this industry. Concentration of impurities and toxic substances in processed water mainly limits recycling benefits because it adversely affects processes, equipments and paper quality. Organic wastes are mostly processed through biodegradation and bioremediation using anaerobic digestion (methane production) followed by aerobic digestion (inducing sludge processing). Although, biological processing is economical and eco-friendly but treatment of wastes including non-biodegradable recalcitrant compounds mostly limits its broad application. Therefore, many other innovative approaches have been exploited to tackle this problem. Advanced oxidation process (AOP), novel biodegradable polymeric flocculants, electrocoagulation and photocatalysis etc. are used as alternative ways to facilitate detoxification and recycling. In this chapter, we emphasised and provided an in-depth knowledge about the various wastewater treatment strategies linked to paper and pulp industry.

Keywords Wastewater · Pulping · Pulp and paper waste · Water recycling · Recalcitrant

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R. L. Singh, R. P. Singh (eds.), *Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future*, Applied Environmental Science and Engineering for a Sustainable Future,
https://doi.org/10.1007/978-981-13-1468-1_2

2.1 Introduction

Economic strength of a nation relies on the industrialization however, it also badly affects its environment (Hossain and Rao 2014; Raj et al. 2014). The pulp and paper industry is considered to be one of the most important industrial sectors in the world due to its important contribution in the economic health of a country. Still now, pulp and paper mills are facing challenges with the energy efficiency mechanisms and management of the consequential pollutants, considering the environmental feedbacks and enduring legal requirements (Kamali and Khodaparast 2015). The pulp and paper industry totally relies on the natural resources because it is known to be a major consumer of wood, water and energy (fossil fuels, electricity) along with its major contribution in discharge of toxic effluents and pollutants into the environment. The pulp and paper industry stands at sixth position after oil, cement, leather, textile and steel industries. The pulp and paper industry typically generates a large quantity of wastewater which requires proper treatment and recycling prior to its discharge; otherwise it may lead to serious threat to the environment and economic wealth of a country.

The natural raw materials being used for the manufacturing processes are wood, cellulose, vegetables, bagasses, rice husk, fibers and also waste-paper materials (Fig. 2.1) resulting into large amount of wastewater after processing. The paper making is a water-intensive process because it requires plenty of fresh water for the production processes (about 250–300 m^3 per tons of paper) and water consumption depends upon the raw material used in industrial processes. The paper and pulp

Fig. 2.1 Different types of pulp and paper waste

industry effluent consists of several toxic and recalcitrants including sulphur compounds, organic acids, chlorinated lignin, resin acid, phenolics, unsaturated fatty acids and terpenes (Prasongsuk et al. 2009). The industrial effluents without treatment are hazardous to the environment because of a high Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), chlorinated compounds measured as adsorbable organic halides (AOX), suspended solids, recalcitrant organics, pH, turbidity, high temperature and intense colour (Chandra et al. 2007). These industries are utilizing a huge amount of lignocellulogic materials and water during the manufacturing process, and release chlorinated lignosulphonic acids, chlorinated resin acids, chlorinated phenols and chlorinated hydrocarbon in the effluent.

The highly toxic and recalcitrant compounds, dibenzo-p-dioxin and dibenzofuran, are formed unintentionally in the effluent of pulp and paper mill. The wastewater resulting from pulp and paper industry contains wood extract, tannin resins, synthetic dyes etc. in form of colouring bodies. The increasing public awareness of the fate of these pollutants and stringent regulations established by the various authorities and agencies are forcing the industry to treat effluents to the required compliance level before discharging in to the environment (D'Souza et al. 2006). A reduced usage of toxic chemicals and improved wastewater treatment in modern mills, have significantly contributed to reduction in effluent toxicity (Van den Heuvel and Ellis 2002) and thereby are eco-friendly (Sandstrom and Neuman 2003). For decolorization of pulp and paper mill effluents, a number of treatment methods have been applied; these are classified into physical, chemical and biological methods. Physical and chemical methods are less economical and also do not remove BOD and low molecular weight compounds (Singh and Thakur 2004). The biological colour removal process is particularly attractive since in addition to colour and COD it also reduces BOD and low molecular weight chlorolignins (Nagarthnamma et al. 1999). This chapter reviews the pulp and paper mill wastes, characteristics, effects and treatment methods and includes both traditional and advanced processes.

2.2 Pulp and Paper Wastewater

2.2.1 Pollutants Released from Pulp and Paper Industry

Pulp and paper industry heavily consumes raw materials e.g. wood, chemical, energy and water. The waste material resulting from this industry includes 41.8% as bleached pulp, 4.2% as solid waste, 5.25% as dissolved organic matter and 2.3% as suspended solids (Table 2.1) (Nemade et al. 2003). The key pollutants from pulp and paper mill are grouped into following categories:

(a) **Organic compounds and chemicals**

- Suspended solids including bark particles, fiber, pigments and dirt.
- Dissolved colloidal organics like hemicelluloses, sugars, lignin compounds, alcohols, turpentine, sizing agents, adhesives like starch and synthetics.
- Color bodies, primarily lignin compounds and dyes.

Table 2.1 Major pollutants released from pulp and papermaking process

Process stage	Effluent content
Raw material preparation	Suspended solids including bark particles, fiber pigments, dirt, grit, BOD and COD
Pulping	Color, bark particles, soluble wood materials, resin acids, fatty acids, AOX, VOCs, BOD, COD and dissolved inorganics
Bleaching	Dissolved lignin, color, COD, carbohydrate, inorganic chlorines, AOX, EOX, VOCs, chlorophenols and halogenated hydrocarbons
Paper making	Particulate wastes, organic and inorganic compounds, COD and BOD

COD Chemical oxygen demand, *BOD* Biochemical oxygen demand, *AOX* Adsorbable organic halogens

- Dissolved in organics such as NaOH, Na_2SO_4 and bleach chemicals.
- Thermal loads.
- Toxic chemicals.

(b) **Gases**

- Malodorous sulphur gases such as mercaptans and H_2S released from various stages in kraft pulping and recovery process.
- Oxide of sulphur from power plants, kraft recovery furnace and lime kiln.
- Steam.

(c) **Particulates**

- Fly ash from coal fired power boilers.
- Chemical particles primarily sodium and calcium based.
- Char from bark burners.

(d) **Solid wastes**

- Sludges from primary and secondary treatment and causticizing in kraft mill recovery section.
- Solids such as grit bark and other mill wastes.
- Ash from coal fired boilers.

2.2.2 *Sources of Pulp and Paper Wastewater Pollutants*

Paper making process includes five basic steps (Table 2.2) and each step may be carried out through a number of methods. Therefore, the final effluent is resulted from the combination of waste water coming out of the five different unit processes and the methods employed there in. Table 2.3 summarizes the source of pollutants normally produced during several steps manufacturing process of pulp and paper industry (Raj et al. 2014; Karrasch et al. 2006).

Table 2.2 Pulp and paper making steps

Name of step	Process
Debarking	Converts the plant fiber into smaller pieces called chips and removes the bark
Pulping	Turns the chips into pulp. This process removes the majority of lignin and hemicelluloses content from the raw material, resulting in a cellulose rich pulp
Bleaching	Brown pulp obtained after pulping in order to meet the desired colour dictated by product standards. Several bleaching agents, including chlorine, chlorine dioxide, hydrogen peroxide, oxygen, ozone, etc. may be used either singly or in combination
Washing with alkali (e.g. caustic soda)	Removes the bleaching agents from the pulp. Generally, an alkali caustic soda is used to extract color and bleaching agents from the pulp and hence, this process is also known as the alkali extraction stage
Washing with filler (e.g. clay, $CaCO_3$)	Paper and paper products are finally produced by mixing the washed pulp with appropriate fillers (clay, titanium dioxide and calcium carbonate) and sizing agents like resin and starch

Table 2.3 Sources of pulp and paper industry wastewater

Sources	Discharge	Intensity of pollution
Fibrous raw material washing	Washing of raw material	Small volume with least pollutants
Digester house	Spills and leakages of black liquor and cooling water	Small volume but high concentration of pollutant
Pulp washing	The final wash often referred as brown stock wash or unbleached wash	Small volume and large quantity of pollutant
Centricleaners	Rejects high concentration of fibres and girt or sand	Small quantity but high-suspended solids
Pulp bleaching	Wastewater from chlorination stage having low pH and high chlorolignins, from caustic extraction stage with dark brown colour and high pH as well as chlorolignins from hypochlorite stage	Very large volume with high concentration of pollutants. About 60–65% of wastewater is contributed from this section. The effluents contain toxic chloro-organic compounds
Paper machine	Often referred as white water	Volume depending upon the extent of recycling. It contains maximum suspended solids like fibres, fines and small quantity of dissolved pollutants
Chemical recovery	Spills of black liquor in the evaporators foul condensates and washings of the cauticiser	Small volumes, but high pollutants

2.2.3 Characteristics of Pulp and Paper Industry Wastewater

The effluents from pulp and paper industry are composed of different parameters in terms of COD, BOD and pH etc. contributing to increased water toxicity (Table 2.4).

Table 2.4 Typical characteristics of wastewater effluents from pulp and paper industry

Unit operations	pH	COD (mg/l)	BOD (mg/l)	BOD/COD	TSS
Wood yard and chipping	7	1275	556	2.29	7150
Thermo-mechanical pulping	4.0–4.2	3343	570	5.86	330–510
Chemical thermo-mechanical pulping	7.43	7521	3000	2.50	350
Kraft cooking section	13.5	1669	460	0.27	40
Pulping process operations	5.5	9065	2440	3.71	1309
Bleaching	8.2	3680	352	10.45	950
Paper machine	6.5	1116	641	1.74	645
Integrated pulp and paper mill	6.5	3791	1197	3.16	1241
Recycled paper mill	6.2–7.8	3380–4930	1650–2565	0.48	1900–3138

COD Chemical oxygen demand, *BOD* Biochemical oxygen demand

2.2.4 Impact of Pulp and Paper Wastewater on Surrounding

The paper industry is known to produce plenty of effluents and wastewater. The untreated effluent from the paper and pulp industry impacts the surrounding environment in various ways.

(a) **Impact on water**

Chemical contamination and reduced level of oxygen, deteriorates the water quality and significantly lowers the survival rate of its aquatic fauna. Oxygen depletion in the aquatic ecosystem occurs due to the high organic load and solid content in the effluent leading to physiological and reproductive alterations in fishes (Springer 2000). These alterations include delayed sexual maturity with lowering in secondary sexual characters in species living in the discharged effluents (Munkittrick et al. 1997). Discharge of greater volume of highly coloured and toxic effluent containing alcohol, chelating agents and inorganic materials that cause hypertrophication of the water bodies. The high molecular weight linin fragments having low biodegradability are responsible for this event leading to an increase in parasitic growth and disease in the species living in the downstream of the discharges (Lehtinen 2004).

The bleaching stage of the process engenders the main effluent bulk containing organic and inorganic compounds primarily comprising of derivatives of lignin or other wood components, such as extractives or carbohydrates. The solid matter usually comprises of fibers and bleaching additives. Resulting wastewater consists of very high biochemical oxygen demand (BOD), total suspended solids, chemical oxygen demands (COD), chlorinated organic compounds and absorbable organic halides (AOX). All these chemicals have an adverse effect on the aquatic life and in the process on the livestock and human population those survive on these water resources.

(b) **Impact on atmosphere**

Air emissions are usually from recovery broiler. Sulphur dioxide mainly, and particulate emissions of nitrous oxides that comes from nitrogen content in the black liquor – dry solid content and support fuel rate used in recovery broiler. The energy generations process produces majorly particulates sulphur dioxide, nitrous oxide etc. Fly ash, SO_2 and NO_x are produced from steam and electricity generating units. These gases along with the particulates result into urban smog resulting into serious human health concerns like eyes, nose throat irritation, coughing, breathing difficulties and lungs ailment. The presence of damaging amounts of sulphur and nitrous compounds upon wet precipitation causes acid rain which in turn results in the acidification of soil and water bodies, ensuing in making the water unsuitable for aquatic animals and wildlife. The acid rain is also seen to rapidly deteriorate buildings and heritage sculptures. The high concentration of nitrogen nutrients greatly accelerates algal growth that affects the animal diversity in the aquatic ecosystem. The particulate density in the air causes haze when the sunlight is obstructed by the same. This conceals the clarity, texture and form of the visual perception.

(c) **Impact on biodiversity**

The spillage of waste water results in the increase of chemicals nutrients like nitrogen and phosphorus. The presence of these nutrients at higher levels promotes excessive algal blooms in water using oxygen and the growth blocks sunlight which hinders the process of photosynthesis of plants under water. The decaying process of these algae also uses oxygen thereby decreasing the oxygen content in water. Blockage of sunlight disrupts the reproductive ability of fish and loss of the natural breeding site. This result in the migration of aquatic organisms to oxygen rich environment and in this process reduction of biodiversity and dead zones are caused.

The waste water pollutants result in the decline of several plant species and increase in the prevalence of hardy species. Also seen are the defoliation, root necrosis, leaves chlorosis, low seedling growth and forest clearance due to premature tree death (Farmer 1990). The studies on mammals and birds show an association between the population decline and loss of relevant food species. The metal contamination correlates to the reduction in reproductive ability in all orders of water dependent species (Tickle et al. 1995). Soil contamination results from the deficiency of microorganisms those play vital roles in soil rejuvenation and fertility thereby affecting micro flora and fauna of the top soil.

(d) **Impact on forest**

Deforestation is a partial result of this industry. The clearance of growing tress to feed the industry has resulted in the increase in the non-cultivable land. The plains and slopes of the cleared forests also pose erosion threats during the monsoons. The untreated wastewater can also influence the forest reserve area causing damage and mortality of ground plants, killing of trees and soil chemistry changes.

(e) **Impact on agriculture**

Waste water with high solid content usually leads to problems of waterlogging, desertification, salinization, erosion affecting the irrigated areas. The downstream degradation of water quality by chemicals and toxic leachates has an impact on the agriculture leading to slow growth of crops and final crop output lowers.

(f) **Impact on public health**

The general health of the human habitation depending on aquatic animals as a source of protein in the diet significantly deteriorates due to low survival rate of aquatic animals resulting from chemical contamination and reduced levels of oxygen in the water.

Surface runoff and consequently non-point source contribute significantly to high level of pathogens in surface water bodies. These usually cause allergies, skin irritation, breathing difficulties, nausea and waterborne infection like diarrhoea. The use of pulp and paper mill wastewater for irrigation contaminates foods during their washing and their consumption as raw vegetables e.g. cabbage, lettuce, strawberries may result in various diseases e.g. cholera, typhoid, amoebiasis and giardiasis etc. due to microbiological contamination.

2.3 Pulp and Paper Production Process

2.3.1 Raw Materials Handling

Paper industry consumes a range of raw materials e.g. cellulosic derived from forest, agricultural residues and waste paper; non-cellulosic coal, chlorine, lime, sodium hydroxide, sodium sulphide, fuel oil, talcum powder etc. Major raw materials used by paper industry are bamboo, wood, bagasse, waste paper and agricultural residue like wheat straw, rice straw, jute sticks, hemp, kenaf, grasses, sea weed etc. Apart from this, paper industry consumes a large amount of chemicals like caustic soda, sodium sulphide, sodium carbonate, chlorine, hypochlorite, mineral acid; coal, talcum powder etc. (Table 2.5).

2.3.2 Pulp Manufacturing

The cellulosic materials are isolated from wood, fibre crops, waste paper and rags using chemical and mechanical methods and are used in formation of pulp which is a key raw material for pulp and paper industry. Pulp formation mostly utilizes heartwood and sapwood. There are a number of methods employed for pulping procedures (given below):

Table 2.5 Details of raw materials for the usage by small and large integrated pulp and paper industries

S.No.	Raw material	Requirement per tonne of paper	
		Small paper industries	Integrated pulp and paper industries
1.	Cellulosic raw material (hardwood, soft wood, agricultural residues etc.) (kg)	2500–3000	2200–2500
2.	Cooking chemicals as Na_2O (kg)	70–90	310–360
3.	Caustic for bleaching	20–35	20–35
4.	Chlorine (kg)	100–160	130–160
5.	Salt cake (kg)	–	60–70
6.	Lime (available CaO 60%) (kg)	70–100	70–100
7.	Lime (available CaO 60%) for causticising section (kg)	–	350–450
8.	Coal (tonne)	1.0–1.35	1.5–3.0
9.	Sulphuric acid (kg)	–	6–7
10.	Alum (kg)	50–60	50–60
11.	Rosin and wax emulsion (kg)	10–12	10–12
12.	Starch (kg)	–	11
13.	Hydrochloric acid (kg)	–	2
14.	Furnace oil (kg)	–	75
15.	Water (m^3)	150–300	150–300
16.	Power (kWh)	1200–1300	1300–1800
17.	Steam (tonne)	6.0–7.0	11–16
18.	Soda ash as % of rosin	7–8	7–8
19.	Talcum (kg)	120–150	150–180

2.3.2.1 Mechanical Pulp

Most modern industries use chips rather than logs and ridged metal discs called refiner plates instead of grindstones. If the chips are just ground up with the plates, the pulp is called refiner mechanical pulp (RMP) and if the chips are steamed while being refined the pulp is called thermomechanical pulp (TMP).

2.3.2.2 Thermomechanical Pulp

Processed wood chips after heat treatment are known as thermomechanical pulp that results from two-step process: stripping of the bark and their conversion into smaller chips.

2.3.2.3 Chemithermomechanical Pulp (CTMP)

The conditions of the chemical treatment are much less vigorous (lower temperature, shorter time, less extreme pH) than in a chemical pulping process since the goal is to make the fibres easier to refine, not to remove lignin as in a fully chemical process. Pulps made using these hybrid processes are known as chemithermomechanical pulps.

2.3.2.4 Chemical Pulp

The high-quality papers are results from these methods because chemical cooking dissolves majority of lignin and hemicelluloses contents found in wood leading to better separation of the cellulose fibres. There are two primary means of chemical pulping.

(a) **The sulphite process:** This cooks wood chips in sulphurous acid combined with limestone to produce calcium bisulphite. The combination of sulphurous acid and calcium bisulphite dissolves the lignin in the wood and liberates the cellulose fibres. Sulphite pulp is soft and flexible, is moderately strong, and is used to supplement mechanical pulps (most typically in newsprint). In order to overcome the issues raised during the process such as types of trees, rules and regulations of pollution laws etc., latest process have been adopted resulting into new chemicals.

(b) **The sulphate process:** It is now the most widely used chemical pulping system. It is evolved from the soda processes developed in the nineteenth century, which used strong bases (alkaline solutions) such as lye to digest wood. Pulpers began adding sodium sulphate to the soda process, and a significantly stronger pulp was produced.

(c) **The kraft process:** It entails treatment of wood chips with a hot mixture of water, sodium hydroxide, and sodium sulphide, known as white liquor that breaks the bonds those link lignin, hemicellulose, and cellulose. This process is more economical, well suited to nearly all known species of trees, increase strength and brightness of pulp. The pulp resulting from this process is much stronger compared to other methods as the name "kraft" suggests and the resulting paper is used in high-speed presses.

To increase pulp whiteness and brightness (unbleached kraft pulp has a dark brown colour), and to remove residual lignin, chemical pulps are bleached. It is at this point that additional non-fibrous materials called fillers are added to the pulp a process called loading and the resulting furnish-the mixture of pulp and fillers-is ready to begin the refining process.

2.3.2.5 Recycled Pulp

Papers with printed ink are recycled using a process termed as deinking, therefore, the recycled pulp is also known as deinked pulp (DIP). A number of industries e.g. newsprint, toilet and tissue paper etc. consumes DIP as a raw material.

2.3.2.6 Organosolv Pulp

Organosolv pulping uses organic solvents e.g. methanol, ethanol, formic acid and acetic acid etc. at temperatures above 140 °C to break down lignin and hemicellulose into soluble fragments. The pulping liquor is easily recovered by distillation.

2.3.2.7 Biological Pulp

In contrast to chemical pulping, biological pulping utilizes a number of microbes e.g. bacteria, algae and fungi those degrade waste lignin (Table 2.6) and cellulose fibres (Ahmad et al. 2011). Lignin peroxidase is a fungal enzyme that selectively degrades lignin (Table 2.7). The treated pulp undergoes bleaching followed by the neutralization step.

2.3.3 Pulp Washing and Screening

Pulping process consumes a high amount of chemicals therefore recovery of chemicals from pulp also known as pulp washing, is required because first they are expensive to replace, second, they interfere with the downstream process and third, they are harmful for the environment.

There are many types of machinery used for pulp washing. Most of them rely on displacing the dissolved solids (inorganic and organic) in a pulp mat by hot water, but some use pressing to squeeze out the chemicals with the liquid. An old, but still common method is to use a rotating drum, covered by a wire mesh, which rotates in a diluted suspension of the fibres. The fibres form a mat on the drum, and showers of hot water are then sprayed onto the fibre mat.

2.3.4 Bleaching

Bleaching process effectively removes total residual lignin content after pulping process because its chromophoric groups contribute in the darkness of the pulp. The modern process employed both bleaching and pulping steps in delignification process. However, traditionally the name ‘bleaching’ is reserved for delignification that

Table 2.6 List of bacteria involved in the treatment of pulp and paper industry wastewater

Bacteria	References
Alcaligenes faecalis	Mehta et al. (2014)
Arthrobacter agilis	Ordaz-Diaz et al. (2014)
Aspergillus niger	Ordaz-Diaz et al. (2014)
Azoarcus tolulyticus	Gauthier et al. (2000)
Bacillus cereus	Mehta et al. (2014)
Bacillus licheniformis	Ordaz-Diaz et al. (2014)
Bacillus seohaeanensis	Ordaz-Diaz et al. (2014)
Bacillu spumilus	Saraswathi and Saseetharan (2010)
Bacillus subtilis	Shanthi et al. (2012) and Tyagi et al. (2014)
Brevibacillus agri	Hooda et al. (2015)
Cellumomonas sp., *Cellulomonas cellasea*	Marquina (2005) and Ordaz-Diaz et al. (2014)
Citrobacter freundii	Shanthi et al. (2012) and Chandra and Bharagava (2013)
Corynebacterium nephridii	Gauthier et al. (2000)
Cronobacter sp.	Kumar et al. (2014)
Enterobacter sp.	Shanthi et al. (2012)
Escherichia coli K12	Gauthier et al. (2000)
Klebsiella sp., *Klebsiella pneumonia*	Kumar et al. (2014) and Gauthier et al. (2000)
Microbrevis luteum	Singh and Thakur (2004)
Micrococcus luteus	Tyagi et al. (2014)
Paecilomyces sp.	Singh and Thakur (2004) and Kumar et al. (2014)
Paracoccus denitrificans	Gauthier et al. (2000)
Penicillum sp.	Ordaz-Diaz et al. (2014)
Pseudomonas alkaligenes	Saraswathi and Saseetharan (2010) and Shanthi et al. (2012)
Pseudomonas stutzeri	Gauthier et al. (2000)
Pseudomonas syringaepv	Kumar et al. (2014)
Rhizopus sp.	Anuranjana Jaya and Vijayan (2016)
Rhodobacter sphaeroides	Gauthier et al. (2000)
Sinorhizobium meliloti	Gauthier et al. (2000)

is taking place downstream of the pulping process. In practice, there are two separate "bleaching" process steps: oxygen delignification and final bleaching.

2.3.4.1 Oxygen Delignification

This process includes treatment of washed pulp with highly alkaline solution of sodium hydroxide because higher pH favours the oxidation of phenolic groups in the lignin through their ionization and thereafter further depolymerization of resulting partial-degraded lignin into low molecular weight biproducts. These are more soluble in water and can be removed from the fibres. It is important that the pulp has been at least partly washed beforehand because the black liquor solids in unwashed

Table 2.7 List of fungi involved in the treatment of pulp and paper industry wastewater

Fungi	References
Alternaria alternata	Zabel and Morrell (1992)
Alternaria solani	Jerusik (2010)
Aspergillus flavus	Barapatre and Jha (2016)
Aspergillus Niger	Sharma and Gupta (2012)
Aureobasidium pullulans	Zabel and Morrell (1992)
Cephaloascus fragrans	Zabel and Morrell (1992)
Ceratocystis moniliformis	Zabel and Morrell (1992)
Ceratocystis rigidum	Zabel and Morrell (1992)
Chaetomium globosum	Jerusik (2010)
Cladosporium spp.,	Zabel and Morrell (1992)
Coriolus versicolor	Hong et al. (2015)
Daldenia concentric	Yamuna et al. (2016)
Fibrodontia sp. *RCK783S*	Kreetachat et al. (2016)
Fomeslividus	Selvam et al. (2002)
Fusarium oxysporum	Jerusik (2010)
Fusarium solani	Marquina (2005)
Lentinus edodes	Wu et al. (2005)
Lenziteseximia	Selvam and Shanmuga Priya (2013)
Lepiota sp.	Yamuna et al. (2016)
Leptographium lundbergii	Zabel and Morrell (1992)
Lasiodiplodia theobromae	Zabel and Morrell (1992)
Ophiostoma ips	Zabel and Morrell (1992)
Ophiostoma piceae	Zabel and Morrell (1992)
Ophiostoma piliferum	Zabel and Morrell (1992)
Ophiostoma pluriannulatum	Zabel and Morrell (1992)
Paecilomyces variotii	Senthilkumar et al. (2014) and Kamali and Khodaparast (2015)
Penicillium funicolosum	
Penicillium notatum	Jerusik (2010)
Penicillium roqueforti	Nilsson and Asserson (1969)
Phanerochaete chrysosporium,	Saritha et al. (2010) and Senthilkumar et al. (2014)
Phiolophora spp.	Zabel and Morrell (1992)
Phlebiaradiate	Senthilkumar et al. (2014)
Pleurotus ostreatus	Wu et al. (2005) and Hong et al. (2015)
Pleurotus citrinopileatus	Ragunathan and Swaminathan (2004)
Pleurotus platypus	Ragunathan and Swaminathan (2004)
Pleurotus sajor-caju	Ragunathan and Swaminathan (2004)
Rhizopus arrhizus	Nilsson and Asserson (1969)
Schizophyllum commune	Selvam and Shanmuga Priya (2013)
Tinctoporia borbonica	Senthilkumar et al. (2014) and Kamali and Khodaparast (2015)
Trametes gallica	Hong et al. (2015)
Trametes hirsute	Saritha et al. (2010)
Trametes serialis	Yamuna et al. (2016)
Trametes versicolor	Selvam et al. (2002) and Kamali and Khodaparast (2015)
Trichoderma lignorum	Nilsson and Asserson (1969) and Marquina (2005)
Tyromyces albidus	Hong et al. (2015)

pulp consume oxygen. After the oxygen delignification stage, the pulp has to be washed very well, as otherwise the organics carry over to the final bleaching process, consuming chemicals there and also decreasing the environmental benefits.

The highly alkaline conditions of oxygen delignification also make carbohydrate fractions in the fibres react with oxygen up to a certain extent however radical oxygen species are harmful for carbohydrates. The formation of radicals is promoted by the presence of certain metal ions. However, it has been found that magnesium salts inhibit metal ion activity, and magnesium sulphate is therefore normally added as a protector in oxygen delignification.

Oxygen delignification can significantly decrease the water pollution from the final (normally chlorine or chlorine dioxide based) bleaching. In addition, it is an effluent free process. All dissolved lignin and other organics (as well as the inorganic chemicals) are recovered in the black liquor and returned to the chemical recovery system, rather than being discharged as effluent as they are in chlorine-based bleaching. Finally, oxygen is a fairly cheap bleaching chemical, although the capital costs are high for an efficient system.

2.3.4.2 Final Bleaching

Final bleaching is a multi-stage process that utilizes various commercial bleaching chemicals including chlorine, chlorine dioxide, sodium hypochlorite, oxygen, peroxide, ozone. This process improves strength of the pulp by efficient usage of the chemicals. Elemental chlorine (Cl_2) produces a large amount of chlorinated organic compounds in the effluent, and strenuous efforts have, therefore, been made to decrease its usage. Modern bleach plants, therefore, use no elemental chlorine. They are called as ECF plants: elemental chlorine free bleach plants. Despite being much toxic to the environment, chlorine dioxide is more effective in preserving pulp strength but less effective in delignification or bleaching compared to Cl_2.

2.3.5 Chemical Recovery

The recovery of the process chemicals and fibres reduces the pollution load to a great extent, where the economy permits; the colour bearing – black liquor is treated for the chemical recovery. However, in this process the lignin is destroyed. The same may also be recovered from the black liquor, by precipitation or acidulation with either CO_2 or sulphuric acid. These recovered lignins have got various uses in other industries. The alkaline lignins of kraft process may be used as a dispersing agent in various suspensions. Lignins may be used as raw materials for various other substances like dimethyl sulphoxide, which is used as spinning solvent for polyacrylonitrite fibres. Activated carbons may also be manufactured from the lignins, recovered from the black liquors. The fibres in the white water, from the paper mills are recovered either by sedimentation or by flotation using forced air in the tank.

2.3.6 Paper Making

Paper making process includes mechanical and chemical treatment of pulp fibres resulting into suspension and, successive pressing and drying of cellulosic fibres to get paper after water removal. The mechanical treatment of the fibre normally takes place by passing it between moving steel bars which are attached to revolving metal discs, known as refiners. This treatment has two effects: it shortens the fibre (fibre cutting) and it fibrillates the fibre. The latter action increases the surface area, and as the fibres bond together in the paper sheet by hydrogen bonding, the increased surface area greatly increases the bonding and strength of the paper. Paper strength is dependent on the individual fibre strength and the strength of the bonds between the fibres. It is usually the latter, which is the limiting factor. Refining increases the inter fibre bonding at the expense of the individual fibre strength, but the net result will be an increase in paper strength. Pressing and calendaring (feeding through rollers) increase density and promote smoothness. Various chemicals are added, e.g. to give water resistance, increased strength, produce coloured paper, or to serve as inorganic filters.

2.4 Methods of Pulp and Paper Wastewater Treatment

2.4.1 Physical Methods

Physico-chemical processes are commonly used in the preliminary, primary or tertiary stages of wastewater treatment. The concentration of contaminants present in wastewaters and their desired removal efficiencies are important factors in choosing the type of physico-chemical treatment process. The presence of lignin and its derivatives contribute to strong colour in most pulp-and-paper wastewaters (Dilek and Gokcay 1994). These wastewaters also contain high concentrations of suspended solids and floating matters. Therefore, the use of a primary treatment, commonly sedimentation (Mulligan 2002) is essential for the treatment process. These processes include various techniques:

2.4.1.1 Sedimentation

Sedimentation is the property that helps to remove most of the suspended particles from the wastewater by employing multiple forces e.g. gravitational, centrifugal and electromagnetic etc. (Thompson et al. 2004).

2.4.1.2 Froth Flotation

Froth flotation is a process for selective separation of hydrophobic materials from a mixer containing hydrophilic substances (Hogenkamp 1999). This process is extensively employed in mineral processing, paper recycling and waste-water treatment.

2.4.2 Physiochemical Methods

2.4.2.1 Coagulation-Flocculation

Coagulation-flocculation is a way to treat chemical water in order to remove the particles before it undergoes sedimentation and filtration. Coagulation step results into gelatinous mass after neutralizing charges whereas, flocculation step involves agglomeration of particles into large masses either by stirring or agitation but in both processes these masses are either settled down or trapped in the filter. These processes add an additional step to purify industrial effluents (Wong et al. 2006). Coagulation is an efficient way to remove suspended solids and COD from industrial wastewater prior to further treatment (Dilek and Gokcay 1994).

2.4.2.2 Activated Carbon Filtration

Activated carbon filtration method is an effective way to get rid of organic contaminants from industrial wastewater through their adsorption on carbon filter but it doesn't involve removal of microbial and other inorganic contaminants. Various parameters such as activated carbon and quality of water etc. determine adsorption efficiency of carbon filters. However, the efficiency and lifetime of carbon filters is drastically increased once they are combined with ozonation process.

2.4.2.3 Chemical Precipitation

Chemical precipitation is the most well known and most commonly used technique for the removal of metals and some anions from wastewater. The aim of precipitation is to precipitate the chemicals from dissolved substances in the wastewater by adding a reagent, which forms an insoluble compound with the to-be-separated matter. Additionally, precipitation also allows to get rid of positive ions e.g. heavy metals and negative ions e.g. phosphates and sulphates.

2.4.3 Biological Methods

Biological treatment is a natural process. Organic matter in water naturally decays as a result of the presence of microorganisms in receiving bodies of water. High organic loads in wastewater will upset the biocenosis (an association of different organisms forming a closely integrated community) of receiving bodies of water and cause other undesirable effects. Biological treatment is engineered to accelerate natural decay processes and neutralize the waste before it is finally discharged to receiving waters. It may be divided in two types:

Aerobic Systems (Activated Sludge (liquid waste), Composting (solid waste))

$$\text{Organic matter} + O_2 \rightarrow CO_2 + \text{new cells}$$

Anaerobic Systems (UASB (liquid waste), Anaerobic Digester (solid waste))

$$\text{Organic matter} \rightarrow CH_4 + CO_2 + \text{new cells}$$

Aerobic processes are usually operated at low dissolved oxygen (DO) concentrations and microorganisms are subjected to varying periods of time when no DO is present. Therefore, many facultative microorganisms will be found in an aerobic process.

2.4.3.1 Aerobic Process

2.4.3.1.1 Activated Sludge Process

Activated sludge is defined as a suspension of microorganisms, both living and dead, in wastewater. The microorganisms are activated by an input of air and the organics in the waste are metabolised to produce end products and new biomass. Mixing must be adequate to prevent the sedimentation of microorganisms and to mix air, waste and nutrients. The aerobic mode of metabolism is the most efficient in terms of energy recovered by the biomass per unit of substrate processed. This results in a relatively large quantity of sludge production, which is the other primary characteristic of this process.

2.4.3.1.2 Composting

Composting is a biological process that uses naturally occurring microorganisms to convert biodegradable organic matter into a humus-like product and is a suitable method for recycling waste treatment sludge. The composting process destroys pathogens, converts nitrogen from unstable ammonia to stable, organic forms of nitrogen and reduces the volume of waste (Zhu 2006). This process is controlled by environmental parameters (temperature, moisture content, pH, and aeration) and

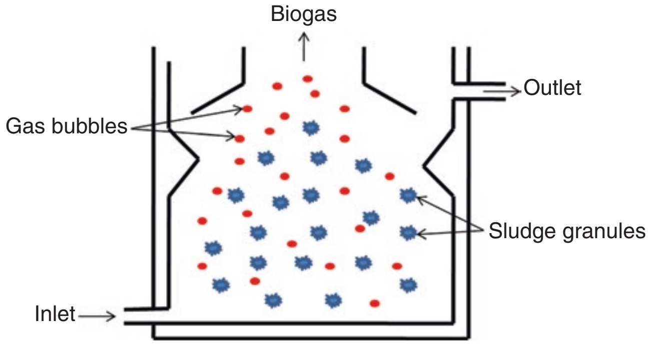

Fig. 2.2 Upflow anaerobic sludge blanket (UASB)

substrate properties (C/N ratio, particle size, and nutrient content) (Kulikowska et al. 2015).

2.4.3.2 Anaerobic Process

Anaerobic processes are more economical in terms of low sludge production and their disposal compared to aerobic processes. This process also yields methane and carbon dioxide, and mostly have been employed during late 1960s e.g. upflow anaerobic sludge blanket (UASB) (Lettinga and Huishoff Pol 1991) expanded granular sludge bed (EGSB) and internal circulation reactor (IC).

2.4.3.2.1 Upflow Anaerobic Sludge Blanket (UASB)

UASB is a methanogenic (methane-producing) digester, evolved from the anaerobic clarigester. It is a single tank anaerobic process for the removal of organic pollutants. As shown in Fig. 2.2, wastewater enters from bottom and flows vertically upwards through sludge blanket filters containing bacteria those help in sludge treatment by anaerobic degradation of organic matter and production of biogas as an energy source. As all aerobic treatments, UASB also require a post-treatment to remove pathogens, but due to a low removal of nutrients, the effluent water as well as the stabilised sludge can be used in agriculture.

2.4.3.2.2 Expanded Granular Sludge Bed (EGSB)

The EGSB reactor is a variant of the UASB for anaerobic treatment of wastewater (Jim and Reyes 2006). A different feature is that a faster rate of upward-flow velocity is designed for the wastewater passing through the sludge bed (Fig. 2.3). EGSB is more suitable for wastewaters with low suspended particles to avoid clogging of sludge bed and less soluble COD values (<1–2 COD/lit).

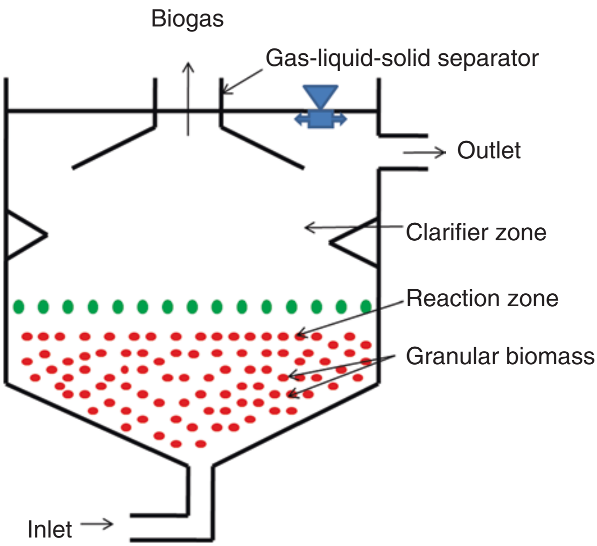

Fig. 2.3 Expanded granular sludge bed

2.4.3.2.3 Internal Circulation (IC) Reactor

Both USAB and EGSB digestion systems give rise to IC reactor with better digestion rates and biogas production (biogas with around 80% of methane). This reactor typically includes an acidification and hydrolysis tank (Fig. 2.4) and results into effluents requiring aerobic treatment to overcome high BOD and COD contents of the discharge. Water is pumped into the bottom of the reactor where it enters in an efficient water distribution system and then mixed with anaerobic granular sludge in the reactor. In the lower part of the reactor (processing zone), most organics are converted into methane and carbon dioxide. Biogas is collected by the lower part of the three-phase separator, producing gas lift power to push water through up-flow column into gas-liquid separator on the top of the reactor. Biogas is separated in the separator while water flows back to the bottom of the reactor. Hence it is known as internal circulation (IC) reactor. In the second section of the reactor, namely the upper part, wastewater is further treated. In this part, the produced biogas is collected by the three-phase separator and clean water is discharged from the top of the reactor.

2.4.4 Innovative Technologies

2.4.4.1 Ozonation

Ozone readily reacts with the substrate on its own compared to oxygen which requires a catalyst e.g. metal ion to start the reaction. An ozonation was also compared with other methods such as combined ozonation with hydrogen peroxide

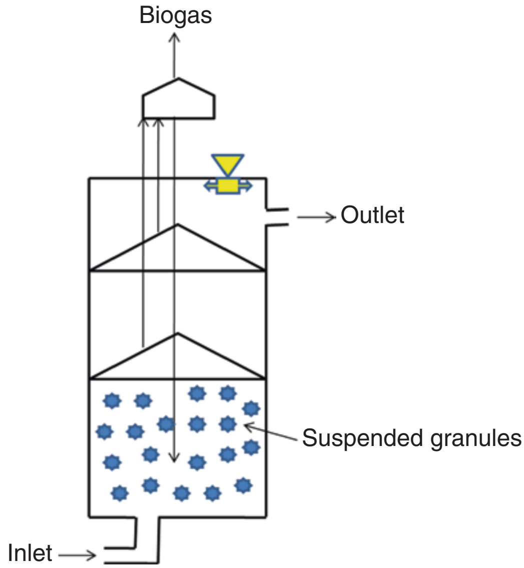

Fig. 2.4 Schematic depiction of IC reactor

mediated oxidation and Fenton's oxidation for the removal of COD and colour from the pulp and paper wastewater (Kishimoto et al. 2010) and found that both, ozonation and ozonation with hydrogen peroxide were successful in decolorization whereas no satisfactory results were found with COD removal. However, the Fenton's oxidation process was found more economical and more efficient in removing both colour and COD compared to ozonation alone, combined ozonation and hydrogen peroxide oxidation. Chemical precipitation using sulfuric acid followed by ozonation was also tried for the treatment of paper-making wastewater that successfully was able to remove large content of high molecular weight contaminants, 96% and 60–70% of colour and BOD, respectively (Santos Ramos et al. 2009). They showed that the pH level, varied with the quantity of sulfuric acid used in the process, affected the efficiency of ozonation.

2.4.4.2 Ultrafiltration

Ultrafiltration is a type of membrane filtration linked with hydrostatic pressure that forces a liquid through semipermeable membrane and has better removal efficiency but less economical which limits its use in the pulp-and-paper industry (Bhattacharjee et al. 2006).

2.4.4.3 Chemical Oxidation

Chemical oxidation oxidises organic pollutants and inorganic components (cyanide) to less harmful substances and eventually results in CO_2 and H_2O. This method may also be combined with biological purification leading to partial oxidation (breakdown of complexed compounds into simplified substances) followed by biological degradation. Chemical oxidisation involves addition of oxidants including ozone (O_3), hydrogen peroxide (H_2O_2), bleaching liquor (NaOCl), chlorine dioxide (ClO_2), chlorine gas (Cl_2), peroxy acetic acid ($C_2H_4O_3$) and pure oxygen (O_2). Among them most active oxidant is hydroxyl radical ($OH^{\cdot}$) resulting from ozone or hydrogen peroxide after activation with a catalyst (e.g. Fe^{2+} in a Fenton reaction) or UV light.

2.4.4.4 Electrolysis

Electrolysis involves electricity flow through treatable water or effluent leading to destabilization of dissolved and colloidal particles, suspended matter so that they may undergo electro-coagulation, agglomeration, electro-flotation for their easy removal (Kishimoto et al. 2010).

2.4.5 Alternative Treatment Methods

Biological treatments of paper and pulp wastes are not enough to degrade non-biodegradable wastes. Therefore, alternative treatments are needed to degrade such industrial wastes.

2.4.5.1 Advanced Oxidation Process (AOP)

This treatment method utilizes the properties of highly reactive hydroxyl radicals in order to transform recalcitrant compounds into biodegradable components and inorganic substances such as carbon dioxide and water. These hydroxyl radicals act on aromatic, polyphenols, halogenated compounds, detergents etc. for their proper mineralization. UV radiation along with hydrogen peroxide (H_2O_2), ozone in combination with UV or H_2O_2 and Fenton's reagent (Fe^{+2} with H_2O_2) in absence and presence of UV are being utilized to accelerate the production of these hydroxyl radicals for AOP method (Covinich et al. 2014). A combination of AOP with biological treatment enhances its efficiency for the waste-water treatment.

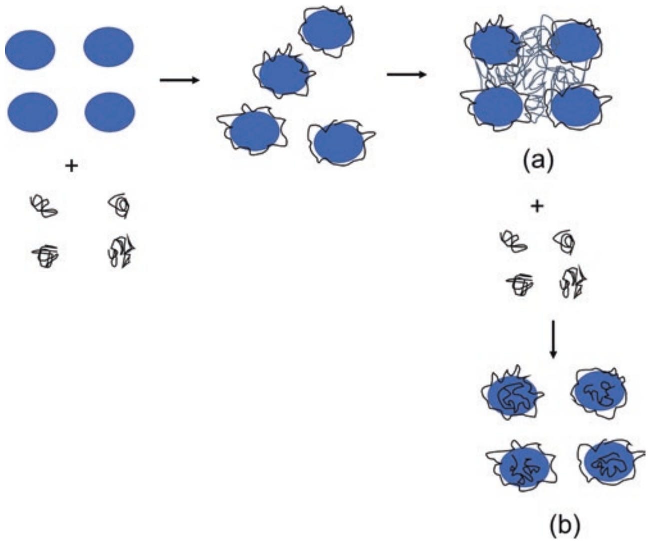

Fig. 2.5 Schematic depiction of (**a**) bridging action and (**b**) re-stabilization by adsorbed polymers leading to flocculation

2.4.5.2 Biodegradable Polymeric Flocculants

Highly toxic recalcitrants e.g. dibenjo-p-dioxin and dibenzofuran resulting from pulp and paper industry are threat to water quality and living aquatic fauna. Physio-chemical and biological approaches still not enough to conquer this problem. Therefore, a novel approach bridging between both approaches could be adopted to treat the waste water of this industry using biodegradable anion polymers (Kumar et al. 2015). The basic principal of this approach is based on two steps: bridging and flocculation (Fig. 2.5). Once, small amount of these long chain polymers is administered to the colloidal particle suspension, they get adsorb on those particles and interlink these particles with each other, the phenomena is known as bridging. But over dosage of the polymers results into destabilization of these particles due to insufficient space available on the surface of these particles and steric repulsion among them for further bridging. Therefore, aggregates of these bridged particles are formed, also known as flocculants (Rose and John 1987). This approach is cost-effective, eco-friendly due to use of biodegradable polymers and it serves as an alternate primary treatment to eliminate toxicity, colour and maintain COD and BOD of the water.

2.4.5.3 Electrocoagulation

Low biodegradability index of paper and pulp effluents limits the usage of biochemical method in waste-water treatment of this industry. Therefore, various approaches such as electro-coagulation, electro-floatation and electro-oxidation have been extensively used for the treatment but out of them, electro-coagulation

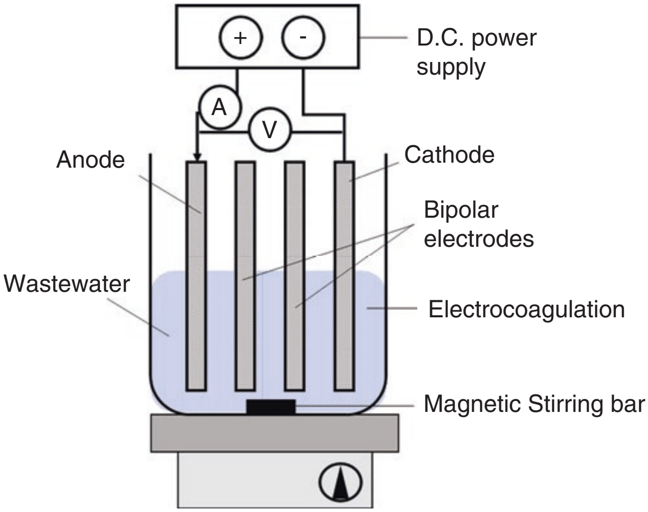

Fig. 2.6 Schematic depiction of batch scale electrocoagulation reactor

has been emerged as most efficient method due to its salient features e.g. low amount of sludge generation, easy handling and complete degradation of resulting pollutants (Fig. 2.6). Electrocoagulation is an independent and complexed process resulting into coagulants by using aluminium as sacrificial anodes. Various parameters i.e. time, current density, pH, salt concentration, speed of stirrer and electrode distance determine reduction of colour, BOD and COD of resulting wastewater from paper and pulp industry (Sharma 2014).

2.4.5.4 Photocatalysis

Wood is a key raw-material of the paper and pulp industry, resulting into major waste-product lignin in the effluent that has to be degraded effectively for water recycling. Therefore, photo-catalysis has emerged an effective method driving oxidation of lignin contaminant up to 2000 mg/lit using photocatalytic slurry reactor with an optimum temperature of 60 °C (Pawar and Hussain 2016).

2.5 Biological Sources of Pulp and Paper Wastewater Treatment

2.5.1 Bacteria

Bacteria are the primary agents of treatment in any biological treatment process (Table 2.6). Taken as whole, their diverse characteristics and minimal growth requirements allow them to proliferate in a wastewater environment.

2.5.2 Fungi

Yeast and fungi are very commonly used in the treatment processes of paper and pulp wastewater (Table 2.7). Their lower nitrogen requirement and ability to survive at lower pH enable them to be used extensively in wastewater treatment. The white-rot fungi have been extensively employed in various biotechnological areas to explore their degradation abilities. The treatment processes including fungi results into conversion of organics present in wastewater into valuable proteins and by-products along with fungal biomass that could be included in human diet and animal feeds (Guest and Smith 2002; Zheng et al. 2005). Yeast bioconversion of wastewater has been attractive to many researchers for ease of cultivation, ability to grow at pH values lower than 5, and growth rates faster than those of moulds (Gonzalez et al. 1992). Additionally, yeasts yield biomass with greater nutrient values and have lesser susceptibility to be contaminated by other microbes (Satyawali and Balakrishnan 2007). Compared to bacteria, fungi are more favourable to treat pulp and paper wastewater. First, fungi contain a group of extracellular enzymes that facilitate the biodegradation of recalcitrant compounds such as polyphenolic compounds through nonspecific oxidation reaction (D'Annibale et al. 2004; Jaouani et al. 2005). Bacterial cells, by contrast, can produce target-specific enzymes for degrading these recalcitrant contaminants (Chrost and Siuda 2002). Second, Fungi also have a greater resistance to inhibitory compounds than do bacterial species. The hyphal growth of fungi provides a greater protection for their sensitive organelles. Third, the cell walls of fungi, a layer of extra-polysaccharide matrix, protect them from inhibitory compounds through adsorption. Moreover, fungi are eukaryotes, having considerably more genes than bacteria, which make them more versatile in tolerating inhibitory compounds (Guest and Smith 2002). Fourth, the higher number of genes in fungi imparts greater reproductive selectivity, which might result in better adaptations to the environment (Bennett and Lasure 1991). One of the major reasons for using bacterial biomass in biological wastewater treatment is its well-understood growth kinetics.

2.5.3 Algae

Algae are natural water purifier and a number of technologies based on algae are used in treatment of wastewater and production of efficient and economical useful products. Many species of algae have been reported for removal of pollutant from pulp and paper industry wastewater (Table 2.8). Microalgae have been employed for the removal of nutrients from wastewater (Gupta and Rao 1980; Kunikane et al. 1984; Gantar et al. 1991; Queiroz et al. 2007; Rao et al. 2011). The algae-bacterial symbiosis contributes in reduction of electricity demand from aeration which constitutes more than 50% of total energy production form wastewater treatment plants.

Table 2.8 List of algae involved in the treatment of pulp and paper industry wastewater

Algae	References
Ankistrodesmus falcatus	Ekendahl (2015)
Botryococcus braunii	Ekendahl (2015)
Chlamydomonas reinhardtii	Ferdowshi (2013)
Chlorella protothecoides	Ferdowshi (2013) and Ekendahl (2015)
Chlorella sorokiniana	Ferdowshi (2013) and Ekendahl (2015)
Chlorella vulgaris	Ferdowshi (2013), Kshirsagar (2013), and Ekendahl (2015)
Chlorella saccharophila	Ekendahl (2015)
Cladophora glomerate	Xiang et al. (2016)
Dictysphaerium pulchellum	Ekendahl (2015)
Eucheuma cottonii	Machmud et al. (2014)
Gracilaria sp.	Machmud et al. (2014)
Nannochloropsis oculata	Gurumoorthy and Saravanan (2016)
Microcystis sp.	Sharma et al. (2014)
Selenastrum capricornutum	Ekendahl (2015)
Scenedesmus dimorphus	Ekendahl (2015)
Scenedesmus quadricauda	Ekendahl (2015) and Kshirsagar (2013)
Scenedesmus obliquus	Ferdowshi (2013) and Kshirsagar (2013) and Ekendahl (2015)
Scenedesmus obtusiusculus	Ekendahl (2015)
Scenedesmus simris	Ekendahl (2015)

2.5.4 Plants

Phytoremediation is an eco-friendly and economical process to convert industrial wastewater into usable water with the help of plants (Lakshmi et al. 2017). The effluents resulting from pulp and paper industry also contaminate surrounding soil with toxic heavy metals those are absorbed by roots of the plants with subsequent transport to aerial plant organs leading to removal of toxins from the affected soil, known as phytoextraction. The sunflower (*Helianthus annuus*) was found efficient for phytoextraction of lead from industrial effluents (Usha et al. 2011). Similarly, a study demonstrated that channel grass *Vallisneria spiralis* effectively reduces COD of pulp and paper effluent (Singhal et al. 2003).

Aquatic weeds e.g. *Typha latifolia, Eichhornia crassipes, Salvinia molesta* and *Pistia stratiotes* also have been found to be efficient for treatment of effluents under laboratory conditions (Table 2.9) (Sukumaran and Dipu 2013). *Eichhornia crassipes* and *Typha latifolia* were found as best options for treatment of the industrial effluents. *Eichhornia crassipes* prominently removed lead whereas *Typha latifolia* was found to remove heavy metals like copper and cadmium from industrial effluents (Sukumaran and Dipu 2013). Another comparative study has been done on three tropical native plants named as *Scirpus grossus, Azola pinnata* and *Salvinia molesta* on the properties of decolorization and COD removal from pulp and paper mill effluent (Ahmad et al. 2017). The authors found that all plants removed 100% COD but showed variable colour removal property. Among all, *Scirpus grossus* was

Table 2.9 List of plants involved in the treatment of pulp and paper industry wastewater

Plant name	Botanical name	Nature of life form	Bioremediation potential
Water velvet	*Azola pinnata*	Aquatic floating plant	Removal of colour and COD
Water hyacinth	*Eichhornia crassipess*	Aquatic floating plant	Biosorption of Pb, Cu, Cd, Hg from contaminated water
Sunflower	*Helianthus annuus*	Rooted annual plant	Removal of Pb
Water pennywort	*Hydrocotyleum bellatta*	Free floating aquatic plant	Removal of nitrogen and phosphorous
Common duckweed	*Lemna minor*	Free floating aquatic plant	Removal of nitrogen, phosphorous and orthophosphate and COD
Water cress	*Nosturtium officinale*	Submerged rooted aquatic plant	Bioaccumulation of Cu, Zn and Ni
Common reed	*Phragmites australis*	Rooted aquatic grass	Removal of heavy metals e.g. Cu, Cd, Zn, Pb, As, Al, Ni, Cr and Mn
Water lettuce	*Pistia stratiotes*	Free floating aquatic plant	Removal of COD, BOD, colour, sulphates, nitrates, phosphates, suspended solids
Water Fern	*Salvinia molesta*	Floating aquatic plant	Removal of Cd, Pb, ammonium and nitrogen
Hard stem bulrush	*Scirpus grossus*	Rooted aquatic plant	Removal of nitrogen
Water caltrop	*Trapa natans*	Aquatic floating plant	Removal of Pb, Cu, Ni, Zn, Cd, Fe, BOD and COD
Cattail	*Typha latifolia*	Rooted herbaceous plant	Removal of COD, BOD and nitrogen
Channel grass	*Vallisneria spiralis*	Aquatic plant	Removal of BOD, COD, colour, lignin. Na and K

found to be a best native aquatic plant for both COD and colour removal (Ahmad et al. 2017). Both water hyacinth (*Eichhornia crassipes*) and water caltrop (*Trapa natans*) have been found in biosorption of Pb and Zn from paper mill effluents (Verma et al. 2005; Kumar and Chopra 2016).

2.5.5 Enzymes

Various enzymes resulting from numerous microbes are involved in treatment of paper and pulp mill wastewater (Table 2.10).

Table 2.10 List of microbial enzymes and their role in treatment of wastewater resulting from paper and pulp industry

Enzyme	Use	References
Alkaline cellulose	Elimination of ink from reclaimed paper	Nomura and Shoji (1988)
Cellulase	Elimination of ink from reclaimed paper	Fukunaga and Kita (1990)
Cellulases (obtained from white-rot fungus *Trametes suaveolens*)	Improved strength properties and reduced beating time	Yerkes (1968) and Seo et al. (2013)
Endoglucanases	Increased tear index apparent density and tear index tensile index properties of handsheets	Kibblewhite and Wong (1999)
Endo-β-xylanase	Enhance the delignification of kraft pulp	Bajpai (1999)
Hemicellulase	Reduction in beating time by 17–25%	Bhardwaj et al. (1996)
Laccases	Facilitate bleaching of kraft pulp in conjunction with organic mediators	Luisa et al. (1996)
Lignin peroxidises	Enhance the delignification of kraft pulp	Luisa et al. (1996)
Lipase	Deinking wastepaper with the incorporation of lipase, removal of ink from recycled paper, reduce pitch and lignin-degrading enzymes remove lignin to soften paper	Sharyo and Sakaguchi (1990) and Guy Vare et al. (1990)
Manganese peroxidise	Decrease in refining energy was found to develop pulp freeness by 25% and delignification of kraft pulps by white rot fungi	Sigoillot et al. (2004) and Reid and Paice (1998)
Mannanases	Pre-bleaching of kraft pulp, reduce bleach required for decolorizing; celluloses smooth fibres, enhance water drainage and promote ink removal	Bajpai (1999)
Novoshape (pectin methylesterase)	Catalyses the hydrolysis of methyl ester groups and has high specificity for pectin substrates	Suutarinen et al. (2002) and Fabienne (2001)
Pectinases	Debarking, retting of flax fibres	Bajpai (1999)
Pectinex smash	Enhance degradation of pectin	Suutarinen et al. (2002) and Micheli (2001)
Xylanases	Pre-bleaching of kraft pulp, reduce bleach required for decolorizing; celluloses smooth fibres, enhance water drainage, promote ink removal and increased tear index apparent density	Bajpai (1999); Kibblewhite and Wong (1999)

2.6 Mechanism of Biodegradation of Major Pollutant of Pulp and Paper Industry

Industrial zones involved in pulp and paper manufacturing and precision machining are contaminated to a large extent by lignin and halogenated hydrocarbons such as dichlororethylene (DCE) and trichloroethylene (TCE), polychlorinated biphenyls (PCBs) and hydroxy-PCBs, polybrominated diphenyl ethers (PBDEs). These chemicals are lipophilic and their release into the environment results in bioaccumulation in adipose tissue and persistence due to their chemical stability and resistance to metabolic breakdown. The more widely used PCBs and benzene hexachloride (lindane) have been identified in almost every component of the global ecosystem including fish, wildlife and humans. Lindane is a persistent organic pollutant. It is relatively long-lived in the environment, transported long distances and can bioaccumulate in food chains. *Lindane* is used as an insecticide on fruit and vegetable crops. The nervous system is mostly effected form the large amounts of lindane resulting into symptoms like headache and dizziness to seizures, convulsions etc. These polychlorinated hydrocarbons are decomposed in the soil, sediment and water by bacteria, fungi and algae (Tables 2.6, 2.7, and 2.8), also known as biodegradation which results into comparatively less harmful by-products. Biodegradation utilizes microbial metabolic activities for transformation or mineralization of organic contaminants into less toxic and harmful substances those are recycled back into biogeochemical cycles. Bioremediation is an economical and non-destructive method which employs natural biodegradation of containments by optimizing limiting conditions (Alexander 1999).

2.6.1 Biodegradation of Lignin

Lignin is an integral cell wall constituent, which provides plant strength and resistance to microbial degradation. The macromolecular properties and structural characteristics of lignin make biodegradation studies difficult. Lignin is chemically modified by demethylation of its phenolic and nonphenolic units (Eriksson et al. 1990) and limited aromatic hydroxylation and ring cleavage (Kirk and Farrell 1987). The ideal isolation method of lignin would allow the collection of chemically unmodified lignin with quantitative recovery and free of non-lignin contaminants. None of the existing methods fulfil all these requirements. Now a day biodegradation is preferred method of recovery of various natural substrates from lignin complex. A wide range of bacteria and fungi have been isolated from different compost environments for study of lignin degradation (Tables 2.6 and 2.7). Actinomycetes are bacteria which form multicellular filaments, thus they resemble fungi. Actinomycetes are able to degrade some cellulose and solubilize lignin, and they tolerate higher temperatures and pH than fungi. Thus, actinomycetes are important agents of lignocellulose degradation during peak heating, although their ability to degrade cellulose and lignin is not as high as that of fungi (Godden et al. 1992). In fungi the most effective lignin degraders are Basidiomycetes. White-rot fungi belonging to the subdivision Basidiomycetes attack either hardwood or softwood, while Ascomycetes probably degrade only hardwood (Kirk and Farrell 1987). Lignin degradation by white-rot fungi is faster than that of any other organisms and they are responsible for most of the lignin decomposition in nature. However, the growth substrate is not only lignin, but also hemicelluloses and cellulose (Buswell and Odier 1987). The growth of fungi decreases in nitrogen or carbon depleted conditions and ligninolytic activity appears as a form of secondary metabolism (Kirk and Farrell 1987). Fungi degrade plant cell wall lignin using extracellular flavooxidases and generate hydrogen peroxide during redox cycling of non-phenolic aromatic aldehydes. Peroxidase one-electron oxidation of lignin units results in an unstable cation radical that experiences different reactions including breakdown of $C\alpha$-C_β and C_4- ether linkage releasing the corresponding aromatic aldehydes that can be intracellularly mineralized (Fig. 2.7).

2.6.2 Biodegradation of Polychlorinated Hydrocarbons

The degradation of aromatic organochlorines occurs via four well characterized mechanisms as follows:

(a) **Oxygenolytic dechlorination**

This occurs via deoxygenative attack on the aromatic nucleus and it is dependent upon the position of chlorine substituents. The oxygenolytic cleavage of the chlorine atom occurs when both the atoms of molecular oxygen are incorporated into the aromatic nucleus. PCBs are principally hydroxylated on the unsubstituted carbons at positions 2 and 3 and 3 and 4. In either case, the mechanism seems to require the presence of adjacent unchlorinated atoms.

(b) **Hydrolytic dechlorination**

In this reaction the incorporation of a hydroxyl group leads to the concomitant release of chlorine substituent. Unlike the above the hydroxyl group is derived from water and the reaction is catalysed by a dehalogenase. The requirement for the water rather than molecular oxygen also permits this chlorination to occur in anaerobic denitrifying conditions.

(c) **Reductive dechlorination**

Reductive dechlorination results in the removal of the chloride substituent with the concurrent addition of electrons to the molecule. Although it has been reported to occur in both aerobic and anaerobic environments but it has been shown to occur primarily in the latter.

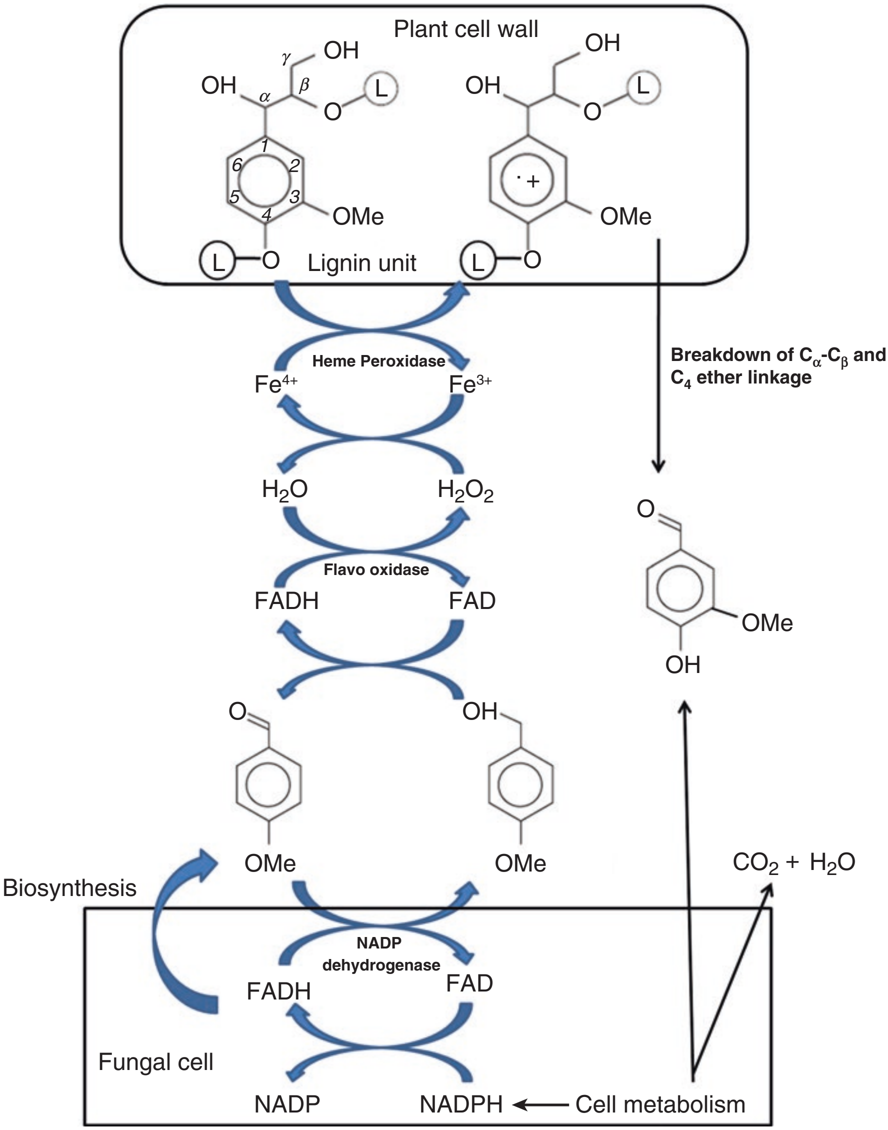

Fig. 2.7 Degradation of lignin by fungi

(d) **Chloride release after cleavage of the aromatic ring**

Both aerobic and anaerobic microbial processes of PCBs degradation involved complete ring opening and final cleavage.

The role of anaerobes play in the degradation of PCBs was first shown by Brown et al. (1987). The first finding was that highly chlorinated PCB compounds (with one to ten chlorine atoms) were present in much higher proportion than less chlori-

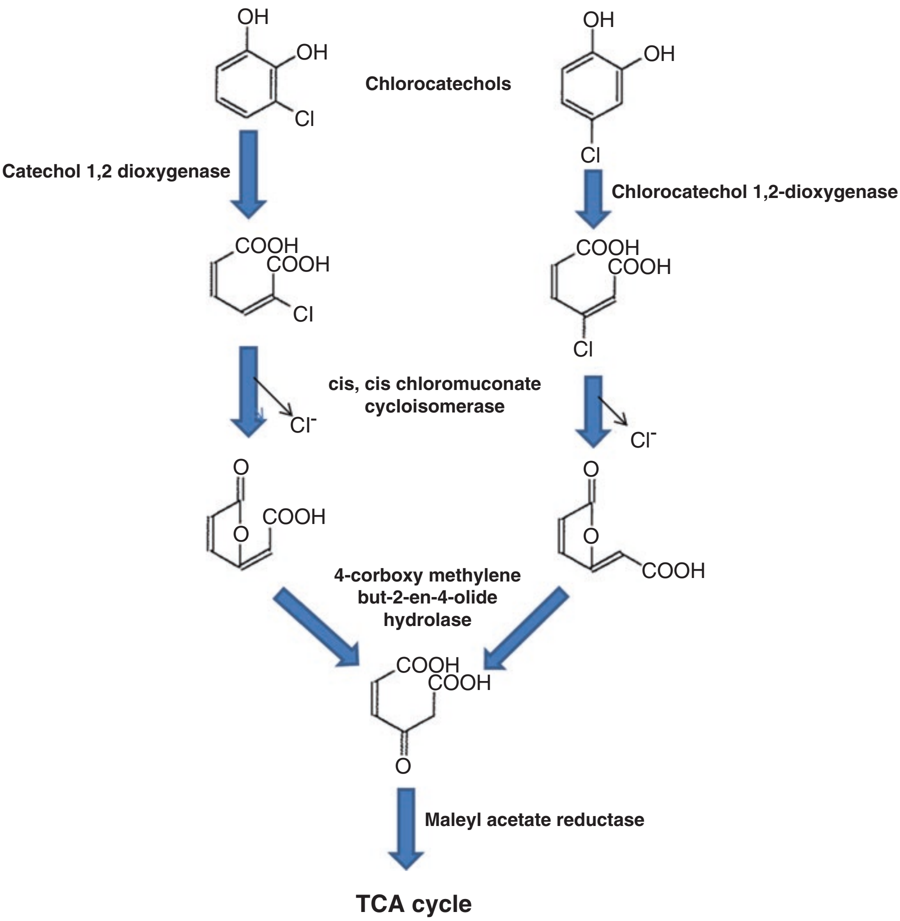

Fig. 2.8 Mineralization of chlorocatechols

nated compounds. Despite this it is clear that the transformations observed specifically involved the removal of ortho, meta and para chlorines. The different position (ortho, meta and para) of chlorine compounds have made advances in the study of anaerobic dechlorination of PCBs. According to Tiedje et al. (1993) the frequency of dechlorination was as follows: meta > para > ortho (Fig. 2.8).

2.7 Pulp and Paper Waste Water Recycling

Increased awareness for environment protection and stringent legislation forced pulp and paper industry to reduce their water consumption and rely on used water recycling. Membrane filtration is one of the methods to clean wastewater to improve its quality. Three types of membrane filters are known to be used here: microfiltration, ultra-filtration and nano-filtration. Recently, a new type of membrane is also being used, known as ceramic membrane with an advantage on carbon filter which is easy cleaning through backflushing (Laitinen et al. 2002). Wastewater pH is also a limiting factor because acidic pH is more suitable for better permeability compared to neutral pH. The reason is that electrostatic repulsions are present in neutral pH but absent in acidic pH. Another method which can be used for water recycling is membrane bioreactor (MBR). In this technique, wastewater from bleaching process is used for treatment and resulting water may be reused as process water (Tenno and Paulapuro 1999).

Water source diagram (WSD) based on the synthesis of mass exchange network via a heuristical algorithmic procedure is an alternate way to minimize the water consumption and wastewater generation (Gomes et al. 2007). This procedure has an ability to minimize about 46% of water consumption and about 76.8% of reusable water generation with an objective to maximize reuse with low fresh water consumption.

2.8 Future Prospects for Paper and Pulp Wastewater Treatment and Recycling

In the era of digitization, the paper and forest product industry is evolving and changing. The education, industrialization and changing lifestyle still could not reduce the demand of papers and its usage for printing, writing and packaging. Paper is mostly used in the printing and writing sector followed by packaging industry. The demand for tissue paper and pulp in manufacturing hygiene products is also growing throughout the world. The graphic paper has less demand these days but the forest product industry definitely seems to be growing.

Although, the demand for newsprint and coated paper is declined regardless of that demand for specialty papers is rising in the market. The industrial packaging including online shopping, delivery, product safety and fabricating procedures also contribute to increasing demand for paper worldwide. The demand for hardwood and softwood fibres is slowly increasing as they are required as raw materials for stronger and lighter weight packaging stuffs.

The dependency of this industry on the raw materials including wood, agro and reused paper at economical prices may force the industry to accelerate and flourish. However, it also requires innovative strategies for recycling and waste treatment for uninterrupted manufacturing and survival of the industry.

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Chapter 3
Treatment and Recycling of Wastewater from Tannery

Tuhina Verma, Soni Tiwari, Manikant Tripathi, and Pramod W. Ramteke

Abstract Tanneries are one of the most important industries of the world, but discharge toxic hexavalent chromium through their waste water into the environment beyond the permissible limit. Such waste water may cause significant damage to the agricultural lands and receiving water bodies due to its higher toxicity and high COD and BOD values and thus is a matter of global concern. To reduce the impact of discharged waste water on all living beings and the environment, several conventional physico-chemical treatment methods are developed to remediate metal polluted sites. However, these methods are costly due to use of non-regenerable materials, high operating cost and generate toxic sludge. Microbial bioremediation is a relatively cheaper and eco-friendly technique for the removal of heavy metals and chloroorganics from tannery waste water and thus has wider implications. Also, there is a chance to recover the economically valuable metal for reuse. Among various microbes, bacteria have proven to be very effective in removing Cr (VI) and pentachlorophenol from tannery waste water. The treated waste water can also be used for various non-potable purposes including agriculture and also during leather tanning. It will ultimately minimize water scarcity problem and will increase the productivity.

Keywords Tannery effluent · Waste water treatment · Chromium · Pentachlorophenol · Bioremediation · Recycling

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R. L. Singh, R. P. Singh (eds.), *Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future*, Applied Environmental Science and Engineering for a Sustainable Future,
https://doi.org/10.1007/978-981-13-1468-1_3

3.1 Overview of Leather Industry

Tanning industry is the third largest contributor in the global industrial sector. In India, tanneries have established an important position as they contribute significantly towards exporting good quality leather products, employment generation, fulfilling the public demand and have an important role in Indian economy. There are more than 3000 tanneries in India, and majorities (90%) of them are engaged in chrome tanning process. Approximately 83 million hides and 140 million skin pieces are processed annually by the tanneries in India and about 50 l of effluent is generated per kg of skin/hide processed. The annual use of chrome salts during tanning in India has been estimated to be ~3000 ton and more than 40% chromium used for tanning remains in the spent tanning liquor, which is finally discharged into the environment.

Despite of several advantages of tanneries, unfortunately, they are one of the most polluting industries as they discharge large quantity of industrial waste water everyday into the environment that contains huge amount of chrome salts, organic and inorganic pollutants, chlorides, sulfides, various salts, dissolved and suspended solids, nitrogenous compounds, pentachlorophenol, tannins, heavy metals, etc. in excess of the maximum permissible limit due to inappropriate treatment and disposal practices. Solid and gaseous wastes are also emanating during the leather manufacturing (Masood and Malik 2011). Thus, the discharged tannery waste particularly uncontrolled release of partially treated tannery effluents to natural water bodies and agricultural lands is ultimately causing soil and water pollution and is a serious threat to human health. Among the various pollutants, chromium (Cr) and pentachlorophenol (PCP) are the major hazardous pollutants discharged through tannery effluent and is of high concern for India and other countries in terms of their environmental impact and health effects. Both Cr and PCP are highly toxic and carcinogenic to all forms of life, hence, listed as priority pollutants by the United States Environmental Protection Agency (USEPA 1999, 2000). Further, these pollutants have permanently affected the surface water and ground water sources in their vicinity due to percolation and subsequent leaching from dumping sites, which has ultimately made the water unfit for drinking and irrigation as well as the land/soil is becoming infertile and is affecting the consumers of different trophic levels (Polti et al. 2010).

Tanneries use basic chromium sulfate [Cr (III)] as a tanning agent in the "chrome liquor" for converting animal skins/hides into leather. It also makes the leather soft, light weight and resistant to heat/water but led to the continuous release of chromium particularly hexavalent chromium [Cr (VI)] through their effluent in to the environment. Chromium exist in several oxidation states, ranging from −2 to +6, but only the trivalent [Cr (III)] and hexavalent species are the most biologically and environmentally stable forms, although they significantly differ in biological, geochemical and toxicological characteristics. Toxic effects of chromium are valency dependent. Chromate is highly soluble than Cr (III) hence Cr (VI) is more mobile and poses greatest threats to humans, animals and plants. Despite the thermodynamic stability of Cr (III), the presence of certain naturally occurring minerals, especially MnO_2 enhance oxidation of Cr (III) to Cr (VI) in the soil environment. The effluent released from leather industry after chrome tanning contains 700–1000 mg Cr (VI) L^{-1} (Aravindhan et al. 2004) and hence the environment is under increasing pressure. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for Cr (VI) and total Cr are 0.05 and 2.0 mg L^{-1}, respectively (Masood and Malik 2011). According to safe drinking water act, maximum contaminant level (MCL) is 0.1 mg L^{-1} for total chromium. Therefore, the treatment plant of tanneries should properly treat their effluent before discharge so that the Cr (VI) levels are reduced in order to meet the discharge limit.

In leather tanning, PCP is used as a biocide for curing and preservation of leather. It is a polychlorinated aromatic compound and recalcitrant to biological degradation. PCP is highly toxic to all living beings and is listed as priority pollutants by the United States Environmental Protection Agency (USEPA), thus its removal has become a matter of prime concern. As per Indian Standard, the recommended limit for chlorophenols in inland surface waters is 0.002 mg L^{-1}, whereas, the similar limit in leachates is 1.0 mg L^{-1} (EPA 1999). The European Council Directive has set a limit of 0.5 μg L^{-1} to regulate the concentration of phenolic compounds in drinking water. Chlorophenolic organics are bioaccumulated in food chains of biological systems, and thus can cause profound problems to the human health. They also contribute to off-flavour problems in drinking water. Chlorophenolic contaminants can damage sensitive cells by permeating cytoplasmic membranes and coagulating the cytoplasm. These compounds are quite inhibitory to living beings, because of their action on membrane function and their ability to uncouple oxidative phosphorylation (Bevenue and Beckman 1967) and sometimes may even be detrimental. Therefore, tannery waste water contaminated with chlorophenolics should be treated carefully before being discharged into receiving water bodies and nearby lands as otherwise it will cause soil and water pollution.

To meet the challenge of pollution resulting from the discharged tannery effluent, an intensive attempt has been undertaken which involves better surveillance on the use of various chemicals during leather manufacturing and improvements in in-plant and end-of-pipe treatment technologies. Regions where treated effluents from the treatment plants of tanneries were disposed of into the cultivable lands have resulted in significant increase in the pollutants particularly the content of chromate and PCP in the soil (Verma and Baiswar 2013). Further, the sludge produced during treatment of tannery effluent in the treatment plants is not safe for land disposal due to the presence of high levels of chromate and chlorophenols and the associated toxicity of their leachates, and thus is of great concern regarding their accumulation in crops (Armienta et al. 2001). Thus, the treatment of tannery effluent before being discharged into the environment has received considerable attention in the past several decades. Towards this direction, tanneries are treating their waste water by the conventional treatment techniques before its release into the environment. It involves chemical reduction followed by precipitation, ion exchange, absorption on coal, alum, activated carbon, flyash and kaolinite, reverse osmosis, electro-diyalysis, membrane filtration, etc. (Cooman et al. 2003). Applications of such traditional treatment techniques need enormous cost and continuous input of chemicals and energy, which becomes impracticable and uneconomical and causes further environmental damage. The concentration of toxic pollutants is lowered but still it remains at a level toxic to flora and fauna (Ramteke et al. 2010). Also, large amount of toxic sludge is produced which requires further remediation before final disposal. Thus, the discharged effluent requires further remediation which otherwise may further aggravate the situation as it ultimately enters the food chain. Hence, easy, economic and eco-friendly waste water treatment techniques would have to be considered with great emphasis. Several microbes are refractory in nature and are capable to survive and colonize such noxious polluted environments. Microbial bioremediation has emerged as an attractive and promising clean remediation technique for the removal of toxic pollutants from the tannery waste water. It has gained increasing attention due to its in situ operation, selective removal and low cost.

In the present time, water is the earth's most valuable resource for sustaining human life and India have already reached the limits of its available water supplies. Tanning industries consumes large quantities of water ~20 to 25 m^3/tone of raw skin for leather manufacturing. Strategies should be aimed to explore suitable methods to minimize the water requirement of tanneries. For this, attempts should be done to collect the industrially treated waste water and it should be re-treated by advance techniques so that the treated water can now be recycled and reused in the tanneries during various stages of leather manufacturing. This will minimize the water scarcity problem and will support the beneficial reuse of water. Apart from minimizing the adverse environmental impacts and health risks to human beings, effective remediation of tannery effluent before its release into the environment, will also offer a wide range of reuse applications for various non-potable purposes without any known significant health risk.

Keeping the above in view, in this chapter information pertinent to tannery effluents and its potential biological treatment processes and advanced treatment techniques of bioremediation to achieve more efficient removal of pollutants from tannery waste water are discussed. Emphasis is also on the recycling practices of treated tannery effluent which will help to minimize the water scarcity problem.

3.2 Pollutants Produced During Leather Manufacturing

Tanning is a chemical process, during which chemical treatments are performed step-wise to obtain highly durable leather from animal skin and hides. The various major steps involved in leather manufacturing are depicted in Fig. 3.1. Since large amount of chemicals are used, and the biodegradation ability of most of the chemicals is very less, so ultimately the tanning process results in various types of pollution like air, water and soil pollution, depending upon the type of wastes produced. In addition to the production of tannery effluent (liquid waste), solid and gaseous wastes are also formed. Waste generated from tanning generally contains much higher concentration of chromium, chlorides, ammonia, pentachlorophenol, sulfate,

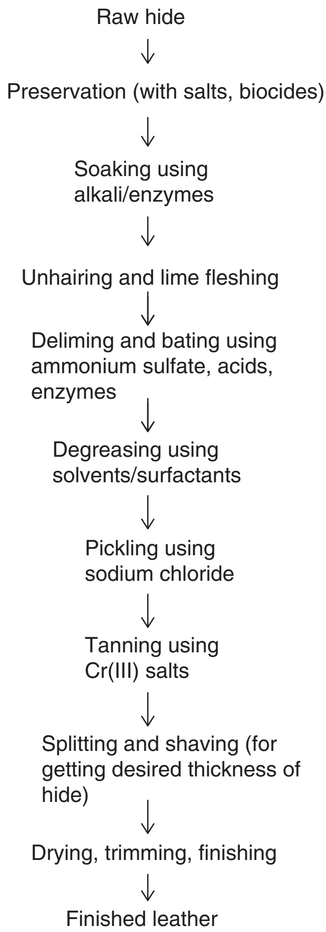

Fig. 3.1 Various steps of leather manufacturing process

phosphate, nitrate, fluoride, oil and grease, total dissolved solids (TDS), suspended solids, heavy metals, etc. (Cooman et al. 2003). The high TDS value in tannery effluent is due to addition of common salt as the major preservative for raw hides. Besides these chemicals, the level of BOD and COD is very high and the DO value is very low suggesting an increase in the organic matter content. Also, mostly the effluent is yellowish-brown in colour which might be hindering the penetration of sun light causing depletion in the rate of oxidation process. It finally contributes to anaerobic oxidation which can be sensed from the putrefying odour of the receiving water bodies (Verma et al. 2008). Further, the slightly alkaline pH of treated effluent could affect biological property of the receiving water body.

Alkaline nature of tannery effluent is due to the presence of carbonate, bicarbonate and hydroxide. Increasing alkalinity suggests an increase in ion concentration, which results in increased conductivity. The higher conductivity alters the chelating properties of water bodies and creates an imbalance of free metal availability for flora and fauna. Further, the higher sulfate level of discharged effluent can stimulate the growth of sulfate reducing bacteria. They produce H_2S which is highly toxic for fishes and other aquatic life, resulting in the increase of eutrophication in the reservoir. Above all, pentachlorophenols are also discharged in significant amount and are not easily utilized by indigenous microorganisms as source of energy and carbon thereby enters the food chain and adds to toxicity. The various types of wastes generated from tannery are discussed below.

3.2.1 Pollution Caused by Liquid Waste

The conventional leather tanning technology is highly polluting as it produces large amount of toxic effluent for disposal. The liquid wastes are produced in sufficient quantities during soaking, liming, dehairing, deliming, bating, tanning (vegetable or chrome) and finishing. In addition to the waste from different processes, washing after different operations also adds to the total volume of the tannery effluent up to an appreciable extent (Bosinc et al. 2000).

3.2.2 Pollution Caused by Solid Waste

Leather industry generates significant amounts of solid waste in the form of untanned and tanned waste from raw hides and skins, semi-processed leather as well as sludge produced during waste water treatment. The production of solid waste in tanneries and its disposal has been recognized as a problem since several years. The solid waste generated in tannery can be classified as (a) non-proteinaceous waste (b) Non collagenous protein waste (c) untanned collagen and (d) tanned collagen waste. Out of 1000 kg of raw hide, nearly 850 kg is generated as solid wastes in leather processing. Only 150 kg of the raw material is converted into leather. A typical tannery generate huge amount of solid waste during various steps of leather tanning process:

- Fleshing and lime fleshing: 56–60%
- Chrome shaving, chrome splits, lime splits and buffing dust: 35–40%
- Skin trimming: 5–7%
- Hair: 2–5%
- Sludge: 30–45%

Over 90% of the organic pollution load in BOD terms emanates from the beam house (pre-tanning); much of this comes from degraded hide/skin and hair matter. During the tanning process at least 300 kg of chemicals (lime, salt, etc.) are added per ton of hides. Excess of non-used salts also gets deposited in the solid waste. If these solid wastes are not properly treated and disposed of, they can cause environmental damage to soil and ground water as well as emissions of odour and poisonous greenhouse gases into the atmosphere. Accumulation of the solid wastes leads to sludge problem and choking of treatment pipes and finally results in decreased efficiency of the treatment plant. Sludge is obtained as a solid waste from equalization and setting of waste waters from different sections of tannery. Treatment of solid waste is also not cost effective, posing economic burden to the tanners. In developing countries, tanneries are facing lot of solid waste disposal problem and many tanneries are closed as they cannot meet the BOD demand and TDS norms.

3.2.3 Pollution Caused by Gaseous Waste

Tanneries discharge noxious gases and smoke into the atmosphere. The main sources of smell in the gaseous discharge of tannery are the compounds containing nitrogen and sulphur. The end products of anaerobic decomposition of protein putrefaction include mainly indole, skatole, mercaptans, aldehydes, etc., all of which are having odours. Some pungent odours released from tanneries are also due to sulphide, fatty acids like butyric acid and caproic acid, solvents, formalin and some of the chemicals used in finishing operations. It also originates from unhygienic practices of skin and hides and delayed disposal of liquid and solid waste. Odours related to tannery waste water are difficult to quantify because they are caused by various compounds and are a nuisance. In the tannery effluent treatment plant the main sources of pungent smell are equalization and sulphide oxidation process, biological aeration, sludge thickening, dewatered sludge storage in the treatment plant and site of sludge disposal. As air pollutants H_2S is released during unhairing and liming process, NH_3 and CO_2 is released during deliming and bating process and acid fumes are released during chrome tanning process. These gases are very poisonous and may result in lethality. Hydrogen sulphide has been reported as frequent killer in tannery accidents, which occur mainly in inadequately ventilated spaces, especially in pits and channels.

3.3 Impact of Pollutants Generated by Tannery

Tannery waste water contains various pollutants and particularly they are responsible for chromium and chloroorganics pollution. In India, nearly 3000 and 7000 mg L^{-1} hexavalent chromium escapes into the environment from the tannery industries through their aqueous effluent, whereas, the recommended permissible discharge limits for Cr (VI) and total Cr are 0.05 and 2.0 mg L^{-1}, respectively, and hence is of great environmental concern (Ahamed and Kashif 2014). However, as per Indian Standard Institution (ISI) limits, the permissible level for phenolic compounds in inland surface waters is 0.002 mg l^{-1}, whereas the similar limit in leachates is 1 mg L^{-1} (EPA 1999). The European Council Directive has set a limit of 0.5 mg L^{-1} to regulate phenol concentration in drinking water.

Chromium contaminated tannery waste is released into the environment due to improper treatment and disposal practices (Verma et al. 2001). Toxic metallic species, once mobilized into the environment, tend to persist, circulate, and eventually accumulate at different trophic levels in members of the food chain. Hexavalent chromium species and dichromate's are extremely water-soluble and mobile in the environment thus pose a serious threat to the environment, and affect plants, animals, and humans (Ackerley et al. 2004). Further, due to high permeability of Cr (VI) through biological membranes it subsequently interacts with intracellular proteins and nucleic acids. Moreover, Cr (VI) is recognized to be highly toxic, carcinogenic, mutagenic and teratogenic in nature and may cause death to animals and human if ingested in large doses (Costa and Klein 2006). Due to its carcinogenic and mutagenic nature, the United States Environment Protection Agency (USEPA) has designated chromium as a "Priority pollutant" or Class A" pollutant (EPA 2000). The resulting types of DNA damage that are produced can be grouped into two categories: (1) oxidative DNA damage and (2) Cr (III)-DNA interactions. Oxidative damage is considered to be an important mechanism in the genotoxicity of Cr (VI). Hence, the need arises to remediate chromium before being discharged. Routes of human exposure to chromium compounds include ingestion of food and water, inhalation of airborne particulates and contact with numerous manufactured items containing chromium compounds.

Chromate has a structural similarity to sulfate $(SO_4)^{2-}$ and thus chromate crosses the cell membrane via the sulfate transport pathway thus has severe impact on human health (Fig. 3.2). Under normal physiological conditions, after crossing the membrane Cr (VI) reacts spontaneously with intracellular reductants (e.g. ascorbate and glutathione) to generate the short-lived intermediates Cr (V) and/or Cr (IV),

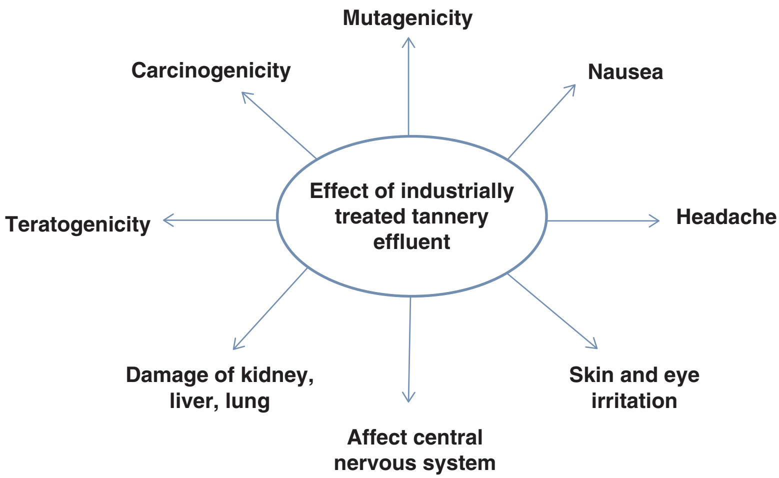

Fig. 3.2 Effect of discharged tannery effluent on human health

free radicals and the end-product Cr (III). Pentavalent chromium undergoes a one-electron redox cycle to regenerate. Therefore, Cr (IV) binds to cellular materials and deters their normal physiological functions. The genotoxic effects of the chromate ion however cannot be solely explained by the action of ROS. Intracellular cationic Cr (III) complexes also interact electrostatically with negatively charged phosphate groups of DNA, which could affect replication, transcription and cause mutagenesis. Moreover, Cr (III) interferes with DNA replication to produce an increased rate of transcription errors in the cell's DNA. Additionally, Cr (III) may alter the structure and activity of enzymes by reacting with their carboxyl and thiol groups. The human health effects of chromium (VI) are lung cancer, respiratory irritation, dermatosis, dermatitis, nausea, vertigo, ulceration of nasal septum, kidney and liver damage, etc. This metal also irritates airways, causes nasal and skin ulcerations and lesions, causes perforation of the nasal septum, asthma, dermatitis and other allergic reactions (Upreti et al. 2004). Ingesting Cr (VI) causes stomach and intestinal damage that may lead to cancer. Chronic liver and kidney damage due to long term exposure of Cr (VI) has also been reported. In lab animals, Cr (VI) damages sperm and male reproductive systems, and in some cases, has damaged the developing foetus (Costa and Klein 2006).

Pentachlorophenol is an important biocide from a toxicological perspective. PCP is a polychlorinated aromatic compound and is recalcitrant to bio-degradation. It is highly toxic to living beings as it causes inhibition of oxidative phosphorylation, inactivation of respiratory enzymes and damage to mitochondrial structure (Bevenue and Beckman 1967). Reductive dechlorination is the primary PCP biodegradation mechanism resulting in formation of partially or fully dechlorinated product which is then more susceptible to ring cleavage. Severe exposure of PCP may result in fatal illness though uncoupling of oxidative phosphorylation. PCP is one of the priority pollutants defined by the US Environmental Protection Agency. The exposure to chromium and PCP increases the risk of dermatitis, ulcer, lung cancer, immunodeficiency and neurological disorders. Due to PCP toxicity, pulmonary oedema, intravascular haemolysis, pancreatitis, jaundice and acute renal failure have been reported (Sharma et al. 2009). However, chronic occupational exposure to PCP causes conjunctivitis and irritation of the upper respiratory tract. Long term exposure has also been reported to result in chronic fatigue, neuralgic pains in legs, impaired fertility and hypothyroidism (Thakur et al. 2001).

Large amount of partially treated tannery waste water generated by tanneries is discharged in to the natural water bodies either directly or indirectly. Even the small tanneries discharge their effluent directly into rivers and streams through open drains without any treatment. The algae, fishes and other aquatic animals present in the water bodies gets exposed to the dissolved chromium and other pollutants of tanneries. This leads to the accumulation of toxic chromium, chloroorganics, etc. in the muscles and tissues of fishes and other aquatic animals that has severe hazardous impact. Many human beings and animals depend for their food on aquatic animals. Consumption of such contaminated foods results in biomagnification of toxic pollutants through food chain and food web and in present scenario it has created alarming situation. Further, the discharged tannery effluent is also rich in sulphides, organic and inorganic constituents. Tannins present in the effluent reacts with iron and impart dark brown colour to the effluent. The sulphide reacts with iron metals causing black precipitate. These contaminants make the water unfit for the growth of algae, fishes and other aquatic life. The sulphide toxicity to fish's increases as the pH value is lowered. The organic and inorganic wastes present in the tannery effluent settles at the bottom of the stream and cover it thereby destroying the bottom fauna necessary for fish as food and also reduces the spawning ground of fisheries. Moreover, bacterial resistance to chromate is mostly plasmid borne and the incidence of plasmids in bacteria is reported to be greater in polluted sites as compared to the cleaner sites (Verma et al. 2009). In the natural environment, such strains will grow rapidly by the horizontal gene transfer and can establish new genetic traits in diverse environments. Tannery strains carrying such plasmid seem to survive well in waste waters. Further, many of the tannery strains have been reported to be pathogenic and the genetic determinants may be present on the same plasmid (Filali et al. 2000; Verma et al. 2002). These plasmids could provide a reservoir of genes and will lead to a very rapid increase in their numbers. These strains were also found to be resistant to multiple antibiotics. Verma et al. (2004) reported that in majority of tannery strains both metal/antibiotic resistance and virulence were plasmid mediated thereby causing serious constraints to therapeutical measures. Thus effort should be made to develop adequate effluent treatment technology otherwise it will lead to a serious public health hazard.

India is agriculture based country and the plant productivity depends on the type of water used for irrigation. Tanneries dispose their large amount of waste water into cultivable lands. Although this waste water contains large amount of valuable plant nutrients but the concentration of toxic pollutants is very high. Thus, decreased plant growth and yield was observed in the plants irrigated with discharged tannery water. This may be due to the increased accumulation of tannery pollutants in the soil, which increases the osmotic pressure of the rhizosphere medium and results in reduced water availability to the plant. The phytotoxic effect of tannery pollutants was observed on crops such as cabbage, water chestnut, tomatoes, pulses, chillies, maize, rice, etc. The effect of toxicity was apparent as symptoms of chlorosis, yellowing, immature fall of leaves, poor growth, retarded flower, fruit and green yields. Repeated exposures of plants affect its physiological processes such as photosynthesis, water relations and mineral nutrition. Metabolic alterations by metal exposure have also been described in plants either by a direct effect on enzymes or other metabolites or by its ability to generate reactive oxygen species which may cause oxidative stress.

3.4 Treatment of Tannery Effluent

The tannery waste water is highly polluted. Thus, its treatment is a great challenge and very important to control the pollution in leather manufacturing countries. The effluent has elevated concentration of organic and inorganic matter as pollutants

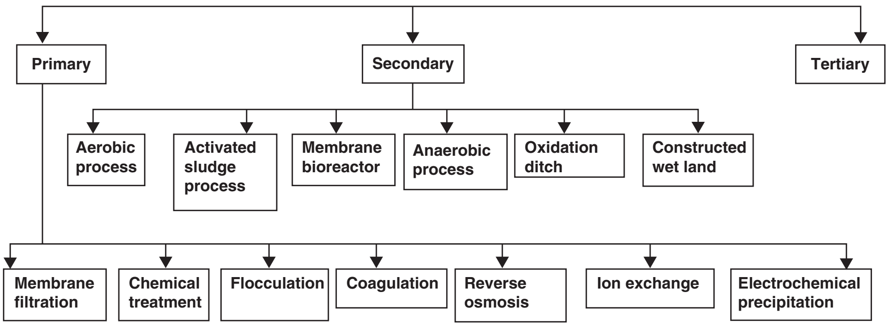

Fig. 3.3 Different techniques for treatment of tannery effluent

which are of conservative and non conservative type (Akan 2007). Treatment of tannery waste water is a multi-stage process by which the tannery effluent can be purified before it is released into natural water bodies, agricultural lands, or it is reused. The overall aim is to decrease the level of pollutants present in the tannery effluent. The pollutants present are not disappeared, rather gets converted into the form which is environmentally more acceptable or easy to dispose in the form of sludge.

The treatment of tannery effluent is required to meet the discharge standards for safe disposal of discharged tannery effluent in the environment. The method of tannery effluent treatment process depends on various factors like competence, expenditure and ecological potential (Costa and Olivi 2009). Also, the waste water characteristics should be considered when choosing the best process (Costa and Olivi 2009). Many authors have previously reviewed the various techniques for treatment of tannery effluent (Aravindhan et al. 2004; Verma et al. 2009). Thus, the tannery effluent is treated in many different ways. The individual small tanneries mostly perform the pre-treatment process and send the effluent to an effluent treatment plant for further treatment. Here the tannery effluent is treated through a series of phases, which are the primary, secondary and tertiary treatments (Fig. 3.3) (Dargo and Ayalew 2014). Thereafter, the solid wastes obtained is processed and allowed to dispose and the treated waste water after quality evaluation is recycled by the industries or may be reused for various non-potable purposes. Each of the treatment processes is described below.

3.4.1 Pre-treatment of Effluent

In several developing countries like India, Pakistan, Bangladesh, etc. many tanneries do not have adequate land as well as financial and technical capacity to set up their individual tannery effluent treatment plants. The effluent outlet channels of such tanneries are connected to the common effluent treatment plants (CETPs). The CETP collectively treat their tannery effluent before releasing it into the environment. But it is essential that the individual tanneries must have pre-treatment units and the tannery effluent is initially treated in this unit and then discharged to the CETP plant for further treatment. The effluent of different processing stages formed during leather manufacturing is mixed and collected in balancing tank, agitated and allowed to settle. It removes large particles, sand/grit and grease up to quite extent. The supernatant is further treated to reduce the concentration of chromium and sulphides before the effluent are discharged into the CETP. The settled solids are then pumped to the sludge settling tanks for re-settling. From here the sludge is pumped to the filter press for further dewatering. The liquid waste is discharged to the sewers while the sludge cake is used in land filling or as fertilizers.

3.4.2 Primary Treatment (Physico-chemical)

During primary treatment the tannery effluent is treated through various physic-chemical methods which do not involve any biological material. Primary treatment is mainly employed to remove the coarse materials, suspended solids, chromium, oil and grease, and sulphides in some cases. However, an appreciable amount of COD, BOD, total suspended solids and total solids are also removed in the primary treatment. In nut shell, the organic and inorganic pollutants are removed by sedimentation and also the floating material (scum) formed by skimming is also removed. Initially the coarse material present in the industrial waste water should be removed as otherwise it will clog/block the pumps and pipes. Thereafter, the effluent from different tannery streams are mixed together to produce a homogenized raw material as then it could be treated in a consistent way. The basic steps followed are screening (self-cleaning of large solids), pumping/lifting of liquid waste to the effluent treatment plant, fine screening to remove fine suspended solids, homogenization to keep all particulate matters in suspension so that it will avoid settling of solids, sulphide elimination mainly through catalytic oxidation, chemical treatment (coagulation, flocculation, etc.), settling and sludge dewatering. Depending upon the nature of the effluent following are the various physico-chemical techniques that are applied for the primary treatment of the tannery effluent.

3.4.2.1 Mechanical Treatment

Usually the first treatment of the raw effluent is the mechanical treatment that includes screening to remove coarse material. Up to 30–40% of gross suspended solids in the raw waste stream can be removed by properly designed screens. Mechanical treatment may also include skimming of fats, grease, oils and gravity settling.

3.4.2.2 Membrane Filtration

Membrane filtration technique has received a significant attention for the waste water treatment (Khalfaouy et al. 2017). It considers the application of hydraulic pressure to bring about the desired separation through the semi permeable membrane. Various types of membranes such as inorganic, polymeric, and liquid membranes can be employed for Cr (VI) removal. A non-interpenetrating modified ultrafiltration carbon membrane was prepared by gas phase nitration using nitrogen oxides (NOx) and hydrazine hydrate. This membrane was used for the separation of Cr (VI) from the aqueous solutions. Studies were done for the removal of Cr (VI) with different nano filtration composite polyamide membranes for varying concentration and pH of the membrane feed solution. Two membranes were used for this investigation: one, a high rejection membrane (NF I) and the other, a low rejection membrane (NF II). The percent rejection of chromium was found to increase with the increase of the pH of feed solution. It has been observed that the effect of feed concentration on the percent rejection was quite low, but the nature of effect varies with the pH of the solution with a transition happening at above pH 7.0. The major disadvantage of this technique apart from being economically expensive are incomplete metal removal, high reagent and energy requirements, inefficient removal of low concentration Cr (VI) in waste water, and generation of large amount of toxic sludge or other waste products that require proper disposal.

3.4.2.3 Coagulation and Flocculation

Coagulation-flocculation process is employed for the removal of suspended solid materials from the effluent of tannery and other industries (Birjandi et al. 2016). The process operate in steps which break down the force which stabilizes the charged particles present in the tannery effluent allowing inter-particle collision to occur, hence, generating flocs (Haydar and Aziz 2009). Suspended solids possess negative charge in water. Since their surface charge is the same, they tend to stabilize and repel one another when they interact with each other. The purpose of coagulation/flocculation process is to destabilize the charged particles of suspended solids. Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers.

Coagulants are mixed in tannery effluent to neutralize the negative charge of the suspended particles. Upon neutralization, the suspended particles fix together to form slightly larger particles. For tannery effluent coagulation, rapid mixing of the coagulant is needed to attain effective collision; this process is followed by a flocculation process where mild addition increases the particle size from sub-microfloc to visible suspended solids. Particles are thus bound together to produce larger macroflocs. To prevent destabilizing of macroflocs an attention is given to the mixing velocity and energy (Ukiwe et al. 2014). The main disadvantage is the production of large amount of sludge containing toxic compounds during the process.

3.4.2.4 Chemical Treatment

Tannery effluent is treated with several chemicals to remove the toxic compounds that are unsafe, so that it can be recycled or released into the natural ecosystem. Several chemicals are used in different phase of the treatment process to separate out solids and remove hazardous substances. Chemical compounds such as lime, alum, ozone, peroxide, etc. are used to treat the tannery effluent. The chemical treatment method involves neutralizing the acid content of the effluent. Acidic effluent typically has a pH value lower than seven and is converted to basic nature through the chemical processes mostly by addition of lime in the acidic tanks in order to neutralize the tannery effluent.

3.4.2.5 Chemical Oxidation Method

Chemical oxidation method is one of the method which use chemical oxidants (H_2O_2, O_3, ClO_2, $KMnO_4$, K_2FeO_4, etc.) for the effluent treatment. In general, chemical oxidation allows removal of the prime organic pollutants upto large extent but complete removal of total organic carbon is more complex (Gao et al. 2010; Sadeddin et al. 2011; Rodrigo et al. 2010; Kilic et al. 2009). Mostly, the sulphides are isolated using H_2O_2 and electro oxidation process (Valeika et al. 2006; Anglada et al. 2009). Oxidation of sulfide by air using activated carbon as catalyst improved its importance for removal of COD, BOD and TOC in addition to the removal of sulfide in waste water (Sekaran et al. 1996). Ozone is a very strong oxidizing agent and it is very effective as a decolourizing agent and as oxidant to treat the organic wastes of tannery effluent.

3.4.2.6 Advanced Oxidation Process

This process has emerged as a promising method for the treatment of tannery effluent containing refractory organic compounds with the potential of developing the maximum reactivity of hydroxyl radicals in driving oxidation. Several technologies like Fenton, photo-Fenton, wet-oxidation, ozonation, photocatalysis, etc. are included in this process and they mainly differ in the source of radicals (Badawy and Ali 2006). Among the various advanced oxidation process, the most widely used method is the solar Fenton process for tannery effluent treatment. However, optimizing the total expenditure of the treatment is a challenge, as this process is much more expensive than the other physico-chemical processes. Hence, a suitable method should not only consider the capacity to decrease the concentration of organic pollutants, but also try to get the required results in a cost effective way (Badawy and Ali 2006).

3.4.2.7 Reverse Osmosis

It is a process in which heavy metals are separated by a semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in waste water. In this process, the concentrated solution is subjected to high pressure (in excess of the osmotic pressure of the solution) as a result of which the solvent is forced out through a semi-permeable membrane to the dilute solution region. The concentrated solution becomes more concentrated and the chromium can be recovered from the concentrated solution. Initially reverse osmosis was used for the treatment of brackish water and desalination, but with the development of cheaper and more efficient membranes, it was also possible to use in waste water treatment. The most commonly used membranes are cellulose acetate and aromatic polyamide. Cellulose acetate is used in waste water treatment. The factors that affect the membrane performance are membrane leakage, membrane fouling and concentration polarization. The disadvantage of reverse osmosis process is that it is expensive, i.e., both capital and operating costs are high (Ukiwe et al. 2014).

3.4.2.8 Evaporation

This process consists of evaporating water from the industrial waste water by supplying heat. The concentrated solution left is subjected for chromium recovery and reuse. Evaporation recovery and reuse are appropriate for almost all processes, with the exception of those, which chemically deteriorate at high temperature. In this method, all non-volatile constituents of the waste water are retained in the concentrated product. In practice, this has been a major disadvantage because of the build-up of impurities on the inside of the evaporator tubes (Badawy and Ali 2006).

3.4.2.9 Electro-Dialysis

This is a membrane separation process in which instead of pressure an electric field is applied across a series of membranes, which are inorganic in nature. The ionic components (heavy metals) are separated through the use of semi-permeable ion selective membranes. Two types of membranes are placed alternatively in the electro-dialysis cell. They are cation exchange membrane and anion exchange membrane. The cathode and anode are placed at the two ends of the cell. Raw waste water is fed continuously into concentrating compartments and treated waste water is withdrawn continuously from the alternate compartments. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane. Further, like reverse osmosis, fouling of membrane and concentration polarization are the common problem which affect the performance of electro dialysis unit. Availability of power at cheaper rates however, decides the economics of these methods. High capital cost, high running cost, initial pH solution and current density are the additional disadvantage of this method.

3.4.2.10 Ion-Exchange

In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. A disadvantage of an ion exchange method for chromium removal is that ion exchange resins are very selective. A resin must be chose that selectively removes the metal contaminant of concern. Further, ion exchange equipment can be expensive and there can be incomplete removal of the chromium from the salt solution. Besides, it cannot handle concentrated metal solution as the matrix gets easily fouled by organic and other solids in the waste water. Moreover, ion exchange is non-selective and is highly sensitive to pH of the solution. Unfortunately, physico-chemical techniques present the disadvantage of producing chemical residues that are harmful to the environment. The above method does not address the final waste disposal problem and is generally expensive due to the high operational cost.

3.4.2.11 Electro-Chemical Precipitation

There is a huge complexity observed in handling of different chemicals and toxic sludge during the chemical coagulation/flocculation processes. Safe disposal of sludge materials in the surroundings has become a main problem mostly in the third world country such as India, Pakistan, Bangladesh or South Asian countries. Considering the challenges, a complete advance chemical treatment method was thought for tannery effluent treatment from the real life experiences. Under this condition, electrochemical treatment has emerged as the new alternative for the treatment of tannery effluent (Min et al. 2004). By this process chromium and other heavy metals could be removed up to parts per million (ppm) levels. This method utilizes an electric potential to maximize the removal of heavy metal from contaminated waste water over the conventional chemical precipitation method. The electrochemical treatment of tannery effluent has been investigated by several researchers (Costa and Olivi 2009; Espinoza-Quinones et al. 2009; Kongjao et al. 2008; Min et al. 2004; Sundarapandiyan et al. 2010) in order to improve the performance of treatment by conventional coagulation and flocculation process. It is also fact, that application of several ionic materials with different electrolytic properties can affect the reactor treatment efficiency (Costa and Olivi 2009). The removal kinetics of organic pollutants as well as nutrients showed very faster removal as compared to biological treatment (Espinoza-Quinones et al. 2009). Although nitrogen, phosphorus, chromium, arsenic and other toxic heavy metals are removed by the electrochemical treatment, still there are certain limitations of this method. The process is cost effective and its efficiency is affected by low pH and presence of other salt ions. Also, the process requires addition of other chemicals, which finally leads to the generation of more sludge. However, electrochemical method can effectively be applied in post-treatment or final finishing stage.

3.4.2.12 Electro-Coagulation (EC)

Electro-coagulation (EC) is the method that combines the function and advantages of conventional coagulation, flocculation, and electrochemistry during tannery effluent treatment. Electrocoagulation is based on dissolution of the electrode material used as an anode (sacrificial anode) which generates metal ions that act as coagulant agents in the tannery effluent (Holt et al. 2005). Electro-coagulation system consists of an anode and a cathode made of metal plates, both sub-merged in the tannery effluent being treated (Emamjomeh and Sivakumar 2009). The electrodes are usually made of aluminum, iron, or stain-less steel, because these metals are inexpensive, readily available, efficient, and less lethal (Zodi et al. 2009). Therefore, they have been approved as the major electrode materials used in EC systems (Kumar et al. 2004). The configurations of EC systems differ. An EC system may include either one or multiple anode-cathode pairs and may be connected in either a monopolar or a bipolar mode (Emamjomeh and Sivakumar 2009). Electrocoagulation is proficient in eliminating suspended solids as well as oil and grease and has been found useful in tannery effluent treatment (Secula et al. 2011).

3.4.2.13 Electro-Oxidation (EO)

Waste water treatment by electro-oxidation goes back to the nineteenth century, when electrochemical decomposition of cyanide was examined (Malakootian et al. 2010). During the last two decades, research works have been focused on the competence in oxidizing various pollutants on different electrodes. The electrochemical oxidation can be achieved by the application of electricity both in direct and/or indirect form. Moreover, its effectiveness strongly depends upon several factors i.e. the treatment condition, tannery effluent composition, the nature of the electrode materials used and mode of operation both in batch or continuous process. The presence of high concentrations of dissolved solids, mainly chlorides, from soak yard makes the tannery effluent particularly amenable for electrochemical treatment (Sundarapandiyan et al. 2010).

In recent years, research attention has been focused on biological methods for the treatment of effluent, some of which are in the process of commercialization (Prasad and Freitas 2003). There are three principle advantages of biological technologies for the removal of pollutants; first, biological processes can be carried out in situ at the contaminated site; Second, bioprocess technologies are usually environmentally benign (no secondary pollution) and third, they are cost effective.

3.4.3 Secondary Biological Treatment

Biological processes are employed as a secondary treatment option after primary treatment of tannery effluent to remove the major portion of organic constituents and nutrients present in the waste water through biological oxidation. It involves the removal of dissolved and colloidal organic matter, sulphides, nitrates, etc. from the waste water obtained after the primary treatment using aerobic and anaerobic biological treatment processes in order to satisfy the standards/limits for its discharge into the environment.

The major type of biological processes includes aerobic, anaerobic and combined biological method which can be suitably adopted in various phases of tannery effluent treatment (Goswami and Mazumder 2014; Abdallh et al. 2016). The aerobic biological processes for tannery effluent treatment include activated sludge process (ASP) Sequential batch reactor (SBR), Wetlands or stabilization pond. Out of various anaerobic processes, Anaerobic filter (AF), Anaerobic digester (AD) and Up flow anaerobic sludge blanket (UASB) are common (Lin and Chuang 1994; Ahmed and Lan 2012).

3.4.3.1 Aerobic Biological Treatment

The principle of the aerobic biodegradation of organic matter is a significant aspect of biological treatment. This is the process where oxygen is needed by degrading microorganisms during degradation at two metabolic sites i.e. at the initial attack of the substrate and at the end of respiratory chain (Pedro and Walter 2006). Oxygenases and peroxidases could be produced by the bacteria and fungi which could help in the oxidation of pollutant and organisms obtain energy in the form of carbon and nutrient during this process. In general, a huge number of bacteria and fungi possess the capability to release non-special oxidase and degrade organic pollutants (Pedro and Walter 2006). There are two types of relationships between the microorganism and organic pollutants; that is the microorganisms use organic pollutant as sole source of carbon and energy, and the microorganisms use a growth substrate as carbon and energy source, while another organic compound in the organic substrate which could not provide carbon and energy resource is also degraded (co-metabolism). The classic aerobic biodegradation reactors include activated sludge reactor and membrane bioreactor (Lin and Chuang 1994; Ahmed and Lan 2012).

3.4.3.1.1 Activated Sludge Reactor

Many researchers have investigated the treatment of tannery effluent using activated sludge process (Murugesan and Elangoan 1994; Jawahar et al. 1998; Eckenfelder 2002; Tare et al. 2003). Activated sludge is a process for treating industrial effluent and sewage using air and a biological floc composed of bacteria and protozoans.

This technique was invented at the beginning of last century by Ardern and Lockett and was considered as a technique for treatment of waste water for larger cities as it required a more sophisticated mode of operation (Wu et al. 2003). Oxygen or air is introduced into a mixture of primary treated or screened effluent combined with organisms to develop a biological floc. The biological floc reduces the organic pollutant of the wastewater, which is largely composed of microorganisms such as saprotrophic bacteria, nitrobacteria and denitrifying bacteria. In general, the process contained two steps, viz; adsorption and biological oxidation. The technique could effectively remove the organic matters, nitrogenous matters, phosphate in the effluent, when there is enough oxygen and hydraulic retention time (Farabegoli et al. 2004). However, the effluent is always short of oxygen, which could cause sludge bulking. The oxygen concentration could be increased by including aeration devices in the system, but research need to be done to find out the optimal value since aeration would cause an increase of the costs of the waste water treatment plants. Also, the excess activated sludge, and the by-product of this process needs to be dealt by the researchers, in a relatively less expensive way (Lin and Chuang 1994).

3.4.3.1.2 Membrane Bioreactor

Membrane bioreactor (MBR) is the combination of a membrane process like microfiltration or ultra filtration with a suspended growth in a bioreactor, and is now widely used for tannery effluent treatment (Chung et al. 2004). The principle of this technique is nearly the same as activated sludge process, except that instead of separation of water and sludge through settlement, the MBR method uses the membrane which is more efficient and less dependent on oxygen concentration of the water. The MBR has a higher organic pollutant and ammonia removal efficiency in comparison with the activated sludge process. Besides this, the MBR process is capable to treat effluent with higher concentrations of suspended solids (SS) concentrations compared to activated sludge process, thus reducing the reactor volume to achieve the same loading rate (Munz et al. 2007). Frequent membrane cleaning and replacement is therefore necessary, but it significantly increases the operating cost (Ahmed and Lan 2012).

3.4.3.2 Anaerobic Biological Treatment

The treatment of tannery effluent anaerobically, is a series of processes in which microorganisms break down biodegradable material in the absence of oxygen. The principle of the anaerobic treatment is as follows: the insoluble organic pollutant breaks down the insoluble substances, making them available for other bacteria. The acidogenic bacteria convert the sugars and amino acid into carbon dioxide, hydrogen, ammonia and organic acid; and then the organic acids are microbiologically converted into acetic acid, ammonia, hydrogen and carbon dioxide. Finally the methanogens convert the acetic acid into hydrogen, carbon dioxide and methane, a kind of gaseous fuel (Pedro and Walter 2006).

The process of anaerobic degradation has a limitation of being slow and less efficient as compared to the aerobic degradation. However, the anaerobic degradation not only decreases the COD and BOD in the effluent, but also produces renewable energy. Furthermore, anaerobic processes could efficiently treat the effluent of several industries such as tanneries, slaughter houses, food industry, etc. with high loads of easy-to-degrade organic materials. Due to these advantages, application of anaerobic microbial mineralization in tannery effluent is of high importance. Anaerobic reactor could be divided into anaerobic activated sludge process and anaerobic biological membrane process. The anaerobic activated sludge process includes conventional stirred anaerobic reactor, upflow anaerobic sludge blanket reactor, and anaerobic contact tank. The anaerobic biological membrane process includes fluidized bed reactor, anaerobic rotating biological contactor and anaerobic filter reactor. Upflow anaerobic sludge blanket reactor and anaerobic filter reactor are selected as the representative of the two kinds of reactors mentioned above.

3.4.3.2.1 Upflow Anaerobic Sludge Blanket Reactor (UASB)

The UASB system was developed in 1970s. No carrier is used in the UASB system, and effluent moves upward through a thick blanket of anaerobic granular sludge suspended in the system. Mixing of sludge and effluent is achieved by the generation of methane gas within the blanket as well as by hydraulic flow. The triphase separator (gas, liquid, sludge biomass) could prevent the biomass loss of the sludge through the gas emission and water discharge. The advantages of this system are that it contains a high concentration of naturally immobilized bacteria with excellent settling properties that could remove the organic pollutants from tannery effluent efficiently and high concentrations of biomass can be achieved without support material which reduces the cost of treatment. These advantages would increase the efficient and stable performance of this system (Leitinga and Hulshoff 1991).

3.4.3.2.2 Anaerobic Bio-Filter Reactor

Anaerobic bio-filter reactor is a kind of highly efficient anaerobic effluent treatment equipment developed in1960s. These reactors use inert support materials to provide a surface for the growth of anaerobic bacteria and to reduce turbulence which allows unattached populations to be retained in the system. The advantages of this system are (a) The filler provides a large surface area for the growth of the microorganisms, and the filler also increases hydraulic retention time of the effluent. (b) The system provides a large surface area for the interaction between the waste water and film. (c) Growth of microorganisms on the filler reduces the run of the degraders. These advantages could increase the efficiency of the treatment of tannery effluent. The limitation of this system is that its working efficiency is affected, especially the water inlet parts when effluents having high content of organic matter are treated (Kassab et al. 2010).

3.4.3.3 Combination of the Aerobic and Anaerobic Biological Treatment

Compared with the individual anaerobic and aerobic reactors, the combination of the anaerobic and aerobic reactor is more efficient for the treatment of tannery effluent (Kassab et al. 2010). There are several advantages of the combined treatment system. (a) The anaerobic process could eliminate the organic matters and suspended solid from the discharged tannery effluent, reduce the organic load of the aerobic degradation and also lessen the production of aerobic sludge, and finally reduce the volume of the reactors. (b) Tannery effluent pre-treated by anaerobic technology is more stable, indicating that anaerobic process could reduce the load fluctuation of the effluent, and therefore there is a decreased oxygen requirement for the aerobic degradation. (c) The anaerobic process could modify the biochemical property of the tannery effluent, making the following aerobic process more efficient. Investigation showed that the tannery effluent from aerobic-anaerobic combined reactor are more stable, indicating that the effluent obtained after such treatment have a huge potential for reuse applications (Durai and Rajasimman 2011). The commonly used aerobic-anaerobic biodegradation reactors for tannery effluent treatment are the oxidation ditch and constructed wetland (Kassab et al. 2010).

3.4.3.3.1 Oxidation Ditch

The oxidation ditch is a circular basin through which the effluent flows. Very small amount of activated sludge as a source of microbes is added to the oxidation ditch so that the microorganisms will digest the organic pollutants present in the effluent. This mixture of raw effluent and returned activated sludge is known as mixed liquor. The rotating biological contactors add oxygen into the flowing mixed liquor, and they also increase the surface area and create waves and movements within the ditches. Once the organic pollutant has been removed from the tannery effluent, the mixed liquor flows out of the oxidation ditch. Sludge is removed in the secondary settling tank, and part of the sludge is pumped to a sludge pumping room where the sludge is thickened with the help of aerator pumps (Peng et al. 2008). Some of the sludge is returned to the oxidation ditch for second round of operation while the rest of the sludge is sent to the waste. Treatment of tannery effluent by oxidation ditch is characterized as a simple process, have low maintenance cost, steady operation, and strong shock resistance property. The effluent obtained after treatment by oxidation ditch has better quality with low concentration of organic pollutants, nitrogen and phosphorus. However, there are some problems which arises while functioning of this reactor, such as sludge expansion, rising of sludge and foam, which overall confines the development of this technique.

3.4.3.3.2 Constructed Wetland

A constructed wetland is an artificial wetland which acts as a biofilter and effectively removes sediments, pollutants such as heavy metals and organic pollutants from the tannery effluent. Constructed wetland is a combination of water, media, plants, microorganisms and other aquatic animals. Constructed wetlands are of two basic types: subsurface-flow and surface flow wetlands (Mook et al. 2012). Physical, chemical, and biological processes combine in wetlands to remove contaminants from the tannery effluent. Besides absorbing heavy metals and organic pollutants on the filler of the constructed wetland, plants can supply carbon and other nutrients such as nitrogen through their roots for the growth and multiplication of the microorganisms. Plants are also the source of oxygen in the circular oxidation ditch which allows the formation of an aerobic and anaerobic area in the deep level of constructed wetland which in turn assists the mineralization of complex organic materials into simpler forms. The microorganisms and natural chemical processes of this constructed wetland are responsible for approximately 65–75% of pollutant removal, while the plants are capable to remove about 15–20% of pollutants (Calheiros et al. 2012).

Constructed wetland is supposed to be a promising technique for the treatment of the tannery effluent in developing countries as it is quite economical, easy to manage and is an eco-friendly reactor. However, this technique was not widely used for the following reasons: (a) Many times the plants are unable to adapt and survive for long period in the tannery effluent obtained after primary treatment. (b) The establishment of this technique demands large area of land (c) The efficiency of this method is relativity lower than other biological effluent treatment methods such as activated sludge process and membrane bioreactor. Thus, efforts should be made in the selection of plants, modification in the way of establishment and to develop combination of multiple treatment techniques to enhance the adaption and efficiency of this method (Calheiros et al. 2012).

3.4.4 Tertiary Treatment

Sometimes even after primary and secondary treatment of effluents in the effluent treatment plants, the quality of final effluent is below the desired quality and does not meet the promulgated standard discharge limits for its discharge into the water streams/sources or agricultural lands due to the presence of refractory BOD, COD or some compounds as the microorganisms of the floc responsible for the treatment were unable to decompose into simple forms. Under these circumstances, more refined and costly treatments i.e. tertiary treatment, also termed as final or advanced treatment like mineralization of organic compound by oxidation with hydrogen peroxide in the presence of ferrous sulphate (Fenton method) and ozonation to destroy part of residual BOD, COD as well as to kill harmful microorganisms are needed (UNIDO 2011).

Through advanced treatment, the waste water is attempted to convert into good quality water, which is safe for specific uses such as domestic, industrial and agricultural. This treatment is capable of removing up to 90–95% of the pollutants. Treatment units are developed for the removal of simple and complex organic substances, nutrients and synthetic compounds. Tertiary treatment technologies to obtain safe water include biological treatment; however, the physico-chemical methods predominate. The unit processes include biological organic degradation, nitrification-denitrification, distillation, crystallization, evaporation, solvent extraction, oxidation, coagulation, precipitation, electrolysis, ion exchange, reverse osmosis, electrodialysis and carbon adsorption (Table 3.1). The applicability and suitability of various technologies for tertiary water treatment towards removal of soluble, suspended, organic, inorganic, biological and volatile impurities is given in Table 3.1 (Gupta et al. 2012). One or more technologies can be used for achieving the desired standards of the tannery effluent.

The liquid effluent after completion of these treatments is disinfected before discharging into the environment. Disinfection of waste waters is necessary to protect the public health when the receiving water is used for the purposes such as downstream water supply, recreation, irrigation and aquaculture. The use of ultraviolet light and ozone for disinfection is more prevalent. In many treatments chlorine is employed for disinfection but then they have to dechlorinate it prior to discharge into the water body or land. Although disposal into water bodies is widely practiced, land application is a feasible alternative to surface water discharge. Land application of waste waters was given substantial recognition in the Federal Water Pollution Control Amendment of 1972 to implement the "national goal that discharges of pollutants into navigable waters to be eliminated by 1985". During the next decade we are likely to give more consideration to land application of the treated liquid tannery waste from the waste water treatment plants.

3.4.5 Processing of Solid Waste

The solid wastes removed from the tannery effluent after every treatment steps (primary, secondary, tertiary and advance treatment) are stabilized and dewatered before its disposal. The sludge drawn from the bottom of the tank is in the form of slurry with a dry-solid content of only 3–5% after primary clarifier and 6–8% after thickened mixed primary and secondary sludge. The mechanical dewatering is done to decrease the volume and weight of material and attain the dry matter to be transported and required for disposal at landfills. In modern waste water treatment plants the major cost of effluent treatment is associated with the processing of solid waste. The various steps of processing are thickening, stabilization, dewatering and safe disposal of sludge (Aravindhan et al. 2004). Thickening is employed to further concentrate the solids or sludge prior to stabilization. Thickening may be accomplished by gravity thickening (sedimentation) or by dissolved air flotation. Thereafter, stabilization is performed by aerobic and anaerobic digestion, composting, chemical

Table 3.1 Applicability and suitability of various technologies for tertiary treatment of tannery effluent

Technologies for tertiary water treatment	Applicable for matter						Suitable for		
	Soluble	Suspended	Inorganic	Organic	Biological	Volatile	Reclamation	Treatment	Source reduction
Distillation	√	×	√	√	√	×	√	√	×
Crystallization (rarely used)	√	×	√	√		×	√	√	√
Evaporation (rarely used)	√	√	√	√	√	×	√	√	√
Solvent extraction	√	×	√	×	×	√	√	√	√
Oxidation (rarely used)	√	×	√	√	×	×	√	√	√
Precipitation	√	×	√	√	×	×	√	√	×
Ion exchange	√	×	√	√	×	×	√	√	√
Micro- and ultra-filtration	√	×	√	√	√	×	√	√	√
Reverse osmosis	√	×	√	√	√	×	√	√	√
Adsorption	√	√	√	√	√	×	√	√	√
Electroysis	√	×	√	√	×	×	√	√	√
Electrodialysis	√	×	√	√	×	×	√	√	√

addition and heat treatment. In case of anaerobic sludge digestion, the solids accumulated by sedimentation are pumped into a separate tank where sludge is digested under controlled conditions. Solids recovered from the aerobic treatment process are also collected in the sludge digester. It is a special tank designed to process sludge under controlled environment through microbial action under anaerobic conditions. The anaerobic and facultative types of bacteria grow in it and perform the function. During sludge digestion they degrade the organic substances of the solid waste into soluble form. Also, large amount of methane and carbon dioxide gas is produced and less amount of hydrogen and nitrogen gas is produced. This gas mixture can be used as a fuel for heating purpose and for operating power.

Dewatering is done by physical methods and is mostly enhanced by the addition of polymer or other chemical coagulants. It is performed by means of vacuum filters followed by belt filter presses, plate and frame presses and decanter centrifuges. Characteristics of sludge dewatering equipment are presented in Table 3.2. The dry solid content of sludge after tertiary treatment varies between 20% and 45%. It is further enhanced by 60–90% after stabilization with calcium oxide mostly after belt press and centrifuge (UNIDO 2011).

Small treatment plants many times use sand filter beds for dewatering. The main purpose of sludge dewatering is not only to reduce the volume and weight of material to be transported but also to attain the dry matter content required for disposal at landfills. The dewatered sludge is mixed with a bulking agent such as wood chips to enhance the air circulation so that the stabilization process could be improved. The mixture of sludge and bulking material is placed in aerated piles and is allowed to biologically decompose for 20–25 days. Thereafter, the sludge is allowed to cure and gets deposited in the form of cakes. The sludge cakes are then carried to incinerators. Here the sludge cakes are finally reduced into ash for final disposal.

Table 3.2 Characteristics of various sludge dewatering equipments

Equipment	Decanter centrifuge	Belt press	Plate filters
Way of operation	Continuous	Continuous	Batch
Sludge conditioning	Required	Required	Not required
Washing water	Not required	Required	Not required
Labour	Only supervision	Only supervision	Required during cake discharge
Sensitivity to sludge variability	Very sensitive	Very sensitive	Less sensitive
Energy requirement	High	Medium	Low
Maintenance	Sophisticated	Medium	Low
Dry solid content	20–30%	20–25%	35–45%

3.5 Sludge Disposal

Tannery sludge is well known to have greater content of organic and inorganic matter, heavy metal especially chromium and sulfur compound as compared to sanitary sludge. However, the main cause of concern is the chromium content of sludge. Though, many solutions including landfill, land application, composting, anaerobic digestion, thermal treatment, vitrification, pyrolysis, brick making are known for utilization as well as safe disposal of tannery sludge but, none of them are satisfactory enough (Krishanamoorthi et al. 2009). There is no universal solution for sludge utilization. Each tannery effluent treatment plant produces sludge of specific characteristics depending upon the treatment process that they have adopted and different countries have different regulations regarding sludge utilization (Ahamed and Kashif 2014). Therefore, a detailed assessment of options should be prepared before construction of any effluent treatment plant. The handling, storage and transport of sludge should be always safe. Most of the treatment plants dispose their sludge for landfilling. Alternatively, few treatment plants spread the stabilized dewatered sludge on the land. Many researchers worked on environmentally safe disposal of tannery sludge (Leena et al. 2016; Geethakarhi 2017). In countries, where the tannery effluent is properly treated, the municipalities are engaged in land-utilization techniques for disposal of treated tannery sludge. However, such practices require cheap lands for sludge disposal.

3.6 Bioremediation of Tannery Waste Water by Microorganisms

The presence of chromate and PCP in the environment inhibits most of the microorganisms, but it also promotes the selection of resistant bacteria. Bacteria are in the front line when it comes to interaction with metals in the environment. Therefore, they have evolved some transport mechanisms for the active uptake of metallic ions or their efflux by the cell, which enables the microbes to regulate their intracellular metal concentration (Cheung and Gu 2007). The indigenous bacteria of polluted site are scavengers of Cr (VI) and PCP and have ability to colonize such noxious polluted environments. Bacterial reduction of Cr (VI) to Cr (III), using PCP as a sole carbon source offers an efficient and eco-friendly strategy for environmental restoration. The Cr (III) species forms an insoluble precipitate, such as $Cr(OH)_3$, which can be removed from waste water. Many indigenous microbes are reported to detoxify the toxic Cr (VI) from the polluted site. The processes through which the microbes interact with the toxic heavy metals for their removal are bioreduction, biosorption and bioaccumulation (Jeyasingh and Philip 2005; Singh et al. 2013; Mosa et al. 2016). Many times bioremediation is achieved by incorporating microorganisms into the contaminated/polluted site to enhance the remediation efficiency, the process is then referred as bioaugmentation. It is environmentally compatible and cost effective technology.

3.6.1 Bioreduction of Cr (VI) by Bacteria

Microbes are able to alter the oxidation and reduction state of toxic heavy metals. The mechanisms by which microorganisms reduce Cr (VI) are variable, and are species specific. Some microbial strains use hexavalent chromium as the ultimate electron acceptor in their respiratory chain, while in other microbes soluble enzymes are responsible for reduction of Cr (VI) to Cr (III). Bioreduction of Cr (VI) to Cr (III) decreases the toxicity of chromate in living beings, and also helps to precipitate chromium at neutral pH for further physical removal. Microbial bioreduction of Cr (VI) to innocuous Cr (III) has gained increasing attention for selective removal of chromium from the contaminated sites (Masood and Malik 2011). Chromate is actively transported across the biological membranes. Once inside the microbial cell, Cr (VI) being a strong oxidizing agent is reduced to Cr (V) intracellularly in the presence of electron donors. The Cr (V) is an unstable short lived intermediate and its formation from Cr (VI) is the first step of chromium toxicity. The Cr (V) reacts with DNA, RNA, proteins and other cellular components, and produces mutagenic, carcinogenic and teratogenic effects on the biological systems. Being less stable in nature the Cr (V) is reduced to stable Cr (III) via another unstable intermediate Cr (IV). This ultimately results in precipitation of chromium. Further, the trivalent chromium is less soluble in nature and hence less toxic. This process takes place either spontaneously or is enzyme mediated.

The microorganisms capable to grow and survive in chromate rich environment have developed resistance for Cr (VI) and also could reduce the toxic chromate to its innocuous Cr (III) form, which allows the survival of microorganisms in such a polluted environment. Isolation of indigenous bacteria from such contaminated sites will be ideal for obtaining microbes with high chromate detoxification ability. The microorganisms reducing toxic Cr (VI) to the innocuous Cr (III) form are termed as chromium reducing bacteria (CRB). Microorganisms reduce toxic Cr (VI) to its trivalent form in the presence or absence of oxygen. It was demonstrated that among CRB, gram positive CRB are significantly tolerant to Cr (VI) toxicity at relatively high concentration, while gram negative CRB are more sensitive to Cr (VI) (Morales-Barrera et al. 2008). In 1977, the first reported chromate reducing bacterial strain, *Pseudomonas* sp., was isolated from chromate (CrO_4^{2-}) contaminated sewage sludge by Russian scientists N.A. Romanenko and V. Korenkov. Thereafter, several chromate reducing bacterial strains such as *Bacillus cereus*, *B. megaterium*, *B. brevis*, *B. subtilis*, *E. coli*, *Pseudomonas fluorescens*, *Pseudomonas aeruginosa*, *Enterobacter aerogenes, Enterobacter cloacae*, species of *Arthrobacter*, *Desulfovibrio, Shewanella, Rhodobacter*, *Alcaligens*, etc. have been isolated (Kashefi and Lovley 2000; Park et al. 2002; Aguilera et al. 2004; Tekerlekopoulou et al. 2010; Verma et alh. 2016). Maximum Cr (VI) reduction is attained when the bacterial density is very high. However, resistance to Cr (VI) and its reduction to Cr (III) are not related to each other because many times the chromate resistance is due to the efflux mechanisms and the Cr (VI) resistant microbes are able to extrude CrO_4^{2-} ions. The Cr (VI) reduction activity is generally associated with soluble proteins that use NADH as an electron donor for enhanced activity and Cr (VI) as a terminal electron acceptor in their respiratory chains. Organisms may also reduce Cr (VI) either by a soluble chromate reductase enzyme; a membrane bound chromate reductase or both (Panda and Sarkar 2012). The reductase enzyme catalyzes the reduction of toxic Cr (VI) to less toxic Cr (III), leading to decreased uptake of chromium.

In intracellular process, the Cr (VI) is reduced in the cytosol using cytoplasmic soluble reductase enzymes. These enzymes play an intermediate role between associated biological electron donors i.e. NADH and NADPH, which is active within a wide range of temperature from 20 to 70 °C and pH 4–10 (Faisal and Hasnain 2004). During intracellular Cr (VI) reduction, Cr (III) could not be removed from the cells as long as cell membrane remains intact. The extracellular Cr (VI) reduction pathway was observed in sulphate reducing bacteria by Smith and Gadd (2000). Formation of $Cr(OH)_3$ (aq) under the higher pH intracellular environment is expressed and represents a physiological reaction which protects cells by forming a barrier from Cr (VI) toxicity and confers a low cell membrane permeability to Cr (VI). The bacterial growth as well as its Cr (VI) reduction efficiency is dependent on the pH, temperature and Cr (VI) concentration. Time for overall Cr (VI) reduction increases with increasing chromate concentration and the bacterial chromate reducing ability is growth-dependent. Further, since the Cr (VI) reduction activity is enzyme mediated so any change in pH will affect the enzyme activity because the ionization degree of chromate reductase enzyme and the protein conformation will alter. Similarly, temperature will also affect the bacterial growth, thereby affecting the chromate reductase activity.

3.6.2 Biosorption of Cr (VI) by Bacteria

Studies revealed that in addition to the living microorganisms dead microbial cells biomass is also able to bind chromate and other metallic ions on the surface of their cell wall through various physico-chemical interactions. It is thus a metabolism independent strategy. This new finding attracted a lot of attention towards the biosorption strategy for Cr (VI) removal. The biosorption is based either synergistically or independently on a number of mechanisms such as ion-exchange, chelation, complexation, physical adsorption, coordination and precipitation (Owlad et al. 2009). The biomasses of algae, bacteria, fungi and yeast have the property to bind with metal ions from the aqueous solutions and are thus used in biosorption. Biosorption can be either metabolism dependent or non-metabolism dependent. Metabolism dependent is a slow process which includes transport of chromate ions across the cell membrane followed by precipitation. While the non-metabolism dependent biosorption is a rapid process that include among any of these mechanisms viz. ion -exchange, chelation, complexation, physical adsorption, coordination and precipitation (Pun et al. 2013).

The biosorption process involves a solid phase which is a biological material that act as sorbent or biosorbent and a liquid phase containing a dissolved species to be sorbed. Due to higher affinity of the sorbent for the sorbate species the latter is attracted and bound with different mechanisms. This process continues till the equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. Any biological material which exhibits affinity towards a metal solution and concentrates the metals from dilute aqueous solutions is called as biosorbent. The heavy metals adsorb on the surface of cell biomass thus, the biosorbent becomes enriched with metal ions in the sorbate. The advantages of an ideal biosorption process are the reusability of biomass, removal of Cr (VI) and other metals from highly toxic effluent irrespective of toxicity, short operation time until equilibrium is reached and no secondary compounds are produced. Some chromate resistant bacteria like *Pseudomonas fluorescens* (Bopp and Ehrlich 1988), *Enterobacter cloacae* and *Acinetobacter* sp. (Srivastava and Thakur 2007), etc. have been shown to remove chromium from the industrial effluent through biosorption.

3.6.3 Bioaccumulation of Cr (VI) by Bacteria

Bioaccumulation of metals by microbes is a promising technology for the removal and recovery of Cr (VI) and other metals from waste streams and contaminated environments. Bioaccumulation of Cr (VI) takes place by adsorption, intracellular accumulation and bio-precipitation; all of which result in the uptake of bioavailable metal ions by living cells (Gupta et al. 2009). Microbial heavy metal accumulation often occurs in two stages. First, an initial rapid and passive process occurs in which metals are physically adsorbed or metallic ions are exchanged at the cell surface. Second, a slower phase occurs, that involves active metabolism dependent transport of metal into bacterial cells. This second phase is inhibited by low temperature, absence of an energy source and presence of metabolic inhibitors and uncouplers. Rate of uptake is also influenced by the state of the cells and the composition of external medium. The initial chromate concentration also affects the rate of Cr (VI) uptake. During bioaccumulation process, several features within a living cell may occur such as intracellular sequestration followed by localization within specific organelles, metallothionein binding, particulate metal accumulation, extracellular precipitation and complex formation (Devi et al. 2012).

Bioaccumulation is an active process so the physiological state of cells affects the process. Starved cells of a denitrifying bacterial consortium showed 10–15% higher amount of Cr (VI) bioaccumulation. More than 100% of Cr (VI) was in the cell wall fraction of the starved cells in comparison to the fresh cells (Aravindhan et al. 2004). This may be due to reduction of Cr (VI) to Cr (III) in the cell wall. In fresh cells, maximum amount of chromate was present in the soluble fraction. The pH of the solution is known to modulate cellular metabolism and sites of interactions that may produce changes in both the accumulation and toxicity of metals. Several researchers reported the significant effect of pH on Cr (VI) bioaccumulation activity of microorganisms. Srivastava and Thakur (2007) studied the effect of pH on chromium bioaccumulation in *Acinetobacter* species. Congevaram et al. (2007) isolated chromium resistant microorganisms (*Aspergillus* sp. and *Micrococcus* sp.) from a heavy metal contaminated environment. The maximal Cr (VI) removal (92% and 90%) occurred at pH 5.0 and 7.0, respectively. Srinath et al. (2002) studied this relationship at pH 6.3 to 9.0 for Cr (VI) accumulation in *Bacillus cereus*.

3.6.4 Microbial Degradation of Pentachlorophenol

The microbial biodegradation of PCP has been studied by a number of researchers in soil, sludge, and aquatic environment (Srivastava et al. 2007; Verma and Singh 2013; Maurya and Verma 2014). Reductive dechlorination has been suggested as the primary PCP biodegradation mechanism by which chlorine can be removed from the aromatic ring resulting in formation of partially or fully dechlorinated product which is then more susceptible to either aerobic or anaerobic attack. The aromatic ring is thus totally dechlorinated prior to ring cleavage. Further degradation results in the production of methane and carbon dioxide (CO_2) (Parker et al. 1993). Under aerobic conditions, the biodegradation pathways of PCP are more diverse than under anaerobic conditions. Ring cleavage can occur either before or after removal of the chlorine substituents, giving rise to a whole array of intermediates of varying toxicity. Application of the enriched PCP-degrading microorganisms would significantly enhance the PCP removal from the contaminated sites.

Biodegradation of pentachlorophenol by reductive dechlorination has been reported in flooded soil and anaerobic sediment environments but much less often in aquifer environments. A common pathway via initial ortho dechlorination followed by para dechlorination to 3,5-dichlorophenol has been reported for various microbial consortia but initial meta or para dechlorination has also been observed (Shah and Thakur 2003). Often, dechlorination is not complete resulting in daughter products, the di-, tri-, and tetrachlorophenols. It is thought that the processes of reductive dechlorination and ring cleavage are carried out by separate microbial populations, one group using the chlorinated compound as an electron acceptor (reductive dechlorination) and the other using the remaining phenol group as an electron donor (oxidative degradation). The process of reductive dechlorination is expected be most likely under strong reducing conditions such as methanogenic and sulfate-reducing redox environments but not under aerobic and possibly not under nitrate-reducing conditions. Oxidative degradation of the remaining phenol mostly occurs under anaerobic redox condition but most rapidly under nitrate-reducing conditions. Pentachlorophenol can also be biodegraded through aerobic pathways (Srivastava et al. 2007). The intermediates formed during pentachlorophenol degradation are 2,3,4,6-tetrachlorophenol, 2,3,5,6-tetrachlorophenol, 2,3,5-trichlorophenol, 2,3,4-trichlorophenol and 2,4,5-trichlorophenol. A study utilizing acclimated microbes in sewage sludge demonstrated that PCP was degraded to lower chlorinated phenols, including dichlorophenols (Stanlake and Finn 1982). In anaerobic systems, pentachlorophenol is biodegraded mainly through reductive dechlorination, and the degradates 3,5-dichlorophenol and 3-chlorophenol may accumulate; complete dechlorination to phenol and its subsequent mineralization to methane and carbon dioxide was also observed. Studies have demonstrated that a chlorine present in the *meta* positions (as in 3, 5-dichlorophenol and 3- chlorophenol) is more resistant to degradation than when it is present in the ortho or para positions. Metabolic intermediates in the biodegradation of PCP also include tetrachloro-*p*-benzoquinone and 2, 6-dichlorohydroquinone. It has been reported that, based on the identified degradates, metabolism of PCP in soil resulted from four reaction mechanisms: reductive dechlorination, methylation, conjugation, and incorporation into insoluble macromolecules (Orser and Lange 1994).

The reaction mechanisms and enzymes responsible for the degradation of polychlorinated phenols have been studied in several microorganisms. *Flavobacterium* sp. strain ATCC 39723 oxidizes pentachlorophenol (PCP) to tetrachloro- *p*-hydroquinone (TeCH) by PCP 4-monooxygenase and then converts TeCH to 2, 6-dichloro-*p*-hydroquinone (2,6-DiCH) by TeCH reductive dehalogenase. Ring cleavage dioxygenases using 6-CHQ (6-chloro-1, 2, 4-trihydroxybenzene) and hydroxyquinol (1, 2, 4-trihydroxybenzene) as substrates have been purified and characterized from *Azotobacter* sp. strain GP1 and *Streptomyces rochei* 303. Further 2, 6-DiCH is a common metabolite in the degradation of polychlorinated phenols, such as PCP, 2,3,5,6-tetrachlorophenol, and 2,4,6-trichlorophenol (2,4,6-TCP), by various microorganisms. *Sphingobium chlorophenolicum* (formerly *Sphingomonas chlorophenolica*) strain ATCC 39723 is one of the bacteria capable of completely mineralizing PCP into succinyl-CoA and acetyl-CoA. They are common metabolic intermediate of several cellular metabolic pathways and can be channelled into the tricarboxylic acid cycle for complete mineralization.

However, few indigenous bacterial strains such as *Brevibacterium casei, Pseudomonas* sp.*, Bacillus* sp.*, Serratia marcescens,* etc. are able to degrade PCP and bioremediate toxic Cr (VI) simultaneously (Srivastava et al. 2007; Verma and Singh 2013; Verma and Maurya 2013). Most of the researchers have reported the detoxification of either Cr (VI) or PCP. Very few researchers have reported towards simultaneous detoxification of Cr (VI) and PCP. Therefore, isolating microbial strains having the potential to degrade PCP and simultaneously bio-accumulate chromium would be valuable for effecting binary-compound bioremediation. Many researchers have degraded PCP by bacteria isolated from industrial waste but the microorganisms suffered from substrate inhibition at high phenol concentration, whereby growth is inhibited. Use of immobilized cells appears to be an attractive and promising strategy to overcome substrate inhibition regarding simultaneous bioremediation of Cr(VI) and PCP. Further, the ability of a co-culture to utilize a wide range of aromatic pollutants for reduction of Cr (VI) illustrated the potential for simultaneous detoxification of chromate and various aromatic contaminants.

3.6.5 Fungal Bioremediation

Fungal biomass acts as biosorptive material and is very efficient and economical sorbents for Cr (VI) removal from polluted sites and even dilute aqueous solutions due to the presence of high percentage of cell wall material and tremendous metal binding capacity. Many fungi and yeasts, such as species of *Rhizopus, Aspergillus, Hirsutella, Trichoderma, Streptoverticillum, Saccharomyces,* etc. have excellent biosorption potential for various heavy metals. Biosorption of Cr (VI) ion onto the cell surface of *Trichoderma* species under aerobic conditions was investigated (Vankar and Bajpai 2007). The fungus is biosorbed 97.39% chromate at pH 5.5. The results of FT-IR analysis suggested that the chromium binding sites on the fungal cell surface were most likely carboxyl and amine groups. Interestingly, many negatively charged functional groups act as active sites capable of binding numerous metal cations during biosorption. The major functional groups of fungi include carboxyl, hydroxyl, sulfate, phosphate, and amino groups. It is regarded as a complex ion exchanger similar to a commercial resin (Congevaram et al. 2007; Gautam et al. 2014). Differences in cell wall composition can cause significant variation in the type and amount of metal ions binding capacity and uptake.

The most common problem encountered while working with bacterial systems is the harvesting of cells after treatment. On the other hand, fungal biomasses are easy to grow and produce high biomass and are comparatively easier to harvest. Further, the crucial aspects of an efficient fungal biosorption process are localization of metal deposition sites within the biosorbent biomass, understanding the metal-sequestering mechanism, elucidation of the relevant metal solution chemistry, and chemical structure of the metal deposition site (Fukuda et al. 2008). The biosorptive capacity of dead fungal cells has been studied extensively in comparison to living cells (Dwivedi et al. 2012). The main reasons include the high surface area associated with the dead cells as adsorption of metals on fungal biomass is the physical adhesion of metal ions (adsorbate) on to the two-dimensional solid cell wall (adsorbent) due to interaction between them. On the other hand, small size and low mechanical strength of living fungal cells make them less ideal as biosorbent. As a result, a substantial hydrostatic pressure is required for suitable and efficient flow rate and disintegration. Other reasons include the absence of toxic effects to the dead biomass, and also the system could be operated at different pH and temperature. Moreover, it is cost-effective to use dead biomass as it cuts the expenses of media for the fungal growth. Along with this, dead biomass can be further reused after regeneration of biomass, which is quite complicated in the case of live material. Further, the biosorptive capacity of dead cell biomass is much better than living cell biomass because to achieve dead cells, the live cells are ruptured after heat treatment and such treatment yields cells that have more binding sites. The increased biosorption performance of dead cells over living ones was observed with *R. arrhizus*, *A. niger* and *S. cerevisiae* for numerous heavy metals, including chromium, nickel and cobalt (Garcia et al. 2005; Chhikara et al. 2010; Gautam et al. 2014).

The fungal biosorption of chromate ions is influenced by several environmental factors. The pH of the metal solution is one of the most influential factors affecting the surface properties of the fungal biomass and metal speciation. The uptake of metallic cations by cells/biomass is reduced below pH 2.0 and above pH 8.0. At acidic pH, lower metal uptake has been observed due to increased competition between H^+ and metal ions. At alkaline pH, metal absorption becomes restricted due to precipitation. Moreover, the optimum value of pH is very important to get the highest metal sorption efficiency (Das et al. 2008).

Biosorption is also affected by the contact time between biomass and the metal solution. Biosorption proceeds fast, and most metals are adsorbed at the very beginning of the process. For attaining equilibrium, knowing the duration of contact between the biomass and the metal ions is relevant. Such information is also essential for economical industrial exploitation. Biosorption occurs rapidly, if equilibrium is optimally attained within a few hours. At a pH of 2.0, 82% Cr (VI) biosorption by *R. arrhizus* was rapidly achieved within 1 h and 92.5% chromate biosorption was attained after 8 h. Further incubation did not enhance the adsorption of chromate. Srinath et al. (2002) reported that biosorption of Cr (VI) by microbial biomass occurred rapidly; attaining equilibrium within 60 min and further incubation upto 240 min increased the Cr (VI) biosorption by only 4.0%. Various steps occur as a metal transfers from the bulk solution to binding sites of the biomass (Dias et al. 2002). The first step is rapid, because of mixing and smooth flow. The second step is film transport involving diffusion of the metal through a thermodynamic boundary layer around the biosorbent surface. The third step is actual adsorption of the metal ions by active sites on the biomass. The fungal strain showed a remarkable capacity to completely reduce very high concentrations of Cr (VI) suggesting that it could be potentially useful for detoxification of Cr (VI)-laden waste waters.

Srivastava et al. (2007) employed a fungal strain *Aspergillus niger* and a bacterial isolate *Acinetobacter* sp. individually for bioremediation of chromium and PCP in a sequential bioreactor. The tannery effluent treated in set-1, with *Acinetobacter* sp. followed with fungus treatment, respectively remediated 90% of Cr (VI) and 67% of PCP in 15 days. In the set-2 sequential bioreactor, wherein the effluent was first treated by the fungus and then by the bacteria, removed only 64.7% and 58% of Cr (VI) and PCP, respectively within 15 days. The higher level of chromium removal in the set-1 bioreactor was attributed to the utilization of PCP as a food source in step-1 by *Acinetobacter* sp., thereby exerting no inhibitory effect of PCP on fungus for removing chromate in step-2. However, in the set-2 bioreactor, the growth of the fungus was inhibited by PCP in step-1, thereby decreasing the extent of chromium removal, which led to the bioaccumulation of Cr (VI) in the fungal mycelium.

3.7 Recycling of Tannery Waste Water

Tanneries consume large quantity of water during leather manufacturing. The tannery effluent obtained after final treatment is intended for reuses by the tanneries itself at various stages during leather processing. The objective is to reduce the consumption of water and reagents (chromium salts, sodium chloride, alkalizing agents, etc.). Further, substantial water savings can be achieved by the reuse of treated waste water for various non-potable purposes such as aquaculture, cultivation of crops and vegetables, washing of vehicles, etc. and will hence support water conservation. The effluent recycling concept will significantly save the raw material and the water consumption which is one of the biggest natural resources. This will also result in the less discharge of tannery effluents into the water bodies and agricultural lands and will also provide pollution abatement. Since the amount of chemical agents to be used during leather manufacturing is decreased, so the amount of chromium and other chemicals discharged through the tannery waste in the successive rounds of leather manufacturing will also decrease and it will ultimately reduce the costs of leather goods and sludge management. The salinity of the final discharged effluent will also be decreased which will thus improve the efficacy of the tannery waste water treatment plants. To adapt this technology in the tanneries of India and other countries re-adjustment of the operational parameters as well as the dimensions of the tanning industries will be needed. In a directive of the Central Pollution Control Board (CPCB), New Delhi, India, tanning industries have to meet the zero liquid discharge (ZLD) norms because of the potential threat to the environment and all forms of life due to discharge of tannery effluents (CPCB 2008). This directive has encouraged tanneries to adopt advanced treatment methods so that the treated water obtained could be reused in the tanneries.

The waste from the tanning industry rich in toxic heavy metals can be used as raw material to produce pigments and ceramics. Interestingly, nanoparticles are produced by a modified sol-gel process using solid and liquid tannery wastes mixed with natural organic materials. Further, the tannery wastes are used in the catalytic reduction of nitrophenol and alumina pigment production. Sabumon (2016) also discussed various perspectives on biological treatment for recycling of tannery effluent.

Katsifas et al. (2004) studied the chromium recycling of tannery waste through microbial fermentation. They reported nearly 97% liquefaction of tannery waste was achieved by *Aspergillus carbonarious* isolate in solid-state fermentation. The liquid obtained was thereafter used to recover chromium. The resulting alkaline chromium sulfate solution was useful in tanning process. Furthermore, proteinaceous liquid was also obtained which has applications as a fertilizer or animal feed additive. The Federal Ministry of Environment proposed a project on recycling of tannery waste water in the years 1990–1994. In this project, the waste water was recycled by the precipitation, flocculation and electro-floatation so that it can be reused again. Through these methods, about 75% of the treated tannery waste water is recirculated for the leather production.

Recycling systems can be classified as closed and open, and are mostly used in conventional tanning processes (Infogate 2002). Closed systems are mostly based on reusing only spent tanning floats and sammying water in successive cycles of leather production. They are utilised when working with short floats and powder chrome tanning agents. In open systems, the float volume increases during recycling and number of cycles are not limited. In industries various open-system recycling techniques are being employed. Further, recycled floats are used in pickling and tanning processes of leather production during consecutive cycles. In open system, the mixture of tanning float and sammying water is reused in pretanning and tanning processes. According to the extent of the use of recycled waste water, about 70–95% increase in chrome utilisation is observed. Further, there is a decrease in chrome discharge and sulphate load in the tannery effluent (Infogate 2002).

The recycling systems are also based on the alkali precipitation of chrome containing effluents. Common precipitation agents include MgO, $Ca(OH)_2$, NaOH, etc. After settling, thickening and dewatering of the chrome oxide suspension, the filter cake is dissolved in sulphuric acid (Katsifas et al. 2004). Thereafter, the pH is adjusted in the basic range and the basic chromium sulphate solution can be reused for tanning by recycling into the tanning process. It is to be noted that recovery/recycling techniques differ in terms of the alkalis used for precipitation, flocculation temperatures, settling and dewatering conditions, as well as the way of handling and reusing the filter cake. With a well-managed tannery effluent collection and processing system, a decrease in the amount of chrome discharged in the tanning effluents from 2–5 to 0.1–0.25 kg $tone^{-1}$ raw hide was observed (Protrade 1995). This will finally lead to more leather production and increased profitability in India without causing environmental pollution. Further, the treated waste water reuse applications will help the community to meet the water demand.

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Chapter 4
Treatment and Recycling of Wastewater from Dairy Industry

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Abstract Dairy industry is considered as one of the major water consuming industries in the world and the waste generated from dairy industry severely contaminates the environment. World is facing severe water crisis, therefore, it is needed to process the waste water for reuse purpose. The processing of raw milk result in production of high concentration of organic matter such as proteins, carbohydrates, lipids, suspended solids, high nitrogen concentration and oil/grease contents. The waste water thus released from the dairy industry has high biological oxygen demand (BOD) and chemical oxygen demand (COD), high variation in pH usually being slightly alkaline in nature, further on fermentation of milk sugar it is converted to lactic acid and rapidly becomes acidic. If the waste water is released untreated in the environment, these organic and inorganic contaminants from the dairy industries can disrupt terrestrial and aquatic ecosystems and there by imbalance the ecosystem. Thus, there is an urgent need to develop efficient techniques for the treatment of dairy effluents. Waste water from dairy industries can be treated by various methods such as physical, chemical and biological. However, to reduce the operational cost, increase in efficiency, recycling and reuse of waste water and to decrease disruptions of environmental resources, further advancements in the treatment methods have become the need of the hour.

Keywords Dairy industry · Wastewater · Contaminants · Biological treatment · Recycling

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R. L. Singh, R. P. Singh (eds.), *Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future*, Applied Environmental Science and Engineering for a Sustainable Future,
https://doi.org/10.1007/978-981-13-1468-1_4

4.1 Introduction

The increasing demand of the milk has increased to several folds in last few decades because of growing world population. Number of dairy industries has been increased after operation flood in 1970s which lead to increased generation of waste products which are being discharged to water bodies and land. The dairy industry uses processes such as homogenization, pasteurization and chilling which involves processing of raw milk and transformed into sour milk, yoghurt, cheese, cream, butter and many other milk products (Tikariha and Sahu 2014). Milk is a complex biological fluid and consists of water, milk fat, proteins, lactose and mineral salts. Further the method of manufacturing dairy products may also contain sugar, salts, flavors, emulsifiers, stabilizers and preservatives. The waste water released from dairy plants are mostly from transport pipes, equipments of operational production unit, cleaning of tanks and washing of milk products. Butter milk, whey and their derivatives are the typical by-products released by dairy industries. The waste water is primarily generated during cleaning and washing operations of the milk in the processing plants. Dairy industry waste water entitled to be crucial issue because processing industries discharges untreated waste in environment which directly imposes its hazardous effects and severely affect living organisms. The concentration of various organic loads present in dairy waste water is depending upon its operation and products being manufactured. The constituents of dairy waste water are casein, lactose, inorganic salts, detergents and sanitizers used during washing. The main contributors in dairy waste water for increasing organic load are dissolved sugar, proteins, fats and other additives and preservatives. The organic content of dairy industry effluents reduces the amount of dissolved oxygen (DO) and when discharges into receiving streams creates various issues like eutrophication, increase in vector born disease such as dengue fever, yellow fever and chicken guinea (Kumar 2011). Besides causing serious environmental problems, the pollutant of dairy industry waste water also affects the aquatic life. The dairy effluents have high butyric acid and protein concentration responsible for foul odor and heavy black flocculated sludge mass. There is also present a class of volatile fatty acid (VFA) which are most abundant in dairy manure and largely responsible for foul odor (Page et al. 2014). It has also been reported that the offensive odor of dairy industry waste water is due to the formation of hydrogen sulphide often creates a problem to nearby areas and affects the population health as well as aquatic life (Shete and Shinkar 2013). Dairy waste water has nitrogenous compounds like nitrate which are being converted into nitrite that serves as ambient environment for development of methemoglobinemia (Kushwaha et al. 2011; Ulery et al. 2004). Waste water from dairy industry constitutes of high biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids, CO_2 concentration that creates high organic load and also rich in calcium, magnesium, compounds of nitrogen and phosphorous (Tikariha and Sahu 2014). The wastewater generated from different dairy industries varies in their characteristics mainly due to discontinuous manufacturing process and high production heterogeneity in the milk processing. Presence of excessive amounts of harmful heavy metals like $Fe^{2+,}$ Cu^{2+}, Zn^{2+} and Mn^{2+} can cause chronic poisoning in aquatic animals and enter the food chain. These heavy metals also get accumulated in plant tissues posing threat to humans and animals feeding on these plants and leads to contamination of entire food chain. The methods involve in the treatment of dairy waste water are generally physical, chemical and biological. This book chapter discusses about the standard procedures involved in the treatment of dairy industry wastewater such as anaerobic digestion, aerobic bioconversions, electrochemical treatment and catalytic membrane treatment processes for proper treatment and disposal of dairy industry effluents to protect environment and focus on biological treatment processes. The purpose of this chapter is to highlight the effective, economical and environment friendly methods of treatment of dairy industry waste water and to review contemporary research and dairy waste water management for clean and safe environment.

4.2 Waste Water Characteristics

Water plays a crucial role in all step of milk processing; the large quantity of waste water comes from manufacturing process. On an average, 2.5–3.0 L of wastewater is generated out of a liter of milk processed in dairy industry. Dairy industry is considered as one of the most polluting industry among all agro-food industries both in terms of the volume of effluent generation as well as in terms of the characteristics of wastewater. However, in general the dairy waste water is characterized by variable pH, increased temperature, high COD, BOD, nitrogen and phosphorous concentration as well as various cleaning agents and detergents. The key parameters of dairy waste water are ranging at pH range from 5.5 to 7.5, TSS (mg/L) 250–600, turbidity (NTU) 15–30, TDS (mg/L) 800–1200, COD (mg/L) 1500–3000 and BOD (mg/L) 350–600 (Shete and Shinkar 2013). The characteristics of dairy wastewater vary with type of methods used for producing dairy products and also vary with type of product produced such as cheese, yoghurt, milk, butter, ice-cream and various desserts (Kolarski and Nyhuis 1995). Effluents generated by industries using acid and alkaline cleaners and sanitizers show a high variation in pH (Kasapgil et al. 1994; Danalewich et al. 1998; Demirel and Yenigun 2002). Nitrogen is present in dairy wastewaters in the form of NH_4^+, NO_2^- and NO_3^- while phosphorus is present in the form of orthophosphate (PO_4^{3-}) and polyphosphate ($P_2O_7^{4-}$) or some organic forms (Guillen et al. 2000). Coagulated milk and flavouring agents generates suspended solids. Certain elements like sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), ferrous (Fe), nickel (Ni), manganese (Mn) and cobalt (Co) are also present in dairy wastewaters. High concentration of sodium (Na) is because of large amount of alkaline cleaners used during the processing of milk in dairy plant. Carbohydrates present in dairy wastewaters are easily biodegradable while proteins and lipids are less biodegradable. Lactose is the main carbohydrate in dairy wastewater which serve favorable environment for growth and an increase in anaerobic bacteria.

4.2.1 Temperature

The average temperature of dairy effluents ranges from 17 to 18 °C during winters and 22–25 °C during summers. Higher temperature of wastewater not only adversely affects the ecosystem and provides favorable condition for growth of phytoplankton and other aquatic life forms (Tikariha and Sahu 2014). This temperature serve ambient environment for growth of various pathogenic microorganisms and insects.

4.2.2 Hydrogen Ion Concentration (pH)

A wide variation in pH ranging from 4.7 to 11 is observed in dairy wastewater. Liquid acidification by lactic acid fermentation of dairy wastewater on prolonged exposure to anaerobic conditions leads to decrease in pH. The variation in pH value affects survival of various micro-organisms and the quality of soil as well (Tikariha and Sahu 2014).

4.2.3 Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)

Dairy wastewater characterized by high BOD and COD values ranging from 350 to 1500 mg/L, respectively which is mainly due to the high organic load of rapid assimilable carbohydrate, slowly degrading proteins and lipids, detergents and milk byproducts (Venetsaneas et al. 2009). The COD value depicts organic strength of effluents; its measurement determines the waste water quality in terms of the total quantity of oxygen required for oxidation to CO_2 and H_2O. BOD can be defined as the amount of oxygen required by bacteria in aerobic condition to decompose organic matter present in waste water.

4.2.4 Suspended Solids

Proteins, fats and other impurities like sand particles forms bulk of sediments in dairy effluents. Although the concentration of settleable solids in the dairy wastewater is low, yet periodic cleaning is required as they may cause clogging to sewage pipes.

4.2.5 *Total Nitrogen (TN) and Total Phosphorous (TP) Concentration*

Nitrogen compounds are mostly in the form of urea, uric acid, ammonical nitrogen, nitrate and nitrite. The wastewater from the dairy and butter plants shows 4.2–6% of the TN concentration and 0.6–0.7% of the TP content which may be responsible for increased eutrophication in receiving water bodies.

4.3 Dairy Industry Wastewater Treatment Processes

The present day dairy effluent processing plants are designed to achieve minimum waste discharge to environment, recycling/reuse of wastes, and maximum resource recovery of milk products as well as to prevent depletion of environment. Primary and secondary treatments are generally performed to remove contaminants from dairy wastewater. Primary treatment includes physical screening and chemical treatment methods while secondary treatment involves use of various methods like biological treatment, physico-chemical treatment and membrane treatment methods (Fig. 4.1). Combination of different methods and new innovations can be used to achieve high performance and efficiency to treat dairy waste. For example,

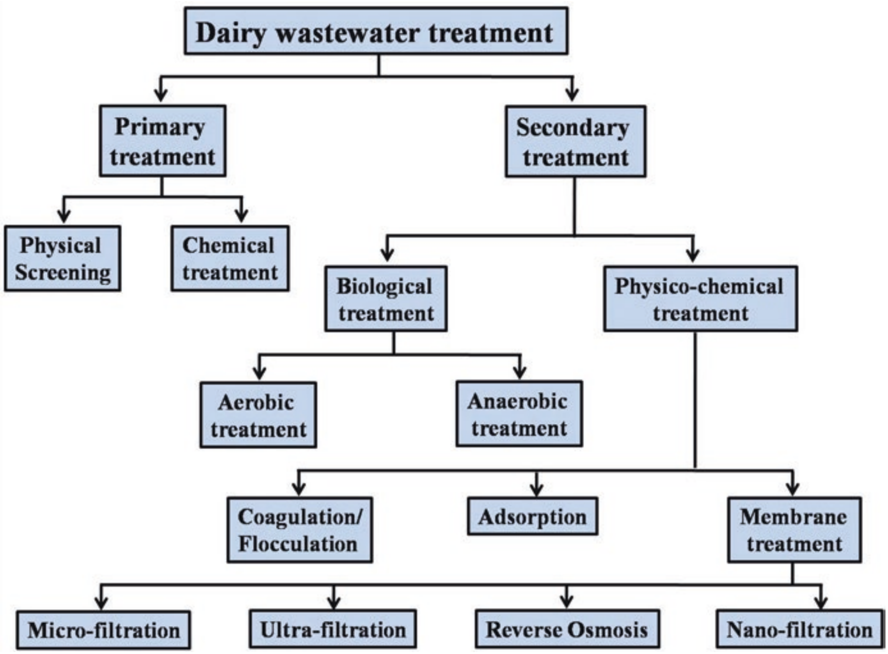

Fig. 4.1 Overview of methods involved in dairy wastewater treatment

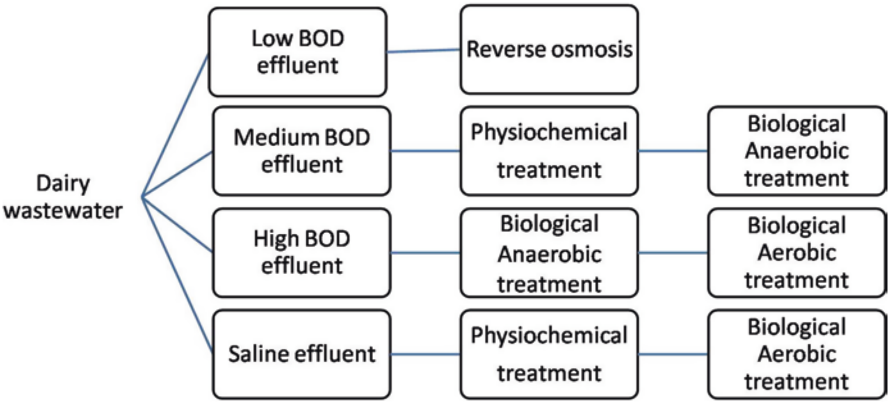

Fig. 4.2 Treatment of waste water through combination of physical, chemical and biological process. (Adapted from Environment Protection Authority (EPA) 1997)

aerobic-anaerobic combination treatment gives better results; physico-chemical treatment methods may be combined with the aerobic and anaerobic treatment in order to reduce the energy consumption and better recyclying (Fig. 4.2). Membrane treatment methods (RO/NF/UF) can be combined with the primary treatment methods, biological methods or with the physico-chemical treatment methods which can be proved to show promising results in waste water management. In order to reduce the cost and energy requirements and to meet the water quality requirements, new innovative and more compact equipment are need to be designed. Judicious use of water and its recycle will reduce the volume of waste generation to a great extent. Industrialist should use raw materials that are less toxic for the environment and government should have a check on quality control. Various conventional treatment processes are existing but the treatment methodology selected should be comprehensive and safe enough so as to safeguard the environment and life. The conventional treatment methods based on pond and land system are sustainable, require less investment and operational cost and are very effective in reducing BOD and bio-degradable pollutants. Some of the dairy wastewater treatment strategies are discussed in the following sections.

4.3.1 Physical Screening

The dairy industry waste water screened physically to remove large debris that may cause downstream clogging and damage to pumps. Delay in the physical screening of the dairy effluents may lead to rise in COD due to solid solubilization. It also promotes total oxygen depletion due to high organic load, thus results in anaerobic condition and affects aquatic life and subsequently creates environmental damage.

4.3.2 Chemical Treatment

Chemical treatment includes processes like reagent oxidation or pH balance which are useful for the removal of colloids and soluble contaminants present in dairy effluents. The dairy industry wastewater shows pH range in between 4.7 and 11 and poses side effects as it could be highly detrimental to microbiological assemblies in biological processes as well as it increases the corrosion of pipes and, therefore, it should be corrected to reduce its damaging effects. Treatment of cheese waste water with $FeSO_4$ and H_2O_2 showed 80% of fat removal. Electrochemical treatment is another method which involves the use of ion electrode to treat simulated dairy wastewater. It is very efficient in treating nutrient rich wastewaters such as generated from restaurant wastewater. Some researchers use iron electrode while others use aluminium electrode (Sengil and Ozacar 2006). The use of aluminium electrode is effective in removal of COD, nitrogen and turbidity up to 61%, 81% and 100%, respectively (Tchamango et al. 2010). In this method, COD is measured by double beam UV visible spectrophotometer, total nitrogen is measured by Kjeldahl method while chlorine is measured by titrimetric Vollhard method. COD removal by electrochemical treatment employs electro-coagulation, electro-floatation and electro-oxidation. Sludge and scum generated from electrochemical treatment can be dried and used as a fuel in boilers and for the production of fuel-briquettes (Kushwaha et al. 2010). It has many advantages as it offers high removal efficiencies in compact reactor with simple tools for control and operation process and high potential to reduce pollutants. The EC process was found to be very effective as the process yielded 84% COD and 86% color reduction at current density 178 A/m^2, initial pH 6 and electrode gap 20 mm in 2 h of treatment.

4.3.3 Physico-chemical Treatment

In dairy industry, physico-chemical treatment process destroys and reduces the milk fat and protein colloids. In dairy effluents fat, oil and grease (FOG) are major contents to be treated which is generated in production of unskimmed milk, separation of milk and whey, cheese and butter but these generally do not occurs with skimmed milk. By increasing temperature in waste water treatment, separation of fat may be reduced (Carvalho et al. 2013; Karadag et al. 2015). In dairy waste water, the precipitation of protein and fat content removed by employing thermal coagulation, thermo-calcic coagulation and using various chemical compounds such as aluminum sulphate, ferric chloride, and ferrous sulphide (Kasmi et al. 2017; Rusten et al. 1993). The method of dissolved air flotation is more productive by reducing organic load and disrupted protein and fat colloids with coagulants ($Al_2(SO_4)_3$, $FeCl_3$ and $FeSO_4$) and flocculants. This method employs expensive and synthetic chemicals which creates problem to environment and also less removal of soluble matter obtained (Gupta and Ako 2005). Some researchers showed that natural coagulation can be obtained by using certain lactic acid bacteria. This bacterium denatures milk protein in waste water and converts lactose to lactic acid. The use of carboxymethyl cellulose (CMC) with lactic acid bacteria removes the total COD up to 65–78%. The COD removal rate gets reduced 49–82% with chitosan (Dyrset et al. 1998; Seesuriyachan et al. 2009). The physico-chemical analysis of polluted water is essential before used for drinking, domestic, agricultural or industrial purposes because it helps us to get an idea about the quality of water and to compare results of different physico-chemical parameters values with the standard values. Analysis of different samples for pH, color, hardness, chloride, alkalinity, TDS etc. have been performed by researchers to test the physico-chemical parameters and the results are then compared with drinking water quality standards set by World Health Organization (WHO). The physico-chemical treatment consists of processes like coagulation/flocculation, adsorption and membrane processes which include Microfiltration (MF), Ultra filtration (UF), Reverse Osmosis (RO) and Nano-Filtration (NF).

4.3.3.1 Coagulation/Flocculation

The coagulation-flocculation process are widely used in treatment of waste water by removing suspended and solid particulates, and decreasing BOD and COD by clearing the turbidity of waste water. Treatment of dairy effluents by different combinations of coagulants such as iron chloride ($FeCl_3.6H_2O$), aluminum sulfate ($Al_2(SO4)_3.18\ H_2O$) and calcium hydroxide $Ca(OH)_2$ showed effective results but the synthetic chemicals are expensive and responsible for various environmental issues (Gupta and Ako 2005). The performance of a particular coagulant is basically depends upon the quality of the wastewater. Addition of coagulants causes destabilization of the particulate matters present in the waste water followed by particle collision and floc formation which results in the sedimentation. There are a variety of inorganic coagulants used in water treatment plants. Alum was found to be most effective coagulant in reducing solids, organics and nutrients in the dairy industry effluent (Hamoda and Al-Awadi et al. 1996. Ferric chloride showed better results in the removal of COD, suspended solids and color as compare to alum. Performance of the coagulants is mainly dependent on pH and dosages (Song et al. 2004). Inorganic coagulants have some disadvantages like they may result in the production of huge volume of sludge and aluminum or iron salts may retain in the treated water. Synthetic polymeric coagulants are found to have some advantages over these inorganic coagulants. Polyaluminium chloride is one of the most commonly used polymeric coagulants used in wastewater treatment. Treatment of secondary effluent with polyaluminium chloride at pH 6.0 resulted in removal of 95% turbidity as compared to alum and ferric chloride (Delgado et al. 2003). Even though polymeric coagulants produce lesser amount of sludge and its effectiveness is not good and it dependent on the pH of the water. Uses of these coagulants are restricted because of the production of chlorinated and several other by-products in water which impart adverse impact on water bodies (Lee et al. 1998). Chitosan is a high molecular weight organic compound obtained from natural source like shells of shrimp, crab and lobster and it is biodegradable and non toxic in nature. Chitosan at very low dosage (10 mg/L) is found to be a better coagulant compared to inorganic and organic coagulants. Performance of chitosan depends on pH (Krajewska 2005). Activated charcoal treatment has been performed after coagulation process eradicates the color and odor of dairy waste water to improve taste of drinking water (Hargesheimer and Watson 1996). Generally coagulation and flocculation are applied in the primary treatment and only in some cases in the secondary and tertiary treatment of dairy waste water. With the application of certain lactic acid bacteria, which denatures milk proteins in the dairy wastewater by fermenting soluble lactose to lactic acid, natural coagulation in the dairy effluent could be achieved and COD removal obtained more than 90% at 0.01 g/L of protein content and 10–25% at 0.7–0.8 g/L of milk sugar (Seesuriyachan et al. 2009; Dyrset et al. 1998).

4.3.3.2 Membrane Treatment Processes

Dairy industries have been producing large quantity of waste among all agro-food industries and need efficient and economically sustainable treatment technology. Membrane treatment process is extensively used for the treatment of dairy industry wastewater. Dairy wastewaters contain high concentrations of organic compounds such as proteins, carbohydrates, lipids and high BOD and COD. Suspended solids and suspended oil-grease are also present in high concentrations. The dairy wastewaters, being different in their flow rates, volume, pH and the amount of suspended solids, have become difficult to be treated properly (Demirel et al. 2005). To overcome this difficulty, the dairy industries need to develop more elaborate and cost-effective treatment systems. Nowadays, biological wastewater treatment is combined with membranes. The membrane treatment process are considered better than conventional biological processes because they have higher degradation efficiency, better quality of treated water, controls suspended solid, retention of all microorganisms, and the operating conditions can be easily controlled (Xing et al. 2003; Bouhabila and Ben 2001). Due to the presence of membrane, sludge is totally rejected. A JLMBR (jet loop membrane bioreactor) is used in the treatment of dairy wastewaters. Membranes used in dairy waste water treatment can be cleaned by backwashing with compressed air (CA) and also by the use of chemicals (first immersing in alkali solution, then in acidic solution). The dairy waste water passed through a cross flow of reverse osmosis membrane system generates very good quality of permeate water. Generally, the membrane used for dairy waste water treatment is made up of cellulose acetate and have more than 99% NaCl rejection (Sarkar et al. 2006). Suarez et al. (2014) used RO spiral-wound membrane (8.4 m^2 surface area) in pilot plant and obtained high quality boiler water. An effective RO membrane should have good retention capability, proper mechanical strength, chemical and thermal stability, long service life and should be cost-effective (Berk 2009). RO membrane has limitations regarding the protection against fouling. Fouling generated by dairy waste water can be reduced using spiral-wound RO membrane with

MF pretreatment before RO, in order to arrest the molecules that are bigger in size such as the fat molecules. RO membrane treatment caused a decrease in BOD and COD values of wastewaters to 8 mg/L and 16.5 mg/L, respectively. This technology uses a semi-permeable membrane that allows the movement of certain compound and monitoring the passage of other components which not to pass in liquid medium. Its affinity for certain compounds makes its perfect for separation of waste water treatment (Saxena et al. 2009). Membrane separation process involves resistant to temperature change which helps to prevent denaturation of proteins from dairy effluents. It also employs various separation aspects using ion exchange and solution diffusion that leads to selectivity in separation. Membrane separation process requires minimum maintenance and can be optimized according to need and no efficient manpower is needed to handle it.

4.3.3.2.1 Micro-filtration

Microfiltration is a low pressure driven membrane filtration process. In dairy industry, this process is used for bacterial reduction and fat removal in milk and whey.

4.3.3.2.2 Ultra-filtration

Ultra filtration is a medium pressure driven membrane filtration process. UF has applications in decalcification of permeates from dairy industry wastewater and in reduction of lactose concentration from milk. In ultra filtration process, the solutes and suspended effluents vary in their size which triggers movement due to hydrostatic forces and performs separation in two phases: one is permeate and another retentate. The ultra filtration process is commonly used for the separation of whey from dairy waste. Another modification of ultra filtration is high performance tangential flow ultra filtration (HPTFF) which exploits the differences in size and charges on particles leads to higher selectivity (Cheang and Zydney 2003). Luján-Facundo et al. (2016) used ultrasound in combination with two membrane systems which is flat sheet and tubular nature and suggested that the ultrasound unit with membranes is effective in cleaning of dairy wastewater at lower frequencies of 20–25 kHz.

4.3.3.2.3 Reverse Osmosis

Reverse Osmosis (RO) is a high pressure driven membrane treatment process. RO treatment of dairy waste water is used to generate water for reuse in plant and to reduce the effluent volume. Large volume of effluents produced during the starting, equilibrating, rinsing and stopping of the dairy processing units. Reverse osmosis treatment of these waste water produces purified water which can be re-used as boiler make-up water and for cooling purposes in the dairy industries. Treatment of

100 m^3/day of wastewater with 540 m^2 RO units produced 95% of water recovery (Vourch et al. 2008).

Reverse osmosis widely used in dairy industry waste water treatment establishes highest water quality with applications of high retention capacity of effluents, no interference to cleaning agents, no effect to chemical and thermal changes, resistant to microbial interactions, long durability and cost effective (Berk 2009). In some instances, RO shows limitation when applied on removal of organic matters (Bódalo-Santoyo et al. 2004). In dairy industry RO can be used in one step process or in combination to nanofiltration and adds on with another RO stage (Vourch et al. 2008).

4.3.3.2.4 Nano-filtration

Nano filtration (NF) membrane separation process is medium to high pressure driven membrane treatment process. NF membrane treatment process operates at lower pressure, lower energy consumption and shows higher permeate recoveries than reverse osmosis (RO) membrane treatment process, hence NF is becoming a viable alternative to the conventional treatment over RO. Tertiary treatment of wastewater effluents by NF showed an efficient COD removal of 98% while the total nitrogen and phosphorus removal of 86% and 89%, respectively. The compounds of high molecular mass can be efficiently removed by NF. In this process, the permeate obtained from membrane bioreactors is nanofiltrated to generate reusable waste water. Increasing the cross-flow velocity of nanofiltration membrane, a rise of 18% was observed on the permeability with wastewater which further improved hydrodynamic conditions of the system. Due to this, the thickness of boundary layer near the surface of membrane reduces and so, fouling is reduced. The permeate obtained from NF can be used for washing floors, trucks and all external areas which require low quality water. Vourch et al. (2005) treated synthetic wastewater comprising whole milk, skim milk and milk whey by nanofiltration. The NF permeates showed a COD of 87 mg L^{-1} and calcium concentration of 3.2 mg L^{-1} (Andrade et al. 2014).

4.3.4 Biological Treatment

The biological treatment for purification of effluents assimilates all the dairy wastewater components and considered as one of the most reliable method for dairy effluent treatment. The biological treatment of dairy waste water includes both aerobic and anaerobic treatment processes. Aerobic and anaerobic treatment of the organic effluents have been found to be effective due to its performance for COD and BOD removal but there are a few drawbacks like anaerobic treatments degrades nutrients partly whereas aerobic processes consumes high energy. All conventional biological processes available for treatment of dairy industry wastewater may not be very feasible due to large land requirements and high operational cost.

4.3.4.1 Anaerobic Treatment

Anaerobic treatment is beneficial for treating wastewater containing high organic content (Rajeshwari et al. 2000). The treatment of dairy waste water is also performed on low cost scale by using anaerobic and facultative systems but it showed less effectiveness towards waste water treatment (Bhatia and Goyal 2014). For the treatment of dairy wastewater UASB reactors, hybrid digester and anaerobic sequencing batch reactors (ASBR) are also employed. Up flow anaerobic sludge blanket (UASB) has been used for treating dairy effluents. A UASB reactor during anaerobic treatment of cheese whey achieves more than 90% of COD reduction (Demirel et al. 2005). UASB reactors in dairy waste water treatment have the organic loading rate of up to 6.2 g COD per day and could be increased up to 7.5 g COD per day. The HRT and loading range of UASB reactors are lies in range of 2.4–13.5 kg COD at HRT of 3–12 h and COD reduction ranged from 95.6% to 96.3% in 3 h. A UASB reactor shows limitation in waste water treatment due to accumulation of fat, oils and grease (FOG) and subsequently increases the time of hydrolysis. To overcome these problems, Passeggi et al. (2012) suggested UASB reactor with modified scum extraction device and lamella settlers. They showed that modified version is efficient in operational unit and is cost effective. Kothari et al. (2017) have reported the production of methane and hydrogen gas using strains of *Enterobacter aerogens* and methanogenic bacteria from dairy waste water. The different concentration of dairy waste water showed maximum biomass growth rate (0.21 per hour) at 75% concentration. The production of methane (190 CH_4 ml/g-COD and 0.59 LCH_4 per litre) and hydrogen up to 105 ml H_2/g-COD and 0.562 L-H_2 per litre was reported from dairy waste water. Hybrid anaerobic digester used in combination with upflow sludge blankets and fixed bed designs at an influent substrate concentration of COD in dairy effluent, the COD removal rate obtained up to 90–97% at an OLR between 0.82 and 6.11 kg COD/(m^3 day) at HRT range of 4.1–1.7 (Strydom et al. 1995). When anaerobic digester used for the treatment of dairy effluent, the methane removed up to 0.354 m^3 CH_4/kg at HRT of 1.7 days. ASBR are reported to enhance the efficiency of dairy effluent treatment in non fat dry milk processing and removes COD and BOD up to 62% and 75%, respectively at HRT of 6 h at low temperature (Banik and Dague 1997). The change in temperature from 5 to 20 °C reduces 62–90% of COD and 75–90% of BOD at HRT between 6 and 24 h for soluble organic loads. ASBR also provides 26–44% volatile solid removal in two stages thermophilic ASBR while removal of volatile solids in mesophilic ASBR systems ranges from 26% to 50% for dairy effluents (Dugba and Zhang 1999).

The advantage of anaerobic treatment over aerobic treatment is that there is no need of aeration and a relatively low area is needed to carry out this process. Anaerobic treatment is of two types: single-phase anaerobic treatment and two phase anaerobic treatment. The single phase anaerobic treatment employs use of filter reactors for low concentration of suspended solids. Removal of COD ranges from 78% to 92% by the use of laboratory-scale plastic medium anaerobic filter reactor. In order to treat very dilute dairy wastewater, an upflow anaerobic filter reactor (UAF) is used. A pilot-scale UAF provides more than 85% COD and 90% BOD removal (Ince 1998). The conventional single phase anaerobic treatment is now being replaced by two phase anaerobic treatment of waste water in which the performance of acid phase (acidogenic) reactor is of paramount importance (Demirel and Yenigun 2002). The two-phase anaerobic treatment system is especially used for the removal of high concentrations of suspended organic solids from wastewaters generated from food and agricultural industries (Guerrero et al. 1999; Demirel and Yenigun 2002). In two-phase anaerobic treatment system, first phase is acidogenic reactor and the second phase is methanogenic reactor (Alexiou et al. 1994). Anaerobic fermentation of wastewaters generated from cheese-making process showed that up to 19% of initial sugar which is converted to volatile fatty acids. Biodegradation of whey generates *n*-butyric acid which can used further. About 95% of carbohydrates, 82% of proteins and 41% of lipids can be degraded by acidogenesis of dairy wastewaters. Both methods are aimed to high extent conversion of waste into methane and other gases that can be used as fuel. Investigation of two-phase anaerobic treatment of dairy waste showed 92% removal of COD in HRT of 4 days. In order to obtain the effluent discharge limits of dairy industry wastewaters, anaerobic treatment process is used in combination with aerobic treatment process. This process aims at reducing BOD by more than 90% and COD removal by 85%. The industrial scale treatment facility of certain factories consists of an anaerobic equalization tank, followed by an UASB and aerated lagoons. Treatment of wastewater from milkhouse and milk parlour by wheat straw biofilter in an aerobic-anaerobic mode at temperature of 8–14 °C showed the reduction of TSS; oil, fat and grease; and COD by 89%, 76% and 37%, respectively (Shah et al. 2002). Uma Rani et al. (2014) investigated the influence of two step sono-alkalization pretreatment anaerobic reactor for high efficiency resource recovery from dairy waste activated sludge (WAS). They reported COD solubilization, suspended solids reduction and biogas production. In optimized condition COD solubilization, suspended solids reduction and biogas production achieved up to 59%, 46% and 80%, respectively, these values are higher when compared with controls. Banu et al. (2008) treated the dairy waste water using anaerobic and solar photocatalytic oxidation methods. They carried out laboratory scale hybrid upflow anaerobic sludge blanket reactor (HUASB) with the working volume of 5.9 L. The organic loading rate (OLR) applied in the range of 8–20 kg COD/m^3 for 110 days. They treated dairy waste water in an anaerobic condition at OLR rate of 19.2 kg COD/m^3 day in combination to secondary solar photocatalytic oxidation treatment. The optimum pH was found to be 5 and catalyst loading up to 300 mg/L for solar photochemical oxidation. The removal of COD from primary anaerobic treatment was observed up to 62% using TiO_2 in secondary solar photocatalytic oxidation whereas 95% COD removal was observed when anaerobic and solar photochemical treatment integrated in dairy waste water treatment. All these parameters make anaerobic treatment followed by solar photocatalytic treatment to be efficient treatment process in dairy industry for waste water treatment and management.

4.3.4.2 Aerobic Treatment

Aerobic treatment process involves biological treatment method to degrade organic matter into carbon dioxide, water and other components by inhabiting microbes grown in oxygen rich environment. Aerobic treatment includes conventional activated sludge process, rotating biological contactors and conventional trickling filters.

Sequential batch reactor (SBR) has various loading capacity and effluent flexibility due to which it becomes a promising technology in dairy waste water treatment. In the treatment of dairy wastewater, a reduction in COD by 91–97%, TS by 63%, volatile solids (VS) by 67%, TKN (total kjeldahl nitrogen) by 75% and TN by 38% were reported by SBR. Moving bed biofilm reactor (MBBR) shows good results when used for treatment of dairy effluents. The COD reduction scores up to 80% and TN up to 13.3–96.2% was reported with MBBR. Membrane bioreactor shows good performance with 95% reduction of 13.3 kg/m^3 COD and 6.5 kg/m^3 BOD. TKN decreased by 96% and TP by 80%, during ice-cream factory effluent treatment. In dairy industry, production of cheese generates large amount of whey constitutes of increased organic matter of 33% of total waste water volume which sums off to highest polluting load that needs treatment in urgent. The gasification process applied for degradation of whey contents involves use of high energy gases like hydrogen and methane (Mozaffarian et al. 2004; Osada et al. 2008; Williams and Onwudili 2006). Aerobic granules are also employed for dairy waste water treatment, it is a kind of biofilm constitutes of self immobilized cells. Aerobic granules due to granule characteristic widely developed for treating wastewater containing high organic loads. Schwarzenbeck et al. (2005) reported the efficiency of aerobic granules for dairy waste water. The total COD removal rate of 90%, total nitrogen 67% and total phosphorous 67% were obtained for volumetric exchange ratio of 50%. Aerobic treatment mostly used for dairy wastewater treatment although they are less efficient in treatment of high lactose concentration which induces microbial growth and low buffering capacity resulting in rapid acidification (Nadias et al. 2010).

4.3.4.2.1 Activated Sludge Treatment Process

Activated sludge treatment process is widely used in treatment of dairy waste water which is rich in fats, lactose and proteins. The removal of carbon, nitrogen and phosphorus are best obtained steadily when used with alternate anoxic/anaerobic and aerobic phases (Gutierrez et al. 2007; Kushwaha et al. 2011). Activated sludge system constitutes of microorganism like bacteria and protozoa that removes contaminants from waste water. This treatment system improves the efficiency of waste water treatment and is advantageous to ecological system because of interaction to microbial entities (Sanz and Kochling 2007). In activated sludge treatment there is abundance of protozoa and they are the key player in microbial food web and its diversity stipulates its performance. Madoni (2003) prepared sludge biotic index (SBI) on the basis of presence and absence of protozoans which indicates the performance and condition of treatment plant and gives numeric value routinely. Tocchi et al. (2012) monitored industrial three reactor plant accommodated with 45m^3 day^{-1} of waste water and applied different regimes of aeration and correlated with performance efficiency of bacterial and protozoans in activated sludge treatment process. The plant treated with on/off cycles of blower (45/15, 15/15, 15/45, 30/30, 30/45 and 30/60 min) provides O_2 in range of 30.2–90.6 kg O_2 day^{-1}. When applied O_2 is 45.4 kg O_2 day^{-1}, COD removal decreases to about 70% from 88% to 94% under aeration regimens 15/45 and 30/60 whereas ammonium ion settled at lowest aeration regime 15/45. Bacterial viable counts and denaturing gradient gel electrophoresis (DGGE) are used to characterize microbes present in activated sludge. After that they observed similar abundance of bacteria and protozoa in three aerated reactors but showed changes when aeration regimen changes. At blower range of 15/45 and 30/60 regimen showed decreased population of protozoa and less SBI reflects less efficiency of activated sludge reactors. There are changes obtained in bacterial community structure when aeration regimen changed and low similarity with DGGE profiles. When dairy waste water was treated with fungal pre-culture, the final yields showed COD removal of 75% on whey and 72% on molasses. Fungi like *Aspergillus niger, Mucor hiemalis* are used for bio-augmentation of activated sludge forming microorganisms present in dairy wastewater. Increase in COD on BOD ratio between inlet and outlet of biological tank is reduced from a range of 451% to 1111% before the addition of fungi to a range of 257–153% after bio-augmentation with fungi (Djelal and Amrane 2013).

4.3.4.3 Use of Microorganisms for Biological Treatment

Microorganisms are widespread, diversified and essential for various life forms including humans. Microbial entities have tremendous properties to degrade the organic loads. Microorganisms make strides on many compounds present in dairy effluents. It is necessary to have information about microbiota composition and its biochemical properties, metabolic activity, physicochemical condition with relation to pollutants to achieve efficient biological waste water treatment. There are various heterotrophic microorganisms present in dairy waste waters such as bacteria including *Psedomonas fluorescens, Pseudomonas aeruginosa, Bacillus cereus, Bacillus subtilis, Enterobacter, Streptococcus faecalis, Escherichia coli* and yeast like *Saccharomyces, Candida, Cryptococcus*.

Dairy waste water constituting of protein, fats and nitrogenous components make it perfect nutritious package for the growth of microbes, and can be used as culture media. The culture media contains mainly carbon, nitrogen, sulphur, phosphorus in which nitrogenous contents are quiet expensive but use of dairy industry waste is an option to prepare culture media. Various studies focused on this aspect of dairy effluents (Andualem and Gessesse 2013; Farhana et al. 2011).

Bio-augmentation method shows positive impact when used with fungal addition on whey and dairy effluents treatment showed removal of COD was increased from 55% to 75% and also significant reduction was reported in COD on BOD ratio. Djelal and Amrane (2013) used the fungal consortium (combination of three fugal species including *Aspergillus niger, Mucor hiemalis* and *Galactomyces geotrichum)* in treatment of dairy waste water. They performed both lab scale and pilot scale using bio-augmentation method for the treatment. They reported that after addition of fungal inoculums COD removal percentage increases from 55% to 75% (Djelal and Amrane 2013). In bioaugmentation process different inoculums made up of individual strains were used which was designed to perform degradation of waste present in local waste water, whereas the degradation capacity of microbial consortium is often more than any single strain and depends on cooperative activities within microbial consortium (Huban and Plowman 1997). The development of inoculum not only targets degradation of dairy wastewater in situ but also persists after getting interacted with microbial community and degradation of effluents (Yu and Mohn 2002). Researchers also designed inoculum constituting of mixed culture of 15 bacteria which showed high degrading capacities of fats, oils and proteins present in organic load of dairy wastewater (Tano-Debrah et al. 1999). Loperena et al. (2009) prepared a consortium of eight isolates which are identified by 16s rRNA gene sequencing includes *Bacillus, Pseudomonas* and *Acinetobacter* and these were tested for their COD removal efficiency and compared with bioaugmentation inoculum. This consortium proves efficiency in COD removal up to 57% which is near to commercially available inoculum that provides 63% COD removal. In terms of nutritious value, it has higher protein content up to 93% while commercial inoculum possesses only 54%. There are different genera which have been isolated from dairy effluents such as *Sporolactobacillus sp., Citrobacter sp., Alcaligenes sp., Bacillus sp., Pseudomonas sp.,* and *Proteus sp.,* (Rajeshkumar and Jayachandran 2004). Kosseva et al. (2003) used *Streptococcus* strain and *Bacillus* strain for the bioremediation of cheese whey. The fat degrading microbes such *Bacillus sp.,* (Gowland et al. 1987; Becker et al. 1997), *Acinetobacter sp.* (Wakelin and Forster 1997; Keenan and Sabelnikov 2000), *Rhodococcus sp.* (Wakelin and Forster 1997; Keenan and Sabelnikov 2000), and *Pseudomonas sp.* (Watanabe et al. 1977; Pabai et al. 1996) were isolated from different resources. These microbes can be used for the treatment of dairy wastewater. Microalgae consortia are used in dairy wastewater treatment for nutrient removal and biodiesel production (Qin et al. 2016). Microalgae generates significant amount of biomass and are suitable to convert it into biodiesel (Chisti 2007; Ahmad et al. 2011). Microalgae cultivated systems reinforces higher COD removal (57.1–62.86%), TN removal (91.16–95.96%) and higher biomass and lipid productivity of 730.4–773.2 mg/L/day and 143.7–153.6 mg/L/day, respectively than those of mono-algae cultivation (674.3 and 142.2 mg/L/day, respectively) (Qin et al. 2016). Dairy effluents (DE) characterized by high BOD and COD, high pH, increased concentration of ammonia, phosphorus and particulates of cleaning and sanitizing compounds are suitable for growth of microalgae and can be used as biofertilizers which may helps small and medium scale farms to improve economy as well as produce biomass (Lincoln et al. 1996; Lu et al. 2015). A two-stage treatment of dairy effluents employs immobilized *Chlorella pyrenoidosa* in the first stage and sand bed filtration technique in the second stage. This two-stage treatment has proved to be a cost effective technique employed to treat the high organic load of dairy effluents (Yadavalli and Heggers 2013). Besides treating these effluents, algal cultivation in the wastewater produces algal biomass which is used for aquaculture, animal and human feed as protein complements, food additives, biogas and fuel production and bio-fertilizer (Cohen 1999). Other algal species such as *Spirogyra* (Khalaf 2008), *Caulerpa lentillifera* (Marungrueng and Pavasant 2005), and *Chlorella vulgaris* (Acuner and Dilek 2004) used in removal of color from dairy waste water by biosorption. They are suitable in conversion of dairy waste into triglycerides which serves as biodiesel and also produces high biomass in comparison to plants. In recent years these algal species are taken seriously for biodiesel production (Barnwal and Sharma 2005). Recently oleaginous microorganisms have become the hot topic in biochemical engineering for biological treatment of wastewaters due to its advantage of easy operation in basic bioreactor and production of valuable bio-products such as microbial oil, chlorophyll, carotenoid, polysaccharides, citric acid, microbial biomass etc. (Huang et al. 2017). Kothari et al. (2012) reported that algal strain of *Chlamydomonas polypyrenoideum* reduces nitrogen content up to 90% in 10 day and 96% reduction in phosphorus content on the 15th day of culture and substantially decreasing dairy rejects. It showed increase in algal biomass production which reinforces the 42% increase in lipid content in 10 days of culture which suggested its role in production of biofuel as well as in phycoremediation. Researchers reported that *Acutodesmus dimorphus* microalgae degrade dairy effluents by lowering the amount of suspended and particulate pollutants. It increases total biomass with overall 25% lipid and 30% carbohydrates which may be used in production of biodiesel and bioethanol (Chokshi et al. 2016). In dairy industry the resource recovery method can be used for conversion of biomass to produce energy producing compounds such as animal feed, ethanol and glycerol using filamentous fungi such as *Aspergillus oryzae* and *Neurospora intermedia* because they produce enzymes capable of breaking complex macromolecules as well as establishes fungi for waste water treatment in environment friendly way (Terabayashi et al. 2010; Ferreira et al. 2013, 2016).

Cultivation of *Chlorella* sp. showed capacity to produce biomass and remove nutrient from raw dairy waste water. The indoor bench-scale cultures produced maximum biomass of 260 mg L^{-1} day^{-1} while that of outdoor pilot-scale cultures produced 110 mg L^{-1} day^{-1}. Dairy effluent contains high concentration of nitrogen and phosphorus which are harmful for environment. Even after biological treatments such as anaerobic digestion of waste waters COD, TN and TP concentrations were found higher than the allowable discharge limits. This led to the need of further developments in the treatment of dairy industry wastewater in order to reduce the level of COD, TN and TP. Oleaginous microalgae have a shorter growth time, higher lipid content and can be cultivated in abandon land and wastewater so they can be used as biofuel feedstock in place of food crops. Culture of microalgae in raw dairy wastewater showed a continuous reduction of TN in the first 2 days of all treatments (Lu et al. 2015). Nitrogen can be reduced either by assimilation by algae (Razzak et al. 2013) or by air stripping (Li et al. 2011). The *C. zofingiensis* cultivating in raw dairy wastewater showed 82.70% of TN removal (Zhu et al. 2013). In anaerobic digestion method, the cultivation of *Chlorella* sp. in dairy wastewater with dilution in multiples of 10, 15, 20 and 25 showed a biomass growth rate of 0.282, 0.350, 0.407 and 0.409 mg/L/day, respectively (Wang et al. 2010a, b). Neerackal et al. (2016) has reported the increase in ammonia emission from dairy waste water *using Alcaligens faecalis* strain 4 by performing treatment in aerated batch reactors which are filled with air or pure oxygen. The air is directly interacted with waste water and ultimately results in removal of total ammonical nitrogen (TAN) in dairy waste water. The intermittent oxygenation reduces the rate of oxygen consumption up to 95% whereas TAN is achieved at same extent with continuous aeration. On the basis of biomass balance nitrogen concentration up to 4% of TAN is released in form of NH_3 gas and large proportion is retained in form of microbial biomass (58%) or transformed into nitrogen gas (36%). They suggested that *Alcaligens faecalis* strain 4 have high efficiency to NH_3 emission and also environment friendly for treatment of dairy waste water. Porwal et al. (2015) extracted the bacterial isolates, yeast isolates and also prepared the mixed culture of these isolates. The mixed culture showed highest removal efficiency of dairy effluents using aeration for 48 h. Bacterial isolates showed effective reduction in EC, TSS, TDS, TS and COD whereas yeast isolates showed effectiveness in decreasing turbidity as compared to bacterial isolates and mixed culture. It was suggested that addition of isolates or mixed culture can be used to increase the performance of activated sludge process and decrease the rate of bulking problem of organic load. Bacterial isolates proved to be best in treatment of dairy waste water. Further activated charcoal powder and sawdust proves to be efficient in removal of waste from dairy industry waste water.

4.3.4.4 Vermifiltration (Lumbifiltration)

The process of vermifiltration (Lumbrifitartion) involves the use of earthworm in filtration system for degradation of organic effluents and facilitates treatment of dairy waste water. This technology proves to be rapid, economic and produces stable detoxified and nutritious organic effluent. Firstly, the vermifiltration performed by Prof. Jose at University of Chile in 1992 (Sinha et al. 2008). Vermifiltration works on the basis of bio-oxidation process in which the interaction of earthworm and microbial community takes place and facilitates the modification and stabilization of organic effluent (Rajpal et al. 2014). The process of vermifiltration can be programmed at local scale and does not require sophisticated machinery, making it economic as well as environment friendly as compared to other treatment technology. It was also reported that aquatic macrophyte when planted on vermifilter bed inhabited by microorganism growth increases its bio filter activity and drive faster the degradation of organic effluents (Wang et al. 2010a, b; Tomar and Suthar 2011).

Eisenia fetida species of earthworm are widely employed in vermifiltration bed with stocking density of 10,000 worms/m^3 in worm active layer. Organic waste present in dairy waste water is convenient for the growth of microbial entities which provides moist environment to earthworms and promotes waste water treatment. Samal et al. (2017) used two vermifilters, first is *Canna indica* with macrophyte assisted vermifilter (MAVF) and other without macrophyte vermifilter (VF) using species of earthworm *Eisenia fetida*. The results indicated that MAVF have higher capacity of processing of organic effluent and nitrogen degradation in treatment process in regular manner without clogging whereas VF shows clogging within few weeks of treatment. The BOD and COD removal efficiencies achieved from MAVF was up to 80.6% and 75.8%, respectively while for VF, the removal efficiencies of BOD and COD were observed 71% and 66.1%, respectively. Displacement of TSS with MAVF and VF were found at the rate of 84.8% and 73.8%, respectively whereas no significant results were obtained for TDS removal.

The different processes used in the treatment of dairy industry wastewater have many advantages but they also have some disadvantages. The following table summarizes the advantages and disadvantages of various treatment methods (Table 4.1).

Table 4.1 Treatment methods and its advantages and disadvantages

Treatment methods	Advantages	Disadvantages
Aerobic treatment	High efficiency in the removal of COD, BOD and nutrients	Requires large area and large reactor size
	Excellence performance in regard to shock loading	High energy input requirement
Anaerobic treatment	Ideal for warm effluents having high COD and organic content	Reduced fats removal efficiency due to inhibitory action of fats to anaerobic process due to formation of long chain fatty acids
	No requirement of aeration	Reduced efficiency of continuous UASB reactor due to buildup of organic matter inside the reactor
	Low amount of excess sludge production	
Physico-chemical treatment	Highly efficient compared to biological treatment process	Availability of selective membranes in the market
	Product recovery is feasible	High initial as well as RMO cost
Membrane treatment	Low energy requirements	High equipment cost
	No phase changes involved	High flow rates used in cross flow feed can damage sensitive materials
	Flexible- is used in the separation, concentration and purification of a huge variety of materials	Poor separation performance if membrane manufacturing process is not precisely controlled

4.4 Recycling of Wastewater

Large amount of wastewater is generated by the dairy industry which accounts a major part of the argro-food industry. An effective approach to produce reusable water and reclaim nutrients of dairy wastewater are provided by membrane treatment processes particularly nano-filtration (NF) and reverse osmosis (RO) (Aydiner et al. 2014; Luo et al. 2011). The process of reverse osmosis allows RO permeate water to be recycled and the retentate can be used to feed animals (Selmer-Olsen et al. 1996). The treated water can be used for irrigation, washing, domestic purposes and in industries. However, during the treatment of dairy wastewater, flux declination occurs due to the formation of concentration polarization layer (CP) and membrane fouling by the proteins present in the wastewater (Luo et al. 2011; Seesuriyachan et al. 2009). Considering the environmental implications of wastewaters, aerobic biological treatments are generally employed which relies on conventional activated sludge plants (Tocchi et al. 2013). To reduce the organic load of dairy wastewater, membrane, chemical and physico-chemical methods are employed. However, either due to the use of external acid sources or flocculating agents, these processes have high operating cost (Seesuriyachan et al. 2009). Effective results were shown in the treatment and reuse of residual fermented dairy products using *Candida* strains, when physico-chemical and fermentation processes were combined (Kasmi 2016). For recycling of waste water an integrated isoelectric precipitation- nano-filtration (NF) – anaerobic fermentation can be used. Most of the proteins can be removed by isoelectric precipitation at pH 4.8 and subsequent centrifugation. NF membrane utilized to reduce fouling by pretreatment of MDW by precipitation at pH 7. High antifouling performance, increased permeability and acceptable permeate quality made NF270 membrane preferable for MDW treatment (Chen et al. 2016).

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Chapter 5
Treatment and Recycling of Wastewater from Distillery

Soni Tiwari and Rajeeva Gaur

Abstract Indian distilleries are using sugarcane molasses for ethanol production and generate large bulk of effluent containing high biological oxygen demand (BOD) and chemical oxygen demand (COD) along with melanoidin pigment. Melanoidin is a dark brown recalcitrant high molecular weight colour compound that causes several toxic effects on living system, therefore, must be treated before disposal. Detoxification/decolourization of different industrial wastewater is gaining importance for environmental safty and aesthetic values. Studies dealing with pure culture of bacteria, fungi, and yeast and their oxidative enzymes (peroxidase, laccase) in decolourization of industrial wastewater to develop a better understanding of the phenomenon of microbial decolourization. This chapter presents an overview of the characteristics of the distillery wastewater in terms of its toxicity and its biological treatment using microbial consortia system.

Keywords Distillery spentwash · Millard reaction · Xenobiotics · Melanoidin · Molasses

5.1 Introduction

Industrialization and urbanization have created great pollution havoc if properly not treated/managed, as these are essential for the development of any country, therefore proper management at economical cost is essential for sustainable environment. It is well documented that microbial system is the only alternative for safe treatment of industrial effluents as well as energy production in the form of methane and hydrogen along with biomass in the form of organic C, N, S and P. The nature is rich reservoir of almost all nutritional types of microorganisms, therefore, potentials of every group for human welfare is expected. However, microorganisms may

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R. L. Singh, R. P. Singh (eds.), *Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future*, Applied Environmental Science and Engineering for a Sustainable Future,
https://doi.org/10.1007/978-981-13-1468-1_5

be isolated and developed for various applications either alone or in consortium for bioremediation of xenobiotic compounds or for production of various microbial metabolites viz. antibiotics, ethanol or any organic acid, vitamins, hormones etc.

Microbial selection on the basis of fermentation process and nature of metabolites production require the optimization of other levels, like water activity, temperature, aeration pH along with nutrition as well as cultivation vessel i.e. fermentor or in a specific design bioreactor in order to achieve maximum productivity. Microbial system is the safest economical and eco-friendly approach to achieve microbial metabolite of human system. Therefore, the current status of the microbial system requires its applications in consortium for which the development of bioreactor is essential to achieve better productivity. In this context, the biosystem selection parameters as well as substrate utilization rate along with biomass and metabolites production should be assessed at the initial level prior to the application of microorganisms in a specialized bioreactor/fermentor.

Selection of the microorganism for industrial applications requires sealing up of the process, as much of the work are only established at laboratory scale in flask culture, while large scale production of metabolites by such microorganisms at commercial level is essential for the welfare of the society. Therefore, selection of such microorganisms and scaling up of the process at industrial scale should be assessed based on the resistance/tolerance towards the substrate concentration, temperature and aeration level for production of primary or secondary metabolites. The fermentation kinetics, also help in the selection of fermentation process where the substrate utilization rate, biomass production rate and rate of metabolite production should be assessed to achieve better productivity. In this approach, the rates of substrate utilization, biomass production and metabolite production should be essential in same scale if the rate of substrate utilization, and metabolites production is the same phase of the growth with the incubation period, then continuous fermentation will be the right approach, which is always economical even from the simple batch process.

Similarly, the growth rate of the microorganisms and cell size which initiate settling factor may also be taken in the account of the design of a bioreactor. However, temperature and aeration then be taken for side by side component for evaluation of complete design. The engineering and mathematical systems like thermodynamic and shearing stress, surface tension, ronold number, viscosity parameters etc. should also be applied during the design assessment. The basic principle in the design of a fermentor requires some of the essential inlets and outlets with the minimum openings in order to prevent contamination. Some of the microbial products in the form of gases that is methane and hydrogen production require a very specialized bioreactor. Different design likes Shulzer, Degremond, Aquatech, etc. have been adopted in a single or two vessels system have been adopted depending upon the nature of effluent. The high BOD and COD of the effluent may require different segmentation in the process according to the growth rate of microorganisms, as well as cultural condition at a particular phase of production. For example, methane production from distillery effluent or any other industrial effluent requires different technology depending upon BOD and COD levels of the effluent. The Shulzer technology has been adopted successfully in a single bioreactor in continuous system with the recycling of biomass through lamella specially designed in such a way to recycle the methanogenic biomass to the fermentor digester. In this chapter, large scale treatment which requires specialized fermentor system in which all the three phases of treatment of distillery effluent through methanogenic bacteria has been discussed.

5.2 Distillery Spentwash

Alcohol industry is one of the major agro-based industries, which utilize molasses as raw material for production of rectified spirit. In addition to rectified spirit, distilleries also produce power ethanol, which can mixed with diesel and used as the biofuel, which help in reducing import of crude oil thereby saving foreign exchange. Ethanol manufacture from molasses generates large volumes of high strength wastewater that is of serious environmental concern. The effluent is characterized by extremely high COD (80,000–100,000 mg/l) and BOD (40,000–50,000 mg/l), apart from low pH, foul odor and dark brown color (Kumar and Thankamani 2016). Its dark brown color is due to the presence of brown polymers called melanoidins which are formed by the Millard amino-carbonyl reaction.

Spentwash is believed to resemble humic acids in its properties. These compounds are highly recalcitrant and have antioxidant properties which render them toxic to many microorganisms, typically present in distillery wastewater treatment processes. Apart from the high organic content, distillery wastewater also contains nutrients in the form of nitrogen, phosphorus and potassium (Mahimairaja and Bolan 2004) that can lead to eutraphication of water bodies. Further its dark color hinders photosynthesis by blocking sunlight and therefore deleterious to aquatic system (FitzGibbon et al. 1998). Studies on water quality of a river contaminated with distillery effluent displayed high BOD value of 1600–21,000 mg/l with in an 8 km radius (Baruah et al. 1993). In addition to pollution, increasingly stringent environmental regulations are forming distilleries to improve existing treatment and also explore alternative methods of effluent management. This chapter focuses on the advances in molasses-based distillery wastewater treatment by the various groups of microorganism and their effect on the degradation of mainly melanoidin.

5.2.1 Ethanol Production from Molasses

Ethanol can be produced from a wide range of feedstock like sugarcane, beet molasses, cane juice, corn, wheat, cassava, rice, barley, crop residues, sugarcane bagasse, wood municipal solid wastes materials. Ethanol production in distilleries is based on sugarcane molasses represents a main industry in India. The world's total production of alcohol from sugarcane molasses is more than 13 millions m^3/

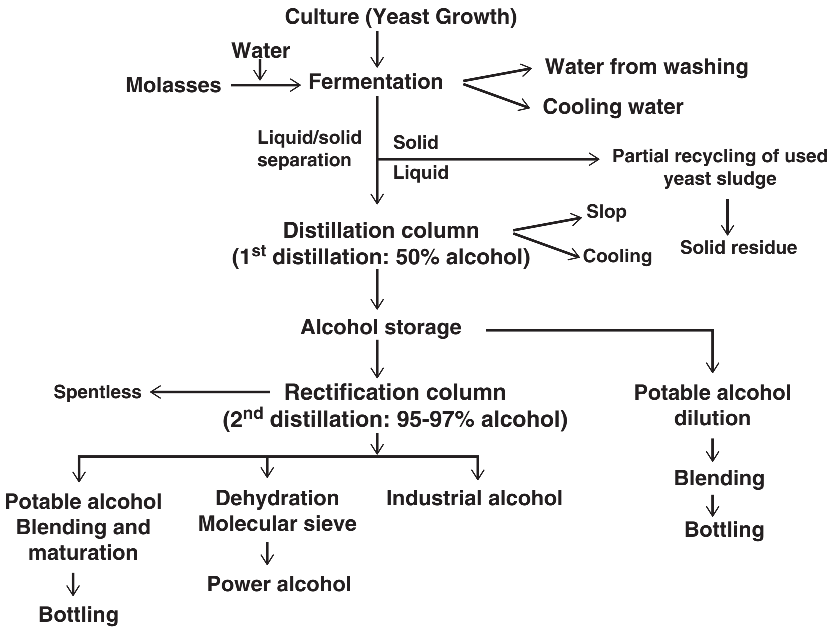

Fig. 5.1 Alcohol manufacturing process

year. The manufacture of alcohol in distilleries consists of four main steps as follow: feed preparation, fermentation, distillation and packaging are mention in flow chart (Satyawali and Balakrishanan 2008b) (Fig. 5.1).

For the production of industrial ethanol, 20–25 brix molasses dilution having pH 5–5.5 is used. General molasses dilution for fermentation which is known as wort has high buffering capacity. It is then supplemented with assimilable nitrogen source like ammonium sulfate or of pH 5.0–5.5, but in some cases it is maintained through using diluted H2SO4 but it is generally avoided. The composition of molasses varies with the variety of cane, the agro climatic conditions, sugar manufacturing process, handling and storage (Godbole 2002) (Table 5.1).

5.2.2 Molasses-Based Distillery Wastewaters and Its Characteristics

Fermentation is facilitated by *Saccharomyces cerevisiae*, a yeast and *Zymomonas mobilis*, a bacterium in all over world. The fermented broth generally known as spentwash comes out in the form of distillery effluent (Nandy et al. 2002; Pathade 2003; Singh et al. 2004; Chandraraj and Gunasekaran 2004). Several workers have used various types of fermentors and fermentation process viz. hydrodynamic,

Table 5.1 Chemical composition of sugarcane molasses

Property	Sugarcane molasses	
	Chen and chou (1993)	Godbole (2002)
Brix (%)	85–92	79.5
Specific gravity	1.38–1.52	1.41
Total solids (%)	75–88	75.0
Total sugar (%)	50–90	44–60
Crude protein (%)	2.5–4.5	3.0
Total fat (%)	0.0	0.0
Total fiber (%)	0.0	0.0
Ash (%)	7–15	8.1
Calcium (%)	NR	0.8
Phosphorus (%)	NR	0.08
Potassium (%)	NR	2.4
Sodium (%)	NR	0.2
Chloride (%)	NR	1.4
Sulfur (%)	NR	0.5

NR Not reported

aerodynamic or even combined form of several others for better fermentation results; after fermentation the fraction distillation large column of stainless steel with glass material have been used. The live heat is used in the bottom of the column for vaporization of the wash and different components if alcoholic products like ethanol, methy alcohol, ethyl acetate, propanol 1 and 2, butanol 1 and 2, isopropyl alcohol having different boiling points are being separated. The efficiency of the column is also worked out by various groups of worker for better results.

The specification of spentwash which has very high chemical oxygen demand (COD) (80,000–100,000 mg/l) and biochemical oxygen demand (BOD) (40,000–50,000 mg/l). Therefore, among several industrial effluents like sugar, textile, tannary or others, distillery effluents is one of the most polluting industries. The aqueous effluent from distilleries known as molasses wastewater is around 12–15 times the volume of the produced ethanol. Though, the quantity and the specification of the sugarcane molasses wastewater are greatly variable and dependent on the raw material and ethanol production process (Pant and Adholeya 2007; Satyawali and Balakrishanan 2008a). The chief source of wastewater is the distillation step wherein bulky volumes of dark brown effluent named as spentwash, stillage, slop or vinasse is produced with a temperature range of 70–80 °C, acidic pH, and with high concentration of organic and solids materials (Yeoh 1997; Nandy et al. 2002). Distillery wastewater also contains nutrients in the form of nitrogen, phosphorus and potassium that can lead to eutriphication in aqueous ecosystem (Table 5.2). Further, its dark color leads to widespread damage to aquatic system (Mahimairaja and Bolan 2004).

Table 5.2 Characteristic of distillery effluent

Parameters	Range	Average
Discharge volume (m^3/ day)	20–450	100
pH	2.5–5.5	4
Temperature (°C)	60–150	98
BOD (mg/l)	17,500–50,00	27,700
COD (mg/l)	57,000–150,000	120,000
COD/BOD	1.90/7.67	4.3
Suspended solid (SS) (mg/l)	5430–24,500	12,345
Total solid (TS) (mg/l)	37,000–130,000	80,000
Total volatile solid (TVS) (mg/l)	31,000–60,000	59,000
Total nitrogen (mg/l)	30–2500	980
Phosphate (mg/l)	30–370	100
Potassium (mg/l)	2500–9000	5000
Sulfate (mg/l)	2000–5300	3900

5.2.3 *Color Compounds of Distillery Effluent*

The recalcitrant character of distillery spentwash is due to the existence of the dark brown colorants, which are biopolymeric colloidal materials that are negatively charged. All colorants have phenolic groups which contribute to their formation except caramel. Infrared spectra of alkaline degradative products specify the occurrence of high molecular weight amino acids. Most of the phenolic colorants are resultant from benzoic and cinnamic acid that are precursors of flavanoids, the yellow pigments of the plants, liable for color formation. The phenolic acids which form colored complexes with iron or get oxidized to polymeric colorants are o-hydroxy or o-dihydroxy acids (Mane et al. 2006). Melanoidins is one of the final products of the Maillard reaction during heat treatment (Kumar et al. 1997; Singh et al. 2004; Mohana et al. 2009). Other recalcitrant compounds present in the wastewater are caramel, different products of sugar decomposition, anthocyanins, tannins and different xenobiotic compounds (Pandey et al. 2003). The nasty odor of the distillery spentwash is due to the presence of skatole, indole and other sulfur compounds, which are not removed during distillation (Sharma et al. 2007).

5.2.4 *Physical and Chemical Properties of Melanoidin*

Melanoidins are dark brown to black colored natural condensation products of sugars and amino acids; they are produced by non-enzymatic browning reactions known as Maillard reactions (Plavsic et al. 2006). Naturally melanoidins are widely distributed in food (Painter 1998), drinks and widely discharged in huge amount by various agro-based industries especially from distilleries using sugarcane molasses and fermentation industries as environmental pollutants (Gagosian and Lee 1981; Kumar and Chandra 2006).

Melanoidin structure is still not fully implicit but it is assumed that it does not have a exact structure as its fundamental composition and chemical structures mainly depend on the nature and molar concentration of reacting compounds and reaction conditions like pH, temperature, heating time and solvent used (Ikan et al. 1990; Yaylayan and Kaminsky 1998). Food and drinks such as bakery products, coffee and beer having brown colored melanoidins showed antioxidant, antiallergenic, antimicrobial and cytotoxic properties as in vitro studies have discovered that products from Maillard reaction may offer significant health promoting effects. Melanoidins can work as reducing agents, metal chelators and radical scavengers (Borrelli et al. 2003; Plavsic et al. 2006). Further, melanoidins also have antioxidant properties, which make them toxic to many microorganisms such as those normally, present in wastewater treatment systems (Kumar et al. 1997). The Recalcitrant nature of melanoidins is evident from the fact that these compounds run off different stages of wastewater treatment plants and lastly comes in the environment.

5.2.5 Melanoidin Development Pathway

During Maillard reaction, melanoidins is formed from highly reactive intermediates through polymerization reactions. A broad series of reactions takes place, including cyclizations, dehydrations, retroaldolizations, rearrangements, isomerizations and condensations. The molecular weight of colored compounds increases as browning proceeds. The complexity of Maillard reaction has been widely studied during recent years and novel significant pathways and key intermediates has been recognized (Martins et al. 2001). A scheme of Maillard reaction is shown in Fig. 5.2. Melanoidins are accepted as being acidic compounds with charged nature. With increasing reaction time and temperature, the total carbon content increases, thus supporting the un-saturation of the molecules. The color intensity rises with the polymerization degree. The degree of browning, usually measured via absorbance at 420 nm, is often used to follow the extent of Maillard reaction.

Methylglyoxal dialkylamine is a C_3 sugar fragment in early stages of browning reaction between sugar and amines or amino acids reported by Hayase et al. (1982). N-substituted 1-amino-1-deoxyketoses, representing an significant class of Maillard intermediates, which were generated during the initial stage of Maillard reaction by Amadori rearrangement of corresponding N-glycosyl amines studied by Fay and Brevard (2004). This kind of reorganization was termed after Mario Amadori who was the initial to reveal the condensation of D-glucose with an aromatic amine. This reaction would generate two structurally dissimilar isomers, N-substituted glycosylamine, which was more labile than the other, N-substituted 1-amino-1-deoxy-2-ketose, towards hydrolysis. Therefore, these Maillard reaction intermediates were termed as Amadori compounds.

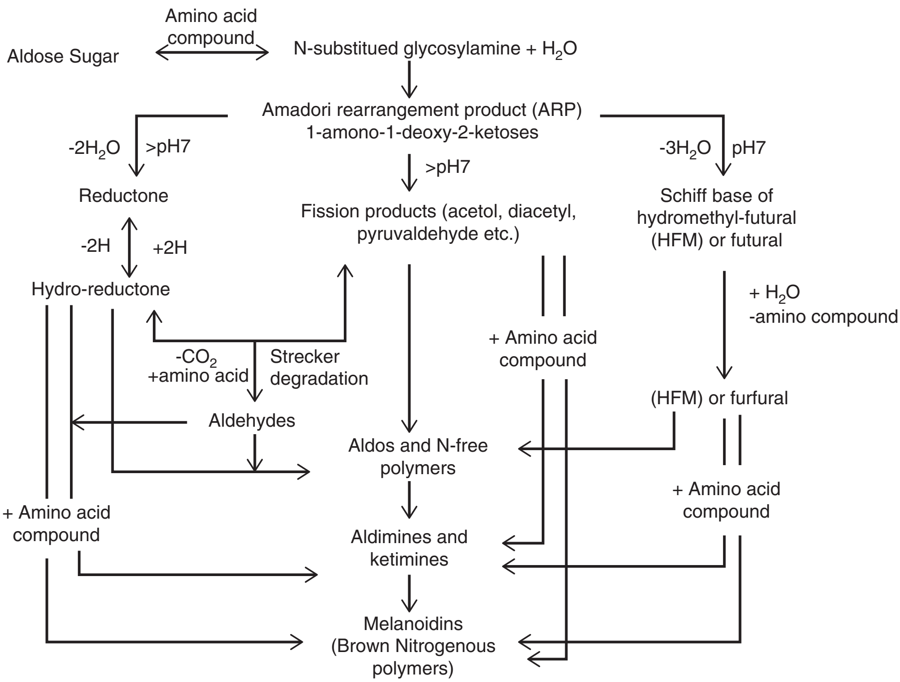

Fig. 5.2 Scheme of Maillard reaction. (Martins et al. 2001)

The C_3 imine formation followed the model of C_2 imine formation, and was well associated to decline in the quantity of glucosylamine and raises in the formation of Amadori products (Hayashi and Namiki 1986). Amadori products when react with n-butylamine quickly generated C_3 compound in a similar manner to that of glucose-n-butylamine system. These results showed the opportunity of contribution of Amadori products in the formation of C_3 compound. In spite of huge research effort done on the Maillard reaction, several parts as mechanism of melanoidins formation at later last stages of Maillard reaction are still unclear. However, the proposed mechanisms indicate that Maillard reaction performs amino-carbonyl reaction.

5.2.6 Structure of Melanoidin Polymer

The clarification of the melanoidins chemical structure is not easy due to the complexity of the Maillard reaction. A main repeating unit of melanoidins is glucose and butylamine (pH 5.0–6.5) under anaerobic conditions was reported by Kato and Tsuchida (1981). However, altering reaction situation play a significant role in the basic structure of melanoidins. This means that it cannot be unspecified that melanoidins have an expected composition with repeating units. On basis of these facts, Cammerer and Kroh (1995) represent a common structure for melanoidins formed from monosaccharides and glycine. The chemical structure presented in Fig. 5.3.

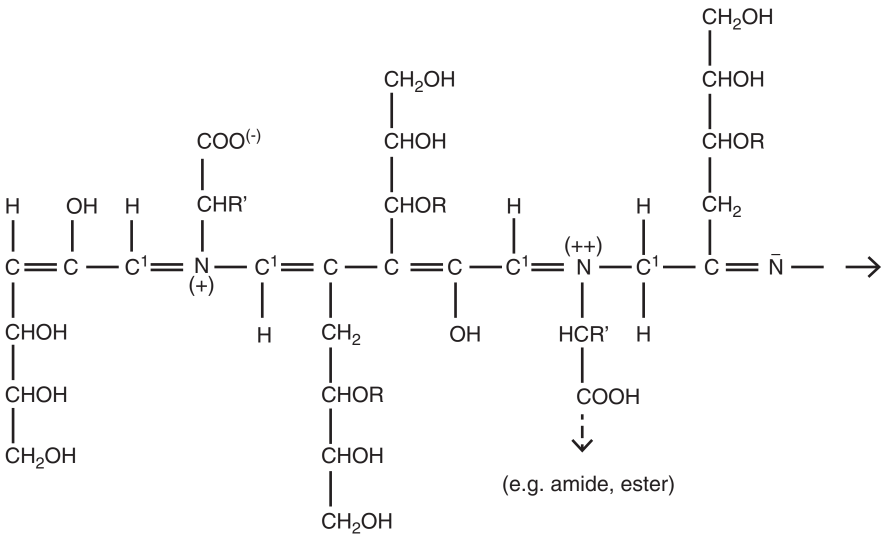

Fig. 5.3 Proposal for the general structure of the melanoidin polymer (Cammerer and Kroh 1995). R:H or saccharides. R': side chain of amino acid

The fundamental structure is formed by á-dicarbonyl Maillard reaction intermediates, partially branched by amino compounds and with several reactive centers that create further decarboxylation and dehydration reactions. The structure of the actual melanoidins is liable to be a result of several reactions from the crucial framework. The structure was consistent with the one proposed by Cammerer and Kroh (1995).

The FTIR spectrum clearly indicates that melanoidin has 1607 cm^{-1} spectrum band tends to higher conjugation, while amadori products, such as pyrazines, pyrroles, pyridines and furans etc. are the result of Pyrolysis. The basic skeleton of melanoidins is carbohydrates and amino acid suggested by Cammerer et al. (2002) (Fig. 5.4). Though the chemical structure of melanoidins is not obviously implicit, but some part of the chemical structure of melanoidins have newly been explained by different spectral studies like 1H NMR, CP-MAS NMR, etc. (Larter and Douglas 1980; Ikan et al. 1990, 1992).

The chemical analysis has exposed that natural and synthetic melanoidins both have analogous elemental (CHON) compositions, spectroscopic characters and electrophoretic motilities at different pH (Ikan et al. 1990, 1992; Migo et al. 1997). Though, the nitrogen contents, acidities and electrophoretic activities of the melanoidins all reveal functional group distributions innate from the amino acids (Hedges 1978).

Despite these facts, the melanoidins chromophore has not been yet recognized, thus the chemical structure of the melanoidin is still not clear, as it does not has a definite structure and exist in different forms of melanoidins depending on the reactants and reaction conditions as pH, temperature and reaction time. Furthermore, it needs exhaustive analysis with more refined modern and highly developed techniques for the explanation of chromophore structure to assume the core skeleton of melanoidin polymer.

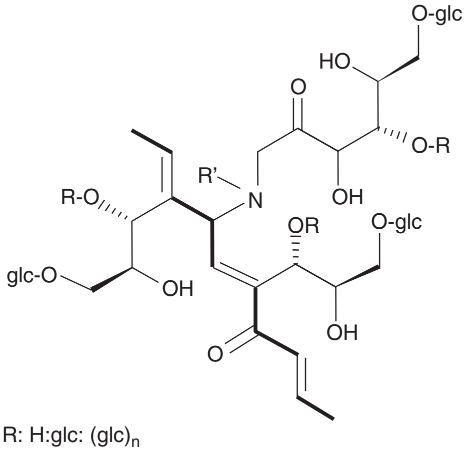

Fig. 5.4 Most common form of melanoidin structure formed from carbohydrates and amino acid. (Cammerer et al. 2002)

5.3 Hazardous Effects of Distillery Effluent

Distillery wastewaters dumping into the surroundings are hazardous and have high pollution prospective. Due to high BOD, COD, total nitrogen and total phosphate content of the distillery effluent may result in eutrophication of aquatic ecosystem (Kumar et al. 1997). Dark brown color of spentwash diminishes sunlight dispersion in rivers, lakes or lagoons which in turn reduce both photosynthetic activity and dissolved oxygen concentration. The toxic effect of distillery spentwash (varying concentration) on common guppy, Lesbistes reticulates has been done and observed significant behavioral changes by Kumar et al. (1995). Hematological changes in fresh water catfish and Channa punctatus was observed when exposed with distillery effluents (Kumar and Gopal 2001).

Juwarkar and Dutta (1990) evaluated the impact of distillery spentwash on soil ecosystem. They observed that, distillery spentwash use for irrigation purpose it reduced overall bacterial and actinomycetes count and also reduced population of *Rhizobium* and *Azotobacter* which responsible for nitrogen fixation. On the other hand, population of fungi improved. Microbial population also reduced when irrigated with anaerobically treated spentwash but not as much as that of the raw spentwash.

The existence of inorganic and organic salts in the distillery spentwash affects the oxygen consumption ability of *Labeo rohita* a fresh water fish during respiration (Saxena and Chauhan 2003). The coagulation of gill mucous reduced dissolved oxygen consumption causing asphyxiation. Different concentration of Distillery spentwash also shows toxicity for fresh water crab, *Barythephusa guerini* (Matkar and Gangotri 2003). Discarding of distillery effluent on terrestrial ecosystem is evenly dangerous to the plants and reduces soil alkalinity and manganese availability, thus reducing seed germination (Kumar et al. 1997).

Growth and germination of *Vigna radiata* seeds affected at very low concentration (5%, v/v) of distillery spenwash (Kannan and Upreti 2008). Application of distillery spentwash to soil without appropriate monitoring, extremely affects the groundwater quality by changing its physico-chemical properties like color, pH, electrical conductivity, etc. due to leaching down of the organic and inorganic ions (Jain et al. 2005).

5.4 Treatment Processes for Distillery Wastewater

Several technologies for the treatment of such pollutants are being processed through physic-chemical and microorganisms. These methods decolorize the distillery spentwash by either concentrating the color into the sludge or by breaking down the colored molecules. These treatment processes are discussed in detail in the following section.

5.4.1 Physico-chemical Methods

5.4.1.1 Physical Aspects of Adsorption

Among the physico-chemical treatment methods, adsorption on activated carbon is generally working for elimination of color and specific organic compounds. Activated carbon is used as adsorbent due to its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity. In earlier studies, melanoidin decolorization is attained by adsorption on commercial as well as indigenously prepared activated carbons (Satyawali and Belakrishanan 2008a). Commercially existing activated carbon as well as activated carbon formed from sugarcane bagasse used for synthetic melanoidins decolorization (Bernardo et al. 1997, Satyawali and Balakrishnan 2007). The adsorptive competence of the different activated carbons was found to be quite analogous.

Twenty-four granular activated carbons (GACs) prepared from four binders includes coal tar, sugarcane molasses, sugar beet molasses, and corn syrup alongwith three agricultural products viz. rice hulls, rice straw, and sugarcane bagasse which were effectively reduced the color of spentwash (Pendyal et al. 1999). Therefore, the ability to remove sugar colorants appears to be by-product dependent with the binder playing a minor role. Chemically modified bagasse using 2-diethylaminoethyl choride hydrochloride and 3-chloro-2-hydroxypropyltrimethylammonium choride was capable of decolorizing diluted spentwash (Mane et al. 2006). Significant decolorization was observed in packed bed studies on anaerobically treated spentwash using commercial activated charcoal (Chandra and Pandey 2000). Complete decolorization (>99%) was obtained with 70% of the eluted sample, which also displayed over 90% COD and BOD removal. Adsorption by commercially available powdered activated carbons resulted in only 18% color removal; however, combined treatment using coagulation-flocculation with polyelectrolyte followed by adsorption resulted in almost complete decolorization (Sekar and Murthy 1998). Ramteke et al. (1989) reported color removal upto 98% with pyorchas as adsorbents.

Mall and Kumar (1997) compared the color removal using commercial activated carbon and bagasses flyash. Lalove et al. (2001) studied the treatment of distillery wastewater using chitosan as an anion exchanger is a natural carbohydrate polymer derived from the exoskeleton of crustaceans. At an optimum dosage of 10 g/l and 30 min contact time, 98% color and 99% COD removal was observed.

Nure et al. (2017) investigated the removal of chemical oxygen demand (COD) and colour from a melanoidin solution using activated carbon produced from bagasse fly ash (BFA). The surface area of the BFA was determined as 160.9 ± 2.8 m^2/g with 90% of particle less than 156.8 μm in size. Characterization of the BFA by Fourier transform infrared spectroscopy (FTIR) showed the presence of hydroxyl and carbonyl functional groups, whereas X-ray diffraction analysis indicated its amorphous nature. Moreover, scanning electron microscopy analysis showed a heterogeneous and irregular shape of pores. The removal of COD and colour from a melanoidin solution with this activated carbon was carried out using an experimental design taking four factors into account. These were adsorbent dose, contact time, pH and initial COD concentration, with removal of COD and colour as response variables. COD reduction was influenced by initial COD concentration whereas colour removal was dominated by contact time, which was in line with the findings of principal component analysis. The maximum COD removal recorded was 61.6% at the optimum condition of adsorbent dose of 4 g in 100 mL, contact time of 4 h, pH 8 and initial COD concentration 6000 mg/L, whereas the decolourization of melanoidin solution was 64% at adsorbent dose of 4 g, contact time 4 h, pH 3 and initial COD concentration 6000 mg/L. Hence, activated BFA is a promising option for simultaneous removal of COD and colour from molasses spent wash under the stated conditions.

5.4.1.2 Oxidizing Agents

Ozone is one of the important oxidizing agents for water and waste water treatment. When ozone dissolved in water, it reacts with a large number of organic compounds in two paths. First is by direct oxidation as molecular ozone and second is by indirect reaction during production of secondary oxidants like free radical species (hydroxyl radicals). Both ozone and hydroxyl radicals are strong oxidants and are proficient of oxidizing numerous compounds (Bes-Pia 2003). Ozone oxidation process could get maximum 80% decolorization and 15.25% COD reduction for biologically treated distillery spentwash. Although, ozone only alters the chromophore groups but does not degrade the dark colored polymeric compounds in the distillery spemtwash (Alfafara et al. 2000; Pena et al. 2003). In another study, when Ozone and UV radiation combindally used for effluent treatment it enhanced molasses wastewater degradation in terms of COD. However, ozone with hydrogen peroxide illustrated only minor reduction even on a very dilute spentwash (Beltran et al. 1997).

The Fenton's oxidation is also an extremely high oxidation process which has ability to produce hydroxyl radicals (OH). Fenton's reagent, which involves homogeneous reaction and is environmentally acceptable, is a mixture of hydrogen peroxide and iron salts (Fe^{2+} or Fe^{3+}) which produces hydroxyl radicals which ultimately leads to decolorization of the effluent (Pala and Erden 2005). Another option is photo-catalytic oxidation that has been studied using solar radiation and TiO_2 as the photocatalyst (Kulkarni 1998). Use of TiO_2 was found to be very effective as the destructive oxidation process leads to complete mineralization of effluent to CO_2 and H_2O.

It has been observed that the use of an individual process alone may not treat the wastewater completely. A combination of these processes is necessary to achieve the desirable norms.

5.4.1.3 Coagulation and Flocculation

Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles (flocs). Inance et al. (1999) reported that coagulation with alum and iron salts was not effective for color removal. $FeCl_3$ and $AlCl_3$ were tested for decolourization of biodigested effluent and showed similar removal reduction efficiencies. About 93% reduction in color and 76% reduction in TOC were achieved when either $FeCl_3$ or $AlCl_3$ was used alone. The process was independent of choride and sulphite ion concentration but was adversely affected by high fluride concentration. However in the presence of high flocculent concentration (40 g/l), addition of 30 g/l CaO enhanced the decolorization process resulting in 93% color removal. This was attributed to the ability of calcium ions to destabilize the negatively charged melanoidin; further, formation of calcium fluoride ions.

Complete color removal (98%) of biologically treated distillery effluent has been reported with conventional coagulants, such as ferrous sulphate, ferric sulphate and alum under alkaline conditions (Pandey et al. 2003). The best results were obtained from Percol 47, an organic anionic polyelectrolyte, with ferrous sulphate and lime combination. This resulted in 99% reduction in color and 87% and 92% reduction in COD and BOD respectively. Same findings have been reported by Mandal et al. (2003). Coagulation on spentwash after anaerobic-aerobic treatment has also been conducted using bleaching powder followed by aluminum sulphate (Chandra and Singh 1999). This resulted in 96% removal in color, accompanied by up to 97% reduction in BOD and COD.

Flocculation is the action of polymers to form bridges between the flocs, and bind the particles into large agglomerates or clumps. Bridging occurs when segments of the polymer chain adsorb on different particles and help particles aggregate. Generally coagulation seems to be an expensive step taking into account expenses of chemicals and sludge disposal (Ecologix Environmental system, LLC 2008).

5.4.1.4 Membrane Based Treatment Process

Prior to anaerobic digestion, Pre-treatment of molasses wastewater with ceramic membranes was done which reduced the COD from 36,000 to 18,000 mg/l (Chang et al. 1994). The whole membrane area was 0.2 m^2 and the system was function at a fluid velocity of 6.08 m/s with 0.5 bar trans-membrane pressure. Electro-dialysis has been investigated for desalting molasses effluent by cation and anion exchange membranes resulting reduction of potassium content (50–60%) (De Wilde 1987).

Electro dialysis having stainless steel cathode, titanium alloy anode and NaCl (4%, w/v) used for the treatment of vinasse (beet molasses) which reduced 88% COD at pH 9.5 (Vlyssides et al. 1997). While, the COD reduction percentage declined at higher spentwash feeding rates. Recently, pilot trials on distillery effluent using a hybrid (NF) and reverse osmosis (RO) process have been reported by Nataraj et al. (2006). Nanofiltration was mostly efficient for color reduction and colloidal particles accompanied by 80% and 45% reduction in total dissolved solids and chloride concentration, respectively, at an optimum supply pressure of 30–50 bars.

5.4.1.5 Drying and Desiccation Method

Distillery spentwash containing 4% solids can be concentrated to a maximum of 40% solids in a quintuple-effect drying system with thermal vapor recompression (Bhandari et al. 2004; Gulati 2004). The condensate with a COD of 280 mg/l can be used in fermenters. The concentrated effluent is spray dried using hot air (180 °C) to get a desiccated powder. The powder is normally mixed with agricultural waste (20%) and blistered in boiler. Desiccation is also an efficient method of on-site vinasse removal as it is accompanied by production of potassium rich ash that can be used for ground application (Cortez and Perèz 1997).

5.4.1.6 Radiation and Coagulation Approach

Radiation tools used for treatment of distillery spentwash is also effective but costly (Pikaev 2001). In this process, a combined treatment of electron beam and coagulation using $Fe_2(SO)_3$ efficiently reduce the decolorization by 65–70%. The ultrasound technology has also been used for the treatment of distillery effluent. The ultrasonic irradiation as a pretreatment step was efficient for the treatment where bioremediation efficiency was improved (Sangave and Pandit 2004). Chaudhari et al. (2008) projected a novel catalytic thermal pretreatment or catalytic thermolysis to improve the greater part of its energy content with resultant COD and BOD deduction. After thermolysis, the formation of settleable solid residue and the slurry has been achieved, exhibited very good filtration. It can be applied as a fuel in the combustion furnaces and the ash achieved can be blended with organic manure and used in agriculture/horticulture. Various physico-chemical methods such as adsorption, coagulation-flocculation, and oxidation processes like Fenton's oxidation, ozonation, electrochemical oxidation using various electrodes and electrolytes, nanofiltration, reverse osmosis, ultrasound and various combinations of these methods have also been studied for distillery effluent treatment. As mentioned above, distillery wastewaters have been reported to be decolorized by various physico-chemical methods which are summarized below (Table 5.3).

Physico-chemical treatment methods are effective in both color and COD removal. Nevertheless the drawbacks associated with these methods are excess use of chemicals, sludge generation with subsequent disposal problems, high opera-

Table 5.3 Summary of various physicochemical treatments used for the treatment of Sugarcane molasses-based distillery wastewaters and their efficiency

Treatment	COD removal (%)	Color removal (%)	References
Adsorption			
Chitosan, a biopolymer was used as anion exchanger	99	98	Lalvo et al. (2000)
Chemically modified bagasse			Mane et al. (2006)
DEAE bagasse	40	51	
CHPTAC bagasse	25	50	
Activated carbon prepared from ago industrial waste			Satyawali and Balakrishanan (2008a)
Phosphoric acid carbonized bagasse	23	50	
Commercially available activated carbon			
AC(ME)	76	93	
AC(LB)	88	95	
Oxidation processes			
Fenton's oxidation	88	99	Pala and Erden (2005)
Ozonation	15–25	80	Pena et al. (2003)
Coagulation- flocculation			
Flocculation of synthetic melanoidin was carried out by various inorganic ions			
Polyferric hydroxysulphate (PFS)	NR	95	Migo et al. (1997)
Ferric chioride ($Fecl_3$)	NR	96	
Ferric sulphate ($Fe_2(SO_4)_3$)	NR	95	
Aluminium sulphate ($Al_2(SO_4)_3$)	NR	83	
Calcium oxide (CaO)	NR	77	
Calcium chloride ($CaCL_2$)	NR	46	
Membrane technologies			
Reservse osmosis	99.9		Nataraj et al. (2006)
Nanofiltration	97.1	100	
Electrochemical oxidation			
Lead dioxide coated on titanium	90.8	98.5	Manisankar et al. (2004)
Ruthenium dioxide coated on titanium	92.1	99.5	
Electrocoagulation and electro fenton	92.6	NR	Yavuz (2007)

NR Not Reported

tional costs and sensitivity to variable water input. Considering the advantages and the disadvantages of different treatment technologies, no single technology can be used for complete treatment of molasses wastewater. Hence, there is a need to establish a comprehensive treatment approach involving several technologies sequentially.

5.4.2 Biological Treatment

In general, a biological treatment employing fungi and bacteria have been investigated essentially for decolorize the distillery spent wash. The microbial decolorization is an environment-friendly and cost competitive alternative to chemical decomposition process. Optimum microbial activities and optimum results are found when effluent is supplemented with additional nutrients as well as diluting the effluent. So it is felt that the ideal cost effective and commercial treatment scheme should comprise of physico-chemical treatment.

Biological treatment of molasses wastewater is either aerobic or anaerobic, but in most cases a combination of both is used. Anaerobic treatment is an accepted practice and various high rate reactor designs have been tried at pilot and full scale operation. Aerobic treatment of anaerobically treated effluent using different microbial populations has also been explored. Majority of biological treatment technologies remove color by either concentrating the color into sludge or by partial or complete breakdown of the color.

5.4.2.1 Anaerobic Treatment

High BOD and COD of distillery make anaerobic conditions having microbial degradation of organic compound by anaerobic bacteria. Anaerobic bacteria are limited and mainly clostridium and few others along with methanogenic bacteria combindly eliminate organic load as well as produce methane which can be used as energy source and cut 70–80% BOD, COD and other nutrient efficiently (Jain et al. 1990). Molasses wastewater treatment using anaerobic process is a very promising re-emerging technology which presents interesting advantages as compared to classical aerobic treatment. It produces very little sludge, requires less energy and can be successfully operated at high organic loading rates; also, the biogas thus generated can be utilized for steam generation in the boilers thereby meeting the energy demands of the unit (Nandy et al. 2002). Further, low nutrient requirements and stabilized sludge production are other associated benefits (Jimenez et al. 2004). However, the performance and treatment efficiency of anaerobic process can be influenced both by inoculum source and feed pretreatment.

The anaerobic treatments is facilitated by a series of sequences of microbial types having different types of physiology and metabolic pathways to produce various types of aliphatic acids and other products of protein, carbohydrate and lipids feeding to different groups of microorganisms and products. Therefore, the bioreactor technology and architecture is designed to get their optimum utilization of various important products in which the hydraulic retention times (HRT) is adjusted according to the design and microorganism nature (Patel and Madamwar 2000).

Anaerobic lagoons are the simplest alternative for anaerobic treatment of distillery spentwash. Rao (1972) carried out an experimental work in the area of distillery effluent management by employing two anaerobic lagoons in series, resulting 82–92% BOD reduction. However, the lagoon systems are rarely operational, souring being a common trend. Outsized area requirement, aroma problem and probability of land water pollution are drawbacks (Singh et al. 2004).

Continuous stirred tank reactors (CSTR) are the simplest type of closed reactors with gas collection. Distillery effluent treatment in Continuous stirred tank reactors has been mentioned in single/biphasic operations, resulting in COD reduction (80–90%) within 10–15 days (Pathade 2003). Anaerobic sequencing batch reactor (ASBR) has been used for the treatment of winery wastewater. The reactor was operated at an OLR of 8.6 kg COD m^{-3} d^{-1} with soluble COD reduction efficiency better than 98% with HRT of 2.2 days (Ruiz et al. 2002).

Biomethanation of distillery effluent in mesophilic and thermophilic range of temperatures in semi-continuous batch digester has been investigated by Banerjee and Biswas (2004). The study revealed that there was a significant effect of the temperature of digestion and of substrate concentration in terms of BOD and COD loading on the yield of biogas as well as its methane content. Maximum BOD reduction (86.01%), total gas production and methane production (73.23%) occurred at a BOD loading rate of 2.74 kg m^{-3} at 50 °C digestion temperature.

In fixed film reactors, the reactor has a biofilm support structure (media) for biomass attachment. Fixed film reactor offers the advantages of simplicity of construction, elimination of mechanical mixing, better stability even at higher loading rates and capability to withstand toxic shock loads. The reactors can recover very quickly after a period of starvation (Rajeshwari et al. 2000; Patel and Madamwar 2002). Perez-Garcia et al. (2005) studied the influent pH conditions in fixed film reactors for anaerobic thermophilic treatment of wine distillery effluent.

The upflow anaerobic sludge blanket (UASB) process has been effectively used for the treatment of different kinds of effluent (Lettingar and Holshoff Pol 1991). UASB reactor systems related to the group of high rate anaerobic effluent treatment and thus it is one of the most accepted and widely used reactor designs for distillery wastewaters treatment. The success of upflow anaerobic sludge blanket (UASB) depends on the formation of active and settleable granules (Fang et al. 1994; Sharma and Singh 2001; Uzal et al. 2003).

In anaerobic fluidized bed reactor (AFB), the medium which hold bacteria attachment and growth is maintained in the liquid condition by pull forces exerted by the up flowing effluent. The media used are minute particle size sand, activated carbon, etc. In the fluidized state, each medium grants a huge surface area for biofilm formation and growth. It enables the attainment of high reactor biomass hold-up and support system competence and firmly. Kida et al. (1995) studied the biological treatment of Shochu distillery effluent using an anaerobic fluidized bed reactor.

5.4.2.2 Aerobic Treatment

Anaerobically treated distillery effluent still contains high concentrations of organic compounds and then cannot be liberated directly. The moderately treated effluent has high BOD, COD and suspended solids. It can decrease the accessibility of crucial mineral nutrients by trapping them into immobilized organic forms, and may generate phytotoxic substances during corrosion. Rigorous rules on release of colored effluent hinder direct discharge of anaerobically treated distillery effluent (Nandy et al. 2002). Consequently, aerobic treatment of sugarcane distillery effluent has been generally attempted for the decolorization of melanoidins, and for reduction of the COD and BOD. Numerous microorganisms such as bacteria (pure and mixed culture), cyanobacteria, yeast and fungi have been isolated in current years and are proficient for remediate melanoidins and thus decolorizing the molasses effluent. The aerobic methods have been described below.

5.4.2.2.1 Activated Sludge Treatment

The most widespread aerobic wastewater treatment is the activated sludge in which a efforts are targeted at enhancements in the reactor design and performance. For instance, aerobic sequencing batch reactor (SBR) was reported to be a hopeful solution for the wineries treatment (Torrijos and Moletta 1997). Aerobic reactor reduces 93% COD and 97.5% BOD within 7 days of incubation. Several workers have focused on the distillery effluent treatment by pure cultures under aerobics condition. Though aerobic treatment like the conventional activated sludge process is presently practiced by various molasses-based distilleries and leads to significant reduction in COD, the process is energy demanding and the color removal is still unsatisfactory.

Biocomposting is a activated bioconversion method by aerobic pathway, whereby heterotrophic microorganisms act on carbonaceous resources depending on the accessibility of the organic source and the presence of inorganic resources important for their growth. Degradation is mainly efficient in converting the wet materials to a usable form thereby stabilizing the organic materials and killing the pathogenic organisms in addition to considerable drying of the wet substrates. In the composting process, thermophilic degradation of organic materials at 40–60% moisture content occurs to form relatively stable, humus-like materials under aerobic conditions (Kannan and Upreti 2008).

5.4.2.3 Fungal System

Several worker have been reported the role of numerous fungi in melanoidins decolorization by adsorption to mycelia and the role of ligninolytic enzyme (Watanabe et al. 1982; Raghukumar and Rivonkar 2001; Vahabzadeh et al. 2004) (Table 5.4). However, the long growth cycle and spore formation limit the

Table 5.4 Different microorganisms employed for treatment of distillery effluent

Culture	Treatment	COD removal (%)	Color removal (%)	Enzymes
Fungi				
Coriolus no.20	Synthetic melanoidin solution was decolourized by the fungus free cells as well as Ca alginate immobilized cells decolorized the distillery effluent	–	80	Sorbose oxidase
		–	85	
			59%	
Phanerochaete Chrysosporium	Free cells as well as Ca alginate immobilized cells decolorized the distillery effluent	–	85 (free)	–
			59 (immobilized)	
Aspergillus niger	Maximum colour removal was obtained when $MgSO_4$, KH_2PO_4, NH_4NO_3 and a carbon source was added to wastewater	–	63	–
Geotrichum candidum	Fungus immobilized on polyurethane foam showed stable decolourization of molasses in repeated-batch cultivation	–	70	–
Aspergillus niveus	The fungus could use sugarcane bagasse as carbon source and required other nutrients for decolourization	–	56	–
Trametes versicolor	Anaerobically treated distillery effluent supplemented with sucrose and inorganic N sources was decolorize by the culture in shake flask studies	75	80	–
Phanerochaete Chrysosporium	The cultures decolorized to reduced the COD of effluent in presence of (3–5%) glucose and 0.1%yeast extract	73	53.5	–

(continued)

Table 5.4 (continued)

Culture	Treatment	COD removal (%)	Color removal (%)	Enzymes
Coriolus versicolor	The culture decolorized to reduced the COD of effluent in presence of (3–5%) glucose and 0.1%yeast extract	70	71.5	–
Coriolus hirsutus	Synthetic as well as wastewater melanoidin was decolorized by the fungus in a medium containing glucose and peptone	–	80	MiP and MnP and presence of extracellular H_2O_2
Coriolus hirsutus IF044917	The fungal culture was immobilized on PUF and used for decolourization of melanoidins present in heat treated liquor	–	45%	–
Flavodon flavus	Distillery effluent was decolorized using marine basidiomycetes in presence of 5% glucose	–	80	Glucose oxidase accompanied with hydrogen peroxide
Penicillium sp.	All fungi produced decolourization from first day of incubation, with maximum being shown by *P. decumbens* at fourth day with a reduction of 70% of the phenolic content of the wastewater	–	30	–
Penicillium Decumbens	Aerobic/anaerobic biodegradation of beet molasses wastewater	50.7	41	–
Coriolus versicolor	The cultures were incubated along with cotton stalks in vinasses, media in static condition. No synthetic carbon or nitrogen sources were used	49	63	
Funalia trogii		62	57	
Phanerochaete Chrysosporium		57	37	
Pleurotus pulmonarius		34	43	
Phanerochaete chrysosporium 1557	Effect of Veratryl alcohol and Mn (II) on decolorization of distillery effluent was studied	–	75	LiP and MnP

(continued)

Table 5.4 (continued)

Culture	Treatment	COD removal (%)	Color removal (%)	Enzymes
Phanerochaete chrysosporium ATCC 24775	The fungus was immobilized on different support materials such as PUF and scouring wet and the decolorization was carried out in a RBC	48	55	
Phanerochaete chrysosporium NCIM 1106	The cultures were employed to study the decolourization of molasses in medium containing 2% w/w glucose in static as well as submerged conditions	–	82	LiP and MnP
Phanerochaete chrysosporium NCIM 1197		–	76	LiP and MnP
Marine basidiomycetes NIOCC	Experiments were carried out with 10% (v/v) diluted effluent	–	100	–
Aspergillus Fumigates G-26	Thermophilic strain tried for molasses wastewater Decolourization but colouring compounds hardly degraded	–	56	–
Mycelia Sterilia	Organism required glucose for the decolourizing activity	–	93	–
Aspergillus Oryzae Y-2-32	The thermophilic strain absorbed lower molecular weight fractions of melanoidin and required sugars for growth	–	75	–
Rhizoctonia sp. D-90	Mechanism of decolourizatin of melanoidin involved absorption of the melanoidin pigment by the cells as a macromolecule and its intracellular accumulation in the cytoplasm and around the cell membrane as a melanoidin complex, which was then gradually decolourized by intracellular enzymes	–	90	–

(continued)

Table 5.4 (continued)

Culture	Treatment	COD removal (%)	Color removal (%)	Enzymes
Pycnoporus coccineus	Immobilized mycelia removed 50% more colour than free mycelia	–	60	–
Coriolus hirsutus	A large amount of glucose was required for colour removal but addition of peptone reduced the decolourization ability of the fungus	–	80	–
Phanerochaete Chrysosporium JAG-40	This organisms decolourization synthetic and natural melanoidins when the medium was supplemented with glucose and peptone	–	80	–
Citeromyces sp. WR-43	Organism required glucose, sodium nitrate and KH2PO4 for maximal decolourization	–	68.91	–
Aspergillus niger UM2	Decolourization was more by immobilized fungus and it was able to decolorize up to 50% of initial effluent concentrations	–	80	–
Aspergillus UB2	This was with diluted wastewater with optimum values of supplemented materials	–	75	–
Flavodon fiavus	MSW was decolourization using a marine basidiomycete fungus. It also removed 68% benzon (a) pyrene, PAH found in MSW	–	80	–
Planerochaete Chrysosporium	Sugar refinery effluent was treated in a RBC using polyurethane foam and scouring web as support	–	55	–

(continued)

Table 5.4 (continued)

Culture	Treatment	COD removal (%)	Color removal (%)	Enzymes
Planerochaete Chrysosporium NCIM	Molasses medium decolourization was checked in stationary and submerged cultivation condition	–	82	–
Pleurotus florida Eger EM 1303	Hydroponocally treated distillery effluent was subjected for treatment by fungus	–	86.3	–
Aspergillus oryzae JSA-1.	The percent reduction of total color of effluent was found on effluent medium	–	77.7	–
Pleurotus sp.	It was seen that mushroom spawn showed better growth on medium prepared in100% molasses spent wash as compared to 75%, 50% and 25% and also reduced its dark brown colorization	–	90%	–
Bacteria				
Lactobacillus hilgardii	Decolorization by this bacterial strain when cultivated with melanoidins containing wastewater medium supplemented with 1% of glucose	–	28	–
	Decolorization by immobilized cells on calcium alginate		40	
Lactobacillus L-2	12.5% diluted wastewater was supplemented with 10 g/l of glucose	57	31	–
Bacillus sp.	The decolorization was studied under anaerobic and thermophilic conditions	–	35.5	Decolorization enzyme
Aeromonas formicans	Study on pre-digested distillery effluent	57	55	–
Pseudomonasfluorescence	Immobilized cells on porous cellulose carrier.	–	76	–

(continued)

Table 5.4 (continued)

Culture	Treatment	COD removal (%)	Color removal (%)	Enzymes
Xanthomonas fragariae	All the three strains needed glucose as carbon source and NH4Cl as nitrogen source. The decolourization efficiency of free cells was better than immobilized cells	–	76	–
Pseudomonas putida U	Anaerobically treated distillery spent wash in two stage bioreactor (first stage: *Pseudomonas putida*; second stage: *Aeromonas* strain *Ema*)	44.4	60	–
Aeromonas strain Ema		44	–	
Bacillus cereus	Experiments were carried out with distillery effluent	81	75	–
Acetogenic bacteria strain no. BP103	Decolorization by the bacterial culture when cultivated in molasses pigments medium containing glucose 3%, yeast extract 0.5%	–	76	Sugar oxidase
Bacillus thuringiensis	Addition of 1% glucose as a supplementary carbon, source was necessary	–	22	–
Bacillus subtilis	Showed maximum decolorization using (w/v) 0.1%, glucose; 0.1%, peptone; 0.05%, MgSO4; 0.01%, KH2PO4; pH -6.0 within 24 h of incubation under static condition	–	85	–
Pediococcus acidilactici B-25	This bacterium exhibited maximum decolorization, COD using 0.1%, glucose; 0.1%, peptone; 0.05%, MgSO4; 0.05%, K2HPO4	85	79	–

(continued)

Table 5.4 (continued)

Culture	Treatment	COD removal (%)	Color removal (%)	Enzymes
Lactobacillus plantarum MiLAB393	A microbiological method of coloured compounds removal from BMV. The conditions of the process (pH and temperature) and vinasse concentration were optimized. The bacteria *Lactobacillus plantarum* MiLAB393 applied showed the decolourization activity in medium consisted of 30% v/v of BMV at pH0 = 6.5 and 35.8 °C	–	30	–
Mixture of all six isolates: *Pseudomonas, Enterobacter, Stenotrophomonas, Aeromonas, Acinetobacter* and *Klebsiella*	Study on decolorization of molasses spent wash	44	–	–
Mixed culture of *Bacillus thuringiensis Bacillus brevis Bacillus* sp. (MTCC6506)	The decolorization was studied with 4 types of synthetic melanoidins as follow:	53.91	45.12	Sugar oxidase and peroxidase
	GGA (glucose-glutamate-acid)	36.13	28.88	
	GAA (glucose-aspartic-acid)	63.39	50.56	
	SGA (sucrose-glutamate-acid)	54.51	46.08	
	SAA (sucrose-aspartic-acid)			

(continued)

Table 5.4 (continued)

Culture	Treatment	COD removal (%)	Color removal (%)	Enzymes
Microbacterium hydrocarbonoxydans Achromobacter xylosoxidans	All the 15 isolates grown on effluent supplemented medium as a sole carbon source	86.14	75.5	–
Bacillus subtilis				
Bacillus megaterium				
Bacillus anthracis				
Bacillus licheniformis				
Achromobacter xylosoxidans				
Achromobacter sp.				
Bacillus thuringiensis				
Bacillus licheniformis				
Bacillus subtilis				
Staphylococcus epidermidis				
Pseudomonas migulae				
Alcaligens faecalis				
Bacillus cereus				
Pseudomonas aerugenosa PA01	The decolorization was studied in effluent with low nutrient medium	67	51	–
Stenotrophomonas maltophila				
Proteus mirobilis				
Mixed culture of *Bacillus subtilis* and *Pseudomonas aeruginosa*	Maximum color reduction was achieved by bacterial consortium when supplied by additional carbon source (glucose 1%)		84.45	
Mixed culture of *Pediococcus acidilactici* and *Candida tropacalis*	Consortium exhibit maximum decolorization on glucose supplimented effluent medium		82	
Yeast				
Citeromyces sp. strain no. WR-43-6	Decolorization was observed on stillage from an alcohol distillery (U-MWW)	99.38	68.91	–
Candida Sp.	A yeast strain was isolated from the paper and pulp effluent decolorized distillery effluent on glucose supplemented medium	60	60	

(continued)

Table 5.4 (continued)

Culture	Treatment	COD removal (%)	Color removal (%)	Enzymes
Candida tropicalis RG-9	Yeast showed maximum decolorization using 0.2%, glucose; 0.2%, peptone; 0.05%, MgSO4; 0.01%, KH2PO4. Decolorizing ability of yeast was also confirmed by high performance liquid chromatography analysis		75	
Cyanobacteria				
Oscillatoria boryana BDU 92181 (marine cyanobacteria)	Decolorization of pure melanoidins (0.1% w/v)	–	75	–
	Decolorization of crude pigment in distillery effluent (5% v/v)		60	
Algae				
Mixed culture of microalgae:	Study with diluted wastewater (diluted wastewater from ethanol production to 10% of original concentration)	61	52	N-
Chlorella vulgaris				
Macrophyte:				
Lemna minuscule				

performance of the fungal system for effluent decolorization (Kumar et al. 1998). One of the most studied fungus having ability to degrade and decolorize distillery effluent is *Aspergillus* such as *Aspergillus fumigatus* G-2-6, *Aspergillus niger*, *Aspergillus niveus*, Aspergillus oryzae JSA-1, *Aspergillus fumigatus* UB260 brought about an average of 69–75% decolorization along with 70–90% COD reduction (Ohmomo et al. 1987; Miranda et al. 1996; Angayarkanni et al. 2003; Jimnez et al. 2003; Shayegan et al. 2004; Mohammad et al. 2006; Agnihotri and Agnihotri 2015).

Sugarcane distillery effluent treated with ascomycetes group of fungi such as *Penicillium decumbens*, *Penicillium lignorum* resulted better color, COD, and phenol removal (Jimnez et al. 2003). Pant and Adholeya (2007) isolated three fungal cultures and identified as *Penicillium pinophilum* TERI DB1, *Alternaria gaisen* TERI DB6 and *Pleurotus florida* EM 1303. These cultures were produces ligninolytic enzymes and decolorized the effluent up to 50%, 47% and 86%, respectively.

Sirianuntapiboon et al. (2004a) isolated a yeast strain WR-43-6 which showed maximum decolorization (68.91%) when cultivated at 30 °C for 8 days in a molasses solution containing 2.0% glucose, 0.1% sodium nitrate, and 0.1% KH_2PO_4, the pH being adjusted to 6.0. This potent strain was identified as *Citeromyces sp*. and showed highest removal efficiencies on stillage from an alcohol distillery (U-MWW). The color intensity, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) removal efficiencies were 75%, almost 100 and 76%, respectively. In a periodical feeding system, *Citeromyces sp.* WR-43-6 showed an almost constant decolorization of 60–70% over 8 day feeding of 10% fresh medium. In a replacement culture system, *Citeromyces sp.* WR-43-6 also gave a constant decolorization (about 75%) during four times replacement.

Several white rot fungi like *Phanerocheate crysosporium*, *Ganoderma*, *Coriolus* spp. have been used for decolorization of melanoidin but these fungi are slow growing therefore, not much effective against commercial treatment process. The white rot fungi are generally produce lignin degrading enzymes like peroxidase, mono and di-oxygenases, peroxigenases. Thses enzymes are highly reactive to ring structure aromatic hydrocarbon (Wesenberg et al. 2003).

Miyata et al. (2000) isolated a white rot fungus, *Coriolus hirsutus*, exhibited a strong ability to decolorize melanoidins in cultures without supplement of nitrogenous nutrients. Addition of peptone to the cultures lowered the ability of the fungus to decolorize melanoidins, but addition of inorganic nitrogens (Ns), ammonium and nitrate did not bring about any marked reduction in the ability. These results suggested an inhibitory effect of organic nitrogens on melanoidin decolorization. Therefore, for enhancing the decolorization of melanoidins in wastewaters by the fungus, activated sludge pretreatment of the wastewaters was expected to be effective, i.e., activated sludge is capable of converting available organic nitrogens into inorganic nitrogens.

Pazouki et al. (2008) isolated 21 isolates and procured microorganisms were screened for their percentage decolorization. The screening strategy was performed using three different culture media in two main steps. The primary screening was carried out in two stages. In the first stage, ten microorganisms had a lower than 25% decolorization of TDW (with 25% TDW concentration). In the second stage eight microorganisms had more than a 48% decolorization of TDW. In the secondary screening all three different culture media, the effect of TDW concentration, pH and nitrogen source were studied.

Seyis and Subasioglu (2009) reported decolorization of molasses by 17 different fungi in two media was studied. *Trichoderma viride* showed the highest decolorization yield (53.5%) when cultivated at 30 °C for 7 days in Medium 1 which contained the molasses which was diluted to 40 g/L in distilled water. The other *Trichoderma species* and *Penicillium sp.* also gave similar results of 40–45%. Decolorization yield was increased by adding peptone and yeast extract to the production medium.

Badis et al. (2009) isolated three most active strains of actinomycetes from soil surface. These strains were identified based on cultural characteristics and chemotaxonomic analysis and classified in the genus *Streptomyces*. Growth of these strains was assured on a poor liquid medium containing Spentwash (SHAs) as carbon and nitrogen sources and degradation occur only in the presence of glucose. A maximal decolorization extent was obtained for 28 days at 30 °C under shake culture (67%, 66% and 57% for *Streptomyces sp.* AB1, *Streptomyces sp.* AM2 and *Streptomyces* *sp.* AH4, respectively). As compared with initial and final structures of color component of spentwash after incubation (28 days), the structural changes in FTIR spectrum and metabolite products analysed by High Performance Liquid Chromatography (HPLC) indicate the capability of the selected *Streptomyces sp.* strains to degrade SHAs and to play a part role in lignin degradation and humus turnover in local soils.

Ravikumar et al. (2011) presented the standardization of nutrient concentration, pH and temperature required to decolorize the anerobically treated distillery spent wash using the fungus *Cladosporium cladosporioides*. Experiments were carried out to measure the decolorization of distillery spent wash effluent and it was found to be effective in acidic environment. From the results it was observed that a maximum color reduction of 52.6% and COD removal of 62.5% were achieved. The optimum conditions required for the growth of the fungus was found to be 5 g/L of fructose, 3 g/L of peptone, 5 pH and 35 °C. It was also observed that during the process a maximum of 1.2 g of fungal growth was attained. Decolorizing ability of the fungus was confirmed using spectrophotometer and HPLC analysis. Single factorial experimental design was used to optimize the parameters. Apart from decolorization it was observed that fungus also has the ability to degrade the spent wash efficiently. This investigation could be an approach towards control of environmental pollution and health hazards of people in and around the distillery unit. Amber and Sayaad (2010) studies a mesophilic fungal strain *Phanerochaete chrysosporium* for effective decolorization of melanoidin by the immobilization, sodium algenate used as a support material. It show that decolorization of distillery effluent by free cells are equal to immobilized cell (63%) at 30 °C, pH 5 after 8 days.

Agnihotri (2015) identified microbial strains capable of degrading specific pollutants to get a valuable product as a fertilizer for crops is an interesting development in environmental biotechnology. Therefore during last few years attention has been directed towards utilization of specific microbial activity for degrading coloring compounds of distillery effluent. In this study, decolorization study on synthetically prepared colorants by *Aspergillus oryzae JSA-1* was carried out. Media containing melanoidin, caramel and ADP separately in different concentrations were studied for the percent reduction in colorant concentration after fungal growth for 12 days, by reading the absorbance at 330 nm, 283 nm and 264 nm respectively (optimum wave lengths for melanoidin, caramel and ADP) before and after fungal treatment. It indicated that the percent removal of colorants by treatment with *Aspergillus oryzae JSA-1* decreased on increasing concentration of colorants.

Pawar et al. (2017) reported that molasses spent wash is one of the major components of growth media used in many industrial processes but presence of melanoidin, a recalcitrant compound causes several toxic effects on the living system. This is an attempt to study the Physico-chemical characteristics, microbial screening of molasses spent wash and use of mushroom in the decolorization of molasses spent wash. It was seen that mushroom (*Pleurotus* sp.) spawn showed better growth on medium prepared in 100% molasses spent wash as compared to 75%, 50% and 25% and also reduced its dark brown colorization.

5.4.2.4 Bacterial System

Different bacteria capable of both bioremediation and decolorization of molasses wastewater have been isolated by different workers in different periods (Table 5.4). Kumar and Viswanathan (1991) isolated bacterial strains from sewage and acclimatized on increasing concentrations of distillery waste, which were able to reduce COD by 80% in 4–5 days without any aeration and the major products left after the degradation process were biomass, carbon dioxide and volatile acids. Nakajima-Kame et al. (1999) could screen various molasses wastewater-decolorizing microorganisms under thermophilic and anaerobic conditions. Strain MD-32, newly isolated from a soil sample, was selected as the candidate strain. From taxonomical studies, this strain belonged to the genus *Bacillus*, most closely resembling *B. smithii*. The strain decolorized 35.5% of molasses pigment within 20 days at 55 °C under anaerobic conditions, but no decolorization activity was observed when cultivated aerobically. At all the concentrations tested, molasses pigment was effectively decolorized by MD-32, with decolorization yields of approximately 15% within 2 days. The molecular weight distribution as determined by gel filtration chromatography revealed that the decolorization of molasses pigment by the isolated strain is accompanied by a decrease in not only small molecules but also large ones. Acetogenic bacterial strain No.BP103 could decolorize 73.5% of molasses pigments in molasses wastewater supplemented with glucose, yeast extract, and basal mineral salts whereas the decolorization of this strain was decreased to only 9.75% in the absence of supplementary nutrients (Sirianuntapiboon et al. 2004b).

Three bacterial strains viz. *Xanthomonas fragairae*, *Bacillus megaterium* and *Bacillus cereus* were isolated from the activated sludge of a distillery waste water plant which were found to remove COD and color from the distillery effluent in the range of 55–68% and 38–58%, respectively (Jain et al. 2002).

Two bacterial strains *Pseudomonas putida* and *Aeromonas sp.* were used to bioremediate anaerobically treated distillery spent wash in a two-stage bioreactor. In the first stage, *P. putida* reduced the COD and color by 44.4% and 60%, respectively. The *Aeromonas sp.*, in the second stage, reduced the COD by 44%. Algal bioassay was used to evaluate the quality of the spent wash before and after treatment. The spent wash was eutrophic before the experimental treatment, but, after treatment, it showed poor algal growth (Ghosh et al. 2002).

Ghosh et al. (2004) also isolated bacterial strains from effluent discharged field soil capable of degrading recalcitrant compounds which were identified as *Pseudomonas, Enterobacter, Stenotrophomonas, Aeromonas, Acinetobacter and Klebsiella* all of which could carry out degradation of PMDE and maximum 44% COD reduction was achieved using these bacterial strains either singly or collectively.

Chaturvedi et al. (2006) isolated and characterized 15 culturable *rhizosphere* bacteria of *Phragmites australis* growing in distillery effluent contaminated sites. These 15 strains were *Microbacterium hydrocarbonoxydans, Achromobacter xylosoxidans, Bacillus subtilis, Bacillus megaterium, Bacillus anthracis, Bacillus licheniformis, Achromobacter xylosoxidans, Achromobacter sp., Bacillus thuringi-*

ensis, Bacillus licheniformis, Staphylococcus epidermidis, Pseudomonas migulae, Alcaligens faecalis and Bacillus cereus which collectively brought about 76% decolorization and 85–86% BOD and COD reduction of the effluent within 30 days. Typically, the bacterial decolorization may require a mixed culture to decolorize molasses wastewater through combined metabolic mode of individual bacterial strains. Thus, mixed culture studies have been carried out by several researchers for degradation of different effluents such as textile effluents. As the catabolic activities of microorganisms in a mixed consortium complement each other, obviously the syntrophic interactions present in mixed communities lead to complete mineralization of the effluent (Alkane et al. 2006; Kumar and Chandra 2006).

Alkane et al. (2006) reported 69% decolorization of molasses spentwash was using soil samples as inoculum indicated the potential of natural reservoir of such microorganisms. Kumar and Chandra (2006) also reported that the additional of 1% glucose as a supplementary carbon source was necessary for molasses decolorization by *Bacillus thuringiensis, Bacillus brevis, and Bacillus sp.* up to 22%, 27.4%, and 27.4% color removal, respectively. The similar pattern was also observed on the decolorization activity of bacterial consortium, comprising of *Pseudomonas aeruginosa* PAO1, *Stenotrophomonas maltophila and Proteus mirabilis*, which achieved its maximum molasses decolorization (67%) and 51% COD reduction within 72 h in the presence of 0.5% glucose (Mohana et al. 2005). Hence, mixed culture studies seem to be more promising for molasses wastewater decolorization.

Tiwari et al. (2012) isolated a potential thermotolerant melanoidin decolorizing bacterium from natural resources for treatment of distillery effluent at industrial level. Total 10 isolates were screened on solid medium containing molasses pigments. Three potential melanoidin decolorizing thermotolerant bacterial isolates identified as *Bacillus subtilis*, *Bacillus cereus* and *Pseudomonas* sp. were further optimized for decolorization at different physico-chemical and nutritional level. Out of these three, *Bacillus subtilis* showed maximum decolorization (85%) at 45 °C using (w/v) 0.1%, glucose; 0.1%, peptone; 0.05%, MgSO4; 0.01%, KH2PO4; pH-6.0 within 24 h of incubation under static condition. The strain of *Bacillus subtilis* can tolerate higher temperature and required very less carbon (0.1%, w/v) and nitrogen sources (0.1%, w/v) in submerged fermentation.

Tiwari et al. (2013) studied on characterize physico-chemical and microbial population of distillery effluent and isolate a novel thermotolerant bacterium for color, COD, and BOD reduction of spentwash. The level of alkalinity, TSS, DO, COD, BOD, TN, ammonical nitrogen, nitrate nitrogen, phosphorous, potassium, chloride, and calcium of spentwash (SW), bioreactor effluent (BE), and secondary treated effluent (STE) were well above the permissible limits. The level of color, TS, and TDS were under the permissible limits for STE but not for SW and BE. The microbial population was higher in BE. The results revealed that effluent was highly polluted and require suitable treatment before discharge. A novel thermotolerant bacterium, identified as *Pediococcus acidilactici*, was isolated which exhibited maximum 79% decolorization, 85% COD, and 94% BOD reduction at 45 °C using 0.1%, glucose; 0.1%, peptone; 0.05%, MgSO4; 0.05%, K_2HPO_4; pH 6.0 within 24 h under static condition. The ability of this strain to decolorize melanoidin at minimum carbon and nitrogen supplementation warrants its possible application for effluent treatment at industrial level. In addition, it is first instance when melanoidin decolorization was reported by *P. acidilactici*. This study could be an approach towards control of environmental pollution and health hazards of people in and around the effluent distillery unit.

5.4.2.5 Yeast System

Yeast, *Citeromyces* was used for treating Molasses Waste Water and high and stable removal efficiencies in both colour intensity and organic matter were obtained. However, the semi-pilot and pilot-scale experiments are to be tested for checking the stability of *Citeromyces* sp. (Sirianuntapiboon et al. 2004a). Microorganisms associated with a rotating biological contactor (RBC) were studied for the treatment of winery wastewater. One of the yeast isolates was able to reduce the COD of synthetic wastewater by 95% and 46% within 24 h under aerated and non-aerated conditions, respectively. Two flocculant strains of yeast, *Hansenula fabianii* and *Hansenula anomala* was used for the treatment of wastewater from beet molasses-spirits production and achieved 25.9% and 28.5% removal of TOC respectively from wastewater without dilution (Moriya et al. 1990) Dilution of wastewater was not favourable for practical treatment of wastewater due to the longer treatment time and higher energy cost. Color removal from MSW using terrestrial white-rot fungi was shown to be Mn-P dependent in *Phanerochaete chrysosporium* and laccase dependent in *Trametes versicolor*. The process was sorbose oxidase and glucose oxidase-dependent in mitosporic fungi *Aspergillus fumigates* and *A. oryzae* and in the basidiomycete *Coriolus* sp. No. 20. It was demonstrated that MnP-independent decolorization of MSW by the marine-derived fungus NIOCC #312 which decolourized 60% of MSW when added at 50% concentration in seawater medium. There was a direct correlation between concentration of glucose oxidase and decolorization of MSW. As previously discussed in this chapter, that decolorization was dependent on glucose oxidase levels in the culture medium like bacterial decolourization, it was suggested that H_2O_2 produced by glucose oxidase act as a bleaching agent.

Gupta et al. (2011) isolated a yeast strain from the paper and pulp effluent and identified as *Candida* sp., which decolorized distillery effluent by 60% within 4 days of incubation at 38C±1, pH 5.6. Further, this strain also reduced BOD & COD of the effluent by 78% and 60%, respectively. Tiwari et al. (2012) reported that melanoidin is a recalcitrant compound that causes several toxic effects on living system, therefore, may be treated before disposal. They isolated potential thermotolerant melanoidin decolorizing yeasts from natural resources, and optimized different physico-chemical and nutritional parameters. Total 24 yeasts were isolated from the soil samples of nearby distillery site, in which isolate Y-9 showed maximum decolorization and identified as *Candida tropicalis* by Microbial Type Culture Collection (MTCC) Chandigarh, India. The decolorization yield was expressed as the decrease in the absorbance at 475 nm against initial absorbance at the same wavelength. Uninoculated medium served as control. Yeast showed maximum decolorization (75%) at 45 °C using 0.2%, glucose; 0.2%, peptone; 0.05%, MgSO4; 0.01%, KH2PO4; pH-5.5 within 24 h of incubation under static condition. Decolorizing ability of yeast was also confirmed by high performance liquid chromatography (HPLC) analysis. The yeast strain efficiently decolorized melanoidin pigment of distillery effluent at higher temperature than the other earlier reported strains of yeast, therefore, this strain could also be used at industrial level for melanoidin decolorization as it tolerated a wide range of temperature and pH with very small amount of carbon and nitrogen sources.

5.4.2.6 Mixed Microbial Consortium

Several microbial consortia have been used for effective decolorization of distillery effluent in various types of fermentor system especially through continuous fermentation. Some of them are efficient based on the nature of spent wash with various dilutions and stages of treatment. Jet loop reactors (JLR), the efficiency of which has already been shown in both chemical and biological processes have also been evaluated for aerobic treatment of wine distillery wastewater. A JLR of 15 dm^3 working volume was used for the aerobic treatment of wine distillery wastewater (Petruccioli et al. 2002). COD removal efficiency higher than 90% was achieved, with an organic load of the final effluents that ranged between 0.11 and 0.3 kg COD. Most of the isolates belong to the genus *Pseudomonas* and the yeast *Saccharomyces cerevisiae* (Eusibio et al. 2004). JLR have higher oxygen transfer rates at lower energy costs. They also observed *Bacillus* apart from *Pseudomonas* and the yeast *Saccharomyces cerevisiae*. Adikane et al. (2006) studied decolorization of molasses spent wash in absence of any additional carbon or nitrogen source using soil as inoculum. A decolorization of 69% was obtained using 10% (w/v) soil and 12.5% (v/v) MSW after 7 days incubation.

Mohana et al. (2007) isolated microorganisms capable of decolorizing and degrading anaerobically treated distillery spentwash. A bacterial consortium comprising of three bacterial cultures was selected on the basis of rapid effluent decolorization and degradation, which exhibited 67.2% decolorization within 24 h and 51.2% chemical oxygen demand reduction within 72 h when incubated at 37 °C under static condition in effluent supplemented with 0.5% glucose, 0.1% KH_2PO_4, 0.05% KCl and 0.05% $MgSO_4{\cdot}7H_2O$. Addition of organic or inorganic nitrogen sources did not support decolorization. The cultures were identified as *Pseudomonas aeruginosa* PAO1, *Stenotrophomonas maltophila* and *Proteus mirabilis* by the 16S rDNA analysis.

Jiranuntipona et al. (2008) isolated a bacterial strain from waterfall sediments effectively used in other bacterial strains showing an effective consortium for better decolorization of distillery effluent. The effect of culture conditions and medium composition on decolorization activity and growth of the bacterial consortium was investigated. The bacterial consortium was able to grow and decolorize molasses wastewater under facultative and anaerobic conditions in general. Aerobic culture conditions at pH 7 and 9 in molasses wastewater containing Lactose broth (LB) medium exhibited high growth but poor decolorization. The addition of a supplementary nutrient source in molasses wastewater medium significantly increased the decolorization activity of the bacterial consortium up to 26.5% within 48 h under anaerobic conditions. Comparison of 16S rDNA sequences indicated that the bacterial consortium which showed decolorization activity under aerobic conditions consisted of *Acinetobacter sp., Pseudomonas sp., Comamonas sp., Klebsiella oxytoca, Serratia marcescens* and unidentified bacteria, whereas, the anaerobically enriched consortium consisted of *Pseudomonas sp., Klebsiella oxytoca, Bacillus cereus and Citrobacter farmeri*, a mercury-resistant bacterium, and an unidentified bacterium.

Tiwari et al. (2014) reported that, a consortium of bacterium and yeast from natural resources exhibited maximum 82 ± 1.5% decolorization within 24 h when incubated at 45 °C under static condition in effluent supplemented with 0.1% glucose; 0.1% peptone and 0.05% $MgSO_4$. The cultures were identified as *Pediococcus acidilactici* by 16S rDNA analysis and *Candida tropicalis* on the basis of phenotypic level. It is the first time when thermotolerant melanoidin decolorizing consortium (*Pediococcus acidilactici* and *Candida tropicalis*) isolated from distillery soil was capable to decolorizing melanoidin pigment of distillery effluent. Hence, it was observed that consortium has the ability to degrade the spentwash efficiently. This study could be an approach towards control of ecological pollution and health hazards of humans in and about the distillery location.

Wilk et al. (2017) studied a microbiological method of colored compounds removal from beet molasses vinasse (BMV). The conditions of the process (pH and temperature) and vinasse concentration were optimized. The bacteria *Lactobacillus plantarum* MiLAB393 showed the decolorization activity of 26% in medium consisted of 30% v/v of BMV at pH 6.5 and 35.8 °C.

5.4.2.7 Immobilization of Microbial Cells for Decolorization

A continuous decolorization of molasses waste water by immobilized cells of *Lactobacillus hilgardii* W-NS was reported with maximal decolorization yield in the presence of 1% glucose with a medium having pH 5.0 at 45 °C (Ohmomo et al. 1988). During last two decades, several attempts have been made to investigate the possibility of using cell immobilization in the technology of aerobic wastewater treatment (Sumino et al. 1985; Fedrici 1993). Early experiments were restricted to the use of selected pure cultures immobilized on solid supports for the degradation of specific toxic compounds (Livernoche et al. 1983; Anselmo et al. 1985). Later, immobilized consortia of two or more selected strains were employed (Zache and Rehm 1989; Kowalska et al. 1998), but of late activated sludge has been immobilized on different carriers and used for wastewater treatment (Shah et al. 1998).

Fujita et al. (2000) reported a bench-scale bioreactor using immobilized fungal cells equipped with an ultramembrane filtration unit was developed as a means of decolorizing brown color components (melanoidins) arising from the heat-treatment liquor (HTL) of waste sludge. Artificial HTL containing 4200 color units of synthetic melanoidin supplemented with 1000 mg/l ethanol was first subjected to decolorization by the fungus *Coriofus him* & s IF04917 immobilized onto polyurethane foam cubes and was subjected to ultrafiltration to obtain the permeate (filtrate) as the effluent. The retentate (concentrate) of the filtration unit containing the remaining melanoidin of high molecular weight and extracellular decolorizing enzymes was returned to the fungal bioreactor to allow further decolorization. This system was operated in a sequencing batch mode under nonsterile conditions. Contamination of the bioreactor with air/water-born microbes markedly lowered the decolorization efficiency. However, this problem was solved by heating the returned concentrate at 50 °C for 10 min. Under the almost stable condition of a hydraulic retention time of 2 day in a 1 day cycle sequencing batch mode, about 70% decolorization was routinely achieved using the entire system (bioreactor + ultrafiltration), while the contribution of the fungal bioreactor alone to the decolorization by 45% only.

Guimaraes et al. (2002) studied continuous decolorization of a sugar refinery wastewater in a modified rotating biological reactor containing *Phanerochaete chrysosporium* immobilized on polyurethane foam disks with a retention time of 3 days using polyurethane particles for treating aerobic winery wastewater. The highest COD removal rate was with free activated sludge in the bubble column reactor. The most prominent bacterial species isolated from the reactor liquid belonged to *Pseudomonas*, while *Bacillus* was isolated mostly from colonized carriers. *Pseudomonas fluorescens*, decolorized melanoidin wastewater (MWW) up to 76% under non-sterile conditions and up to 90% in sterile samples (Dahiya et al. 2001).

Raghukumar et al. (2004) reported decolorization of such intensely brown colored molasses spent wash (MSW) by *Flavodon flavus*, a white-rot basidiomycete fungus isolated from a marine habitat. They have further attempted to improve the process of decolorization of MSW with the help of this fungus by immobilization. Polyurethane foam-immobilized-fungus decolorized 10% diluted MSW by 60% and 73% by day 5 and 7, respectively. The immobilized fungus could effectively be used for a minimum of three cycles repeatedly to decolorize MSW. Besides decolorization, the fungus also removed the toxicity of MSW. Toxicity bioassay of the fungus-treated molasses spent wash using an estuarine fish *Oreochromis mossambicus* showed no liver damage in contrast to untreated effluent, which showed moderate liver damage. The benzo (a) pyrene, a polycyclic aromatic hydrocarbon (PAH) in the MSW is appears to be one of the causes of toxicity of the MSW. The concentration of PAH in the MSW decreased by 68% by day 5 on treatment with the fungus. This is the first report where decolorization of MSW is accompanied by simultaneous detoxification and decrease in PAH content of the MSW. A comparison of gel filtration chromatography of MSW, before and after treatment with the immobilized *F. flavus* showed disappearance of the most of the colored fractions in the fungus-treated MSW. A possible mechanism of decolorization of MSW is via the action of glucose oxidase accompanied by production of hydrogen peroxide that may ultimately act as a bleaching agent.

Chairattanmanokorn et al. (2005) studied a thermotolerant fungal strain for decolorization of alcohol distillery waste water. The capacity of fungal strain for production of ligninolytic enzyme was examined at 35 °C and 43 °C on agar media containing 2, 2-azino-bis (3-ethylbenzothiazolin-6-sulphonic acid) and $MnCl_2$. *Pycnoporus coccineus* strain showed a higher potential for decolorization, both on agar and in liquid media at 43 °C. Immobilized mycelia on polyurethane foam removed about threefold more total phenol and 50% more color than the free mycelia under shaking conditions at 43 °C.

Guimaraes et al. (2005) reported *Phanerochaete chrysosporium* immobilized on different support materials, such as polyurethane foam (PUF) and scouring web (SW), in shake cultures, was able to decolorize efficiently the sugar refinery effluent in a long-term repeated-batch operation. The decolorization medium composition was optimized using PUF-immobilized fungus. Addition of glucose was obligatory and the minimum glucose concentration was found to be 5 g/l. A rotating biological contactor (RBC) containing *P. chrysosporium* immobilized on PUF disks was operated with optimized decolorization medium in continuous mode with a retention time of 3 days. By simply reversing the feed inlet of the reactor, after 17 days of operation, it was possible to double the active fungal lifetime. During the course of operation the color, total phenols and chemical oxygen demand were reduced by 55%, 63% and 48%, respectively.

Adikane et al. (2006) studied decolorization of molasses spent wash in absence of any additional carbon or nitrogen source using soil as inoculum. A decolorization of 69% was obtained using 10% (w/v) soil and 12.5% (v/v) MSW after 7 days incubation.

Tiwari and Gaur (2014) reported that potential thermotolerant melanoidin decolorizing bacterium and yeast used for consortium development and entrapped in suitable matrix for immobilization at large scale spentwash treatment. A total 58 bacteria and 24 yeast were isolated from soil sample of distillery site in which *Pediococcus acidilactici* B-25 and *Candida tropicalis* RG-09 showed higher decolorization. These two strains were used for consortium development and then entrapped in sodium alginate for the wastewater treatment in a continuous column immobilization system. The immobilized consortium cells showed maximum 85% decolorization with the optimized parameters such as 2% (w/v) sodium alginate, 2% (w/v) calcium chloride with 16 h curing time, 5 g alginate beads with 2 mm bead diameter. The immobilized cells of consortium in alginate beads are more efficient for the wastewater treatment and can be reused for 18 cycles ($24 \times 18 = 432$ h) without any loss in their activity and 22 cycles with 72% residual activity. Immobilization of consortium cells in continuous column system is better than free culture. Among the immobilized cell bioreactors, no doubt that continuous column immobilization is a novel and efficient one, which can be adopted for the treatment of industrial wastewater containing melanoidin compounds and other pollutants. A proper choice of immobilized culture, careful consideration of various design parameters for continuous column immobilization will make treatment process cost effective in the long run (Table 5.4).

5.4.2.8 Algal System

Cyanobacteria are considered ideal for treatment of molasses wastewater as they, apart from degrading the polymers, also oxygenate waterbodies, thus reduce the BOD and COD levels (Mohana et al. 2009). Marine cyanobacteria such as *Oscillatoria boryna* have also been reported to degrade melanoidins due to the production of H_2O_2, hydroxyl, per hydroxyl and active oxygen radicals, resulting in the decolorization of the effluent (Kalavathi et al. 2001). Patel et al. (2001) have reported 96%, 81% and 26% decolorization of distillery effluent through bioflocculation by *Oscillatoria sp., Lyngbya sp.* and *Synechocystis sp*., respectively. Valderrama et al. (2002) studied the feasibility of combining microalgae, *Chlorella vulgaris* and macrophyte *Lemna minuscule* for bioremediation of wastewater from ethanol producing units. This combination resulted in 61% COD reduction and 52% color reduction. First, the microalgal treatment led to removal of organic matter and further treatment with macrophytes removed other organic matter, color and precipitated the microalgae.

5.4.2.9 Phytoremediation

Phytoremediation of effluents is an emerging low cost technique for removal of toxicants including metals from industrial effluents and is still in an experimental stage. Aquatic plants have excellent capacity to reduce the level of toxic metals, BOD and total solids from the wastewaters (Kumar and Chandra 2004). Billore et al. (2001) carried out the treatment of distillery effluent in a constructed wetland which comprised of four cells. After a pretreatment in the two first cells the effluent was channeled to cells three and four which contained plants *Typha latipholia* and *Phragmites karka*. This treatment eventually led to 64% COD, 85% BOD, 42% total solids and 79% phosphorus content reduction. Kumar and Chandra (2004) successfully treated distillery effluent in a two-stage process involving transformation of recalcitrant coloring components of the effluent by a bacterium *Bacillus thuringienesis* followed by subsequent reduction of remaining load of pollutants by a macrophyte *Spirodela polyrrhiza*. A similar biphasic treatment of the effluent was carried out in a constructed wetland with *Bacillus thuringienesis* and *Typha angustata* by Chandra et al. (2008a, b) which resulted in 98–99% BOD, COD and color reduction after 7 days.

5.4.2.10 Potential Decolourizing Oxidative Enzymes

For living cells, the major decolorization mechanism in biodegradation is the production of lignin modifying enzymes (LME), laccase, manganese peroxidase (MnP) and lignin peroxidase (LiP) to mineralize synthetic lignin or dyes (Table 5.4). However, the relative contributions of LiP, MnP and laccase to the decolorization of dyes may be different for each organism. Lignin-modifying enzymes are essential for lignin degradation, however for lignin mineralization they often combine with other processes involving oxidative enzymes. An older concept of ligninolysis re-emerges, enzymatic "combustion". By extension, this enzyme-assisted process is applicable to the degradation of many other recalcitrant molecules including dyes. The main LME are oxidoreductases, i.e., two types of peroxidases, LiP and MnP and a phenoloxidase, Laccase.

5.4.2.10.1 Manganese Peroxidases (MnP)

The most common ligninolytic peroxidises produced by almost all white-rot basidiomycetes and by various litter decomposing fungi are manganese peroxidises (MnP). These are glycosylated glycoproteins with an iron protoporphyrin IX (heme) prosthetic group, molecular weights between 32 and 62.5 kDa and are secreted in multiple isoforms. MnP preferentially oxidize Mn^{2+} into Mn^{3+}, which is stabilized by chelators such as oxalic acid, which is secreted by the fungi itself. Chelated Mn^{3+} acts as a highly reactive (up to 1510 mV in H_2O, low molecular weight, diffusible redox-mediator. Thus, MnP are able to oxidize and depolymerize their natural substrate, i.e., lignin as well as recalcitrant xenobiotics such as nitroaminotoluenes and dyes.

5.4.2.10.2 Lignin Peroxidases (LiP)

Lignin peroxidases (LiP) catalyze the oxidation of nonphenolic aromatic lignin moieties and similar compounds. LiP has been used to mineralize a variety of recalcitrant aromatic compounds, such as three and four ring PAHs, polychlorinated biphenyls and dyes. The extracellular N-glycosylated LiP with molecular masses between 38 and 47 kDa contain heme in the active site and show a classical peroxidase mechanism. Lignin peroxidase requires H_2O_2 as the co-substrate as well as the presence of a mediator like veratryl alcohol to degrade lignin and other phenolic compounds. Here H_2O_2 gets reduced to H_2O by gaining an electron from LiP (which itself gets oxidized). The oxidized LiP then returns to its native reduced state by gaining an electron from veratryl alcohol and oxidizing it to veratryl aldehyde. Veratryl aldehyde then gets reduced back to veratryl alcohol by gaining an electron from lignin or analogous structures such as xenobiotic pollutants. LiP catalyze several oxidations in the side chains of lignin and related compounds by one-electron abstraction to form reactive radicals. Also the cleavage of aromatic ring structures has been reported.

5.4.2.10.3 Versatile Peroxidases (VP)

A third group of peroxidases, versatile peroxidises (VP), has been recently recognized, that can be regarded as hybrid between MnP and LiP, since they can oxidize not only Mn^{2+} but also phenolic and nonphenolic aromatic compounds including dyes. VP has been described in species of *Pleurotus* and *Bjerkandera*. A novel enzyme which can utilize both veratryl alcohol and Mn^{2+}, versatile peroxidase has been recently described as a new family of ligninolytic peroxidases. The most noteworthy aspect of versatile peroxidase (VP) is that it combines the substrate specificity characteristics of LiP, MnP as well as cytochrome *c* peroxidase. In this way, it is able to oxidize a variety of (high and low redox potential) substrates including Mn^{2+}, phenolic and non-phenolic lignin dimers, veratryl alcohol, dimethoxybenzenes, different types of dyes, substituted phenols and hydroquinones. It has an Mn-binding site similar to MnP and an exposed tryptophan residue homologous to that involved in veratryl alcohol oxidation by LiP. It issuggested that the catalytic properties of the new peroxidase is due to a hybrid molecular architecture combining different substrate-binding and oxidation sites.

5.4.2.10.4 Laccases

Laccase is a benzenediol:oxygen oxidoreductase (a multi-copper enzyme) having multi-copper oxidase which has capability of oxidizing phenolic and aromatic compounds. Laccases catalyze the oxidation of a variety of aromatic hydrogen donors with the concomitant reduction of oxygen to water. Unlike peroxidases, it does not contain heme as the cofactor. Neither does it require H_2O_2 as the co-substrate but rather molecular oxygen. Laccase often supports a high degree of glycosylation, which confers a degree of self resistance to attack by proteases.

5.5 Recycling of Distillery Spentwash

5.5.1 The Ferti-irrigation Potential of Spentwash in Agriculture and Biocompost Supplement

Application of industrial wastes as fertilizer and soil amendment has become popular in agriculture. Irrigation water quality is believed to have effects on the soil and agricultural crops. Being very rich in organic matters, the utilization of distillery effluents in agricultural fields creates organic fertilization in the soil which raises the pH of the soil, increases availability of certain nutrients and capability to retain water and also improves the physical structure of soil. Mostly the distillery wastewaters are used for pre-sowing irrigation. The post-harvest fields are filled with distillery effluents. After 15–20 days, when the surface is almost dried, the fields are tilled and the crops are sown and subsequent irrigation is given with fresh water. However, the effluent is diluted two to three times before application on crops (Kamble et al. 2017). Apparently, the irrigation with distillery wastewater seems to be an attractive agricultural practice which not only augments crop yield but also provides a plausible solution for the land disposal of the effluents. One cubic meter of methanated effluent contains nearly 5 kg of potassium, 300 g of nitrogen and 20 g of phosphorus. If 1 cm of post methanation effluent is applied on 1 ha of agricultural land annually, it will yield nearly 600 kg of potassium, 360 kg of calcium, 100 kg of sulphates, 28 kg of nitrogen and 2 kg of phosphates. The distillery effluent contains 0.6–21.5% potash as K_2O, 0.1–1.0% phosphorus as P_2O and 0.01–1.5% Nitrogen.

Haroon and Bose (2004) conducted an experiment on chemical composition of untreated distillery spentwash and primary treated distillery effluent. There was a considerable change in pH of untreated and primary treated spentwash with acidic (3.8) and alkaline (8.0) reaction, respectively. Electrical conductivity of untreated and primary treated spentwash was 30.0 and 32.5 dS m^{-1}, respectively. Total solids content in untreated and primary spentwash was 90,000 and 81,000 mg L^{-1}, respectively. It contains high amount of nutrients such as nitrogen, phosphorous, potassium, sulphur and a large amount of micronutrients. The land application of distillery spent wash often benefits water pollution control and utilization for agricultural production (Kanimozhi and Vasudevan 2010, Kamble and Hebbara 2015). So it can be applied directly to the land as irrigation water as it helps in restoring and maintaining soil fertility, increasing soil microflora, improving physical and chemical properties of soil leading to better water retaining capacity of the soil. The effluent is ideal for sugarcane, maize, wheat and rape seed production (Diangan et al. 2008). It has been reported that waste water from different industries produced continuously could cater the needs of irrigated crops (Mallika 2001; Kamble et al. 2016). Thus the distillery spent wash will not only prevent waste from being an environmental hazard but also served as an additional potential source of fertilizer for agricultural use. Diluted spent wash increased the growth of shoot length, leaf number per plant, leaf area and chlorophyll content of peas (Rani and Srivastava 1990). It was also reported that the water holding capacity and cation exchange capacity increase the availability of nitrogen, phosphorus, potassium, copper, zinc, iron, manganese; but with reduced biochemical oxygen demand (BOD) with addition of sewage sludge to a course textured sandy and calcareous soil (Badawy and Elmataium 1999). An increase in the soil organic matter by 1% with sugar factory effluent applied to soils was observed in Cuba. Many workers reported an adverse effect of higher concentration of different types of industrial effluents in the growth rate of different crops (Dutta and Boissya 1997; Karunyal et al. 1993; Mathur and Davis 1987). There have been studies related to the application of distillery spentwash to agriculture in India as well as other part of the world. Spentwash at the rate 35–50 m^3 ha-1 was recommended as optimum dose for higher sugsr yield in Brazil and Australia. The distillery effluent can be conveniently used as source of irrigation in crop production. But, it has to be used judiciously because of high organic and chemical load (Banulekha 2007), while continuous usage of the effluent on the same land might result in development of sodicity, if the soils are ill drained. Several researchers concluded that non-judicious use of spentwash adversely affected crop growth and soil properties by increasing soil salinity (Mahimairaja and Bolan 2004; Kamble and Hebbara 2015; Kamble et al. 2016). Salinity causes reduction in leaf area as well as the rate of photosynthesis, which together result in reduced crop growth parameters. Also, high concentration of salt was reported to slow down or stop root elongation and reduction in root production. In the initial years, the beneficial use of spentwash to the sugarcane was due to its nutritive and growth promoting effect. However, long-term use of spentwash not only polluted the environment but also resulted in the accumulation of salts in the root zone. Soil salinity has been considered a limiting factor on sugarcane productivity in arid and semiarid regions. Soil saturated extract (ECe) conductivities greater than 1.7 dS m^{-1} was reported to decrease yield (Mass and Hoffman 1977). In Sau Paulo, Brazil, the crop productivity was two to ten times higher as compared to the untreated lands. Distillery spent wash was found to increase the cane yield in sugarcane and decrease the potassium fertilizer. In Philippines, spent wash application at the rate of 80–240 m^3 ha^{-1} in addition to chemical fertilizers increased the cane yield by 10–12% and sugar yield by 13–16% compared to normal irrigation. In Cuba, spent wash application at the rate of 90–150 m^3 ha^{-1} increased the potassium content of the soil, with increased cane yield and sugar recovery. In a study conducted in Kiev, Ukraine has shown increased yield of grasses, maize and fodder beet by 45–100% using distillery effluent. In India, extensive studies on distillery spent wash have been carried out successfully with respect to various crops in different agro-climatic regions (Mahimairaja and Bolan 2004; Mallika 2001).

In spite of the toxic nature of spent wash there are several important potential applications in the area of agriculture and biocompost thbrough which the toxic component of spentwash can easily be transform into useful products with the help of specific microorganisms present in the natural ecosystem. Soil is rich reservoir of various groups of microorganisms in which few are very efficient in the degradation of xenobiotic compounds. Spentwash also contain such compound like melanoidin which require such group of microorganisms having capability to produced mono-oxygenases, di-oxygenase, peroxidases, laccasaes, and others which have capability to degraded organic compounds. It has already been investigated that the distiller effluent is very important for methane production thereafter the effluent which is purified by 70–80% of its BOD, COD and melanoidin and rest of the 20% toxic components can be detoxified by irrigating agriculture land after suitable dilution as well as such for compost supplement. Several researchers have categorized it as a dilute organic fertilizer with 7–9% solids and 90–93% water. Above 75% of the solids are organic in nature and about 25% are inorganic. The presence of nitrogen in colloidal form permits it to work as a slow release fertilizer and better than any inorganic source of nitrogen. The presence of phosphorus in the organic form has also facilitated a better accessibility. It has been predicted that the 40 billion liters of spent wash being discharged every day could provide 480,000 tonnes of potassium, 52,000 tonnes of Nitrogen and 8000 tonnes of phosphorous per annum. This manurial potential has further been expected to meet the potassium requirement of 3 million hectares, nitrogen requirement of 0.25 million hectare and phosphorous requirement of 0.2 million hectare land, if two crops are taken in a year. Owing to its high organic matter, the spent wash is also a potential resource of bioenergy. If this energy is trapped, distilleries producing 3.2 billion litres of alcohol can generate 5 trillion kilo calories of energy yearly. Spent wash also contains large amounts of Copper (Cu), Manganese (Mn) and Zinc (Zn). It also contains 29.1% reducing sugar, 9.0% protein, 1.5% volatile solids, 21.0% gums, 4.5% combined lactic acid, 1.5% combined organic acids and 5.5% glycerol. The spent wash contains organic and inorganic compounds could bring significant changes in the physical, chemical and biological properties of soils and thus, considerably influence the fertility of soil. Organic compounds extracted by alkaline reagents have been found to be humic in nature and similar to those in soil. They also do not contain any toxic elements or compounds and the highly acidic nature and rich calcium and magnesium contents make them a good agent for reclamation of non saline sodic soils. The following options appear to be available for the utilization of spent wash in agriculture like biomethanation followed by irrigation, biomethanation and secondary treatment followed by irrigation, composting after or without biomethanation, controlled land application, after or without biomethanation, raw spent wash as an amendment to non calcareous sodic soil.

5.5.2 The Economics of Using Spentwash in Agriculture

The practice of applying post methanated effluents in agricultural fields either as pre-sown or post-sown show to be valuable. Appropriate balancing for nutrient supply needs to be done to resolve the difficulty of extreme salt loading. The usual approach to treating effluents even up to secondary or tertiary levels does not give an eco-friendly solution. Agricultural consumption of waste water offers a low cost option where the manure and irrigation value of spent wash are utilized and savings generated in fertilizers and water use. Farmers could save Rs. 1335 crore per year that they spend on nitrogenous fertilizers if only 200 of the existing distilleries recycled there wastes to the agricultural fields. The secondary and tertiary treatment systems for distillery effluents are highly energy intensive and may need 350 MW installed load to cater the secondary and tertiary systems involving high cost.

5.5.3 Impact on Crop Yields and Soil

Raw, post-methanated and diluted spent wash have been successfully utilized (where applied) as manure in cultivating various crops like rice, maize, wheat, pulses, cash crops, paddy, sugarcane, oil seed crops, medicinal plants, flowering plants and vegetables like potato, lady finger, pumpkin, bottle gourd, brinjal, beans, cauliflower, cucumber, etc. The application of spent wash as manure has resulted in increased yield of crops, increased root and shoot length, leaf area index, chlorophyll content and pod formation. Substantial increase was also recorded in case of germination, oil and protein content of crops, nutrient availability of soil, nutrient uptake by crops and mineralization of soil. It has also enhanced the nutrient availability and uptake without any post harvest detrimental impacts on the soil texture, chemistry and biology.

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Chapter 6
Treatment and Recycling of Wastewater from Winery

Sivakumar Vijayaraghavalu, Ritambhara, Himanshu K. Prasad, and Munish Kumar

Abstract Wine production is a multi-step process that consumes large quantities of water for various cleaning activities under different stages of its production. The effluent from winery is mostly acidic, but can vary from slightly acidic to basic. It contains organic acids, lees, ethanol, sugars, aldehydes, phenolic compounds and detergents. These contaminants in the winery waste water have high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) which is detrimental to flora and fauna, if released un-treated into the environment. Production facilities equipped with recently developed water conservation equipments reduce the water consumption by 20% but results in more concentrated waste stream. Further if the facility have also a distiller, then the effluent BOD and COD level doubles. Hence, compliance to appropriate treatment protocols is necessary to reduce the toxicity of the effluent. However further advancement in treatment methods are needed to increase the efficiency and decrease the environmental foot print of the effluents. This book chapter discusses the various procedures followed for the treatment of winery waste water as well as highlights the recently developed advanced operation procedures that are at bench-side or in pilot-scale study.

Keywords Winery · Pollutants · Wastewater · Treatment · Recycling

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R. L. Singh, R. P. Singh (eds.), *Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future*, Applied Environmental Science and Engineering for a Sustainable Future,
https://doi.org/10.1007/978-981-13-1468-1_6

6.1 Introduction

Wine production is a multi-step process requiring almost 1100 gal of water per ton of grapes. Water usage in winery depends on the water conservation practices followed in the production facility. In general, production unit equipped with equipment's developed after 1990 has reduced water consumption of about 20%; thereby results in more concentrated waste stream. Winery waste arise from number of activities during the production including cleaning of production tanks, washing equipment(s) and floors, rinsing of the transfer lines, bottling facilities and filtration units. If the facility is also a distiller that produces alcohol from wine and its production waste, then the stillage (distillation waste), biochemical oxygen demand (BOD) and total suspended solids (TSS) can double or triple in the daily effluent. In addition sediments of dead/residual yeast (lees), bacteria, grape pulp and other particulate matter can have BOD and TSS concentration in excess of 100,000 mg/L (Napa Sanitation District 2009).

6.1.1 Need to Treat Winery Effluent

The wineries pose a great challenge for waste water treatment. The effluent from the industry contains various contaminants such as sugars, ethanol, organic acids, aldehydes, phenolic compounds, other microbial fermentation products and detergents from cleanup operations (Petruccioli et al. 2000). Organic acids produced during fermentation process, and the pH of winery waste water is slightly acid (6.5–6.9), but can vary from mildly acidic (5.0) to basic (10) during cleaning operations (Napa Sanitation District 2009). Due to increase in BOD and chemical oxygen demand (COD) release of untreated winery water to the environment could be detrimental to both flora and fauna. Disposal of winery waste into natural water bodies could deplete the dissolved oxygen, which leads to suffocation of aquatic and amphibious life. Further, disposal of winery effluent in soil could alter the physiochemical property of the ground water. It could affect the odor, color and pH by leaching the organic and inorganic ions in to ground water (Christen et al. 2010). Usage of untreated winery water in agricultural fields could reduce the plant growth. Also due to high electrical conductivity of this organic acid rich water; germination of seeds may be delayed (Melamane et al. 2007). In addition, low levels of phenolic compounds found in the effluent are toxic to all forms of life including humans (Nair et al. 2008). Hence, treatment of winery effluent following appropriate protocol is of prime importance in protecting the environment.

6.2 Winery Effluent Treatment Process

Although the characteristics of pollutants in the winery effluents are well classified, it is difficult to define the toxicants in the effluent prior to production, because it is source – centric, that is, it depends on the wine making protocol and the technologies adopted for it (Brucculeri et al. 2005). Various treatment processes are developed and/or in development with a goal of reducing the BOD, COD, TSS, chemicals and water usage at the reduced investment and operational cost. These processes focus on reliability and ease of management. Treatment systems vary from simple and direct discharge of the effluent to septic tanks to more complex, capital – intensive systems, including aeration ponds and aerobic digesters (Mosse et al. 2011). Biological treatment systems that heavily rely on ponds and land based treatment systems are most appropriate and are described under different headings in this chapter. These traditional systems are sustainable with less operational and investment cost on comparison to some of the advanced systems that are still at pilot study level. Further, it reduces the BOD, TSS and bio-degradable pollutants at minimal operational cost. Conversely the refractory pollutants in the effluents mostly exceed the levels stated European Directive 91/271/EEC. Hence combination of one or many other treatment processes such as filtration or physical/chemical processes could yield better water quality than employing biological treatment alone and can be safely disposed in the environment. The winery water treatment processes are discussed under different headings in this chapter, which are as follows.

6.2.1 Waste Water Treatment Ponds

Most commonly wineries world-wide have waste water ponds/lagoons in which the effluent is treated to lower the BOD and adjust the pH. The BOD in the effluent can range from 5000 to 20,000 ppm for spills, pure wine or juice. High levels of BOD are directly proportional to the sugars in the effluent. Usually regulatory bodies recommend the effluent pH between 5 and 9 and BOD levels below 200 ppm prior used for irrigation or other purposes (Napa Sanitation District 2009). Mostly this system uses a mechanical aerator to increase the dissolved oxygen in the pond; thereby the organic matter can be degraded efficiently. The major advantages of ponds/lagoons are its simplicity in operation, low energy consumption than other conventional mechanical treatment systems, natural pH buffering, nutrient uptake and solar induced disinfection. Though it is a simple system depending on the characteristics of effluent the operating parameters and the types of ponds used for the treatment may vary (Welz et al. 2016).

Water treatment ponds are usually classified as aerobic, anaerobic, facultative and maturation. Facultative or mechanically aerated ponds are most commonly used in wineries (Welz et al. 2016). Anaerobic ponds are designed to deal effluents with high organic loading and are devoid of dissolved oxygen. Hence they may need longer detention time to degrade organic matter. Anaerobic decomposition of organic matter results in gases such as methane and carbon dioxide which can be used for electricity generation. Most often the upstream anaerobic bio-reactors are connected to the anaerobic lagoons to increase its efficiency.

Anaerobic biological treatment of winery waste water was reported to achieve significant reduction in COD. For instance, a study by Ruiz et al. (2001) have shown that employing anaerobic sequencing batch reactor (ASBR) with hydraulic retention time (HRT) for 2 days attained more than 98% COD removal. The process involves two stages; initial acidification of organic matter and then breaking down of volatile fatty acids to form methane. Both the stages followed zero-order reactions.

The anaerobic processes rely majorly on the type of sludge seeded in the reactor, temperature and pH. A study done by Keyser et al. (2003) have shown that *Enterobacter sakazakii* enriched granular sludge seeded in the up-flow anaerobic sludge blanket (UASB) reactors with microbial conditioning step reduced the start-up time of the UASB reactor to 17 days and removes more than 90% COD on comparison to conventional sludge feed (<70% after 90 days); thereby reduced the operational cost. A different study report that the good granule (microbial aggregates) growth occurred in seed sludge at mesophilic conditions (35 °C) than at sub-mesophilic conditions (18–21 °C) (Kalyuzhnyi et al. 2000). Yet another study done by the same group reported that application of non-preacidified sludge at the temperature of 10 °C to the UASB reactor increased the organic loading rate and COD removal by 70%. Organic contaminants such as sugars, ethanol and butyrate were efficiently removed and only trace amounts found in the treated effluent. Also the hydrogen gas levels in the reactors headspace was minimized significantly. Low temperature acts as rate limiting step for propionate conversion (Kalyuzhnyi et al. 2001). Thus by controlling the temperature and organic load, on an average of 90% COD reduction can be achieved with successful start-stop operation of the UASB reactor.

In contrast to UASB the up-flow sludge bed-filter (USBF) reactor was shown to be more efficient in reducing COD (96–98%) and methane production (70–80%). Because of high methane yield this process is highly advantageous in terms of energy recovery (Wolmarans and Villiers 2002). Ganesh et al. (2010) studied three different upflow anaerobic fixed-bed reactors, these reactors differed by the size and surface area of the low density supports in them. Smaller reactors are better because of increased organic loading rate, retention of volatile solids and increased biomass activity and higher reduction in COD. Additionally these reactors produced less sludge and consume less energy. However, like any other anaerobic reactors, the effluent from it contains high levels of residual COD (average – 3900 mg/L), and makes it unsuitable to discharge without prior treatment. In line with this, a different study investigating the efficiency of anaerobic moving bed biofilm reactor (AMBBR) also concluded that the reactor performance increased with increase in surface area of the carrier used (Chai et al. 2014). Hence, conceptually it can be generalized that increase in surface area of the bed/carrier could support better granular growth, and thereby increase the efficiency of anaerobic digestion (Ganesh et al. 2010; Chai et al. 2014).

In general, the anaerobic digestion of winery effluent generates biogas with 60–70% methane for every 400–600 L/kg COD removed (Daffonchio et al. 1998). At comparable operating conditions the levels of residual organic recalcitrant are higher with lower methane production in red wine effluent than from white wine effluent. One of the major reasons for this difference is due to generation of high levels of acetic acid from volatile fatty acid (VFA) in white wine effluent on comparison to red wine effluent (25% acetic acid from VFA) (Daffonchio et al. 1998). Amongst the anaerobic processes the ASBR and USBF are two most efficient treatment processes for winery waste water with COD reduction of up to 98% (Daffonchio et al. 1998; Molina et al. 2007). ASBR is often used as alternative to continuous system due to its ability to produce high quality effluent at low operational cost. USBF combines the main advantages of up-flow anaerobic filter (UAF) and UASB reactors for biomass retention. In this way it is possible to minimize clogging or biomass flotation problems (Fernandez et al. 2001). After biological treatment COD value is reduced to 900–5440 mg/L. Also, the residual BOD ranges from 101 to 1060 mg/L (Nair et al. 2008). Consistently, numerous studies showed that recalcitrant high molecular weight compounds such as polyphenols tannins and lignin are not mineralized by biological treatment. Based on these facts it can be generalized that the biological treatment alone cannot achieve complete mineralization and hence need combination of other advanced processes to produce high quality effluents that can be safely discharged in the environment. Facultative ponds involve an aerobic upper – and anaerobic lower – layer. The aerobic system is maintained using aquatic plants and aerators (Butler et al. 2017). Most of the wineries use only floating aerators to increase the oxygen content (Fig. 6.1). However, this method is not very efficient because the amount of oxygen transferred to the water is approximately 3%.

Some wineries also use more efficient aerators known as bubble diffusers. This method uses a rotary blower to deliver high volumes of air at low pressure. The air sucked from atmosphere is delivered to fine bubble diffusers that produce small bubbles (Oliveira et al. 2009). The smaller the bubble greater the oxygen transfer.

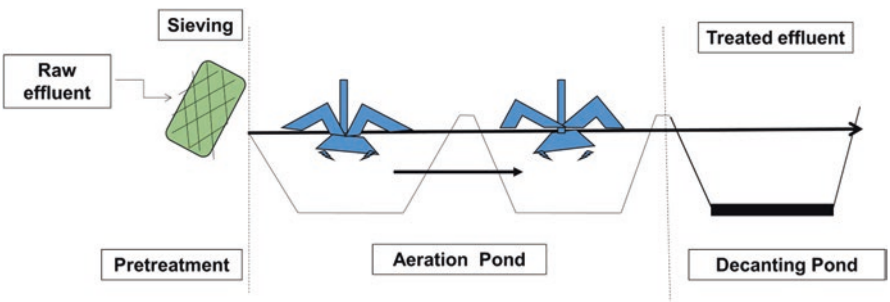

Fig. 6.1 Schematic diagram showing winery waste water treatment pond. Effluents passed through sieve are stored in series of ponds equipped with aerators for treatment. Recalcitrant pollutants were decanted at the decanting pond and then the treated water is collected for re-use or for irrigation purpose

This method is highly efficient than the simple floating aerators. Efficiency of aerating the ponds is directly proportional to its size; smaller ponds are aerated better than the larger ones. If the wineries increase the production then the waste water generation increases, which in-turn requires more acres of land to increase the pond size and the amount of aeration required to lower the BOD levels, as a result, investment and operation cost increases. Thus to overcome such a hurdle, wineries can maintain an optimal pH (7.0), so that the biomass (microbes) that actually reduces the BOD can survive and aerate the effluent (Bories et al. 2005). Many wineries also do bio-augmentation, adds freeze – dried microbes to consume the sugars and reduce the BOD levels in the effluents.

Additionally to increase the efficiency of BOD reduction, some wineries install the bio-reactors upstream of the ponds (Andreottola et al. 2005). A bioreactor is a series of tanks where the effluent is highly aerated and pH adjusted, the effluent is then allowed to flow into a clarifier where the bacteria settle down. The settled organisms are then returned to the incoming high BOD stream. Resultant of aerobic treatment is odor free whereas anaerobic treatment generate odor (Montalvo et al. 2010). The biological treated effluents still may contain recalcitrant molecules and warrants further treatment employing other processes before being discharged in the environment for irrigational or recreational purposes. The nutrient rich degraded biomass can also be used to enrich the soil (Fig. 6.2).

Maturation ponds are shallower than other ponds and allow algal development to increase the dissolved oxygen and use ultraviolet (UV) rays of sunlight for disinfection. These shallow ponds are most suitable for small wineries. Because of its simplicity and low operation cost, pond systems are considered as the most sustainable type of treatment process. The treated water with low BOD can be used for irrigating the vineyard or sent to ornamental ponds constructed for recreation purpose within the winery or elsewhere (Fig. 6.2). The sludge formed due to biodegradation of

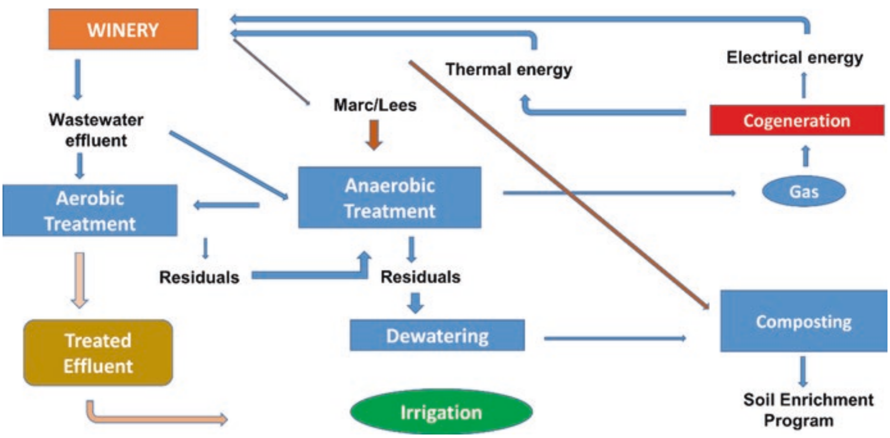

Fig. 6.2 Summary of winery water treatment process using pond system – schematic representation

organic matter can be removed periodically (2–5 years) using a pontoon mounted pump and then delivered to dewatering system and the resulting solid mass can be disposed at landfills or spread on the land. Alternatively, the sludge can be treated in the bioreactors and the resulting compost can be used to nourish the soil in the vineyard (Petruccioli et al. 2002).

6.2.2 Land Treatment Systems

Controlled application of waste water on the land surface with aim of reducing the pollutants through natural physical, chemical and biological processes that happens on and in the soil niche is called land treatment. This process is highly advantageous in terms of operating and maintenance cost and in terms of least technical sophistications over other conventional and advanced methods of water purification methods. The most common classification of land treatment methods are slow rate (SR), overland flow (OF), rapid infiltration (RI), subsurface soil absorption or drain field (DF) and dry wells (DW). Various organic and inorganic minerals in the effluents are potential toxicants when discharged in natural water courses, but if they are applied under controlled conditions to a vegetative land, it could serve as nutrients to the plants and will have a positive economic value (Bustamante et al. 2005). In this view land treatment is advantageous over other methods of water treatment (Christen et al. 2010).

6.2.2.1 Slow Rate (SR)

In this method the waste water is allowed to flow through the plants and soil matrix in a cultivated land. The water is applied evenly throughout the land either by spray or drip irrigation technology or using the vehicle mounted apparatus or by other surface techniques such as graded-border and furrow irrigation. Usually, the water to be treated is applied at regular intervals (4–10 days) to the fields to maintain aerobicity in the soil. A portion of the applied water can percolate through the soil to reach the ground water table, a part of it is absorbed by plants and the remaining is evaporated naturally (Fig. 6.3).

In some treatment process the waste water reaching the ground water is intercepted by construction of drains or recovery wells; so that the water can be reapplied on the vegetated soil. The treatment of the waste water occurs while it is interacting with the plant-soil matrix (Mousavinezhad et al. 2015). Pollutants that contribute to the BOD are mostly adsorbed on the soil particles and/or catabolized by bacterial activities. Suspended solids in the effluent are filtered while it is percolating through the soil particles (Mousavinezhad et al. 2015). Nitrogen is assimilated by vegetation or eliminated by microbial action and/or stored in the soil. Phosphorus undergoes chemical immobilization (precipitation and adsorption) and/or used up by the plants. Monovalent and multivalent ions are adsorbed in the soil

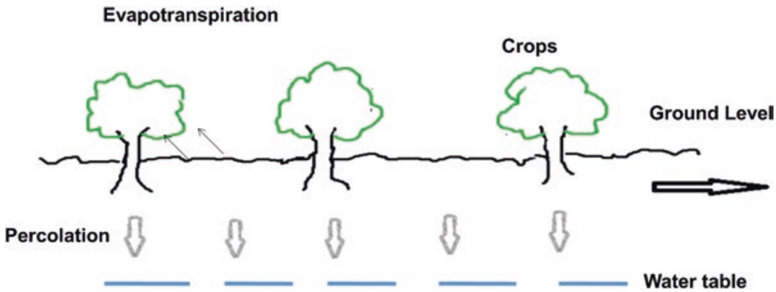

Fig. 6.3 Land treatment system – Slow Rate (SR) System. Winery effluent intermittently allowed to interact with plant-soil matrix to remove BOD, COD and TSS. Pollutants are partly adsorbed to soil particles and a part is degraded by soil microbes and a part of it is assimilated by cultivated plants. Water purified while slowly percolating through the soil to reach ground water table

or precipitated or undergo complexation with the soil particles and also a part of it is absorbed by the plants. Pathogens in the effluents are eliminated by adsorption, desiccation, radiation, or predation by soil microbes. Trace organics are decomposed by sunlight (photodecomposition), or undergo volatilization and/or degradation.

The SR system is classified into two types, the first category focuses only on water purification, no vegetation is employed, whereas the second category focuses on crop production and water re-use. Unlike first category, only sufficient amount of water required for crop growth is added intermittently in the second category. SR system has highest water treatment potential than all other natural systems (Mousavinezhad et al. 2015).

6.2.2.2 Rapid Infiltration (RI)

Water is applied intermittently through highly permeable soil. The suspended solids are filtered as the water flows through the soil matrix. Organic and inorganic chemicals are precipitated and adsorbed during water percolation (Christen et al. 2010). Biological oxidation, assimilation and reduction of pollutants occur in the top few layers of the soil. No vegetation is used in this method; the volume of effluent released into the soil and water evaporation from the soil surface is high when compared with other land treatment methods (Fig. 6.4) Since the waste water receives minimal treatment prior mixing with the ground water; this method is most cost effective and needs site specific pretreatment to protect the ground water quality. Some of the wineries also recover the water by construction of spreading basins in the loose soils. The basins will have collecting pipes embedded at the bottom of the soil, the filtered water reaching the collecting pipes is directed to small streams or to drains wells for re-use (Christen et al. 2010).

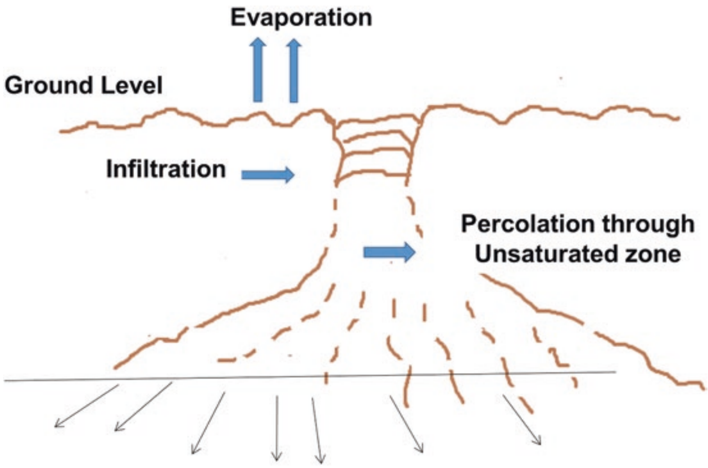

Fig. 6.4 Rapid infiltration (RI) system. Water treatment occurs as it rapidly percolates through highly permeable soil. Biological oxidation, adsorption and reduction of pollutants occur in the top few layers of the soil

6.2.2.3 Overland Flow (OF)

The water to be purified is applied at the upper end of the vegetated slopes and collected at the lower end for re-application/re-use (Fig. 6.5). The applied water is partly absorbed by plants, while the remaining is evaporated or collected at the bottom. In contrary to the SR and RI method, this process is carried on relatively impermeable soil. Water treatment is majorly depends on the action of soil microbes. Complex organic substances are degraded by microbes as a result BOD is reduced. Elements like nitrogen and phosphorus are absorbed by plants. Nitrogen is also removed by microbial de-nitrification. Mostly, this process is used as a secondary treatment, advanced secondary treatment or for nutrient removal. Constructed wetlands are secondary treatment systems; therefore a primary system or pre-filter is essential for solid removal before wastewater is applied to the wetlands (DEQ 2015; Thullen et al. 2005).

6.2.2.4 Dry – Wells

Dry well is also a conventional method used for the treatment of waste water. Constructed dry wells are used to collect, detain and percolate the waste water which cannot be discharged directly to the natural water bodies.

Generally dry wells increase the ground water recharge capacity and augment low flow stream conditions. One of the major problem in using dry well system is the water infiltration to the surrounding soils can be clogged and could decrease the volume filtered through the soil and reaching the ground water. The reduction in

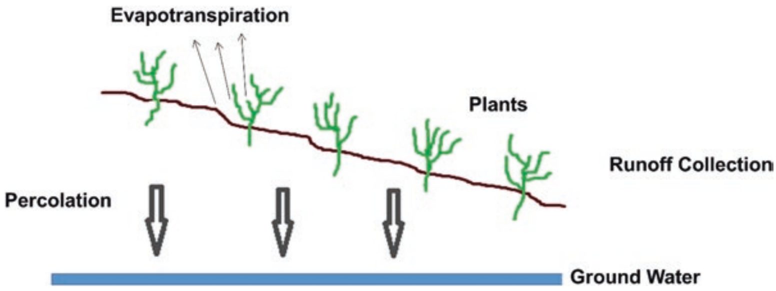

Fig. 6.5 Overland flow (OF) system. Effluent is applied at the top of the vegetated slopes and collected at the bottom. The soil is relatively impermeable; so water treatment depends on microorganisms in the soil. Pollutants are degraded by microbial action, assimilated by cultivated plants and also adsorbed in top layer of the soil

infiltration also results in longer periods of standing water in the well and overflow from the well. Hence to avoid clogging, sediment loads in the waste water needs to be monitored regularly. Since this process has potential to contaminate the ground water; this method is least preferred and alternative methods are advised (DEQ 2015).

All land treatment process mentioned above is highly efficient in BOD removal and rely on natural phenomenon occurring in and on the soil such as filtration, adsorption, biological reduction and oxidation. For instance in SR and RI, the BOD reduction happens on the soil surface or in the near surface soil where the microbial activity is intense. Since OF uses relatively impermeable soil, the reduction heavily depends on the biological growth and slime formation on the OF slope. Additionally, because water flows as thin film in OF the particulate matter settles relatively faster than SR/RI systems. Since by principle all these systems mainly depend on microbes for BOD reduction, as long as the favorable conditions are maintained for growth of microbes, these systems are capable of sustained BOD removal. Some of the pilot studies done earlier shown that BOD removal were independent of pre-treatment of waste water, soil type or infiltration rate. Hence for land treatment systems high levels of pre-application treatments are not recommended for BOD removal (Bhargava and Lakmini 2016).

Of all the land treatment systems the SR is most efficient in metal removal from waste water. The fine-textured soils and increased interaction of effluent with the soil matrix favors higher percent of metal removal in this system. Since RI uses highly permeable soil and the water percolates faster to reach the water table, the distance between the soil surface and water table determines the effectiveness of metal removal. More the distance betters the removal. In OF system due to minimal contact of waste water with soil matrix the metal removal is comparatively poor and it depends on the type of metals in the effluent. One major problem with metal pollutants is that they could accumulate in the soil and have potential to enter the food chain via crops or animals (Bustamante et al. 2005).

Due to existence of nitrogen in various forms including elemental nitrogen to different states of oxidized forms and as ammonia; its removal using the land treatment method significantly depends on the soil type, method and water characteristic. Hence it is appropriate to estimate the type of nitrogen pollutant and its concentration in the water before selecting the soil type. For example in SR and OF method, nitrates and ammonium are majorly removed by plant assimilation. Additionally other process such as denitrification and volatilization also contribute to nitrogen removal; whereas in RI, ammonia adsorption on the soil particles followed by nitrification is the major process of nitrogen removal from waste water (Houlbrooke et al. 2004).

Phosphorus removal in land treatment also occurs through plant uptake, microbial, chemical and/or by physical processes. Since RI system has no crop, greater travel distances of water in the soil is requisite for effective phosphorus removal, whereas in SR system slow percolation of water through soil-plant matrix favors effective assimilation of phosphorus by plants and the remaining are precipitated. Due to limited water-soil interaction in OF phosphorus removal is in the range of 40–60%, so its removal can be improved by chemical addition and precipitation on the treatment slope. Phosphorus removal in the soil significantly depends on the chemical reactions happening in the soil which are not renewable; as a result retention capacity of soil could reduce with time, but not exhausted (Bhargava and Lakmini 2016).

In land treatments, especially in SR and OF systems, the microbes that live in microsphere of roots also play a critical role in purifying waste water by breaking down the organics and removal of colloidal solids. As mentioned above, maintaining the aerobicity of soil sustains the growth of crop and microbes and thereby purifies water effectively for re-use or to recharge the ground water. Like any system, land treatment has its own caveat. Land treatment obviously requires large area for treatment. Not all the sites are candidates for land application; it depends on the type of soil that exists in the industrial area. Land treatments are subjective to weather conditions, they are best utilized in summer; when the evapotranspiration rates are high in the irrigated fields, whereas in winter or in monsoon periods the rate of evapotranspiration rates in the fields are poor thereby leading to escalated costs and decreases the effective filtration. Despite its dis-advantages, it is the most cost effective treatment process; wineries can use the filtered water to irrigate the grape fields or can use it in forestry in or away from the site.

6.2.3 Biological Treatment Processes

Wine industries throughout the world are producing billion of liters of winery wastewater annually. Generally, before disposal, these waste are treated using biological methods, such as anaerobic digestion and activated sludge reactors. However, this kind of treatments represents high costs to the winery industry. An alternative to these costly treatment methods is the use of efficient, low cost and environment friendly option using microorganisms. The microbial species including fungi, bacteria, and algae have been exploited for their capacity to remediate toxic chemical pollutants present in various industrial wastewater including wineries.The unique metabolic characteristics of the microorganisms help them to survive in wine making environments and for that reason could be potential candidates to act as inoculum in the winery effluent treatment. This section will highlight the roles of microbial systems in winery effluent treatment and use of microbial fuel cell systems for efficient treatment of the winery wastewater.

6.2.3.1 Role of Bacteria and Bacterial Communities in Winery Wastewater Treatment

A wide variety of bacterial and yeast species have been isolated from various treatment processes employed for winery wastewater. These isolates have the potential to be used in biological treatment owing to various unique physiological adaptations. Studies on the microbial community in waste water aerated bioreactors indicated that bacteria dominated over the fungi (Eusébio et al. 2004; McIlroy et al. 2011). These bacteria show remarkable tendencies to tolerate acidic pH, high ethanol concentration and utilization of a diverse carbon source (Joyeux 1984; Drysdale and Fleet 1988). *Acetobacter aceti* and *Acetobacter pasteurianus* were the most adaptive species. These bacteria were persistent even after 9 months of the storage in barrels, which is a good indicator of the capacity of these microorganisms to survive to adverse conditions. *A. pasteurianus, Acetobacter liquefaciens* and *Acetobacter hansenii* can survive in winery conditions (Du Toit and Lambrechts 2002). In fact, the aerobic treatment of winery wastewater by activated sludge bioreactors are rich in microbial populations of *Pseudomonas* sp. followed by *Bacillus* sp., *S. cerevisiae,* and *Flavobacterium* sp. (Petruccioli et al. 2000, 2002). Also, in a jet-loop activated sludge reactor the microbes isolated were *Pseudomonas* sp*., Bacillus* sp*., Candida* sp*., Agrobacterium radiobacter* and *Acinobacter* sp. (Eusébio et al. 2004). *Enterobacter sakazakii, Bacillus licheniformis, Bacillus megaterium* and *Staphylococcus species* were isolated in winery effluent medium by Keyser from the upflow anaerobic sludge blanket (UASB) process (Keyser et al. 2003). Apart from the bacterial communities in the wine waste waters, the communities present during wine making process itself represent a good source of organisms having the potential for use in various wine waste water treatment procedures. Several microbial communities analysis studies have been done to assess the wine waste water impact on bacterial communities (Rohr et al. 2011; Ramond et al. 2013). Using molecular phylogenetic methods to monitor seasonal changes in the composition of the microbial community in a natural wetland several members of dominant genera were identified. These includes genus *Clostridium, Citrobacter, Acinetobacter, Syntrophus, Rhodocyclus, Frateuria, Propionibacterium, Pelobacter* and *Syntrophobacter* (Rohr et al. 2011). Several unidentified tolerant microbial communities were reported to be prsent that result in high degradation of the wine wastewater discharge (Ramond et al. 2013). In a very recent report by de Beer et al.

(2018) used next-generation sequencing startegies to understand the microbial communities, their metabolic capabilities prevelant in the biofilm of the two towers of a high rate biological contact reactor treating winery wastewater. They have identificated 19 groups at genus level including *Acetobacterium, Actinomyces, Aeromicrobium, Amaricoccus, Arcobacter, Bdellovibrio, Bosea, Devosia, Dysgonomonas, Fluviicola, Kaistia, Lactobacillus, Leadbetterella, Mezorhizobium, Myroides, Paracocci, Patulibacter, Pseudoxanthomonas* and *Trichococcus.* Recently, a novel group of nitrogen-fixing bacterial communities was identified in biological sand filter for winery waste water remediation owing to a high C:N ration in these effluents. The value addition of winery effluent is a promising prospect for waste utilization. One of the prospects is to use the waste to grow microbes producing industrially useful compounds, like xanthan. Xanthan is used in food, pharmaceutical, petrochemical, cosmetic and other industries as a stabilizer, emulsifier, gelling and thickening agent (García-Ochoa et al. 2000). Indeed few reports are existing which confirmed that cultivation of *Xanthomonas campestris* could produce xanthanon from wastewaters (Rončević et al. 2015, 2017; Bajić et al. 2015). Few studies have reported the use of winery waste water as substrate for *Gluconacetobacter xylinus* for the production of cellulose (Wu and Liu 2013; Krzywonos et al. 2009). Similarly, technological advancements in the generation of electricity from waste effluents have contributed to the development of microbial fuel cell (MFC) and their derivatives for simultaneous treating and electricity generations (Xu et al. 2015; Pandey et al. 2016). By using microorganisms under anaerobic conditions, MFCs are an example of an ecofriendly bio-electrochemical systems capable of metabolizing organic matter into electricity (Pant et al. 2010; Zhou et al. 2011). A MFC uses the anaerobic oxidation of biodegradable organic substrates by microbes (Pant et al. 2013; Patil et al. 2012). These microorganisms are capable of converting a wide variety of biodegradable organic compounds into CO_2, water, and energy (Pandey et al. 2016). Few studies have reported the winery waste water treatment with MFCs and in those studies only *Acetobacter aceti, Gluconobacter roseus* and activated sludge were used as anodic inoculum. Using wine waste water (2200 mg COD l^{-1}), a maximal electrical energy of 31.7 Wh m^{-3}, 27% COD removal and 18% columbic efficiency (CE) has been reported (Cusick et al. 2010). Furthermore, Cusick et al. (2010) analyzed the microbial community present in the biofilm produced during the winery wastewater treatment by using a microbial electrolysis cell (MEC), the predominant bacteria in the biofilm were *Geobacter sulfurreducens* (44%), *Roseivivax* sp. (14%), and *Rhodopseudomonas palustris* (3%). A two chambered MFC with bad wine (7.8 g/l of COD) as substrate with *Acetobacter aceti* and *Gluconobacter roseus* as biocatalysts was used by Rengasamy and Berchmans (2012). They reported 3.82 Wm^{-3} power density (P_d), 41% COD removal and 45% CE. Penteado and coworkers (2016) reported 105mWm^{-2} P_d, COD Removal about 17% and 2% CE, and demonstrated that the unbalanced nutrients/COD ratio is a major challenge in the winery waste water treatment and efficient electricity production. Sciarria et al. have reported the use of air cathode MFCs for bio-electricity generation using white and red wine lees (262 mWm^{-2} and 111 mWm^{-2} respectively) (Sciarria et al. 2015).

6.2.3.2 Role of Yeast and Fungi in Winery Wastewater Treatments

Yeast and fungi is an essential player in the biodegradation of material and are essential in natural biofilm communities (Elvers et al. 1998). Yeasts are well-known as an important group of microorganisms in biotechnology fields such as fermentation, food, pharmacy (Fleet 2007; Jespersen et al. 2005). The application possibility of yeasts in wastewater treatment was early reported by some Japanese scientists (Moriya et al. 1990; Chigusa et al. 1996). Within fungi, yeasts are more representative than filamentous fungi, ranging from 10^{-2} to 10^{-5} CFU g^{-1} of sludge and are specific to wastewater treatment plants, varying with wastewater type. The most-frequently isolated yeast populations in the wastewater treatment plants were genera *Rhodotorula*, *Candida, Trichosporon* and *Pichia*. Yeasts are facultative anaerobic microorganisms that can utilize alcoholic fermentation pathway to convert sugars into ethanol under anaerobic conditions. This anaerobic process is involved in the processing of different alcoholic beverages, such as beer or wine, and in bioethanol production. Due to its efficient adaptive physiologies like tolerance to acid environments, high osmotic and ethanol tolerance and formation of biofilms, *S. cerevisiae,* along with other yeasts are work horses of beverages industries (Masneuf-Pomarede et al. 2016; Ciani et al. 2016). Eusébio et al. (2004) isolated *S. cerevisiae* strain during the microbial characterization of activated sludge in the aerobic winery wastewater treatment. Yeast were also found in the liquid and biofilm of anaerobic jet-loope dactivated sludge reactor for the degradation of winery wastewater. *Trichosporon capitatum* and *Geotrichum peniculatum* was reported as their hyphal forms, which formed communities with other microbes such as *Pseudomonas*, metazoan microbes and *Saccharomyces cerevisiae* (Petruccioli et al. 2002). Biofilm aggregation to a rotating biological contactor (RBC) in the winery waste water treatment showed the potential role of dynamic microbial populations in remediation (Malandra et al. 2003). They identified dominat yeast species from the biofilm aggregation to a rotating biological contactor which included isolates of *Eremothecium gossyphi, Williopsis saturnus, S. cerevisiae*, *Candida intermedia*, *Hanseniaspora uvarum and Pichia membranaefaciens* and suggesting that RBC as an effective biological system for lowering the COD of winery wastewaters because they provide sufficient aeration for the biofilm formation by several yeast. Recently, waste water treatment by the lipid producing oleaginous yeasts attracts much attention for its low cost (due to the use of simple bioreactor), effiecient waste water treatment within short period of time with generation of value added chemicals. For the biological treatment of waste waters, the oleaginous yeasts used mainly includes the yeasts from genus of *Rhodotorula* such as *Rhodotorula glutinis* and *Rhodotorula mucilaginosa*, genus of Trichosporon such as *Trichosporon cutaneum*, *Trichosporon dermatis* and *Trichosporon coremiiforme*, genus of Cryptococcus such *as Cryptococcus curvatus*, *Cryptococcus albidus*, *Cryptococcus laurentii*, and *Cryptococcus podzolicus* and some other kinds of oleaginous yeasts such as *Rhodosporidium toruloides* (Huang et al. 2017). In an innovative study design Santos et al. (2014) used a combination of biological and chemical processes to treat waste water removal. The combined system consisting of a biological

(*Cryptococcus. laurentii* AGG 726, a basidiomycetes yeast) degradation followed by a chemical (Fenton reagent) treatment of waste water achieved a final reduction of 98% and 96%, for COD and TPP. A metagenomic approach for community structure analysis by de Beer 2018 identified several fungal population including *Candida, Trichosporon*, *Fusarium* and an unidentified genus of *Nectriacea.* As compared to yeast communities, filamentous fungi exhibit certain advantages for bioremediation process. Foremost being their ability to produce several extracellular hydrolytic enzymes for the assimilation of complex carbohydrates without prior hydrolysis. This quality makes possible the utilization of complex substrates. Another advantage is the easy separation of biomass by filtration due to the filamentous structure. In comparison to yeasts, filamentous fungi are less prone to variations in nutrients, aeration, temperature, and pH and have a lower nucleic content in the biomass. In an attempt to use filamentous fungi for treatment of winery wastewater, microfungi like *Trichoderma viride, Aspergillus niger and Aspergillus oryzae* showed potential for both the production of fungal biomass protein at a 5 g/L and a simultaneous reduction of COD to 90% (Zhang et al. 2008). In another exapmle, the use of white rot fungi to lower the chemical oxygen demand, total phenol and to decrease the colour in wine distillery wastewater was reported by Strong and Burgess (2007).

6.2.4 Physico-chemical Process

Various physicochemical processes have been in use to treat the winery waste water, such as chemical precipitation of contaminants by using chelating agents, sedimentation of pollutants by adding flocculants. Also other methods in use are coagulation/flocculation and electrocoagulation. The efficiency of different physiochemical processes are determined by measuring the TSS, turbidity and COD removal. Andreottola et al. (2007) studied the chemical precipitation method using trimercaptotriazine as the chelating agent. The study showed that the chemical chelation reduced 90% of TSS, 96% Cu and 76% Zn from the effluent. But the COD removal was only 9% of COD (Andreottola et al. 2007). Considering various parameters such as low COD removal, operating cost, plant management, chemical cost and dose, effluent quality controls, electricity, sludge disposal and manpower needed this method is not efficient.

Hence coagulating the toxicants using metals or natural organic coagulant like chitosan was studied. Rizzo et al. (2010) reported that chitosan is better than conventional metal based coagulants, because it could produce potentially reusable organic sludge and its efficiency was high. Chitosan removed 73% COD and 80% of TSS in the effluent. But, no further improvements in reducing the TSS was reported by varying the pH, this indicates that instead of charge neutralization or adsorption mechanism, inter-particle bridging could be the major cause for particle aggregation. In other study, use of $Ca(OH)_2$ dramatically reduced the TSS levels (95.4%), but the COD removal was lesser on comparison to chitosan (68% vs 73%).

To efficiently remove the COD, a combination of long-term aerated storage (LTAS) followed by coagulation with $Ca(OH)_2$ was attempted. By this method approximately 85% of COD, 99% TSS and 97% of turbidity was removed. Some wineries also use electrocoagulation (EC) as a method to treat the effluent. Using this method up to 42% COD and moderate reduction in BOD (28%) was achieved. Ozone addition to EC was reported to marginally increase the COD removal by 6% (Braz et al. 2010).

In order to further increase the COD removal efficiency, a combinatorial approach of EC and pond aeration may be followed. The effluent is initially treated with EC and then allowed to stand still in a pond system containing floating aquatic plants such as *Hydrocotyle umbellate* and *Eichhornia crassipes*. Further to increase the dissolved oxygen in the pond water, aerators are employed, as a result 98.2% of COD and 95.6% of BOD removal was achieved. Overall EC alone is efficient in removing color, odor and turbidity but its efficiency on COD removal is moderate (Kirzhner et al. 2008). Hence EC process can be combined with biological treatment techniques to achieve better result. Comparing the above mentioned studies coagulation with chitosan was found to have high efficiency in COD removal. Also use of bio-polymer (chitosan) is non-toxic, non-corrosive and safe to the environment.

In a most recent laboratory scale study Karpe et al. (2017) utilized ultra-sonication and fungal enzymes to effectively degrade winery biomass (grape pomace) and produced commercially useful compounds from it. Basically, in this study, the grape pomace was ultrasonicated in alkaline condition for 20 min prior to addition of fungal enzymes. The crude enzymes from *Phanerochaete chrysosporium* and *Trametes versicolor* (1:1, v/v) was added to biomass and incubated for 18 h initially. In the second phase enzymes from the following fungus; *Aspergillus niger, Penicillium chrysogenum, Trichoderma harzianum and Penicillium citrinum* were added at the ratio of 60:14:4:2 (v/v) and incubated for additional 18 h. Only fungal mixture added to the biomass and incubated for 16 days served as the control and the results were compared with combination treatment to estimate the efficiency. Study results shown that combination of ultra-sonication and fungal enzymes treatment effectively degraded the biomass in shorter duration (36 h) than fungal alone treatment (16 days) (Karpe et al. 2017). Hence, by this method the 2 weeks of operating cost could be saved for each batch treated. Additionally, the degradation also yielded commercially important compounds such as gallic acid, lithocholic acid, glycolic acid and lactic acid in significantly higher quantities on comparison to biological only treatment. Several small scale wine producers across the globe may not have sufficient financial resources to treat waste water employing costly physicochemical- or biological (aerobic/anaerobic) – treatments. Though constructed wet lands or other land treatments seems to be cost-effective alternative, the caveat is need to own enough land which again pose an economic burden, additionally it may not generate the effluent quality defined by environmental protection agencies (EPAs) (Christen et al. 2010). Hence to overcome these problems Litaor et al. (2015) recently developed and reported a cost-effective mobile treatment system; with two series of aerated cells that are integrated with coagoflocculation module using nanocomposite to reduce TSS, COD and other contaminants. Each series of cells has four portable containers (1.5 m^3) filled with volcanic tuff of a decreasing progressive particle –size structure. The system also includes forced air apparatus to maintain minimal oxygen level (1.5 mg/L) and thereby treatment capacity is greatly enhanced. As appropriately named (mobile) the entire system was mounted on two flat lorry beds equipped with special hooks for ease of transportation. The test results were highly convincing, it was shown to reduce the TSS, COD and TP by 95% consistently for two consecutive vintage seasons. However, the aerated cells are susceptible to clogging, but this problem was addressed by using hoist- sack method and/or treatment with H_2O_2 solution which can be implemented without affecting normal operation of the system (Litaor et al. 2015)

6.2.5 Membrane Filtration Process

Membrane filtration is increasingly used globally in water treatment and waste water reclamation, when the high level reduction of dissolved solids, inorganic ions and organic compounds are desired (Ferrarini et al. 2001). Typically, in a membrane process, a membrane separates two adjacent phases and allows the transport of one or few components than other components in a mixture. The driving force for the transport of molecules across the membrane can be dependent on various gradients such as pressure, temperature, concentration or an electrical potential gradient. Effluent when passed through membrane is divided in to two streams; one the retentate or concentrate stream and the other one is permeate stream (filtered water from the winery effluent) (Van Der Bruggen et al. 2003) (Fig. 6.6).

Consistently it was observed that various recalcitrant pollutants including high molecular weight compounds such as polyphenols, tannins and lignins are not mineralized by the biological treatment process. As well the COD and BOD concentration of the biologically treated effluent ranges from 110 to 5440 mg/L and 101–1060 mg/L, respectively; thereby biological treatment does not completely

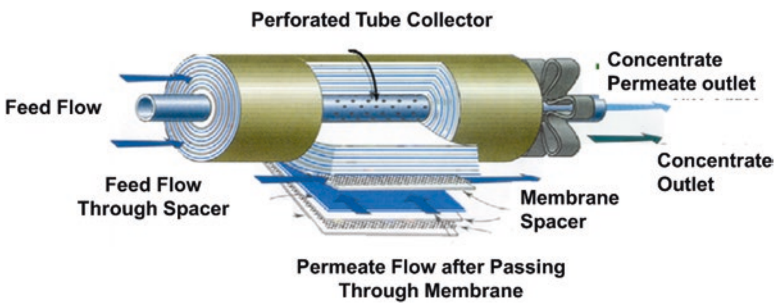

Fig. 6.6 General structure of spirally wounded membrane. The feed (effluent) is filtered through membrane and collected via perforated tube collector as permeate at the outlet. The remnants (pollutants in water) are collected at concentrate outlet

degrade the organic matter in the effluent (Bellona et al. 2004). Therefore other technology or combination of different technologies needs to be applied to purify the effluent; so that it can meet the regulatory standards for safe disposal in the environment. In this view membrane separation could be highly advantageous, because, it can generate high quality permeate from the winery effluent. The other major advantages with the membrane technology are its selective permeability without requiring any additives and it can be performed isothermally at low temperatures utilizing low energy (Wintgens et al. 2005).

As well up- and down-scaling the membrane process can be done at ease without compromising the quality of permeate. Further, this process can function alone or in synergy with other separation or retention processes easily. Some of the membrane filtration process is discussed below.

6.2.5.1 Reverse Osmosis (RO)

In RO, higher external pressure is applied on the feed water to overcome the osmotic pressure, as a result water flows in the reverse direction to its natural flow across the membrane leaving behind the monovalent ions, multivalent ions, virus, bacteria and all other organic and inorganic compounds in it. No heating or pH change is needed for this process. Only major requirement is application of high pressure to the effluent (Van Der Bruggen et al. 2003).

In a pilot scale study RO was shown to reduce the COD by 97% and TSS by 94%, as well demonstrated much lower ecotoxicity by reducing the recalcitrant pollutants. The RO treated water had no toxicity on *Daphinia magna* (fresh water plankton), whereas the feed water (effluent) completely inhibited its mobility (100%). Further, phytotoxicity studies comparing the RO treated and untreated water on seed germination, root and shoot growth of three different plant species (Sinapisalba, Lepidiumsativum and Sorghum saccharatum) shown the toxicity of treated water decreased by 79% on comparison to untreated water. This is expected because RO is the tightest possible membrane process in liquid/liquid separation and offers highest water quality (Ioannou et al. 2013). However RO has its own drawbacks. It is well known that the membrane separation process cannot degrade the pollutants, instead concentrate them into smaller volumes of waste water (concentrates). The concentrates generated in this process contains very high levels of recalcitrant organic and inorganic pollutants and it is difficult to degrade them by other conventional methods and their direct discharge in the environment could be toxic. The fouling RO membrane needs periodical replacement and the high operation cost adds up to the drawbacks of RO (Wang et al. 2012). The toxic concentrate formed in the RO process can be treated successfully by photo-Fenton oxidation. Thus combination of RO and photo-Fenton oxidation could result in environmentally safe and re-usable water from the winery effluent (Ioannou et al. 2013).

6.2.5.2 Nanofiltration

The basic principle of Nanofiltration (NF) treatment is to use the pressure to separate the soluble ions out of water through a semi permeable membrane. Unlike dead end filter, the membrane operates under a different hydraulic profile which is also known as cross flow filtration. Mostly the nanofiltration membranes are composite materials supported by polymer substrate and manufactured in a spiral design instead of flat sheet or tube geometry. Nanofiltration connects the technological gap between ultrafiltration and RO filtration (Fig. 6.7). It can be considered as loose or lower rejecting RO membrane or a tight ultrafiltration membrane with pore size in the range of 0.01–0.001 μ (Van der Bruggen et al. 1999).

Conclusively NF is a pressure driven membrane with properties between RO and ultrafiltration (UF) membrane. Though RO membranes produce very good quality of permeate, the operational cost is considerably high. Hence a membrane was needed that could produce good quality permeate by applying comparatively low pressure than that is needed for RO; thereby the cost on the energy could be saved. This idea resulted in low-pressure reverse osmosis membranes, which otherwise called as NF membranes. As the name indicates these membranes separates particles even at nanometer range. Due to its smaller pore size (~1 nm) NF membrane can separate molecules in the range of 200–1000 Da and small neutral molecules (Van Der Bruggen et al. 2003). Additionally, because of their surface electrostatic charge, these membranes can remove multivalent ions to an extent and charged molecules. Since wide ranges of NF membranes are available in market, based on the requirement, wineries can select appropriate membrane. In general NF membranes are characterized by their molecular weight cut-off, charge, membrane roughness, hydrophobicity, retention and permeability properties. Hence prior set-

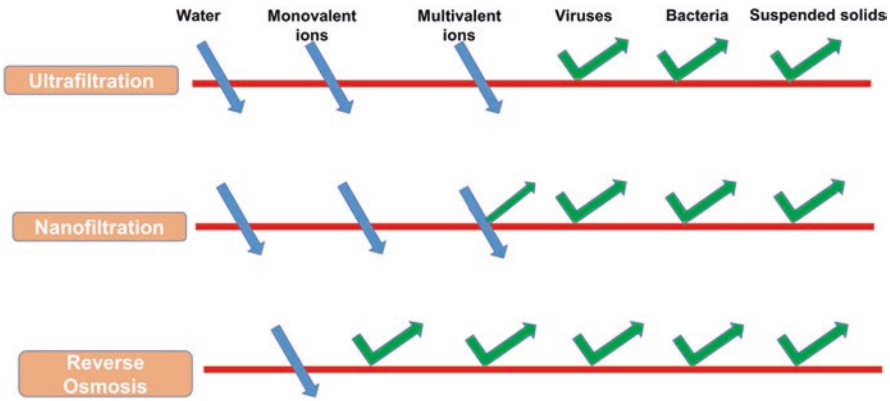

Fig. 6.7 Schematic diagram showing difference among various membrane processes. Reverse osmosis process is widely used and it could produce superior quality water. The red horizontal line represents membrane. The blue – and green – arrows indicates the permissible and impermeable molecules through the membrane respectively

ting up the industrial scale NF membrane simulation studies can be done to gain insight on the separation process and operation cost (Ferrarini et al. 2001).

The other advantage of NF membrane process is it offers flexibility to design wide range of membranes based on the membrane salt rejection rate. Membranes with lower salt rejection rate utilize lesser energy and it is more preferred for operating the facility during non-vintage season, because of less pollutant load in the effluent. So, membranes with 40–75% salt rejection can be used during non-vintage than the membranes with 95–99%. This flexibility is not available with RO system, because any system with less than 99.5% salt rejection is considered inferior (Van der Bruggen et al. 2001). Another study has reported that NF membrane was able to reduce the total phenolics by 74%. The same study also determined the parameters that could be manipulated to increase or decrease the yield. For example, the permeability of NF membranes could double by increasing the pressure from 32 to 45 bars. Also the increase in temperature increased the permeate flux. For each degree rise in temperature, 3% increase in the permeate flux was observed. Further the fouling index was found to be dependent on factors related to grape juice composition and membrane must interaction (Ferrarini et al. 2001). Both the NF and RO are similar technologies that use membranes to filter the waste water. Unlike RO, NF can allow monovalent and multivalent ions to pass through thereby permeate from NF membrane could support the growth of plants better than permeate from RO process. Further, more pilot scale and industrial scale studies are needed to assess the advantages and cost effectiveness of NF over RO process.

6.2.5.3 Ultrafiltration

Ultrafiltration (UF) systems have diverse membrane filtrations where hydrostatic pressure pushes solvents against a very fine membrane. They block suspended particulates and solids that are large, while water and solutes with a lower molecular weight are allowed to flow through the membrane.

Ultrafiltration (UF) is a membrane filtration process that uses diverse membranes with pore size in the range of 0.1–0.001 μ and filter molecules in the range of 1000–300,000 da at relatively low operating pressure (1–5 bar) than both NF and RO process. UF removes high molecular weight substances, bacteria, colloidal materials, organic and inorganic compounds, whereas the low molecular weight compounds below the cut off range mentioned above are allowed to pass along with the permeate. Additionally mono-valent and multivalent ions are passed along with water. One of the major advantage of UF over the RO/NF is its ability to generate high flux (amount of permeate/unit area of membrane in given time) rates at low pressure. UF could achieve the flux in the range of 50–200 gal per square foot per day (GFD) at 50 psi, on the contrary RO could attain 10–30 GFD at very high pressure (200–400 psi. In principle, like RO and NF, it is a cross-flow separation technique. The feed flows along the membrane surface and produce the concentrate and permeate. Unlike, conventional membrane filters the UF membrane will not trap the suspended particles in their membrane, hence frequent replacement is not needed as it is required for conventional membrane filters. (Van Der Bruggen et al. 2003).

Another important factor that decides the quality of permeate is the membrane type and module. Membranes commercially used in UF are mostly made of polysulfone or cellulose acetate (Nabe et al. 1997). For high pure filtration, the membranes must be compatible with the chemicals present in the effluent. A pilot scale study to assess the membrane compatibility with real winery effluent will always be helpful before undergoing an industrial scale study. Usually membranes are categorized based on the molecular weight cutoff. For example a membrane that removes dissolved solids with molecular weight 8000 or above has the molecular weight cutoff of 8000 da. However, the membranes with same molecular weight cut off could have different pore sizes and could remove the molecules differently. So, only molecular weight cut off may not be useful guide for selecting the membrane; the pore size of the membrane must be considered for removing different molecules. Proper membrane selection is the critical in attaining high efficiency UF. In addition, the membrane module also plays a role in UF process. UF membrane modules come in plate, frame, spiral, wound, capillary and tubular configurations. To obtain highly pure water the spiral-wound and capillary configurations are generally used, whereas for more concentrated effluents more open configurations like plate or frame and or tubular modules are used. Further, while choosing the module the optimal operating conditions such as flow velocity, pressure, power consumption and operating cost should be considered (Van Der Bruggen et al. 2003).

The permeate yield is directly proportional to the operating pressure and temperature. As mentioned above usually the UF works around 50 psi, but due to membrane fouling and compaction the pressure could reach around 100 psi and rarely exceeds above it. Among various membrane modules the operating pressure for capillary module is mostly lower than 50 psi due to the physical strength limitation imposed by the module. Permeate rate increases with increase in temperature for any membrane system. However for UF it is not a controlled variable. The knowledge about the effect of temperature on the membrane flux; might be useful to state the reason for any drop in permeate quantity while operating the system. Thus daily records of feed- and permeate-flow, feed – pressure and – temperature and the pressure/temperature drop across the system could be highly useful for uninterrupted operation of the system. Membranes should be cleaned if the permeate rate drops by 10% or more. If the system is shut for 2 days or more then the bactericide should be circulated through the membranes and then while restarting the system, the initial permeate generated should be diverted to drain until all the bactericide is removed from the membrane (Van Der Bruggen et al. 2003).

6.2.6 Advanced Oxidation Process (AOP)

The recalcitrant pollutants in the winery waste water resist biodegradation and poses toxicity to plants and microbes that are used in the conventional systems. Hence to degrade or transform it advanced oxidation process (AOPs) alone or in combination with conventional treatment methods are applied. By principle, AOPs generate highly reactive free radicals that could react rapidly and non-selectively with all most all electron-rich organic compounds and destroys it. (Mosteo et al. 2008).

Several methods are included under the broad title of AOPs. Most of them use strong oxidizing agents (H_2O_2 or O_3) with catalysts (transition metal ions) and/or irradiation (ultraviolet/visible light). Among AOPs; methods that generate hydroxyl radicals such as Fenton's reaction, hydrogen peroxide/UV light process and titanium dioxide/UV light process are most commonly used for waste water treatment. On comparison to conventional oxidants (H_2O_2 or $KMnO_4$), hydroxyl radicals (HO•) have high oxidation potential (2.33 V) and exhibit faster oxidation rates. Once generated it can react with organic chemicals by radical addition (R + HO• → ROH), hydrogen abstraction (R + HO• → R• + H_2O) or by electron transfer (Rn + HO• → Rn-1 + OH-); in these reactions R denotes organic compound (Gogate and Pandit 2004).

6.2.6.1 Photo-Fenton Process

A mixture of hydrogen peroxide and ferrous iron (catalyst) was developed as an analytical reagent by Henry John Horstman Fenton in 1890s; which was later named as Fenton reagent and widely applied as an oxidant for organic contaminants in waste waters. The following sequence of reactions represents the oxidation of an organic compound by Fenton reagent (Neyens and Baeyens 2003).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet \tag{6.1}$$

$$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^- \tag{6.2}$$

$$HO\bullet + RH \rightarrow H_2O + R \tag{6.3}$$

$$R\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+} \tag{6.4}$$

The hydroxyl radical generated in this exothermic process is a powerful non-selective oxidant. It rapidly reacts with organic compounds and eventually results in the formation of carbon dioxide and water. Various factors that influence the rate of the reaction were very well studied. Light enhances the rate of the reaction and hydroxyl radical formation, as a result organic compounds are broken down at faster rate when compared with Fenton reaction carried out in absence of light. Since this reaction can be done efficiently with low energy photons. Solar irradiation is most commonly used in the waste water treatment and the process itself is called as photo-Fenton reaction (Torrades et al. 2004). Additional factors that affect the Fenton reaction is the concentration of the reactants (ferrous ion and H_2O_2), pH of the waste water and concentration of pollutants (Gogate and Pandit 2004). The optimal pH for Fenton reagent should be in the range of 2–4, at pH higher than 4 the Fe^{2+} ions are readily oxidized to its more stable form, Fe^{3+} ions. In contrast in alkaline conditions, H_2O_2 another start up reactant is broken down into oxygen and water thereby loses its oxidizing ability (Neyens and Baeyens 2003). Due to these reasons, waste water pH should be in the acidic range for optimal reaction rate. Increase in Fe^{2+} ion and H_2O_2 concentrations also increase the rate of the reaction (Lin and Lo 1997). However, if this process is used as pre-treatment for biological treatments; then the increased H_2O_2 concentration could be toxic to microbes and reduce the treatment efficiency of biological process. Further, presence of phosphates, sulfates, and halides at higher levels as pollutants could inhibit the Fenton reaction by scavenging the hydroxyl radical or by precipitating the iron ions (Pignatello et al. 2006).

An alternative Fenton process that utilizes the electrochemical reaction for in situ generation of the start-up reactants is called electro-Fenton process. Ferrous ion can be formed by oxidative dissolution of anodes such as iron metal (Arienzo et al. 2001) or by reduction of ferric ions using inert platinum cathode (Qiang et al. 2003), while H_2O_2 is generated by dioxygen reduction at the cathode (Casado et al. 2005). Fenton reactants formation is affected by the cell potential, solution conditions and nature of the electrodes used. Despite its wide application in waste water treatment, Fenton reaction has its own hassle to combat. It needs regular clearance of iron oxide sludge, maintenance of acidic pH of the waste water, limiting the pollutants that could complex with iron and inhibit the reaction (Pignatello et al. 2006).

6.2.6.2 Hydrogen Peroxide/UV Light Process

This process is similar to Fenton process by principle, instead of iron ions UV light (200–280 nm) is used to break the O-O bond in H_2O_2 to generate hydroxyl radical, which in-turn reacts with refractory organic compounds and converts/transforms them into degradable molecules. The reaction sequence is as follows (Buxton et al. 1988).

$$H_2O_2 + h\nu \rightarrow 2\,HO\bullet \tag{6.5}$$

$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O \tag{6.6}$$

$$H_2O_2 + HO_2\bullet \rightarrow HO\bullet + H_2O + O_2 \tag{6.7}$$

$$2\,HO\bullet \rightarrow H_2O_2 \tag{6.8}$$

$$2\,HO_2\bullet \rightarrow H_2O_2 + O_2 \tag{6.9}$$

$$HO\bullet + HO_2\bullet \rightarrow H_2O + O_2 \tag{6.10}$$

Various studies were done to standardize the optimal conditions required to achieve higher treatment efficiency of waste water using this process. An abstract of observation from several studies were as follows, the photo-lysis of hydroxyl radical production is directly proportional to the initial H_2O_2 concentration added and inversely proportional to the bicarbonate ions (Rezaee et al. 2008). The optimal H_2O_2 concentration needed at the start of the reaction was in the range of 2–2.5 mmol/L. Lower levels of H_2O_2 results in large residues of refractory organic compounds, while higher levels could react with hydroxyl radical to form HO_2• (Daneshvar et al. 2008). Slightly basic pH of the water to be treated was found to be optimum than high basic or acidic conditions. At high basic pH the reaction was inhibited. So, like Fenton reaction proper maintenance of pH is a requisite. Further, combination of ultrasonic waves to UV light was found to increase the rate of H_2O_2 lysis and water purification. Temperature in the range of 294–307 k was also found to increase the rate of the reaction (Ugurlu and Kula 2007). One major disadvantage of this process is that it cannot use sunlight as the source of UV light because high energy photons are required to photolyse the oxidizer. Since H_2O_2 poorly absorbs the UV and water matrix also could absorb UV light from solar radiation, special reactors with UV illumination is required for effective treatment of waste water (Oller et al. 2011).

6.2.6.3 Titanium Dioxide (TiO2)/UV Light Process

In this process TiO_2 absorbs UV light to generate hydroxyl radical needed to oxidize the recalcitrant organic compounds in waste water. In particular exposure of TiO_2 to UV light results in the formation of conduction band electrons (ecb) and valence band holes. Then the electrons in the conduction band interact with molecular oxygen to form superoxide anions and the valence band holes interact with water to form hydroxyl radical (Comninellis et al. 2008). The following set of equations denotes the mentioned process.

$$\mathrm{TiO2} + h\nu \rightarrow \mathrm{ecb} + \mathrm{h}+ \tag{6.11}$$

$$\mathrm{ecb} + \mathrm{O2} \rightarrow \mathrm{O2} - \bullet \tag{6.12}$$

$$\mathrm{h} + + \mathrm{H_2O} \rightarrow \mathrm{H} + + \mathrm{HO}\bullet \tag{6.13}$$

The organic compounds are oxidized to harmless end products such as CO_2 and H_2O by the interaction with one or many of the end products formed such as hydroxyl radicals, superoxide anions, and valence band holes and/or with valence band electrons. One major advantage of this process is usage of cheap and readily available raw material (TiO_2). Some of the rate limiting factors of this process is initial organic load, amount of catalyst, reactor's design, UV irradiation time, temperature and pH (Chatterjee and Dasgupta 2005). Reactor vessels should be designed in such a way that uniform irradiation of the catalyst surface is achieved (Ray 1999). Varying the temperature in between 20 and 80 °C has negligible effect on the process. However increasing the temperature above 80 °C was reported to reduce the reaction rate (Herrmann 1999).Unlike other mentioned oxidation process, this optimal performance can be achieved both at acidic and alkaline pH. But, it is subjective to the nature of pollutants present in the waste water. For instance, acidic pollutants are more in number, then the photocatalytic oxidation is more effective at acidic pH (Andreozzi et al. 2000), alternatively, if influent has higher percent of alkaline pollutants, rate of oxidation is better at alkaline conditions than in acidic conditions (Choi and Hoffmann 1997). Presence of ionic species also was reported to affect the degradation process (Andreozzi et al. 2000).

6.2.6.4 Ozonization

This process involves usage of highly unstable ozone gas to treat waste water. Ozone is made up of three oxygen atoms, which readily dissociates to molecular oxygen and superoxide anion. The anion formed is highly reactive with various organic and inorganic molecules. As well it is toxic to microorganisms. Ozone oxidizes the metallic ions to its respective oxides, hence this process needs post filtration or sedimentation step to remove the metallic oxides (Glaze et al. 1987) (Fig. 6.8).

The conventional methods use either corona-discharge (CD) or UV – light to split the oxygen in the feed gas to form ozone. Basically, in CD method, dried air/oxygen is passed through an electric field cloud (corona). The current causes the splitting of molecular oxygen to unstable atomic oxygen, which then rapidly reacts among themselves to form ozone. Since this an exothermic reaction; a cooling unit is required to quench the excess heat. Passing of dry feed gas (~ −80 °F) is critical for ozone formation. Because, moisture in air is inversely proportional to the amount of ozone formed. In addition the air moisture could hinder the process by favoring the formation of nitric acid which could potentially damage various parts of CD generator, necessitating equipment failure or parts replacement regularly. Due to the extended life span, high yield and cost efficiency, CD generators are most com-

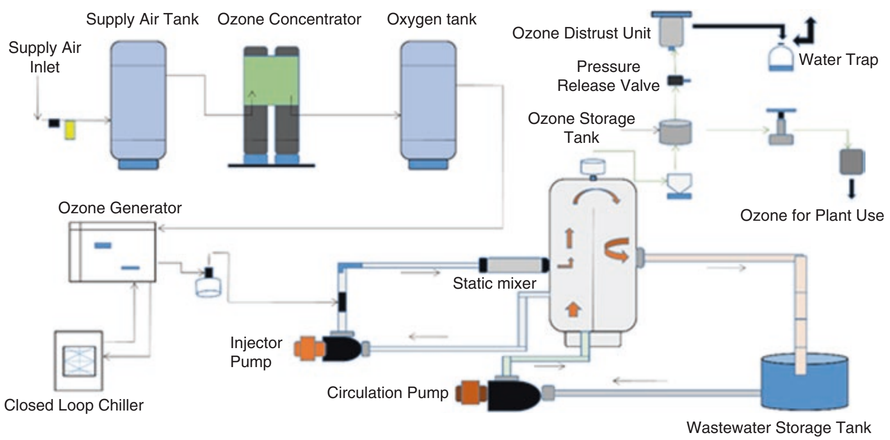

Fig. 6.8 Ozonization process. Figure shows the series of steps involved in water treatment using ozone

monly used on comparison with UV illumination process. Unlike other AOPs, ozonation can be performed at wider pH range and does not require addition of any other chemicals for water purification. Though ozonation can effectively eliminate pathogens; its effect is transient and cannot inhibit regrowth of the residual microbes in the treated water.

Further, in a study Beltran et al. reported even to remove moderate levels of organic matter high levels of ozone is required; thus to obtain higher water quality, high doses of ozone is required; which in-turn increases the electricity consumption, operation cost and frequency of maintenance (Beltran et al. 1999). Hence with a view to reduce the operational cost and to achieve higher efficacy Gimeno et al. (2007) investigated the combination treatment of UV/TiO2 and ozonation process. The study reported that under optimal conditions COD and TOC depletion was closer to 80% and 85% respectively. The combination process was effective at acidic conditions (pH 3), whereas maximum efficiency is achieved only at alkaline (pH 11) conditions for ozone alone treatment. Also, quantitatively lesser biorecalcitrants were formed in combination treatment than in ozone alone treatment (Gimeno et al. 2007). Hence the combination of ozone with other AOPs could be highly efficient in achieving higher standards of re-usable water.

6.3 Recycling and Reuse of Treated Waste Water

As mentioned above in this chapter the winery waste water is a useful resource for irrigation purposes in regions of drastic water scarcity (Laurenson et al. 2012). However, it is best to know the effect of treated water on soil and plant health and its long time implications while used for irrigation. The organic and inorganic contaminants in the winery waste water can be reduced by conventional biological methods which are discussed above in this chapter. The recalcitrant molecules including monovalent ions such as sodium and potassium may be of concern when used for irrigation (Laurenson et al. 2012). Because higher concentrations of these ions could lead to structural degradation of soil and affect the soil quality (Laurenson et al. 2012). Thus the biological treatments need to be combined with other advanced methods such as membrane filtration process which are effective in removing monovalent ions. The treated water can be used for irrigational purposes in wine yard itself or in other horticultures or for afforestation. Unlike sewage water the winery water may not have coliforms, so it can be used to irrigate the golf courses, cemeteries, freeway landscapes and landscapes within the wineries and somewhere else including the mountain-scape. If the quality of purified water meets the local governmental regulations it can also be used to irrigate parks and other areas where public have access. Sewage water is used for aquaculture in Calcutta, India therefore treated water from large scale –wineries can also be used for fisheries, it could be safer in terms of sanitation and health on comparison to aquaculture using sewage water. Further the treated waters with low BOD and COD can be used to construct recreation ponds within the wineries for public use or lagoons elsewhere for recreation purposes. In dry arid conditions stream channels can be constructed in and around wineries that could function both as humidifier and recreational. As well the water with low monovalent ions can be drained in the dry wells for the purpose of re-charging the ground water table in the water scarce regions. Also the treated water with contaminants within the environmental protection agency (EPA) limits can be discharged in the natural water bodies such as rivers, lakes or streams.

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Chapter 7
Treatment and Recycling of Wastewater from Sugar Mill

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Abstract Sugar is the most important food supplement of our daily diet. During the production of sugar, large volume of water is used by sugar mills for processing, and produces large amount of wastewater. The sugar mill wastewater have color, organic compounds, low pH, high temperature, BOD, COD, total dissolve solid (TDS), sludge, press mud and bagasse etc. If this wastewater is released in the environment before the treatment, it will cause harmful effect on aquatic life, animals, plants, human being and also change the soil properties. Therefore, it is necessary to treat the wastewater before their disposal. Three important treatment methods i.e. physical, chemical and biological are employed to treat the wastewater. Biological treatment of sugar mill wastewater has several significant advantages over other available methods. Treatment of sugar mill wastewater mainly affected by pH and temperature of effluents, biomass during the reaction, reaction time, type and speed of reactions, aerobic or anaerobic conditions, presence of catalyst, inhibitor, nutrients and concentration of the sulfide and its other compound in the wastewater. The treated wastewater can be reused in the industry for processing and may also be used for ferti-irrigation for agriculture or other purposes like compost and biofertilizers within the limit prescribed by the Central Pollution Control Board. Reuse of treated effluent can reduce the fresh water demand in various sectors. Treated effluent contains well balanced chemicals with low toxic metal ion. The diluted treated effluent have shown significant increase in chlorophyll,

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R. L. Singh, R. P. Singh (eds.), *Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future*, Applied Environmental Science and Engineering for a Sustainable Future,
https://doi.org/10.1007/978-981-13-1468-1_7

carotenoids, total sugar, amino acids, protein contents and suitable for seed germination and seedling growth over the bore well water and undiluted treated effluent.

Keywords Sugar · Wastewater · Biological methods · Bagasse · Eco-toxicology

7.1 Introduction

As world population growing fast, requires increased demand for food leading to massive increase in both agricultural and industrial practices. Rapid industrialization without sufficient environmental safety measures lead to pollution of water, which results in lack of good quality water both for irrigation and drinking purposes. Every human civilization, whether urban or rural require technological advancement resulting the releases of some kind of waste products which ultimately affects the normal functioning of the ecosystem and has undesirable effect on plants, animals and humans. Sugar is obtained from sugarcane crops and it is one of the most important parts of human diet and it is vital product of the human life. Bagasse, a byproduct of sugarcane used to provides energy in the form of fuel for the generation of steam and electricity (Renouf et al. 2008). Worldwide bagasse is used as energy resource in 80 sugarcane producing countries (Botha and Blottnitz 2006). Initially, sugar mills produced only sugar but presently they are also involved in the production of electricity and ethanol. Hence, sugar industry is now called as the cane industry (Ramjeawon 2008). Globally, the top 5 countries as India, Brazil, Thailand, Australia, and China (Table 7.1) accounted for nearly 40% of the total world sugar production. Sugar crops are cultivated in approximately 115 countries of the world. The sources of sugar produced by these countries are different, for example, out of 115 countries, 67 countries produced sugar from sugarcane, 39 countries from sugar beets and 9 countries from sugarcane as well as sugar beets (Lichts 2007). It is better to say that the sugar is produced 70% from sugarcane and 30% from sugar beet and cassava etc. (Contreras et al. 2009). Worldwide, Brazil and India are positioned at first and second rank in sugarcane production countries, respectively. Both are producing 275 million tons of sugarcane annually (Prakash

Table 7.1 List of large scale sugarcane producing countries

Country name	Annual production (million ton)	Harvest area (million hectare)	Average income (t/ha)
Australia	34	0.39	87.10
Brazil	648	8.14	79.70
China	124	1.71	73.10
Colombia	39	0.38	100.4
Cuba	16	0.38	41.30
India	348	5.06	68.90
Mexico	51	0.67	76.70
Pakistan	64	1.24	51.50
South Africa	21	0.43	48.20
Thailand	73	1.05	69.70

et al. 1998). Sugar mills are basically seasonal in nature and operate only for 150–210 days in a year (November to May) (Kolhe et al. 2000). Considerably large amount of wastewater is produced during the production of sugar. Wastewater from these mills contains a moderate amount of pollution load including suspended solids, dissolved solids, organic matter etc. A number of chemicals that are used in sugar industries mainly for removal of impurities and refining of end products are also present in wastewater. The waste water discharged from sugar mill not only offers potent threat to the environmental quality but also possess energy value which is not fully utilized despite the fact that they are cheap and abundant in most parts of the world.

Water is essential for all living organisms because it plays a most valuable and important role in the natural metabolic cycles. It is believed that among the whole water availability, only 3% fresh water is available on the earth for drinking and irrigation purposes. Industries and domestic or anthropogenic activities facilitate the entry of significant amount of pollutants in the available fresh water sources. In the present scenario of conservation policies plays a significant role in the conservation of fresh water bodies as well as water quality. Large amount of fresh water is used for the production purposes which is stored in the industry for continuous supply of water. It is estimated that the amount of consumption of fresh water is equal to the amount of discharge of wastewater as effluent (Kumar and Srikantaswamy 2015). Rapid urbanization and industrialization leads to severe problems in collection, treatment and disposal of effluents in the many developing countries. Untreated organic waste portions from industries, municipalities and agricultural area are naturally decomposed in the environment ensuing large scale contamination of water, air and land imposing serious public health problems and environmental degradation. Most of sugar mills in developing countries release their wastewater without proper treatment due to lack of knowledge, financial support and sometimes unwillingness to spend on treatment of wastewater. However awareness of environmental problems and the potential hazards caused by sugar mill wastewater has endorsed by many countries to prevent the discharge of wastewater.

7.2 Physico-chemical Properties of Sugar Mill Wastewater

The physico-chemical analysis showed that the sugar mill wastewater is acidic in nature and have dark yellowish color. It is very rich in total suspended and dissolved solids with large amount of Biological oxygen demand (BOD) and Chemical oxygen demand (COD) with low dissolved oxygen (DO). Higher concentration of chloride, sodium, potassium, calcium, magnesium, iron, sulfur and their oxidized and reduced compound is also present in the released sugar mill wastewater. These effluents severely affected the plants, soil microbes, soil properties and texture when used for irrigation purposes. The wastewater or spillage products from such mills include massive quantity of dissolved organic matter, heavy metals along with other hazardous pollutants. Their discharge into fresh water bodies affects the aquatic life severely with decrease in the quality of water and irrigation land. The unmanaged sugar mill wastewater could possibly lead to soil deterioration and low productivity. The pollution standards specify that BOD of wastewater should be less than 30 mg/l for disposal into inland surface waters and less than 100 mg/l for disposal on land. Whereas, the sugar mill wastewater has a BOD of 1000–1500 mg/l (Amin et al. 2010).

In the developing countries sugar mill wastewater is used as fertilizer and has gained much importance, considered as a good source of organic matter along with plant nutrients, and also serves as good fertilizer. Sugar mill wastewater holds considerable amount of potentially harmful stuffs including soluble salts and heavy metals such as iron, copper, zinc, manganese and lead etc. (Vermeulen and Vawada 2008). The continuous application of sugar mill wastewater for irrigation objectives contaminates soil to such an extent that it becomes toxic to plants and soil (Fakayode 2005). The effects vary from crop to crop because each plant species has its own tolerance of the different wastewater concentrations. According to the permissible limit suggested by Bureau of Indian Standards (BIS), the physico-chemical parameters of sugar mill wastewater are temperature (30 °C), turbidity (84.7 NTU), pH (8.1), electrical conductivity (5530 dSm), chloride (1894 mg/l), total alkalinity (254 mg/l), total hardness (342 mg/l), BOD (6856 mg/l), COD (7432 mg/l), total dissolved solids (2516 mg/l), sulphate (540 mg/l), phosphate (224 mg/l), total acidity (45 mg/l), calcium (364 mg/l) and magnesium (151 mg/l), but almost all the water quality parameters in the sugar wastewater have been found to be very high and well above the permissible limits (Shivappa et al. 2007).

The physico-chemical characteristic (Table 7.2) such as silt, clay, water holding capacity, electrical conductivity, organic matter, total nitrogen contents and

Table 7.2 Range and average value of water quality parameter of sugar mill wastewater prescribed by BIS (1983), India

Parameters	Range	Average
pH	6.4–9.5	8.1
Temperature	25–35 °C	30 °C
Electrical conductivity	4900–6800 dSm	5530 dSm
Turbidity (NTU)	78.5–99.6	84.7
Alkalinity	120–398	254
DO	0–1.0 mg/l	0.5 mg/l
BOD	5630–7015 mg/l	6856 mg/l
COD	6763–8840 mg/l	7432 mg/l
Total dissolved solid	914–3698 mg/l	2516 mg/l
Calcium	281–476 mg/l	364 mg/l
Chloride	1692–1907 mg/l	1894 mg/l
Magnesium	99.8–272 mg/l	151 mg/l
Sulphates	498–608.5 mg/l	540 mg/l
Phosphates	182–310 mg/l	224 mg/l
Total hardness	270–465 mg/l	342 mg/l
Total acidity	35–55	45
Total solids	1070–4610 mg/l	3070.1 mg/l
Oil and grease	0.9–1.25 mg/l	1.1 mg/l

microbial population were significantly higher in the samples collected from sugar industry wastewater dump sites (Nagaraju et al. 2009). Analysis of sugar mill effluents and soil samples had shown high metal content than the permissible limits except lead. Further, analysis of plant samples have indicated the maximum accumulation of iron followed by manganese and zinc in root, shoot, leaves and seeds of mustard and wheat. The above mentioned physical and chemical characteristics of sugar mill wastewater make it useless for drinking and other purposes thus it is necessary to treat this wastewater before release into environment to minimize its harmful effects. In view of this, scientist searches the treatment methods which are cost effective and efficient.

7.3 Eco-toxicological Concerns of Sugar Mill Wastewater

In the present scenario immense concern has been given throughout the globe regarding the environmental pollution. Sugar mills are the backbone of rural, agricultural and socio-economic progress in many countries. Many industries are directly or indirectly rely on sugar mills which in turn are responsible for overall development of particular country. In view of this sugarcane production has vital significance for its products and by-products. It has been reported that an average of 30,000–40,000 l of wastewater was generated per tons of sugar processed (Belliappa 1991). The sugar mill wastewater, as it released has a relatively clear appearance. However, after stagnating for sometime it turns black and starts emitting foul odor (Baskaran et al. 2009). The waste water entering the water bodies from sugar mills are one of the key sources of environmental toxicity. Internationally, water pollution is the serious and significant threat mainly due to the contamination of aquatic bodies like rivers, canals, lakes, oceans and ground water resources (Richardson and Temes 2011). Contamination of water usually begins when wastewater from industries, agriculture and domestic regions are released into the surrounding water bodies without adequate treatment to remove hazardous chemicals constituents (Dougherty et al. 2010).

Sugar mill wastewater not only affects the value of drinking water but also has harmful effect on the soil micro flora and aquatic ecosystems. Soil is the most favorable habitat for a broad range of microorganisms such as bacteria, fungi, algae and protozoa. Industries continuously release wastewater which is quite toxic for the soil micro flora whether it is from sugar mill or other industries. The organic, inorganic and non biodegradable material such as toxic chemicals of wastewater adversely affects the soil parameters and soil fertility up to large extent (Kisku et al. 2000). Sugar mill wastewater has an unbearable odor and unlikable color when poured into the environment without appropriate treatment. Farmers have been using this wastewater for crop irrigation found that the soil health was compromised. Such harmful wastewater is injurious to plants, animals and human beings in many aspects. The effects of various sugar mill wastewaters on seed germination, growth and yield of crops have captivated the attention of many workers. In addition, sugar mill effluent released in the environment leads serious health hazard to the rural and semi-urban populations that use water stream and river water for domestic purposes. Sugar mill wastewaters entering in agricultural land contribute largely to fish mortality and spoils paddy crops leading to agro-economic losses (Baruah et al. 1993).

Several anomalous changes were found in the physico-chemical properties, for example, pH, temperature, odor, color, TDS, DO, COD, BOD, conductivity and turbidity etc. of natural aquatic bodies due to the release of the wastewater mainly from the sugar and allied industries (Kolhe et al. 2009). Several studies are available for the physico-chemical characteristic features of sugar mill wastewater and their undesirable effects on aquatic life and the influence of sugar mill wastewater on the seed germination of various commercially important crops such as maize, pine, green gram, rice, wheat and Jowar etc. (Siva and Suja 2012). The growth of certain aquatic plants such as water hyacinth and water lettuce was also greatly influenced by the effluent discharged from the sugar industry (Ayyasamy et al. 2008). Untreated wastewater from sugar mills contains total dissolved solid (TDS) and total suspended solid (TSS) up to significant amount. The high value of TSS in wastewater offers salt deposition in land which decreases soil porosity. The presence of high concentration of different solids in the wastewater reduces the growth and development of the new seedlings. High TDS value in wastewater may also have undesirable effect on agricultural crop plants. A TDS of 500–1000 ppm may have negative effect on susceptible crops.

However, various types of metallic and nonmetallic elements of wastewater act as important nutrients but at the higher concentration they may show toxic effect on seed germination and seedling growth which ultimately adversely affecting plant growth and yield in agricultural field. Therefore, the polluted wastewater directly or indirectly affects the living organisms which are found nearby the water sources not only in the industrial area but also in agricultural fields, river and river beds (Nath et al. 2005). Although in some of the industries, the wastewater may have high level of nutrients, heavy metals and hazardous chemical compounds which may help to the microorganism's growth during the biological treatment of the wastewater (Malaviya and Rathore 2007). Thus it is well established fact that the sugar mill wastewater has direct and indirect adverse effect on living organisms of different habitats by diminishing their growth, reducing energy supply and photosynthetic efficiency.

7.4 Treatment of Sugar Mill Wastewater

The large amount of sugar mill wastewater is released in environment per day throughout the world which has harmful effect on all living organism. Globally several treatment methods are used to treat this wastewater before their release into

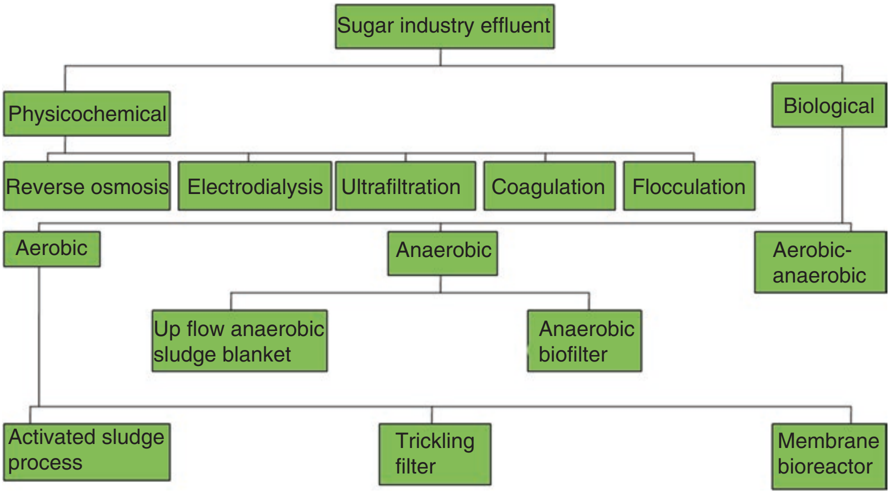

Fig. 7.1 Different techniques for treatment of sugar industry wastewater

water bodies. The physico-chemical and biological methods are employed for removal of pollutant from sugar mill wastewater. Several physico-chemical methods such as coagulation, flocculation, ultrafiltration, electrodialysis and reverse osmosis are used to treat sugar mill wastewater. The biological methods are frequently used in bioremediation of sugar wastewater which is very effective and offer some advantages over physico-chemical methods (Fig. 7.1).

7.4.1 *Physico–chemical Methods*

7.4.1.1 Chemical Oxidation Method

Chemical oxidation method is one of the physico-chemical methods used for chemical oxidant (H_2O_2, O_3, $KMnO_4$, etc.) to oxidize the hazardous pollutant in slightly toxic, harmless substances or transform it into convenient form. Though, chemical oxidation methods comprise the use of oxidizing agents such as ozone and hydrogen peroxide, exhibit lower rates of degradation. Ozone is a gas at normal pressure and temperature. Its solubility in water is function of its partial pressure and temperature. Ozone is produced by high voltage discharge in air and oxygen. Ozone is unstable and tends to react to form:

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$$

Ozone is a very strong oxidizing agent and much effective for decolorization.

7.4.1.2 Coagulation and Flocculation

Coagulation-flocculation process is employed for removal of suspended solids materials from sugar mill wastewater. The process operates in steps which break down forces, which stabilize charged particles present in the waste allowing inter particle collision to occur, hence, generating flocs. The purpose of coagulation/flocculation process is to destabilize the charged particles of suspended solids. Addition of coagulants with opposite charges of the suspended solids destabilizes the particles charge. Coagulants are mixed in wastewater to neutralize the negative charge of suspended particles. Upon neutralization, the suspended particles fix together to form slightly larger particles.

7.4.1.3 Reverse Osmosis

It is a process in which heavy metals are separated by a semi permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. The disadvantage of this method is that it is highly expensive.

7.4.1.4 Electrodialysis

In this process, the ionic components are separated through the use of semi-permeable ion selective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage of this technique is the formation of metal hydroxides which clog the membrane.

7.4.1.5 Chemical Precipitation

Precipitation of pollutants is achieved by the addition of coagulation such as alum, lime, iron salts and other organic polymers. The main drawback of this method is the production of large amount of sludge during the process which contains toxic compounds.

7.4.1.6 Electro-oxidation (EO)

Wastewater treatment by electro-oxidation goes back to the nineteenth century, when electrochemical decomposition of cyanide was examined. Extensive study of this method initiate since the late 1970s. During the last two decades, research works have been focused on the competence in oxidizing the various pollutants on different electrodes, improvement of the electrocatalytic activity and electrochemical stability of electrode materials, investigation of factors affecting the process performance, and exploration of the mechanisms and kinetics of pollutant degradation. The electrochemical oxidation can be achieved by the application of electricity both in direct and/or indirect form. Moreover its effectiveness strongly depends upon several factors i.e. the treatment condition, waste composition, the nature of the electrode materials used and mode of operation both in batch or continuous process.

7.4.2 Biological Methods

Industrial pollution is one of the major factors causing the degradation of the environment around us. Also, increasing industrialization is not only consuming large areas of agriculture lands, but also simultaneously causing serious environmental threats (Saranraj and Stella 2014). In India, sugar industries have an important position in economic development. However, the wastewater released from these industries bear a high extent of pollution. Sugar industries generate nearly 1000 L of wastewater for 1 ton of sugar cane crushed (Kushwaha 2013). If wastewater is discharged without proper treatment, it poses pollution problems in environment. The generation of organic compounds as liquid effluents is one of the important environmental problems in sugarcane processing industry. The inadequate and indiscriminate disposal of such wastewater in soils and water bodies has gained much attention because of their environmental toxicity. There are several conventional technologies involves physical and chemical methods that have been used for treating sugarcane industry waste. However, these methods are expensive and ecologically not fit as chemical methods may cause secondary pollution. Thus, nowadays eco-friendly and cost effective biological methods are used for treating such waste generated from sugar mill. The present technology has initiated the zero discharge by using wastewater in press mud, bagasse burring and in biofertilizer production unit of the industry.

Biological treatment is a better alternative for treating sugar industry wastewater. The biological treatment over other physical and chemical treatment processes is better due to economic advantage, both in terms of capital investment and operating costs. Major biological methods involve aerobic, anaerobic and combined biological treatments that can be suitably adopted in different processing steps of sugar mill wastewater treatment process. The aerobic biological methods for sugar mill wastewater treatment occurs through sequential batch reactor (SBR), activated sludge processes (ASP), wetlands or stabilization pond. Among the different anaerobic methods, anaerobic digester (AD), anaerobic filter (AF) and Upflow anaerobic sludge blanket (UASB) are mainly used for the treatment of wastewater.

Aerobic treatment processes occurs in the presence of oxygen using aerobic microbes to assimilate organic impurities i.e. convert them in to carbon dioxide, water and biomass. The anaerobic treatment processes, on other hand take place in the absence of oxygen by anaerobic microorganisms to assimilate organic impurities into methane and carbon dioxide gases and biomass (Fig. 7.2a, b).

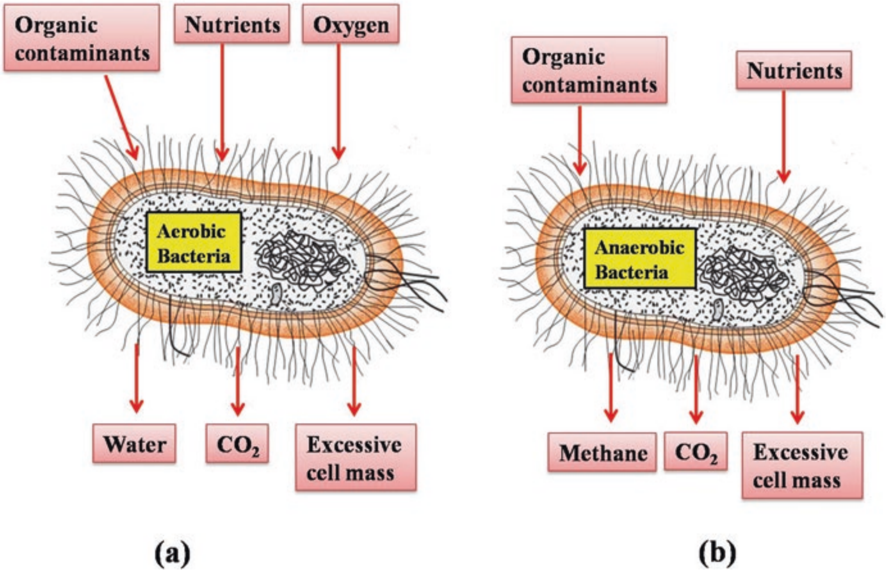

Fig. 7.2 Bacterial treatment of contaminants using aerobic (**a**) vs. anaerobic (**b**) processes

7.4.2.1 Anaerobic Biological Treatment

The high organic content of wastewater from sugar cane industry makes anaerobic treatment attractive in comparison to direct aerobic treatment. Therefore, biomethanation is the primary treatment step and is usually followed by two-steps aerobic treatment before discharge into a water bodies. Anaerobic treatment method converts half of the effluent COD into biogas and it can be successfully operated at high organic loading rates; also, the biogas thus generated can be utilized for steam generation in the boilers thereby meeting the energy demands of the unit. Further, low nutrient requirements and stabilized sludge production are other associated benefits (Rais and Sheoran 2015).

Anaerobic lagoons are the simplest way for the anaerobic treatment of wastewater (Wilkie et al. 2000). It was reported that employing two anaerobic lagoons in series resulted in final BOD levels up to 600 mg/l. However, large area requirement, odor problem and chances of ground water pollution restrict its usage (Rais and Sheoran 2015). These reactors offer the advantage of separating the hydraulic retention time (HRT) from solids retention time (SRT) so that slow growing anaerobic microbes can remain in the reactor independent of wastewater stream (Mall and Kumar 1997).

Anaerobic treatment converts the wastewater organic pollutants into small amount of sludge and large amount of biogas as source of energy whereas aerobic treatment method needs external input of energy for aeration (Ayati and Ganjidoust 2006).

Anaerobic processes could treat the effluent with high loads of easy to degrade organic materials (effluent from the sugar industry) efficiently. Anaerobic method can be categorized into anaerobic activated sludge and anaerobic biological membrane processes. The anaerobic activated sludge method involves conventional stirred anaerobic reactor, upflow anaerobic sludge blanket reactor (USAB), anaerobic contact tank, etc.

7.4.2.1.1 Upflow Anaerobic Sludge Blanket Reactor (UASB)

The upflow anaerobic sludge blanket (UASB) reactor is by far the most widely used high rate anaerobic treatment system for variety of wastewater (Van Haandel and Lettinga 1994). The most characteristic device of UASB reactor is the three phase separator or settler. The presence of the settler on the top of the digestion zone enables the system to maintain a large sludge mass in the UASB reactor, while effluent essentially free of suspended solids is discharged. In this process, mixing of sludge and waste water occurs through the production of methane within the blanket as well as by hydraulic flow and the triphase (gas, liquid, sludge biomass) separator which could restrict the loss of biomass sludge via the gas emission and release of water. The benefits of USAB system are as follows:

1. It has a high population of naturally immobilized bacteria with good settling characteristic, and also remediates the organic contaminants from wastewater of sugar industry.
2. In USAB system, increased concentrations of cells biomass can be achieved without support materials that reduces the cost that make the process feasible and efficient.

Hampannavar and Shivayogimath (2010) studied the treatment of sugar industry wastewater in a UASB reactor seeded with nongranular anaerobicallly digested sewage sludge. They also reported a maximum COD removal efficiency of 89.4% was achieved at ambient temperature and Successful reactor startup with granulation was achieved within 95 days of operation.

7.4.2.1.2 Anaerobic Biofilter

Anaerobic biofilter is a type of efficient anaerobic treatment equipment which was developed in 1960s for treatment of wastewater. These reactors use inert support materials to make available a surface for the development of anaerobic bacteria and to decrease disorder to allow free bacterial populations to be retained in the anaerobic biofilter.

7.4.2.2 Aerobic Biological Treatment

After post-anaerobic treatment step, the anaerobically treated waste has still high organic load and is dark brown in color, hence it is generally followed by a secondary, aerobic treatment. Solar drying of bio-methanated sugar mill waste water is one way but the large land area need restricts this practice (Rais and Sheoran 2015). Other techniques that have been demonstrated for bio-methanated sugar mill effluent are aquaculture, constructed wetlands (CWs), biocomposting, and microbial (bacteria, fungi and algae) treatments. Biological techniques employing aerobic processes such as activated sludge, biocomposting, etc. are presently used by many sugar industries. Only a part of the wastewater gets consumed in biocomposting due to the large volumes generated. Biocomposting utilizes sugarcane press mud as the filler material; thus it is typically employed by sugar mills. Since sugar manufacturing is a seasonal operation, press mud availability is often a constraint. Further, biocomposting requires large amount of land. Also, it cannot be carried out during the rainy season (Rais and Sheoran 2015).

Microbial treatment has been considered as an eco-friendly and cost competitive technique involving the natural way which results in conversion of hazardous toxic organic and inorganic compounds into nontoxic forms. This technique involves compatible microbes in the polluted water system and the pollutants are bioremediated during the microbial metabolism process. Sugar industries consume large quantities of water for various processes and discharge equally large volumes of waste waters containing variety of pollutants and coloring matter. Microorganism due to their inherent capacity to metabolize a variety of complex compounds have been utilized since long back for biodegradation of complex toxic and recalcitrant compounds present in various industrial wastes for environmental safety (Gupta and Mukarji 2001). Microbial treatment systems have advantage of being simple in design and low in cost (Banat et al. 1996). Several species of fungi, bacteria and algae have been used for the removal of pollutant from sugar mill wastewater. Buvaneswari et al. (2013a) reported the role of *Staphylococcus aureus, Bacillus cereus, Klebsiella pneumoniae, Enterobacter aeruginosa* and *Escherichia coli* in bioremediation of Sugar mill waste water. Similarly, Saranraj and Stella (2012) studied the sugar mill effluent bioremediation by immobilized bacterial consortium (*Bacillus subtilis* + *Serratia marcescens* + *Enterobacter asburiae*). They reported that the immobilized bacterial consortium used for bioremediating the effluent showed a sharp decrease in the levels of COD, TSS, TDS, heavy metals and other physical properties after 6 months of treatment. To overcome the contamination caused by polluted soil of sugar industry the addition of some seeds of *Moringa oleifera*, *Acacia nilotica*, *Tamarindus indicus* and cow dung were used by Shinde et al. (2016) in that polluted soil.

Fungi, their biology, economic value and pathogenic capabilities are not new to human society. They have been used from fermentation of foods to production of pharmaceuticals. Fungi thrive well in hospitable habitats with environmental extremes because of their enzyme systems (Cooke 1979). Fungi are involved in the biodegradation of undesirable materials or compounds and convert them into harmless tolerable or useful products. Fungi are recognized for their superior aptitudes to produce a large variety of extracellular proteins, organic acids and other metabolites and for their capacities to adapt to severe environmental constraints. Fungal systems appear to be most appropriate in the treatment of colored and metallic effluent. Fungi not only produce various metabolites like citric acid, homogeneous proteins, heterogenous proteins, peroxides but have shown their effectiveness for removal, reduction and detoxification of industrial effluent ingredients. Several fungi have been used for treating sugarcane industry waste such as *Aspergillus niger*, *Penicillium* sp. and *Fusarium* sp. (Buvaneswari et al. 2013b).

Many biological methods have been investigated for the treatment of wastewater from sugarcane industry. Due to high COD, the anaerobic treatment with biogas recovery is employed mainly as the first treatment step that reduces the organic pollution load and brings down BOD to 80–95% of the original value; however, the bio-digested effluent still contains BOD in the range of 5000–10,000 mg/l (Rais and Sheoran 2015). Further the problem of color associated with sugar mill waste water not only remains unsolved but actually gets aggravated under anaerobic conditions (Patil et al. 2003). Therefore anaerobically treated effluent is darker in color compared to untreated wastewater and needs several-fold dilution by fresh water prior to discharge. Biological treatment using aerobic processes like activated sludge, biocomposting etc. is presently practiced by various sugar mill industries.

Due to the large volumes generated, only a part of the wastewater gets consumed in biocomposting. Biocomposting utilizes sugarcane press mud as the filler material; thus it is typically employed by distilleries attached to sugar mills. Since sugar manufacturing is a seasonal operation, press mud availability is often a constraint. Further, biocomposting requires large amount of land; also, it cannot be carried out during the rainy season. Though aerobic treatment like the conventional activated sludge process leads to significant reduction in COD, the process is energy intensive and the color removal is still inadequate. Thus several pure cultures of fungi, bacteria and algae have been investigated specifically for their ability to decolorize the effluent as discussed earlier. In all instances, supplementation with either nitrogen or carbon source is almost always necessary because the microbial species are not able to utilize the wastewater as the sole carbon source. Further, high dilution (typically up to 1:10-fold for untreated wastewater) is required for optimal microbial activity. In addition, these studies are mostly limited to laboratory scale investigations and no pilot/commercial scale operations are reported as yet.

Kushwaha (2013) reviewed about sugar industry wastewater. The wastewater generated from these industries bear a high level of pollution. Most of the studies on sugar industry wastewater treatments have been carried out by anaerobic treatment processes. However, oil and grease are not easily degraded by anaerobic processes. Anaerobic-aerobic combined systems can remove organics completely. However, more work is needed in use of combined systems (Kushwaha 2013).

The aerobic microbial degradation have significant role in biological treatment. In this process, the oxygenases and peroxidases synthesizing microbes are mainly used. The microbes get the energy, carbon and nutrient elements released during the degradation process. The classic aerobic biodegradation process involves activated sludge reactor and membrane bioreactor.

7.4.2.2.1 Activated Sludge Reactor

It is frequently used technique for treating wastewater generated from industry that uses oxygen and microorganisms to biologically degrade organic pollutants. In the process, there is an aeration tank (Fig. 7.3), a setting tank or clarifier is present to allow the waste sludge to settle. Part of the waste sludge is recycled to the aeration tank and the remaining waste sludge is removed for further treatment and ultimate disposal.

Activated sludge process is used to treat sugar mill wastewater using air and a biological floc composed of microbes. In general, the process occurs in two steps, viz; adsorption and biological oxidation. The technique could effectively remediate the organic pollutants of the wastewater.

7.4.2.2.2 Trickling Filter Method

A trickling filter consists of a bed of rocks, gravel, slag, peat moss, or plastic media over which sugar industry wastewater flows downward and contacts to microbial slime covering the bed. Aerobic conditions are maintained by forced air flowing through the bed. Trickling filter process involves adsorption of organic compounds of the wastewater by the microbial slime layer and diffusion of air into the slime layer to provide oxygen required for the biochemical oxidation of the organic compounds. The end products include carbon dioxide gas, water and other products of the oxidation.

7.4.2.2.3 Membrane Bioreactor

This process is the combination of microfiltration or ultra filtration with a suspended growth bioreactor, and is used for industrial wastewater treatment including sugar mill wastewater. The technique is nearly the same as activated sludge process, except that instead of separating water and sludge via settlement. This processes is capable to treat effluent with higher suspended solids (SS) concentrations compared to activated sludge process, thus reducing the reactor volume to achieve the same loading rate.

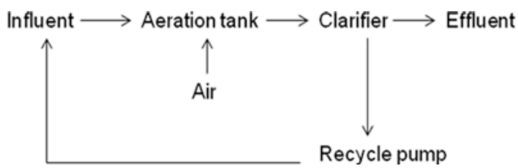

Fig. 7.3 Diagrammatic illustration of activated sludge process

7.4.2.3 Combination of the Aerobic and Anaerobic Biological Treatment

The combination of the anaerobic and aerobic reactor is more efficient in sugar mill wastewater treatment compared to the single anaerobic and aerobic reactors. The benefit of using combined process viz., anaerobic process could modify the biochemical property of the wastewater, making the following aerobic process more efficient. The combined aerobic-anaerobic reactors include A/O reactor, A2/O reactor, oxidation ditch, constructed wetland. The two classic aerobic biodegradation reactors such as oxidation ditch and constructed wetland are briefly discussed here.

7.4.2.3.1 Oxidation Ditch

In this method, the effluent treatment occurs in which a circular basin through that the effluent passes. The microorganisms will digest the organic pollutants in the wastewater when activated sludge is added to the oxidation ditch process. Raw wastewater and returned sludge is known as mixed liquor. The addition of oxygen into the flowing mixed liquor occurs through rotating biological contactors. Once the organic waste has been removed from the polluted water, the mixed liquor flows out of the oxidation ditch and sludge is removed in the secondary settling tank, and part of the sludge is pumped to a sludge pumping room where the sludge is thickened with the help of aerator pumps in oxidation ditch. The oxidation ditch is characterized by simple process, low maintain consumption, steady operation, and strong shock resistance.

7.4.2.3.2 Constructed Wetland

It is an artificial wetland which could act as a biofilter, removing sediments and pollutants from wastewater. Constructed wetland is a combination of water, media, plants, microbes. Other physical, chemical, and biological also combine in wetlands to remove pollutants from the effluent. Constructed wetland method is economical and eco-friendly. Thus, it is supposed to be a promising technology to treat the effluent in developing country.

7.5 Factors Affecting the Treatment of Wastewater from Sugar Mill

India is one of the largest producers and consumers of sugar per annum in the world. In rural economy of India, sugar industry plays an important role by uplifting the livelihood and creation of employment. Byproducts of sugar industry are also used as raw materials in different industries. However, effluents of sugar industries have a great environmental impact upon the surrounding environment due to presence of various pollutants. A significant large amount of waste are generated during the manufacture of sugar, which contains a high amount of pollutants in terms of suspended solids, organic matters, biological and chemical oxygen demand effluent including sludge, press mud and bagasse (Yadav and Daulta 2014). Near about 526 sugars mill are operating in India that produced 33.69 million tons of sugarcane in the year of 2015–2016 (Mane et al. 2015). To crush one tone of sugarcane nearly 2000 l water required, which generated nearly 1000 l of wastewater (Kolhe et al. 2009). If untreated wastewater is discharged on land, decaying organic solids present in the wastewater clog the soil pores and will change soil properties (Reddy et al. 2015). Sugar mill effluent represents an environmental problem due to its high organic load, intense coloration and presence of phenolic compounds. Most of the organic matter present in the effluent can be reduced by conventional biological treatments but the color is hardly removed by such treatments. The remaining color can lead to a reduction of sunlight penetration in rivers and streams which in turn decreases both photosynthetic activity and dissolved oxygen concentrations causing harm to aquatic life. Hence, purification of sugar industry wastewater is a not challenging task due to fewer amounts of pollutants.

The principle factors which mainly affect the ability of sugar mill wastewater treatment are pH, aerobic or anaerobic conditions, temperature, reaction time, type and speed of reactions for the treatment of wastewater, biomass in the aeration tank in each moment during the reaction, catalyst, inhibitor, nutrients and the concentration of the contaminants in the wastewater. Combined sugar mill effluents generally contain high amount of suspended solids, dissolved solids, BOD and COD which have an adverse environmental impact. Wastewater with a high TDS level would have adverse impact on aquatic life, unfit for drinking, and reduce crop yields if used for irrigation. Suspended solids reduce light penetration and, as a result, photosynthetic activity reduces with increasing turbidity and can also clog fish gills. Sugar mill effluents generally change the natural pH level of the receiving water body to some extent. Such changes in pH can disturb the ecological balance of the aquatic system (Roy et al. 2007). The effluents with its high BOD rapidly deplete available oxygen supply when they enter into water ecosystem causes adverse condition for aquatic life. The high BOD also creates septic conditions, generating foul smelling due to hydrogen sulphide, which in turn can precipitate iron and any dissolved salts, turning the water black and highly toxic for aquatic life (Behera and Mishra 1985). A high COD value of effluents indicates the presence of high inorganic and partly organic non-biodegradable content in the effluents. Its effects on the receiving water body are similar to that of a high BOD. Aerobic decomposition of components can decrease oxygen availability while anaerobic decomposition can produce hydrogen sulphide and are unaffected in lack of oxygen (Saranraj and Stella 2014). For the treatment of sugar industry effluent, several biological treatment technologies like aerobic as well as anaerobic methods were used. Wastewater organic pollutants are converted into small amount of sludge and large amount of biogas as source of energy during anaerobic treatment whereas aerobic treatment needs external input of energy for aeration. Anaerobic digestion is ideal for waste treatment, having several significant advantages over other available methods. The advantages become more pronounced when dealing with strong industrial wastes including sugar cane waste which is nutrient deficient. Inspite of that the analyzed parameters of treated wastewater are well within the prescribed by the central pollution control board (CPCB) for the discharge of effluent to on-land standards and discharged wastewater could be used for the agriculture purposes or any other purposes.

7.5.1 pH

pH is one of an important biotic factor that serves as an index for pollution. Any change in the pH value can change the rate of biological and chemical reaction and survival of various microorganisms present in the water. The presence or absence of different anions and cations can have direct relation with pH of the waste water (Doke et al. 2011). From the literature, it has been found that pH of sugar mill effluents varies from 4.8 in the raw waste water and 6.9 in the treated waste water. Khan et al. (2003) observed the pH of sugar industry wastewater was 9.5 however, Maruthi and Rao (2001) observed the pH of the sugar mill effluent discharges from Tummapala sugar factory, Anakapalli (Andhra Pradesh) was 6.5–8.8. Different study showed the difference in pH of sugar mill wastewater (Senthil et al. 2001; Matkar and Gangotri 2002). The reaction between waste water flowing from open drainage system with the soil has direct relevance to the pH of waste water. If the water in a stream is too acidic or basic, the H^+ or OH^- ion activity may disrupt the biochemical reactions of aquatic organisms. Wastewater pH has been identified as one of the parameters which influence the effective wastewater treatment (Aboulhassan et al. 2006). The lower pH of the reactor contents may be due to acid production by activities of acidogenic bacteria whereas acetogenic and methanogenic bacteria increase the pH by the consumption of the generated acid during methane formation. These bacteria have different growth rates and perform activities at different stages. At pH below 6.2, the growth of methanogens is inhibited; however, fermentative bacteria will continue to function even when pH has dropped to 4.5–5.0. Lower pH values of both treated and untreated effluents may be also due to use of phosphoric acid and Sulphur dioxide during cleaning of sugar cane juice. Low pH of the digester system may be due to inhibition of methanogenic bacterial action. For efficient operation of an anaerobic reactor, pH is an important indicator and a continuous drop in the pH is a sign that all is not right. Hence, before a stable population of each bacterial groups established in an anaerobic digester, external control is done by adding chemicals such as lime and bicarbonates or carbonates of either sodium or potassium. Omol (1997) observed that anaerobic digesters may operate at the satisfactory pH range of 6.2–8.0 while the optimum range is 6.8–7.2. He also noted that low pH of system may be due to accumulation of volatile fatty acid. To see the effect of initial pH on COD and color reduction in waste water treatment, an experiment was carried out from sample pH 2 to 10 at 3 kg/m^3 mass loading with treatment temperature 65 °C, reaction time 3 h and in presence of catalyst copper oxide. Maximum 39.7% COD and 43.6% color reduction was found at pH 8 whereas 38.5% COD and 42.5% color reduction was found at pH 4 (Sahu 2016). The COD reductions are due to a combined effect of the active functional groups of effluents which react at certain pH and the catalyst reactivity which varied with pH. Tiwari and Sahu (2017) reported that removal of color 54%, 62%, 66% and COD 51.5%, 59.5%, 63.5% was increased with increased in pH 3.0, 4.5 and 6.0, respectively during the treatment of sugar mill waste water.

7.5.2 Temperature

Temperature is basically one of the most fundamental parameter which largely affects the chemical and biological reactions of aquatic organisms (Shelavale and Shinde 2016). The temperature of sugar mill waste water depends on season, time of sampling, distance of sampling from sugar mill etc. When effluent is discharged from industries, it has generally higher temperature which affects the aquatic biota and land adversely. In general, the temperature of aquatic condition lies between 20 and 27 °C but the temperature of untreated and treated effluent of sugar industry has 48 °C and 30 °C, respectively. The temperature of the discharge waste water should not exceed 35 °C otherwise it will produce adverse effect on aquatic system, agricultural field and yield of the crop (Beruch et al. 1993). Siddiqui and Waseem (2012) also suggest that the temperature of the discharged wastewater should not exceed 35 °C. The high temperature of the untreated effluent i.e. above 35 °C also affected the germination process. The increased temperature may accelerate the rate of chemical reaction and chemical changes in the aquatic condition (Poddar and Sahu 2017). The activity of various anaerobic bacterial population is depends on temperature. Different bacterial species are functional at different temperature ranges. Omol (1997) observed that anaerobic digestion can occur over a wide range of temperature which may be subdivided into three separate ranges as indicated below. Temperature ranges for bacterial action are:

Type	Range (°C)	Optimum range (°C)
Psycrophillic	2–30	12–18
Mesophilic	20–45	25–40
Thermophilic	45–75	55–65

From above observation, it is expected that any variation in temperature may affect the performance of anaerobic reactors. During anaerobic treatment, acetogenic and methanogenic bacteria are extremely sensitive to temperature variation with even a drop of 2–3 °C affecting the performance of reactors. Souza (1986) observed that an increase in temperature above 15 °C, the rate of anaerobic digestion also increased, but large variations in temperature should be avoided due to adverse effect of it on bacteria. Sahu (2016) showed the effect of reacting temperature (55–95 °C) on COD and color reduction at treatment time 9 h, optimum mass loading and pH. From the experimental data, it has been found that with an increase in temperature (55 °C, 65 °C, 75 °C, 85 °C) decreased the COD (55%, 60%, 65%, 73%) and color (57.5%, 63%, 68% 76%), respectively. It was found that the preheating period up to 85 °C is sufficient for affecting the COD 73% (994.15 mg/l) and color removal 76% (84 PCU), no further increase in COD and color removal was observed even the reactor is maintained at 95 °C temperature. The large molecules of the organic matter present in waste water breaks into smaller molecules and leads to carbon enriched solid residue formation. The decomposition of the large molecules at high temperature resulting in the deposition of the insoluble charred residue, leads to reduction in COD of the treated wastewater (Kumar and Srikantaswamy 2015). Gaseous products formed during decomposition have pungent and foul smell, which escape when the valve is opened after cooling of the reactor. The gases may consist of methane and/or nitrogenous and sulphurous compounds.

7.5.3 Aerobic and Anaerobic Condition

Biological treatment of effluents can be achieved by two processes, aerobic and anaerobic processes. Aerobic processes are occurs in presence of oxygen and usually limited by the waste strength. Aerobic processes require maximum oxygen exchange rate from the gas phase to the liquid phase to treat the waste water aerobically. In compare to aerobic treatment of wastewater, anaerobic treatment process has two distinct advantages (Artsupho et al. 2016). First, due to their low energy yield, the excess biomass is utilized to fulfill the energy requirement. Secondly, the problem of excess sludge disposal is significantly reduced. Because of low sludge generation, the requirements of nutrients are considerably lower in anaerobic treatment as compare to aerobic processes. Many industrial waste water including sugar mill waste water are often nutrient deficient, hence anaerobic treatment has an important advantage over aerobic treatment of sugar mill effluent.

7.5.4 Mass Loading

Sugar mill waste water is characterized by high organic waste load, large volume and high suspended solid content. Anaerobic treatment process was considered as effective treatment procedure for sugar mill effluent when it was compared to aerobic treatment. Anaerobic treatment has several advantages over aerobic treatment. Anaerobic treatment has low nutrient requirement, no limitations of oxygen exchange from gas to liquid phases and can therefore treat stronger organic pollutant of waste water than aerobic process. The effect of mass loading on treatment of waste water, COD and color removal was carried out from 2 to 6 kg/m^3 at optimum pH and treatment time 9 h with copper oxide as catalyst. At minimum mass loading of 2 kg/m^3, 46.5% COD and 50.5% color removal was observed. However, COD removal 51%, 54%, 60% and color reduction 53.8%, 57%, 63% increased with increase in mass loading 3 kg/m^3, 4 kg/m^3 and 5 kg/m^3, respectively. Further increase in mass loading upto 6 kg/m^3, COD (57%) and color removal (63%) decreased. It proves that 5 kg/m^3 is the optimum mass loading for maximum COD (60%) and color reduction (63%) in presence of catalyst. Further increase in mass loading decreases the treatment efficiency (Sahu 2016).

7.5.5 Reaction Time

To see the effect of reaction time on COD and color reduction of sugar mill waste water, treatment was carried out with waste water containing 3 kg/m^3 mass loading for 0–9 h at temperature 65 °C. Experimental data suggest that the removal efficiency increases with increase in time. Maximum 51% COD and 53.8% color removal were observed in the presence of copper oxide as catalyst at 9 h of treatment time. Without catalyst, marginal effect on COD (37%) and color removal (38%) was observed at same treatment time. Heating and absence of oxygen also increases the COD and color reduction (Sahu 2016). Guimaraes et al. (2005) reported that *Phanerocheate chrysosporium* can remove color and total phenols from the sugar mill waste water with retention time of 3 days. During the course of operation, color, total phenols and chemical oxygen demand were reduced by 55%, 63% and 48%, respectively. Deshmane et al. (2016) reported that COD reduces up to 91% in 108 h and reduction of COD over 50% was achieved in only 24 h in presence of *Spirulina*.

7.5.6 Catalyst

The role of catalyst in the treatment of sugar industry wastewater has significant positive impact. In an experiment, maximum 73% chemical oxygen demand and 76% of color removal were obtained at 5 kg/m^3 mass loading, reacting temperature 85 °C, treatment time 9 h and optimum pH 8 with copper oxide as catalyst. In presence of catalysts $CuSO_4$ and CuCl, COD decreased 48%, 44.5% and color removal was 51% and 46%, respectively after 9 h of treatment time whereas in absence of catalyst, 37% COD and 38% color removal was observed at same treatment time (Sahu 2016). Similarly, COD removal by 10.5% and color reduction 11% was observed in the presence of poly-aluminum chloride at pH 7.5 (Tiwari and Sahu 2017). The treated wastewater contained more copper compared with pollution control board dischargeable limits. It required further treatment like adsorption or membrane separation of copper before discharge into the receiving stream. The quality of water was found to be suitable for irrigation after the removal of copper. The high removal of chemical oxygen demand and color from wastewater in presence of copper appreciates its use as catalyst in the treatment of sugar mill wastewater.

7.5.7 Nutrients

Along with the substrates, microorganisms require growth factors, trace elements and nutrients for their growth. Nitrogen (N) and phosphorous (P) are two important nutrients that are vital for bacterial growth. It has been found that the biological growth during the anaerobic digestion depends on different types of substrate. The slowest growth was observed with long chain fatty acids and highest growth was observed with carbohydrate as substrate. Growth of microorganism varies considerably and cannot be predicted from knowledge of waste strength alone, but the components of the waste also need to be considered (Omol 1997). Kiestra and Eggers (1986) studied the nutrient requirements i.e. carbon, nitrogen and phosphorous ratios during aerobic and anaerobic processes and obtained the following ratio; for aerobic process, it was 100:5:1, and for anaerobic process, it was 100:1.5:0.3. Therefore, the above ratios indicate that anaerobic organisms have lower nutrient requirements than aerobes. This may be attributed to the slow cellular growth of anaerobes and is an advantage when dealing with wastewaters with relatively inadequate nutrients. It has been found that the optimum BOD:N:P ratio for successful anaerobic ecosystem is 100:0.5:0.1.

7.5.8 Inhibitors

Inhibitors are substances that adversely affect the rate of biochemical or chemical reactions when they are present above certain concentrations. Inhibitory substances mainly affect the microbial activities of methanogenesis phase because methanogenic bacterial group is consists of only a few sensitive species, unlike the diverse hydrolytic and acidogenic bacteria. Hydrolytic and acidogenic bacteria are required during the first phase of decomposition of organic matter and therefore constantly replenished. However, methanogenic bacterial population is required during the second phase of organic decomposition and once the population is depleted, it takes a long time to recover. During decomposition, ammonia and sulphates are the most common inhibitors (Omol 1997). Although, ammonia and ammonium ion are essential as nitrogen sources for bacterial growth during digestion but they are inhibitory at high concentrations. Sulphate concentration greater than 500 mg/l can reduce methane production and lead to excessive sulphide production.

7.6 Recycling and Reuse of Wastewater

India is a developing country where small/large scale industrial units mainly sugar industry discharge their waste water without any treatments in open areas or in running water bodies such as river, lakes etc. The main difficulties in the treatment of wastewater is cost of treatment plant/processing which add extra pressure to smaller units. Hence, the values of pH, TSS, TDS, BOD and COD are above the permissible limits. These effluents have deleterious effects on the soil making them unsuitable for cultivation purpose. Qureshi et al. (2015) reported that sugar industry wastewater has high oxygen demand which leads to the depletion of dissolved oxygen content in the water bodies. If discharged untreated, it will produce adverse effect on aquatic biota and humans. Damodharan and Reddy (2012) showed that the yield of sugarcane increased when sugarcane crop was irrigated with the waste water as compared to bore well water irrigated crop. The results indicated a significant increase in plant height, shoot diameter, growth pattern, number of leaves and nodes, and biomass of the saplings, irrigated with wastewater when compared to bore well water irrigated crop. The reuse of treated wastewater is good options due to increasing water supplies to agriculture and use of nutrients by plants reduce the pollution load (Goel and Kulkarni 1994).

With increasing population, water demand in various sectors is now increasing. Now, researchers are concentrating to resolve this problem by the use of treated wastewater for irrigation. A large quantity of wastewater is produced from mill and cane handling station, boiler house and as by product during various sugar mill processes. This wastewater goes to common wastewater treatment plant for primary and secondary treatment. There are several initiatives taken by industries to minimize their water consumption and recycle the treated wastewater. However, research is going on to fill the existing gaps to provide a comprehensive and cost effective solution for small and large scale industries to become low water consuming and zero discharge units (Rais and Sheoran 2015).

7.7 Advantages of Treatment

Sugar industry untreated effluent has high COD, BOD, TDS and low contents of DO which causes negative effects on biological system. All the industries use large quantity of water and throw back almost an equal quantity of effluent which contains highly toxic materials in dissolved or suspended form. If this water is properly treated then it can be reused or recycled and a part of water shortage will surely be solved. During the treatment of waste water, all harmful chemical constituents including oil and grease should be removed. Although oil and grease has been removed successfully from waste water but some better technique is still required for the removal of oil and grease from the effluents. The hazardous pollutants of wastewater and their harmful effects can be removed/minimize after the treatment. Treated waste water of sugar industry has well balanced of chemicals. It may be suitable for irrigation purposes, if diluted with other fresh water. The treated wastewater can accelerates and improves the crop production (Rana et al. 2011). Mane et al. (2015) reported that use of treated sugar mill wastewater is a prospective source of different plant nutrients and can be used for irrigation purpose in agricultural practices. It would be beneficial alternative resources of water and due to presence of nutrients; it can act as fertilizer for crop production. Presently sugar industries are consuming their wastewater inside the industry through various processes like bagasse moisturing before the use in furnace, absorb for biofertilizers and so on.

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Chapter 8
Treatment and Recycling of Wastewater from Textile Industry

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Abstract Textile industries are one of the largest generator of wastewater as large amount of water is used in coloring and finishing processes. The effluents released from textile industries contain biodegradable and non-biodegradable chemicals such as dyes, dispersants, leveling agents etc. These effluents are released into water bodies which can modify the physical, chemical and biological nature of the receiving water bodies. Azo dyes are largely utilized in textile industry as coloring agent. During the processing of textile, a lot of dyestuff specifically lost to the wastewater due to inefficiency in dyeing processes which may causes serious health and environmental problems. Therefore, removal of dyes from textile wastewater is necessary prior to their disposal. Several physico-chemical techniques have been utilized for the treatment of wastewater containing dyes, but execution of these strategies have the distinctive limitations of being expensive, unable to the complete removal of dyes from wastewater, and producing noteworthy amounts of sludge that may cause auxiliary pollution issues. The application of microorganisms (bacteria, fungi and algae) and plants for the removal of azo dyes from textile wastewater is an attractive option over the physico-chemical methods. Biological methods are environment friendly, produce less sludge, and inexpensive. Water recycling is the reuse of treated wastewater for valuable purposes such as agricultural irrigation and industrial processes etc. Recycling of textile wastewater is important for restricting the amount of wastewater and expenses of production, and recommended for the protection of environment.

Keywords Textile wastewater · Azo dyes · Microorganisms · Decolorization · Recycling

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R. L. Singh, R. P. Singh (eds.), *Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future*, Applied Environmental Science and Engineering for a Sustainable Future,
https://doi.org/10.1007/978-981-13-1468-1_8

8.1 Introduction

Water is, without a doubt, the most precious natural resource that exists on our planet. It is a basic need for sustenance of all forms of life and life on earth would be non-existent without water. In spite of the fact that we as humans know about this reality, day to day the water pollution issues are far worse around the world, because of human activity and rapid industrialization (Gupta et al. 2015). Industrial wastewaters are the significant contributor to water pollution by polluting rivers, lakes and oceans. These wastewaters are released by different industries such as textile, dyestuffs, paper and pulp, distillery, tannery, oil mill and metal industries. Textile industries are one of the largest generator of wastewater due to extensive volume of water is utilized in dyeing and finishing processes (Saratale et al. 2011). The pollution issues because of textile industries wastewater have expanded as a result of the way that over the most recent couple of decades, there has been rapid advancement in the dye and dyeing industries due to increased demand for textile products. The discharge of wastewater from textile industries has introduced various toxic organic compounds into different components of the environment, making it the major sources of serious pollution issues around the world. Wastewater discharged from textile industries contains biodegradable and non-biodegradable chemicals such as wide variety of dyes, dispersants, leveling agents, heavy metals, dissolved inorganics, acids and alkali that make the environmental challenge for textile industry (Olukanni et al. 2006). The textile wastewater can change the physical, chemical and biological nature of the receiving water bodies by increasing the biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total suspended solids (TSS) as well as alters the pH and gives the intense colorations to water bodies (Singh et al. 2017a). The textile waste water contains diverse chemicals, and among the different chemicals, dyes are accounted as imperative pollutants. The occurrence of very low concentrations of dyes (less than 1 ppm for some dyes) in water is exceptionally noticeable. It influences the aesthetic value, water clarity and solubility of gases in lakes, rivers and other water bodies, decreases photosynthetic activity by hindering light penetration into more profound layers and in addition delineates toxic impacts on aquatic organisms (Rana et al. 2013). Dyes are colored unsaturated organic complex compound having capacity to absorb light in the visible region. They are utilized as a part of expansive amounts in various industries including textile, paper, printing, leather, food, plastic, etc. as coloring material. There are more than 8000 chemical products related with the coloring procedures recorded in the Color Index whereas over 100,000 economically accessible dyes exist with an annual production of 7×10^5 metric tons (Zollinger 1987; Singh et al. 2015a). Dyes comprise a wide range of various chemical structures which is based on substituted aromatic and heterocyclic groups, for example, aromatic amine, phenyl and naphthyl. Among the various chemical classes of dyes, azo dyes (~60 to 70%) are the largest class with considerable diversity of colors. Anthraquinone dyes are the second largest class (~15%) followed by triphenylmethanes (~3%) dyes (Fig. 8.1). These dyes are widely utilized in textile industries and

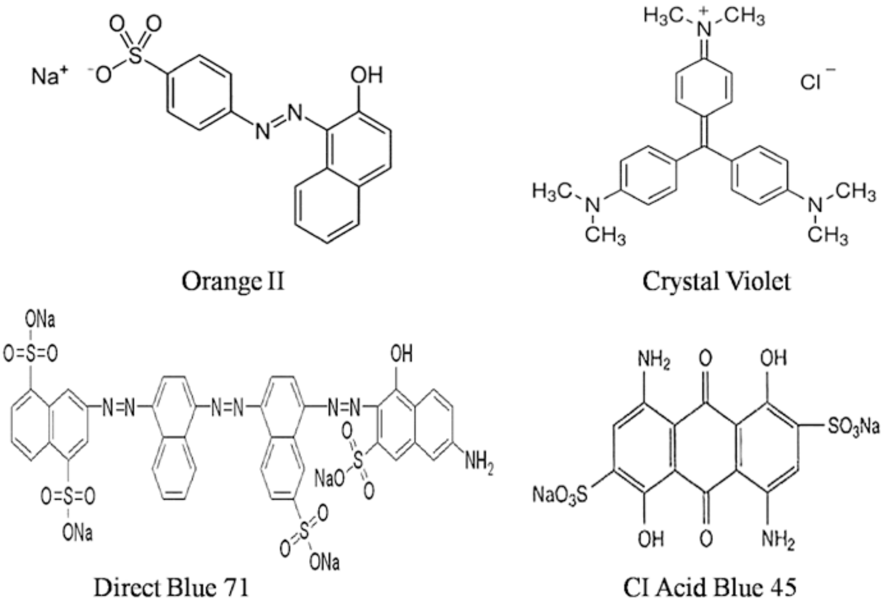

Fig. 8.1 Structure of some textile dyes

are the major well-known synthetic dyes discharged into the environment (Zhao and Hardin 2007).

During the processing of textile, huge amounts of dyestuffs are specifically lost to the wastewater due to inefficiency in dyeing processes which at last finds its way into the environment (Singh et al. 2015a). The amount of dye lost in the wastewater relies upon the applied chemical class of dye, varying from 2% loss (basic dyes) to about 50% loss (in certain reactive dyes). This residual amount of dye is responsible for the coloration and high BOD and COD of the textile wastewater. Release of dye containing wastewater from textile industries into the environment causes serious health and environmental problems. These dyes cannot be degraded easily and some of them are hazardous to humans and other living forms. Moreover, some dyes and/or their degraded intermediate might be either toxic or mutagenic and carcinogenic (Singh et al. 2014). The salts and heavy metals from highly colored wastewater are also toxic to aquatic life. Therefore, wastewater discharged from textile industries has critical ecological concern and removal of dyes from wastewater is necessary prior to their reuse or disposal in order to ensure our water be safe for the future generation.

Conventional treatment processes like adsorption, oxidation, chemical reduction, precipitation, irradiation, membrane filtration, coagulation/flocculation and ion exchange have been utilized in removing various toxic chemicals of general wellbeing and ecological concern. These traditional techniques have their own limitations at large scale (Singh et al. 2014). These methods are not able to completely remove the recalcitrant dyes and their organic metabolites as well as they produce a lot of sludge and secondary waste which need additional treatment and safe disposal (Saratale et al. 2011). Other advance methods, for example, ozonation, electrochemical destruction, treatment using Fenton's reagent and photocatalysis may also used for the treatment of textile wastewater. However, these technologies typically include complicated approach and are very costly. The biological treatment methods can overcome these limitations because it is cost competitive, produces less amount of sludge and eco-friendly alternative to conventional physico-chemical treatment. Biological dye removal strategies with the help of microbes and plants may exhibit a relatively cost effective and environment friendly approach (Singh and Singh 2017). The adaptability of microbial systems makes them able to degrade wide variety of dyes. These methods are generally based on the microbial biotransformation of dyes. The microbes used for the decolorization of dyes are bacteria, fungi, yeast and algae. Over the most recent couple of years, new procedures for the treatment of textile wastewater have been developed. Among them, biological methods are able to remove the dyes with less ecological effect and without the utilization of harmful chemical compounds in mild pH and temperature conditions (Robinson et al. 2001). Together with the environmental and health concerns, textile industries require large volume of fresh water in production process of the textile products. The wastewater volume varies from mill to mill. Due to the large volumes of potable water utilized by the textile industries, the management of wastage of consumable water with recycling and reusing advancements are getting to be imperative for restricting the measure of wastewater and expenses of generation, and recommended for the protection of environment (Dos Santos et al. 2006). Water recycling is the reuse of treated wastewater for useful purposes, for example, agricultural irrigation and industrial processes etc.

8.2 Environmental Concern

Due to rapid urbanization and industrialization, huge amount of chemicals including dyes are produced and are being employed in daily life. Synthetic dyes are extensively used in various industries for example in textile, leather, paper, food, cosmetics and pharmaceuticals etc. About 100,000 synthetic dyes are produced including several varieties of dyes such as reactive, basic, acidic, azo, diazo, anthraquinone dyes with a yearly production of over 7×10^5 metric tons for commercial purposes. Due to inefficient dyeing process 10–50% of the dye used are not bind with the textile fabric and entering the wastewater directly (Pandey et al. 2007). Textile industries produces large amount of colored wastewater because it requires high volumes of water for their processing. Large amounts of chemically different dyes used by the textile industries are poured to the ecosystem and they become a major concern for living organisms as most of the synthetic dyes have complex aromatic structure which is largely toxic, mutagenic, carcinogenic and recalcitrant in nature (Grassi et al. 2011). Dyes in wastewater causes incidence of bladder tumors and it has been reported that dye industry workers are more prone to common population for such incidence. In addition, they reduce the esthetic nature of water and photosynthetic activity of aquatic lives by diminished light penetration valuable for photosynthesis. Several reports are available about the harmful effect of colored wastewater on animals, plants and microorganisms. Because of their stability to temperature, light and microbial attack, they are recalcitrant organic compounds. High suspended solids, acidity, heat, color and many other substances largely contribute to the pollution of textile wastewater. Process of color removal from textile wastewater and dyestuff manufacturing industry's wastewater is a difficult task. Several impurities discharged with untreated wastewater leads to change in dissolved oxygen, biological oxygen demand, chemical oxygen demand and color etc. when accumulated in natural or artificial water ecosystem (Saratale et al. 2013).

These impurities are not only the source of mortality for living organisms but also results in sub lethal stress and have profound effect on growth rate, reproductive success and their ability to compete with other species in the ecosystem. Therefore, their removal from textile wastewater is vital before discharge into the ecosystem water bodies.

8.3 Characteristics of Wastewater from Textile Industry

With the expanded need of textile products, the textile industry and its wastewater have been expanding relatively, making it one of the significant wellsprings of serious pollution issues around the world. The characteristics of wastewater from textile industries are highly variable, depending on the type of dye, type of fabric and the concentration of the added agents. These effluents are complexes of many constituents, including a broad category of dyes, natural polluting influences extricated from the fibers and different products, for example, acids, alkalis, salts and heavy metals (Ashfaq and Khatoon 2014). The wastewater discharged from textile industry is immensely colored having high biological oxygen demand (BOD), chemical oxygen demand (COD), high conductivity and alkaline nature (Singh et al. 2017a). The textile coloring industry utilizes vast volume of water and generates huge quantities of wastewater from various steps in the dyeing and finishing processes (Babu et al. 2007). A large portion of wastewater produced by textile industries is during the wet processing stages which include sizing, desizing, scouring, bleaching, mercerization, dyeing, printing, finishing and ultimately washing (EPA 1997).

- **Sizing:** It is the first preparative step, in which sizing agents are added which provide strength to the fibres and limit breakage. The sizing agents utilized in this step is starch, polyvinyl alcohol (PVA) and carboxymethyl cellulose.
- **Desizing:** In this approach, the sizing materials are removed from the grey fabric prior to weaving. This step is necessary because the presence of sizing agents on the fabric hinders the penetration of other chemicals in the subsequent stages.

- **Scouring:** This procedure is utilized to remove impurities, for example, waxes, natural oils, surfactants and fatty acids from the fibres by using an alkali solution.
- **Bleaching:** In this step unwanted color from the fibres is removed with the help of chemicals such as hydrogen peroxide and sodium hypochlorite.
- **Mercerising:** It is a continuous chemical procedure which is utilized to enhance dye intake capacity of the fabric, lustre, tensile strength and fibre appearance. This process is accomplished by concentrated alkaline solution.
- **Dyeing:** The main purpose of this process is adding dyestuff molecules (color) to the textile fibres. This procedure typically requires extensive volumes of water in the dye bath as well as during the rinsing step.
- **Printing:** This process produces colored patterns on the fabric by using print containing dyestuff, pigments and other auxiliary chemicals.
- **Finishing:** This step includes the final operations necessary for making the textile presentable and attractive such as drying, providing dimensional stability, calendaring, softening etc.

During each step diverse kind of chemicals are utilized, for example, strong acids, strong alkalis, inorganic chlorinated compounds, hypochlorite of sodium, organic compound such as dyestuff, bleaching agent, finishing chemicals, starch, thickening agent, surface active chemicals, wetting and dispersing agents and salts of metals. Different dyes (mostly azo dyes) are utilized during coloring stage for shading purpose and multicolor are utilized to enhance excellence of products. Depending on the coloring procedure of textile, various chemicals like metals, salts, surfactants, organic processing assistants, sulfide and formaldehyde, might be added to enhance the adsorption of dye onto the fibres (Ashfaq and Khatoon 2014). Because of the nature of different chemical processing of textiles, huge amount of wastewater consisting of diverse potential pollutants are released from cotton processing operations (Table 8.1).

Table 8.1 Process involved in textile processing and the main pollutants from each steps

Textile process	Main pollutants	Textile effluent characteristics
Desizing	Sizing agents, enzymes, starch, waxes, ammonia	High BOD, high TS, neutral pH
Scouring	Residues of disinfectants and insecticides; sodium hydroxide, surfactants, detergents, fats, waxes, pectin, oils, sizes, spent solvents, enzymes	High BOD, high TS, high alkalinity, high temperature
Bleaching	H_2O_2, adsorbable organic halogens, sodium silicate or organic stabilizer, high pH	High BOD, high TS, alkaline wastewater
Mercerising	High pH, NaOH and other salts	
Dyeing	Dyes, metals, salts, surfactants, organic processing assistants, sulfide, acidity/alkalinity, formaldehyde	Wasted dyes, high BOD, COD, solids, neutral to alkaline wastewater
Printing	Urea, solvents, color, metals	
Finishing	Resins, waxes, chlorinated compounds, acetate, stearate, spent solvents, softeners	

The wastewater generated during textile wet processing stages are marked by high variations in various parameters such as COD, BOD, TS, TDS, pH, color and water usage. Much of the times BOD/COD ratio of the textile wastewater is around 0.25 that infers that the wastewater having huge measures of organic matter which is non-biodegradable. The composition of textile wastewater will rely upon various types of organic-based compounds, chemicals and variety of dyes utilized in the dry and wet-processing steps of textile industry (Dos Santos et al. 2006). The wastewater released by textile industries is highly colored having huge quantity of various types of dyes mainly azo dyes. These dyes are important sources of environmental pollution pose hazardous effect on aquatic life because of its strong color, high COD, BOD and low biodegradability. Inspite of the dyes, textile effluent additionally contains variable pH and ionic strength, and high salts concentration too.

8.4 Conventional Methods of Treatment of Wastewater from Textile Industry

Textile industries consume huge amount of water and chemicals for wet processing of textiles. Number of coloring agents such as dyes, tannins, lignin and inorganic pigments etc. are used to impart color in textile fibers. Among the textile wastewater various types of coloring agents are present especially dye wastes are predominant. Massive amount of complex compounds with high concentrations are present in the textile wastewater. Nigam et al. (2000) revealed that very low concentrations of dyes in wastewater are highly visible and undesirable. The release of unprocessed wastewater from textile industry is the primary and the most polluting phenomenon of the globe. The conventional methods used to treat the wastewater are physico-chemical and biological methods. The physico-chemical methods include coagulation, flocculation and ozonation etc. whereas biological methods are used for the removal of nitrogen, phosphorous, organics and metal traces. In the last few decades, many techniques or methods have been developed which offers economic and competent means to treat the textile wastewater. The existing literature proves that large number of conventional methods including physico-chemical, biological processes and some new emerging techniques like microbial fuel cells, genetic engineering, biofilms, nanotechnology etc are effective in decolorization of textile wastewater. Robinson et al. (2001) suggested that when two or three methods have to be combined then maximum color removal achieved.

There are various types of physico-chemical methods utilized in the treatment of textile wastewater.

8.4.1 Adsorption

Out of several physico-chemical methods, adsorption is believed as one of the most successful method applied in textile wastewater treatment. Adsorption techniques have gained attention recently due to their great efficiency in the removal of pollutants. It produces a high quality product, and is a process which is economically feasible. In this method, porous material or filter are used to adsorb and remove the pollutants present in wastewater. Activated carbon, kaolin and silicon polymers are commonly used adsorbents having selective adsorption capacity for dyes but activated carbon is gained preference over other popular adsorbents.

The activated carbon has specific characteristic to adsorb dyes, it can efficiently remove the water soluble dyes in wastewater, such as reactive dyes, basic dyes and azo dyes, but on the other hand it can't absorb the suspended solids and insoluble dyes. Many factors such as temperature, pH, dye-sorbent interaction, sorbent surface area, particle size and contact time have largely influence the adsorption process (Kumar et al. 1998). Amino nitrogen based adsorbent like chitin possesses significant amount of adsorption capacity for acid dyes.

8.4.2 Membrane Separation Process

This method is basically based on separation of certain substances present in wastewater by the use of microporous membrane with selective permeability. Presently reverse osmosis, nanofiltration, ultrafiltration and microfiltration are the membrane pressure based separation processes which are used for treatment of dyeing wastewater. Reverse osmosis offers decolorization and removal of all mineral salts, hydrolyzed reactive dyes, and chemical compounds present in dye wastewater in a single step. Nanofiltration, another membrane based separation process used to treat colored wastewater having several nanometers aperture with 80–1000 Da molecular weights of retention capacity. Recently combination of nanofiltration and adsorption exploited for the treatment of dye wastewater in which adsorption step utilized before nanofiltration to increases the process output. The nanofiltration mediated treatment of dyeing wastewater, treatment of solutions with high concentration and complex nature is proved to be very efficient in recent days (Babu et al. 2007).

8.4.3 Ion Exchange

Ion exchange method is not extensively utilized for treatment of textile wastewater as it cannot apply to remove a wide range of dyes (Slokar and Le Marechal 1997). In this method ion exchange resin is used and colored wastewater allows passing over it until the available exchange sites are saturated. This method offers removal of both anionic and cationic dyes from wastewater with some advantages such as no loss of adsorbent, recovery of solvent after use and the removal of soluble dyes. The high operation cost of this method limits its application for the treatment of textile wastewater.

8.4.4 Fentons Reagent

Fentons reagent is a chemical method suitable for the treatment of wastewater which are resistant to biological treatment or toxic to live biomass (Slokar and Le Marechal 1997). It is based on the sorption or bonding process for removal of dissolved dyes from wastewater and also has potential in decolorizing both soluble and insoluble textile dyes. Usually this method is used as pre treatment at higher temperature than ambient however, in large scale treatment plant ambient temperature is use with excess of iron as well as hydrogen peroxide. Hydrogen peroxide is strong oxidizing agent and activated to form hydroxyl radicals which are potent decolorizer of wide range of dyes present in textile wastewater.

8.4.5 Ozonation

Ozone is known to be very good oxidizing agent because it posses high instability (oxidation potential, 2.07) compared to other oxidizing agent like chlorine (1.36) and H_2O_2 (1.78). It is very promising in decolorization of dyes as it can easily reduce the double bond present in the several textile dyes. This method oxidizes a significant portion of COD by inhibiting or destroying the foaming properties of surfactants and useful for the treatment of wastewater containing toxic and high fraction of non-biodegradable components.

8.4.6 Photochemical

This method is used to degrade dye molecules by UV treatment in the presence of water. Hydroxyl radicals which are generated in high concentration are sole source of color removal. H_2O_2 is activated by the use of UV light to generate hydroxyl radical for the efficient removal of dyes. In this method other factors such as intensity of the UV radiation, pH, dye structure and the dye bath composition are largely contribute in treatment process. Some additional by-products like organic aldehydes, metals, halides, inorganic acids and organic acids are also produced during treatment of textile wastewater.

There are advantages of using photochemical treatment over other available methods that it offers no sludge production and foul odors during treatment of wastewater.

8.4.7 Cucurbituril

It is a cyclic polymer of glycoluril and formaldehyde. Cucurbituril so named due to its structure which is in shaped like a pumpkin, and urea (uril) monomer is its important integral part. It has extraordinary sorption capacity to remove various types of textile dyes. The polymer has potential to remove almost all the dye classes such as reactive, acid, basic and disperse etc to achieve complete decolorization.

8.5 Biological Treatment of Wastewater from Textile Industry

The wastewater released from textile industries are complexes of many constituents. The major pollutant of textile wastewater is dyes especially azo dyes. Azo dyes are complex aromatic compounds with one or more azo (–N=N–) groups. These dyes are recalcitrant in nature and not degraded easily (Singh et al. 2015b). Therefore, removal of these dyes is essential before their release into the ecological systems. The removal of dyes from textile wastewater is constantly associated with the decolorization treatment utilized for textile wastewater. As dyes are intended to be chemically stable and durable colorants, they are generally not degraded easily and effectively. The processes based on biological systems have immense ability to degrade the textile dyes and resolve the issue of superfluous pollutants and high BOD/COD of the textile industries effluents. Different taxonomic category of microorganisms (bacteria, fungi, algae) and plants have the potential to remove dyes from textile wastewater (Fig. 8.2). Moreover, treatment of textile wastewater with biological system is environment friendly and inexpensive as contrast with other treatment processes.

8.5.1 Treatment of Wastewater from Textile Industry by Using Bacteria

Different trophic categories of bacteria are often used for removal of dyes present in textile wastewater. These bacteria are easily cultivated, propagate rapidly and suited fine for decolorization, degradation and mineralization of textile dyes under suitable

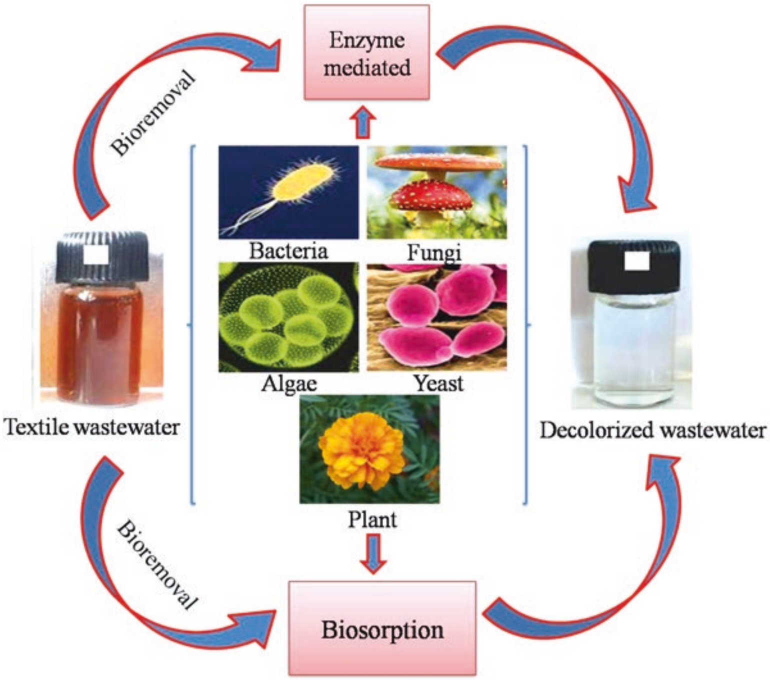

Fig. 8.2 Biological treatment of wastewater from textile industry

conditions (Singh and Singh 2017; Singh et al. 2015a). The process of removal of dye by bacterial system might be anaerobic, aerobic or include a combination of both anaerobic and aerobic conditions. However, physiology of bacteria propagated in aerobic and anaerobic conditions is significantly different (Stolz 2001).

8.5.1.1 Under Anaerobic Conditions

Under anaerobic conditions, the bacterial removal of azo dyes from textile effluent is simple, non-specific and more viable process. It involves the reduction of azo linkage in the dye molecule by a variety of cytoplasmic azoreductases. These azoreductases are soluble and having low-substrate specificity. The reductive cleavage of azo linkage produces colorless aromatic amines which are generally impervious to anaerobic mineralization and might be hazardous or mutagenic to living beings (Saratale et al. 2011). Removal of dyes under anaerobic conditions necessitate complex organic carbon or energy source. The rate of dye removal is reliant on the supplemented carbon source and in addition the structure of dye (Bromley-Challenor et al. 2000). Extensive studies have been accomplished utilizing different species of bacteria like *Citrobacter* sp., *Pseudomonas putida*, *Clostridium bifermentans*, *Pseudomonas luteola*, *Staphylococcus hominis* for removal of azo dye under anoxic/anaerobic condition (Singh et al. 2017b). Inspite of the fact that large numbers of these bacteria were capable to propagate aerobically but removal of dyes was accomplished just under anaerobic conditions. Different bacterial species such as species of *Bacillus*, *Pseudomonas*, *Micrococcus, Proteus, Aeromonas* and purple non-sulfur photosynthetic bacteria were observed to be efficient in the removal of a number of azo dyes under anaerobic condition. In addition, various studies have been accounted for the decolorization of azo dyes mediated by bacterial culture under anoxic/anaerobic condition (Table 8.2).

Table 8.2 Bacterial species/strains used for removal of azo dyes present in textile wastewater under anaerobic conditions

Name of strain	Decolorization process, conditions [pH, temp. (°C), time (h)]	Initial concentration, name of dye and % decolorization	Type of enzymes involved	References
Acinetobacter sp. SRL8	Microaerophilic, 7.0, 30	Disperse Orange SRL, 90%	–	Zhiqiang et al. (2015)
Bacillus cereus	Degradation under static incubation, 6.0–7.5, 37 °C, 72 h	200 ppm, Reactive Red 195, 97%	–	Modi et al. (2010)
Bacillus pumilus HKG212	Anaerobic degradation, 8.0, 30 °C, 30 h	Remazol Navy Blue, >95%	–	Das et al. (2015)
Bacillus sp., *Lysinibacillus* sp.	Degradation under static incubation, 7.2, 40 °C, 12 h	200 ppm, Acid Yellow 36, 100%	Azoreductase	Anjaneya et al. (2011)
Klebsiella oxytoca	Anaerobic degradation, 7.0, 30 °C, 48 h	0.3 mM, Methyl Orange, 96.53%	–	Yu et al. (2012)
Pseudomonas aeruginosa	Static, 7.0, 30, 24 h	200 mg/l, Remazol Orange, 94%	Reductive	Sarayu and Sandhya (2010)
Pseudomonas entomophila BS1	Static, 5–9, 37 °C, 120 h	Reactive Black 5, 93%	Azoreductase	Khan and Malik (2016)
Pseudomonas sp.	7.0, 35 °C, 24 h	Reactive Black 5, 83%	–	Mohamed (2016)
Pseudomonas sp.	Static, 7.0, 35 °C, 70 h	200 mg/l, Reactive Blue 13, 83.2%	–	Lin et al. (2010)
Staphylococcus aureus	Degradation under static conditions, 37 °C, 48 h	6 µg/ml, Orange II, 76%; Sudan III, 97%	Azoreductase	Pan et al. (2011)
Staphylococcus hominis RMLRT03	Static, 7.0, 35 °C, 60 h	100 mg/l, Acid Orange, 94%	–	Singh et al. (2014)

8.5.1.2 Under Aerobic Conditions

The dyes present in textile wastewater as a major pollutant are not readily metabolized under aerobic environment because reduction of azo linkage is generally hindered in the presence of oxygen (Ola et al. 2010). However, some bacteria have ability to metabolize azo dyes by reductive mechanisms under aerobic condition. These bacteria are generally specific towards their substrate and produce an oxygen-insensitive azoreductase which exhibit great specificity towards the structure of dyes and utilizes NADH as cofactors for the activity. The oxygen-insensitive azoreductases reductively cleave the azo linkage of specific azo compound and produce aromatic amines under aerobic condition (Stolz 2001). Different bacterial species and their strains have been reported for removal of azo dyes under aerobic condition (Table 8.3). A large number of these species remove the dyes (azo compounds) in aerobic condition only in the presence of additional carbon sources as they cannot use dye as the substrate for their growth and energy (Padmavathy et al. 2003). A small number of bacteria are capable to grow on azo compounds by utilizing the azo compounds as their sole carbon source. These bacteria catalyze the reductive cleavage of azo (–N=N–) bonds and use the resulting amines for their growth as carbon and energy source. The bacterial strains *Xenophilus azovorans* KF 46 and

Table 8.3 Bacterial species/strains used for removal of azo dyes present in textile wastewater under aerobic conditions

Name of strain	Decolorization process, conditions [pH, temp. (°C), time (h)]	Initial concentration, name of dye and % decolorization	References
Bacillus cereus	Aerobic degradation, 7.0, 35 °C, 5 days	Cibacron Black PSG, 67%; Cibacron Red P4B, 81%	Ola et al. (2010)
Bacillus subtilis	Shaking, 7.0, 37 °C, 120 h	100 mg/l, Reactive Red M8B, 60%	Arulazhagan (2016)
Geobacillus stearothermophilus	Aerobic degradation; 7.0, 50 °C, 24 h	0.050 mM, Orange II, 98%	Evangelista-Barreto et al. (2009)
Listeria sp.	Aerobic degradation, 37 °C, 48 h	50 ppm each, Black B, 69%; Black HFGR, 74%; Red B5, 70%	Kuberan et al. (2011)
Micrococcus sp.	Aerobic degradation, 6.0, 35 °C, 48 h	100 ppm, Orange MR, 93.18%	Rajee and Patterson (2011)
Micrococcus strain R3	Aerobic degradation, 7.0, 37 °C, 6 h	Methyl Red, 98.4%	Olukanni et al. (2009)
Sphingomonas paucimobilis	Aerobic degradation, 9.0, 30 °C, 10 h	850 ppm, Methyl Red, 98%	Ayed et al. (2011)
Staphylococcus arlettae	Aerobic degradation, 30 °C	100 ppm each, Reactive Yellow 107, 99%; Reactive Black 5, 99%; Reactive Red 98, 98%; Direct Blue 71, 96%	Franciscon et al. (2009)

Pigmentiphaga kullae K24 can utilize the Carboxy-Orange I and Carboxy-Orange II dye, respectively for their growth under aerobic condition (Kulla et al. 1983). However, these bacterial strains could not utilize the structurally resembling sulfonated dyes like Acid Orange 20 (Orange I) and Acid Orange 7 (AO7).

8.5.1.3 Using Bacterial Consortium/Mixed Cultures

The removal of dye from textile wastewater by bacteria is proficient and quick, yet individual bacterial strains more often cannot completely mineralize the azo dyes (Joshi et al. 2008). Moreover, these bacteria are generally specific towards a sort of textile dye, and because of the chemical unpredictability of textile wastewater, it is important to elaborate more effective microbial dye removal process. Subsequently, wastewater treatment systems containing mixed microbial populations/bacterial consortia accomplish a more advanced level of biodegradation and mineralization due to the synergistic or co-metabolic action of the microbial groups (Khehra et al. 2005). Several researchers have used the mixed cultures and bacterial consortia for removal of textile azo dyes (Table 8.4). The uses of mixed cultures/bacterial

Table 8.4 Bacterial consortium/mixed cultures used for removal of azo dyes present in textile wastewater

Bacterial consortium/mixed cultures	Decolorization process, condition [pH, temp. (°C), agitation, time (h)]	Name of dye, initial concentration and % decolorization	Type of enzymes involved	References
Bacterial consortium-GR (*Proteus vulgaris* and *Miccrococcus glutamicus*)	Static, 8.0, 37 °C, 24 h	50 mg/l each, Green HE4BD, mixture of 6 reactive dyes, 100%	Oxidative and reductive	Saratale et al. (2010)
Bjerkandera sp. and microorganisms from wood shavings	Anaerobic/aerobic degradation	Reactive Black 5, Reactive Red 2, 200 ppm, 90%	–	Forss and Welander (2011)
Citrobacter freundii, *Enterococcus casseliflavus*, *Enterobacter cloacae*	Microaerophilic, 7.0, 45 °C, 30 min; aerobic, 7.0, 37 °C, 48 h	Amaranth, 100 ppm, 100%	–	Chan et al. (2012)
Enterococcus casseliflavus, *Enterobacter cloacae*	Microaerophilic, 7.0, 45 °C, 60 min; aerobic, 7.0, 37 °C, 5 days	Orange II, 200 ppm, 100%	–	Chan et al. (2011)
Providencia sp., *Pseudomonas aeuroginosa*	Degradation under static incubation, 7.0	Red HE3B, Remazol Black 5B, Red HE7B, 50 ppm, 100%	Lac, Veratryl alcohol oxidase, NADH-DCIP reductase, azo reductase	Phugare et al. (2011)
Pseudomonas, Arthrobacter and *Rhizobium*	Aerobic degradation	Acid Orange 7, 200 ppm, 100%	–	Ruiz-Arias et al. (2010)

consortia for decolorization of dye have extensive preferences over the utilization of pure single bacterial cultures (Saratale et al. 2010). A noteworthy benefit of consortia over the utilization of pure/individual bacterial strains in the removal of azo dyes is that, the diverse bacterial strains in consortia may attack at various positions of the dye molecule or can utilize the metabolic intermediates produced by the co-existing bacterial strains for assist the decomposition, and in some cases accomplishing the mineralization of azo dyes (Jadhav et al. 2010).

8.5.1.4 Mechanism of Removal of Azo Dyes by Bacteria

The removal of azo dyes by the bacterial system can take place through two mechanisms: biosorption and enzymatic degradation.

8.5.1.4.1 Biosorption

Biosorption procedures have picked up an extensive significance because of their effectiveness in the elimination of pollutants (dyes), found to be more stable for conventional methods (Aksu 2005). Biosorption is the straightforward process of color removal by entire bacterial cells via adsorption of the dye molecule onto the bacterial biomass by means of different functional groups of heteropolysaccharide and lipid constituents of the cell wall. Removal of dye based on biosorption process includes the interaction of dye to a solid organic or inorganic matrix. The interaction of dye to the matrix depends on matrix composition and dye structure. Different sorts of interactions, like electrostatic, ionic exchange, Van der Waals forces, complexation or chelation involve in the interaction of dye to the matrix.

The remediation of dye by biosorption is impacted by different determinant, for example, surface area of sorbent, particle size, pH, temperature, contact time, presence of salts, surfactants and metals (Robinson et al. 2001). It must be highlighted that the sorption procedures only change the phase of pollutants from one phase to another and subsequently generate sludge which need to be safe disposal or recovered by some different procedure. The bacterial species such as *Pseudomonas luteola* and *Aeromonas* sp. are capable to remove the Reactive Blue 5, Reactive Red 22, Reactive Violet 2, Reactive Yellow 2 dyes by biosorption (Hu 1994).

8.5.1.4.2 Enzymatic Mechanism

The initial step in bacterial removal of azo dyes is reductive cleavage of azo linkage (chromophore) with the help of soluble cytoplasmic azoreductases. This azoreductase mediated cleavage involves the sequential transfer of four electrons to the azo bond (–N=N–) of dye in the presence of reducing equivalent (NADH) in two

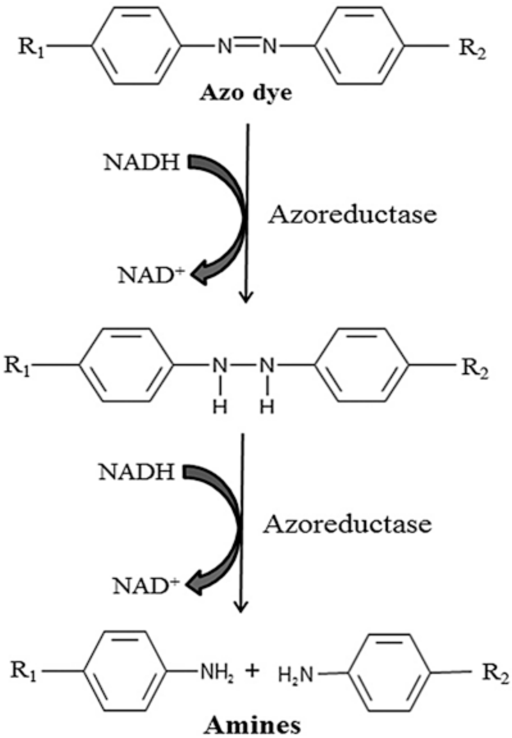

Fig. 8.3 Decolorization of azo dye by azoreductase

successive steps. In each step, two electrons are transferred to the azo bond of dye resulting in the cleavage of azo linkage via a Hydrazo intermediate. This reaction leads to the formation of colorless aromatic amines which may be additionally degraded to simpler or non toxic form under aerobic conditions (Pandey et al. 2007) (Fig. 8.3).

As majority of azo dyes are high molecular weight compounds having sulfonate substituent groups, they are improbable to move across the cell membranes. Thus, reduction of these sulfonated azo dyes occurs through a mechanism that is not reliant on their intracellular uptake (Russ et al. 2000). In this mechanism a link is established by means of redox mediator between intracellular electron transport system of bacteria and the extracellular azo dye (high molecular weight compounds) (Myers and Myers 1992) (Fig. 8.4). The redox mediator compounds having low molecular weight act as electron shuttles between the extracellular azo dye and azoreductase enzyme which is present in the outer membrane of the bacterial cell (Gingell and Walker 1971).

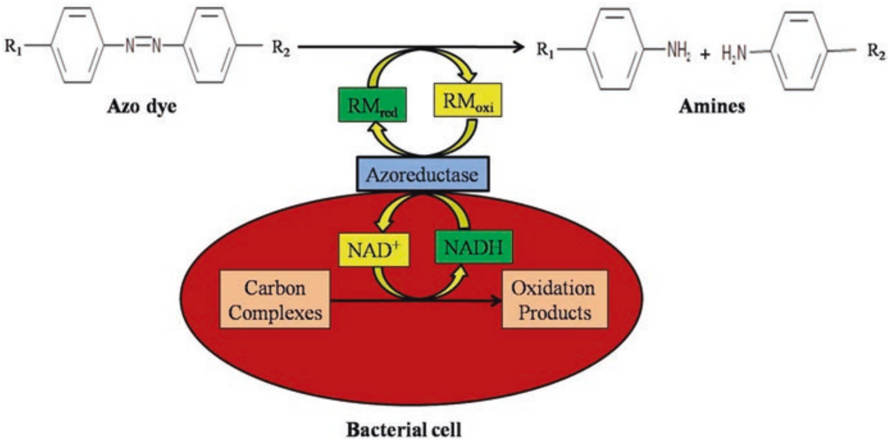

Fig. 8.4 Mechanism of the redox mediator dependent reduction of azo dyes by bacteria

8.5.1.5 Removal of Triphenylmethane and Anthraquinone Dyes by Bacteria

Triphenylmethane and anthraquinone based dyes are the groups of dyes which are usually utilized in textile industries after the azo dyes (Singh et al. 2017a). Triphenylmethane dyes are synthetic dyes with triphenylmethane $(C_6H_5)_3CH$ as their backbones. On the other hand, anthraquinone dyes are characterized by their chromophore group (=C=O), forming an anthraquinone complex. Triphenylmethane and anthraquinone-based dyes are more resistant to degradation because of their synthetic origins and complex aromatic structures. Removal of these dyes from textile wastewater may take place either by biosorption or biodegradation. Biodegradation of these dyes may involve enzymes such as laccase, lignin peroxidase (LiP), tyrosinase, manganese peroxidase (MnP) and DCIP reductase. These enzymes help in removal of triphenylmethane and anthraquinone dyes by depolymerisation, demethoxylation, decarboxylation, hydroxylation and aromatic ring opening reactions (Singh et al. 2015a). Many bacterial species have been reported for the degradation of triphenylmethane and anthraquinone dyes (Table 8.5).

8.5.2 Treatment of Wastewater from Textile Industry by Using Fungi

Among industrial wastewater, textile wastewater requires vigorous treatment processes due to their complex nature. Number of microorganisms has been reported for efficient dye decolorization and degradation from wastewater; these microorganisms include bacteria, algae or fungi. The processes they employ are aerobic, anaerobic or combination of both. Treatment process is principally relying on the

Table 8.5 Bacterial species/strains used for removal of triphenylmethane and anthraquinone dyes present in textile wastewater

Name of strain	Decolorization process, conditions [pH, temp. (°C), time (h)]	Initial concentration, name of dye and % decolorization	Type of enzymes involved	References
Triphenylmethane dyes				
Bacillus cereus, DC11	Anaerobic, 7.0, 20–45 °C, 4 h	55 μM, Malachite Green, 96%	–	Deng et al. (2008)
Bacillus thuringiensis	7.0, 30 °C, 6 h	40 mg/l, Malachite Green, 84.67%	Laccase	Olukanni et al. (2013)
Consortium of Agrobacterium radiobacter, Bacillus sp., *Sphingomonas paucimobilis and Aeromonas hydrophila*	Shaking, alkaline pH, 30 °C 2 h	50 mg/l, Malachite Green and Crystal violet, 91% and 99%	–	Cheriaa et al. (2012)
Kocuria rosea MTCC 1532	static, 6.8–6.9, 30 °C, 5 h	100 mg/l, Malachite Green, 100%	Malachite green reductase and DCIP reductase	Parshetti et al. (2006)
Anthraquinone dyes				
Bacillus cereus	Shaking, 7.0, 27 °C, 72 h	200 mg/l, Reactive Blue 19, 95%	–	Giwa et al. (2012)
Bacillus cereus, DC11	Anaerobic, 7.0, 20–45 °C, 6 h	100 μM, Acid Blue 25, 95%	–	Deng et al. (2008)
Pseudomonas desmolyticum NCIM 2112 and *Galactomyces geotrichum* MTCC 1360	Aerobic, 9.0, 25 °C, 23 days	100 mg/l Vat Red 10 (Novatic red 3B), 55%	–	Gurav et al. (2011)

structure of dye and nature of microorganisms (Keharia and Madamvar 2003). Application of biological organisms leads to partial or complete mineralization of wastewater dyes to CO_2 and H_2O (Mohan et al. 2002). Fungi has been considered as an important living organism for the treatment of textile wastewater and in degradation of dyes. Several species of fungi are known which can biosorb or decolorize various dyes. These living microorganisms encodes enzymes such as laccase, manganese peroxidase (MnP) and lignin peroxidase (LiP) which are nonspecific in nature and involved in biodegradation of dyes. The extracellular nature of these enzymes proved to be beneficial in tolerating high concentrations of the harmful dyes. The dead cell biomass of fungi exhibit biosorption process which rely on several physico-chemical interactions such as adsorption, deposition and ion exchange.

8.5.2.1 Pure Cultures of *Phanerochaete chrysosporium*

The pure culture of *P. chrysosporium* is most frequently used for the removal of textile dyes because of their capacity to produce high concentration of enzyme. The dye removal extent is largely based on the dye-microorganism compatibility and composition of medium. It was observed that many extracellular enzymes such as LiP and MnP and laccase may facilitate the process of decolorization. Enayatizamir et al. (2011) observed degradation of dye Azo Black Reactive 5 when treated with *P. chrysosporium* and achieved 92% decolorization rate after 3 days. It is also a well known fact that to achieve maximum dye decolorization careful selection of fungal strain and appropriate culture condition is required. Chagas and Durrant (2001) identified the role of enzymes Mn-peroxidase, h-glucosidase and laccase produced by *P. chrysosporium* and *Pleurotus sajor-caju* when tested and compared biodegradation of dyes Amaranth, Tartrazine, New Coccine and Orange G. Couto et al. (2000) proved that on addition of activators such as tween 80, manganese (IV) oxide, veratryl alcohol the production rate of lignolytic enzymes by *P. chrysosporium* is enhance and increased Poly R-478 dye decolorization achieved.

8.5.2.2 Pure Cultures of Other Important Fungi

Several other fungi have been employed for the treatment of textile wastewater containing diverse group of dyes. Many genera of fungi have been used either in living or inactivated structure. Yesiladali et al. (2006) stated that *Trichophyton rubrum* LSK-27 is a promising isolate for dye removal processes and can be a potent culture for treatment of textile wastewater under aerobic conditions for non toxic degradation of dye molecule. Wesenberg et al. (2002) reported the decolorization of wastewater from a textile dye producing industry by the agaric white-rot fungus *Clitocybula dusenii* and observed that on optimal conditions up to 87% of the dyes of a fourfold diluted wastewater were decolorized after 20 days of incubation. In last decades decolorization of dyes such as Magenta, Pararosaniline, Malachite Green, Brilliant Green and Crystal Violet by *Kurthia* sp. has been extensively studied. *Ganoderma lucidum* was used for treatment of textile wastewater in a batch reactor under optimized conditions, a maximum decolorization of 81.40% and a COD reduction of 90.30% were achieved.

The white rot fungi *Ganoderma* sp. En3, *Trametes versicolor* and *Irpex lacteus* was highly effective in treatment of textile wastewater and remove more than 90%, 60% and 93% color, respectively. Several pure and mixed fungal cultures are given in Table 8.6 which shows potential for treatment of textile wastewater. Amaral et al. (2004) studied the decolorization of wastewater from a textile industry by *T. versicolor* and reported that for a sevenfold diluted wastewater a decolorization percentage reached to 40% which was much lower than that found for a synthetic wastewater having same color (300 mg/l) whereas a higher decolorization percentage (92%)

Table 8.6 Fungal mediated decolorization of raw colored wastewater of textile industry

Fungus	Wastewater parameters	References
Aspergillus lentulus	COD: 132 mg/l BOD: 58 mg/l pH: 8.11	Kaushik and Malik (2010)
Aspergillus niger	COD: 6410 mg/l BOD: 5200 mg/l pH: 10	Agarry and Ayobami (2011)
Bjerkandera adusta (Willdenow) P. Karsten MUT 3060	COD: 145 mg/l pH: 8.1	Anastasi et al. (2011)
Curvularia lunata URM6179 and *Phanerochaete Chrysosporium* URM 6181	BOD: >167 mg/l COD: 354 mg/l	Miranda et al. (2013)
Ganoderma sp. En3	COD: 24,813.5 mg/l, TOC: 8445.3 mg/l, pH: 9.2	Zhuo et al. (2011)
Mixed culture consisting *Pleurotus ostreatus* IBL-02 and *Coriolus versicolor* IBL-04	BOD: >200 mg/l COD: 82 mg/l	Asgher et al. (2012)
Penicillium ochrochloron MTCC 517	COD: 145 mg/l, BOD: 836 mg/l, pH: 8.5	Shedbalkar and Jadhav (2011)
Phanerochaete chrysosporium	COD: 1500–1600 mg/l BOD; 124 mg/l pH: 5	Sedighi et al. (2009)

was obtained with a 42-fold diluted wastewater (dye concentration 50 mg/l). Different fungal cultures have been used for treatment of number of different dyes from many classes successfully.

8.5.3 Treatment of Wastewater from Textile Industry by Using Algae

Algae are photosynthetic, minute organisms, which typically inhabit aquatic environments (pond, lake and sea etc.), soil and other appropriate area. Microalgae degrade and utilized dyes as a nitrogen source (Table 8.7), contribute their role to overcome eutrophication in the aquatic system (Ruiz et al. 2011) and also they are key scavenger of CO_2 which is a major global warming gas (Mata et al. 2011). Microalgae show tremendous scavenging potential towards heavy metals (Table 8.7). They are used in biofuel production and considered as promising source of renewable energy (Ferrell and Sarisky-Reed 2008). Recently, algae have been used in bioremediation and to cleanup wastewater due to their high efficiency in absorbing both inorganic and organic pollutants, including heavy metals, pesticides, toxic compounds, dissolved nutrients and even radioactive materials (Mata et al. 2011). Microalgae produce around 50% of the oxygen present in the atmosphere by the process of photosynthesis which vital for life on our planet. Microalgae are necessary for the life of ocean and lakes as they are placed bottom of food chain and contribute their role in the stability of aquatic ecosystem.

Table 8.7 Algal species involved in textile wastewater treatment

Algae	Substrate	References
Chlamydomonas sp., *Dunaliella* sp., *Nannochloropsis oculata* and *Tetraselmis terathele*	Heavy metals and organic compounds	AL-Rajhia et al. (2012)
Chlorella vulgaris	Organic and inorganic compound	El-Kassas and Mohamed (2014)
Chlorococcum vitiosum	Alkali metals, Na, K, Mg, and Ca	Chitra et al. (2013)
Desmodesmus sp.	Methylene Blue and Malachite Green	Al-Fawwaz and Abdullah (2016)
Lyngbya sp.	Acid red dye and heavy metals like Zn, Hg, Ni, Cd, Cr and Fe	Nandhini et al. (2014)
Nostoc, Eichhornia crassipes and Pistia stratiotes	Reduction of COD of textile effluents	Roy et al. (2010)
Oscillatoria limosa and *Nostoc commune*	NO_3^-, PO_4^{-3}, SO_4^{-2}, Cl^-	Azarpira et al. (2014)
Oscillatoria sp.	Blue and red dye	Brahmbhatt and Jasrai (2016)
Spirogyra sp.	Reactive Yellow 22 (Azo) dye	Mohan et al. (2002)
Spirogyra sp. and *Oscillatoria* sp.	Blue dye and Red dyes	Brahmbhatt and Jasrai (2015)
Spirulina and *Chlorella*	Heavy Metal Cu^{2+} and Cr^{2+}	Hadiyanto et al. (2014)

The treatment cost of textile wastewater is high because of their very high concentrations of total Nitrogen and Phosphorous and toxic metal (Gasperi et al. 2008). The textile wastewater is also rich in both organic and inorganic compounds and useful for algal biomass as a sustainable growth medium (Green et al. 1995). Microalgae grow and accumulate nutrient from wastewater by making them sustainable and suitable for low cost wastewater treatment (de-Bashan et al. 2010). The species such as *Chlorella vulgaris* accumulate higher lipid content (42%) when grown in wastewaters (Feng et al. 2011). It is beneficial to design the wastewater High Rate Algal Ponds (HRAPs) setup in the vicinity of textile industries to trap sustainable and renewable source of energy. Presently wastewater treatments HRAPs are the only environment friendly and economic system to produce biofuels (Park et al. 2011).

8.5.3.1 Methods and Mechanism of Algal Textile Wastewater Treatment

Microalgae are known to remove textile effluents by bioadsorption and biotransformation.

8.5.3.1.1 Bioadsorption

It is an energy independent process and no requirement of input of synthetic chemical. Operation cost of this method is very low as it is carried out effectively in situ at the contaminated site. Removal of dyes and metal ion from textile wastewater by using plant material as adsorbents is attractive feature of this prominent technology (Mohammad et al. 2012). High affinity between adsorbent and adsorbate species (toxic substances) plays a major role in this process. The process will be continues till the establishment of equilibrium between the solid bound adsorbate species and its reminants in the solution. Mango peel, tree barks, tea leaf powder, coconut bunch waste, banana peel, wheat husk etc. are the several sorbent which were already tested for their adsorption capacity (Nevine 2008).

8.5.3.1.2 Biotranformation (Biodegradation)

Chemical conversion of a substance into a desired product may be done with the aid of whole microbial cell, containing the necessary enzyme(s) or isolated enzyme. Enzymes and whole cell biocatalysts possess many useful properties, which determine preferential use of catalysts for organic synthesis. These catalysts have some characteristic features such as require mild reaction conditions, high chemo and stereo selectivity, usually performed in an aqueous environment but can also be efficient in solvent mixtures for example vinyl acetate, an organic solvents used for esterification by enzymes esterases and lipases (Schmid et al. 2001).

8.5.3.2 Factors Affecting the Algal Growth

(a) **Abiotic, physical and chemical:** light, nutrient concentration, O_2, CO_2, pH, salinity, toxic chemicals
(b) **Biotic factors:** pathogens like bacteria, fungi, viruses
(c) **Operational factors:** mixing, dilution rate, depth, addition of bicarbonate, harvesting frequency

8.5.3.3 Advantages of Algal Textile Wastewater Treatment

(a) Use of microalgae can sort out the problems of global warming by fixing large amount of CO_2 in the atmosphere. It was estimated that 1 kg of CO_2 is required for production of 1 kg algal biomass which is a better option to overcome the problem of global warming.
(b) It is superior in remediation processes as a wide range of dyes, heavy metals, toxic chemicals and other wastes can be treated with algae and they are non pathogenic in nature.
(c) Use of microalgae is environment friendly and not associated with secondary pollution problems.

(d) Recently microalgae are used as biofuel and considered as alternative to conventional fuel that is diminishing very fast.
(e) Microalgae have excellent heavy metal scavenging properties.
(f) Blue-green algae are the suitable organism which performs dual role of wastewater treatment and simultaneously biomass production.
(g) To decrease the space and land requirement in treatment of wastewater by microalgae a hyper concentrated algal culture known as 'activated algae' is utilized which removes nitrogen and phosphorous in less than 1 h.
(h) Microalgae remove N and P nutrients from wastewater in very short period of time as they utilized it for the synthesis of protein, phospholipid and nucleic acid.

Thus algal growth can keep the water clean and make natural waters more suitable for human consumption.

8.5.3.4 Limitation of Algal Textile Wastewater Treatment

(a) Fresh water algae normally start with a small population but by utilization of large amount of sunlight and required nutrients, they slowly develop in large population. They also produce scums and facilitate the removal of water color. When left untreated, these algae could suffocate aquatic flora and fauna.
(b) Lagoon systems want more land space than other treatment process.
(c) Cold climate have adverse effect so they need additional land or longer detention times in these areas.
(d) Odor produced during algal blooms or with anaerobic lagoons limits its use.
(e) Mosquitoes and other insects use unmanaged algal lagoons as site for breeding.
(f) They are as much efficient in removal of heavy metals from wastewater as plants.
(g) Sometimes additional treatment requires for wastewater from lagoons.

8.5.4 Treatment of Wastewater from Textile Industry by Using Plants

Phytoremediation is a green innovation that utilizes plant frameworks for remediation and rebuilding of the polluted destinations. Plants have inbuilt enzymatic apparatus equipped for removing the complex structures of pollutants and can be utilized for cleaning the polluted destinations. It is a naturally stable and maintainable recovery system for bringing contaminated locales into beneficial purpose however, is still in exploratory stage; hence it needs more consideration and logical overview (APHA 2005). Phytoremediation has been appeared to be cost competitive in different aquatic systems. This technique utilizes special plants known as hyperaccumulators to purify heavy metal contaminated sites (Table 8.8). In hyperaccumulation,

Table 8.8 List of some hyperaccumulators

Species	Family	Metal	References
Pityrogramma calomelanos	Pteridaceae	As	Francesconia et al. (2002)
Pteris vittata	Pteridaceae		Wang et al. (2002)
Brassica juncea	Brassicaceae	Au	Kulkarni et al. (2013)
Thlaspi caerulescens and *Arabidopsis halleri*	Brassicaceae	Cd and Zn	Cosio et al. (2004)
Cyanotis longifolia	Commelinaceae	Co	Reeves (1979)
Haumaniastrum robertii	Lamiaceae		Lange et al. (2016)
Hibiscus rhodanthus	Malvaceae		Lange et al. (2016)
Dicoma niccolifera	Asteraceae	Cr	Baker and Brooks (1989)
Salsola kali	Amaranthaceae		Gardea-Torresday et al. (2005)
Sutera fodina	Scrophulariaceae		Brooks (1998)
Aeollanthus subacaulis	Lamiaceae	Cu	Reeves and Baker (2000)
Eragrostis racemosa	Poaceae		Malaisse and Gregoire (1978)
Haumaniastrum robertii	Brassicaceae		Baker and Brooks (1989)
Ipomea alpine	Convolvulaceae		Baker and Walkar (1990)
Pandiaka metallorum	Amaranthaceae		Malaisse et al. (1979)
Sorghum sudanense	Poaceae		Wei et al. (2008)
Pistia stratiotes	Araceae	Hg	Baker and brooks (1989)
Macademia neurophylla	Proteaceae	Mn	Baker and Walker (1990)
Allysum bertolonii	Brassicaceae	Ni	Barzanti et al. (2011)
Berkheya coddii	Asteraceae		Moradi et al. (2010)
Bornmuellera kiyakii	Brassicaceae		Reeves et al. (2009)
Geissois pruinosa	Cunoniaceae		Jaffre et al. (1979)
Pimelea leptospermoides	Thymelaeaceae		Kachenko et al. (2009)
Psychofria douarrei	Rubiaceae		Boyd et al. (1999)
Rinorea niccolifera	Violaceae		Fernando et al. (2014)
Sebertia acuminate	Sapotaceae		Garcia-Leston et al. (2007)
Thalaspi goeingense	Brassicaceae		Wenzel et al. (2003)
Agrostis tenuis	Poaceae	Pb	Barry and Clark (1978)
Arrhenatherum elatius	Poaceae		Deram et al. (2000)
Brassica juncea	Brassicaceae		Blaylock et al. (1997)
Pisum sativum	Fabaceae		Huang et al. (1997)
Thlaspi goesingense	Brassicaceae		Puschenreiter et al. (2003)
Thlaspi rotundifolium	Brassicaceae		Baker and Walker (1990)
Astragalus bisulcatus	Fabaceae	Se	Freeman et al. (2012)
Brassica juncea	Brassicaceae		Mounicou et al. (2006)
Lecythis ollaria	Lecythidaceae		Hammel et al. (1996)
Neptunia amplexicaulis	Fabaceae		Burnell (1981)
Stanleya pinnata	Brassicaceae		Freeman et al. (2012)
Arabidopsis halleri	Brassicaceae	Zn	Baumann (1885)
Potentilla griffithii	Rosaceae		Qiu et al. (2006)
Thlaspi brachypetalum	Brassicaceae		Reeves et al. (1983)
Thlaspi caerulescens	Brassicaceae		Banasova and Horak (2008)

heavy metal pollutants are absorbed by the roots of the plants and are concentrated in the plant tissues or decomposed to less harmful forms. Plants that can assimilate and tolerate high amounts of heavy metals are considered as potent candidates of phytoremediation. The importance of phytoremediation is the low capital costs, aesthetic advantages, reduction in leaching of pollutants and stabilization of soil. It includes principally fertilization and watering for keeping up plant development. In case of heavy metals remediation, extra operational expenses will likewise incorporate in harvesting, disposal of contaminated plant mass and repeating the plant development cycle.

Floating aquatic macrophytes are characterized as plants that buoy on the water surface with submerged roots. Many aquatic macrophytes are potent candidates of phytoremediation as they exhibit solid abilities to retain unnecessary heavy metals and accumulate them in plant tissues (Salt et al. 1995). Additionally, the rapid proliferation and direct contact of aquatic macrophytes with the polluted environment encourages the decontamination procedure and guarantees the sanitation of contaminated water bodies. The most widely recognized aquatic macrophytes being utilized in wastewater treatment are water hyacinth (*Eichhornia crassipes*), penny wort (*Centella asiatica*), water lettuce (*Pistia stratiotes*), and water ferns (*Azolla filiculoides*). *E. crassipes* is potent growers known to twofold their populace in 2 weeks. The plant has high degree of tolerance and high limit for the take-up of heavy metals including cadmium, chromium, cobalt, nickel, lead and mercury, which could make it reasonable for the biocleaning of textile wastewater. *E. crassipes* can remediate different toxic pollutants, for example, cyanide, which is ecologically valuable in territories that have experienced gold mining activities.

8.5.4.1 Properties of Hyperaccumulators

(a) The plant must have the capacity to tolerate abnormal amounts of the element in root and shoot cells. The hypertolerance property is the key which ensure the hyperaccumulation.
(b) In addition to tolerance, the hyperaccumulation properties should be stable. Further, the plant should have the capacity to accumulate several metals.
(c) The plant should be competent to translocate an element from roots to shoots at high rates. Normally, the concentrations of Zn, Cd or Ni in root are at least ten times higher than shoot; but in case of hyperaccumulators, the concentrations of metal in shoot can surpass the root levels.

(d) There must be a quick take-up rate for the element at levels which happen in soil arrangement along with fast growth of the plant and increased biomass production.
(e) The plant must have the ability to grow outside of their area of collection.
(f) The species should be of economic interest.
(g) The plant should be resistant to disease and pests.
(h) Unattractive to animals minimizing the risk of biomagnification.

8.5.4.2 Methods and Mechanism for Plant Textile Wastewater Treatment

Depending on the underlying procedures, relevance and contaminant type, phytoremediation can be done by various techniques and systems.

8.5.4.2.1 Phytoremediation to Treat Organic Contaminants

Phytotransformation (Phytodegradation)
Phytotransformation, is the breakdown of pollutants taken up by plants via metabolic process inside the plant, or the breakdown of pollutants encompassing the plant with the help of enzymes produced by the plants (Schnoor 1997). Complex organic contaminants are degraded into simpler or less toxic forms which are utilized by the plant tissues to enable the plant to become fast grower. Plants contain enzymes that catalyze and enhance the chemical reactions. Some enzymes degrade and change the ammunition wastes while others breakdown the chlorinated solvents and herbicides.

Phytostimulation (Rhizodegradation)
Phytostimulation is the removal of pollutants in the rhizosphere by microbial action that is increased by the nearness of plant roots. It is a much slower process as compare to phytotransformation. Sugars, alcohols and acids are the natural substances produced by the plant roots that give nourishment to soil microorganisms and the extra supplements increase their action. Certain microorganisms can digest fuels or organic solvents that are harmful to humans and breakdown those into innocuous products in a process known as biodegradation. Biodegradation is likewise supported by the way plants loosen the soil and transport water to the territory.

Phytovolatilisation
Phytovolatilisation is the process in which uptake and transpiration of a pollutant takes place by the plant resulting in release of the altered form of pollutant in the climate. Phytovolatilisation happens as growing trees and different plants take up water and the organic pollutants. Poplar trees at one specific investigation site have been appeared to volatilize more than 90% of the trichloroethanol (TCE) they take up (James et al. 2009).

8.5.4.2.2 Phytoremediation for Treatment of Metal Contaminants

Phytoaccumulation (Phytoextraction)
In the process of phytoaccumulation, the uptake of metals from soil takes place by plant roots into over the ground portions of plants. After that plants have been permitted to grow and after some time they are harvested for recycling of the metals through incineration or composting (Irshad et al. 2015). This procedure might be repeated as important to bring soil contaminant levels down as far as possible. In case of incineration, the ash must be dispose safely in a hazardous waste landfill; however, the volume of ash will be under 10% of the volume that would be created.

Rhizofiltration
Rhizofiltration is the adsorption or precipitation of contaminants onto the plant roots that are in solution encompassing the root zone. Rhizofiltration is like phytoextraction, yet the plants are utilized to clean up contaminated groundwater instead of soil. The plants to be utilized for cleanup are grown in greenhouses with their roots in water. As the roots become saturated with pollutants, they are harvested. For example, sunflowers were effectively utilized to remove radioactive pollutants from wastewater (Rahman et al. 2013).

Phytostabilisation
Phytostabilisation is the process in which certain plant species is used to immobilize the pollutants in the soil and groundwater via absorption and accumulation by roots inside the root zone. This method decreases the mobility of the pollutants and avoids their movement to the groundwater or air, and furthermore lessens the bioavailability for entry into the food chain. This method can be utilized to restore a vegetative cover at sites where characteristic vegetation is missing because of high contaminants in surface soils. Hyperaccumulators can be utilized to reestablish vegetation to the destinations, in this way diminishing the potential movement of pollutants through breeze and transport of uncovered surface soils as well as reduces the leaching of soil contamination to groundwater.

8.5.4.2.3 Phytoremediation for Hydraulic Control of Contaminants

Riparian Corridors
Riparian passageways (the bank of a river) or buffer strips are specific employments of phytoremediation that may likewise consolidate parts of phytodegradation, phytovolatilisation and rhizodegradation to control, intercept or remediate pollutants entering in a river or groundwater plume (Hill 1996). In a riparian corridor, plants might be applied along with the water stream, whereas buffer strips might be applied around the border of landfills. The uses of these frameworks prevent pollution from spreading into surface water and additionally groundwater.

Vegetative Cover

Vegetative cover/cap is a self-managing cap made out of soil and plants growing in or over waste in a landfill. This sort of cap is an alternative option to composite clay or plastic layer caps. Plants control erosion and limit drainage of water that could somehow permeate via the landfill and form polluted leachates. Moreover, a vegetative cap can be outlined, not exclusively to control erosion and drainage of water, yet additionally to improve the degradation of underlying materials in the landfill.

8.5.4.3 Advantages of Phytoremediation

(a) **Cost competitive:** cheaper than other remedial approaches.
(b) **Applicability:** applicable to moderately multi-contaminated sites of large extension.
(c) **Favorable public perception:** enhanced aesthetics, decreased noise and bad smell.
(d) **Greenhouse effect reduction:** CO_2 sequestration into biomass.
(e) **Removable energy production:** energy can be recovered from the controlled combustion of the harvested biomass.

8.5.4.4 Limitation of Phytoremediation

(a) **Root depth:** some efficient phytoextractors' roots are situated in depth.
(b) **Applicability:** For the most part, the utilization of phytoremediation is restricted to sites with low to medium pollutant concentrations, top soil contaminant localization, bioavailability of contaminants.
(c) **Treatment rate:** Relatively slow in comparison to bioremediation technologies.
(d) **Seasonal dependence:** Efficiency is strongly reduced during the winters.
(e) **Potential contamination of food chain**: Probability of entry of pollutants into the food chain via consumption of plant biomass by animals.

8.6 Factors Affecting the Treatment of Wastewater from Textile Industry

Ecosystems are active entity with unpredictable abiotic circumstances such as pH, salts, temperature and O_2 etc. Microorganisms are very sensitive towards dyes, high salinity, change in pH and heavy metals. The best suited microorganisms for biotreatment of textile wastewater are isolated from textile industry contaminated background, including soil, wastewater and sludge and further allow growing in adverse condition. Various researches have concluded that the operational parameters must be optimum for the success of biological treatment systems. Thus the effects of these parameters are vital for assessing the potential of a variety of microorganisms for bioremediation of xenobiotics. Maximum rate of dye decolorization are achieved when the various parameter like temperature, pH, aeration and redox potential of the reaction system must be optimized. The composition of textile wastewater varies greatly and may contain nutrients, organics, salts, sulfur derivatives and toxicants as well as the color.

The effect of each of the factors indicated above on the treatment process must be precisely examined prior to use of biological or other methods for the treatment of textile wastewater.

8.6.1 pH

The medium pH is an important parameter for the optimal physiological activity of microbial cultures and decolorization of textile wastewater. It plays a significant role for movement of nutrients through the cell membrane, affects the microbial cell growth and various biochemical, enzymatic processes. It was estimated that the suitable pH for color removal from wastewater is 6–10. Bacteria shows superior decolorization and biodegradation activity at neutral or basic pH while fungi and yeast at acidic or neutral pH. The decolorization potential of anaerobic and aerobic microorganisms is directly affected by the pH of the wastewater. Adaptation of biological organisms to varying pH improves the process of wastewater treatment.

8.6.2 Temperature

It is an important abiotic environmental factor and the remediation potential of microorganisms is largely influenced by the changes in temperature. An optimum temperature is needed for the growth and reproduction of the decolorizers (typically soil bacteria and fungi). Beyond the defined optimum temperature, the process of decolorization reduces due to slow growth and multiplication. The microbial cells countered temperature change by adaptation through biochemical or enzymatic means. Such changes in temperature lead to a rapid alteration of the activation energy in the microbial physiology (Chang and Kuo 2000). The extent of color removal increases with increasing initial temperature.

8.6.3 Dye Structure

Diverse groups of synthetic dyes are present such as acidic, reactive, azo, diazo, anthraquinone, basic, disperse and metal-complex dyes (Banat et al. 1996). These dyes differ in their chemical composition such as either they hold special functional groups or they are isomers. These differences notably influenced the decolorization potential of the microorganisms. Simplicity and molecular weight of dyes present in wastewater have direct correlation with decolorization mechanism. Dyes with simple structures and low molecular weights show faster decolorization, whereas the decolorization of complex and high molecular weight dyes is slow.

8.6.4 Dye Concentration

The decolorization of dye in wastewater largely depends on the initial dye concentration. Rate of color removal decreases step by step with rise in concentration of dye due to dye mediated toxic effect on microbial degrader or the masking the active sites of effectors enzymes by dye molecule with alternative structures (Sponza and Isik 2004). The dye concentration can affect the success of dye removal via combination of factors such as toxicity of dye, higher concentration of co-contaminants and capacity of enzyme to recognize their substrate at very low concentration in target wastewater.

8.6.5 Salts

The textile wastewater contains number of impurities such as salts or metal ions acids and alkalis etc. Wastewaters from dyeing plants and textile processing industries contain considerable amounts of salts in addition to azo dyes. Dyestuff industry wastewaters contain salt concentrations up to 15–20%. Thus, using microbial cultures capable of tolerating salt stress is preferable for treating such wastewaters. The capacity of *Shewanella putrefaciens* strain AS96 in removing four azo dyes with different structure at variable concentrations of NaCl was analyzed. The azo dyes Direct Red 81, Reactive Black 5, Acid Red 88 and Disperse Orange 3 decolorized upto 100% when NaCl concentration was 0–40 g/l. Time for decolorization increased with increase in NaCl concentration (60 g/l) and decolorization extent also decreased drastically (Khalid et al. 2008).

8.6.6 Agitation

Enormous literature is available which correlate the effect of agitation and static condition with microbial decolorization of synthetic dyes containing wastewater. Microorganisms accelerate decolorization under both shaking and static conditions. Higher rate of color removal is found under shaking condition due to better oxygen transfer and distribution of nutrients as compared to stationary cultures but exceptionally agitated cultures of *Pseudomonas* sp. SUK1 and some other cultures showed less decolorization than static conditions.

8.6.7 Nutrients

Nutrients also play a significant role in dye decolorization process. Suitable amount of nutrients have significant effect on the growth of microorganism and enhance the degradation of dyes in wastewaters. *Pseudomonas* sp. BSP-4 isolated from azo dye contaminated soil was capable to decolorize azo dye Black E by utilizing it as nitrogen source upto 300 ppm in 36 h (Sudhakar et al. 2002). Nutrients, such as nitrogen, carbon and sulfur etc. have noticeable effect on wastewater treatment.

8.7 Recycling of Wastewater from Textile Industry

Recycling has turned into a fundamental procedure in the treatment of wastewater and play a role in control the pollution. The significant wastes produced by textile industries are mainly fibers, beaming wastes, dyes and various chemicals. These procedures utilize around 200 l of water/kg of fiber and generate large volume of wastewater (Babu et al. 2007). Textile industry utilizes a number of processes during the production of textile, for example, washing, weaving, dyeing, printing, finishing, quality and process control and warehousing, in addition to garment making. These processes contribute the different type of pollutants in textile wastewater.

A recycled product is the materials which have been recovered or modified from wastes either from the manufacturing process or after usage. There are distinctive strategies for recycling of textile wastewater; physical (mechanical), biological, chemical and thermal recovery. Considering the variability of textile wastewater, various strategies of wastewater recycling must work in a coordinated manner so as to accomplish a notable impact on recycling.

8.7.1 Methods of Textile Wastewater Recycling

The mechanical or physical methods for treatment of wastewater include under primary treatment while use of biological methods for further treatment is part of secondary treatment. The advanced secondary treatment process involved in combined use of chemical and biological system for example disinfection of the water by injecting chlorine. The tertiary treatment is expensive, used to remove traces of chemicals and dissolved solids.

8.7.1.1 Physical Recovery

This is the first step in the recycling process of textile wastewater. In this process the raw waste is passed through the metallic bar screens for the separation of large stuffs like sticks and rags from the water. Water moves through bar screens and reaches into grit chamber (Fig. 8.5) in which the influent water flow is slows for setting down of gravel and sand into the bottom of chamber. Primary clarifiers mediate further slowing of influent water flow so that settleable organics deposit in the bottom whereas greases, oils and fat float to the top. This process useful in removal of almost 50% of the contaminants present in wastewater (Jefferson et al. 1999).

8.7.1.2 Biological Recovery

In this process water runs into aeration tank where oxygen is mixed with it and microorganisms use organic material as food which leads to removal of remaining contaminants, decrease in BOD level. Wastewater biosolids are the end product after the conversion of non-settleable solids into settleable solids of wastewater by microorganisms. Several operators of wastewater recycling plants consider themselves “bug farmers”, because they are in the business of growing and harvesting a healthy population of microorganisms (Vineta 2014). Chemical or substance present in wastewater is harmful to microorganism which can interfere with the biological operation of a water recycling plant. When the water recycling plant is not adequately operating because of chemicals which kill the microorganisms, water reuse programs are threatened and the quality of water discharged to receiving streams is poor.

8.7.1.3 Chemical Recovery

After the bugs (pathogenic microorganism) complete its role, chemical such as chlorine are used to kill the remaining pathogens as a final clarifiers. The residual chlorine must be must be removed from system before discharge into lakes and rivers by using sulfur dioxide (SO_2). Chlorine gas have risks on using and storing as it

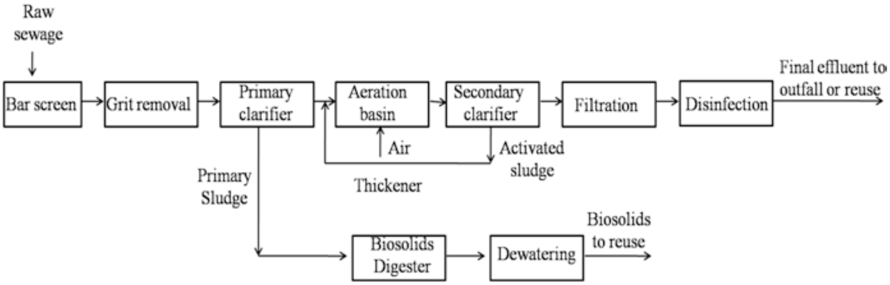

Fig. 8.5 Textile wastewater recycling process

is highly toxic, so use of ultraviolet radiation as an alternative to chlorine provides final disinfection of water.

8.7.1.4 Thermal Recovery

It is useful in the waste recycling technology where higher temperatures are required for the processing of the waste feedstock. This recovery system is believed to be thermal entity and include number of process such as cement kiln, mechanical heat treatment, pyrolysis, gasification, incineration, thermal depolymerization and waste autoclaves.

8.7.2 Advantages of Textile Wastewater Recycling

Enhancing the management of wastewater recycling can be beneficial for business and the environment by:

(a) Reducing expense of acquiring materials and augmenting the proficiency of material use.
(b) Increasing productivity and profitability.
(c) Reducing the expenses of wastewater treatments and disposal.
(d) Reducing the ecological effects by lessening utilization of crude materials and delivering less waste.
(e) Enhancing the public image and employee satisfaction by promoting an eco-friendly image and giving a more secure working environment.

8.7.3 Limitation of Textile Wastewater Recycling

(a) In spite of the fact that the environmental attention to the overall population has expanded in the recent years, their eagerness to effectively take an interest in reducing the waste is still needed to be improved.
(b) There is no economic motivation for waste producers to diminish the waste.
(c) Low qualities, high transportation cost or absence of market interest for recovered or recycled materials.
(d) The majority of small and medium recovery and recycling ventures demoralizes the interest in waste recycling technologies.

8.7.4 Future Scope of Textile Recycling Work

Clothing and textile recycling process reduces the need for landfill spaces, pressure on virgin resources, demand for dyes and fixing agents, saves energy and reduces pollution. As textile mill sludge contains organic matter, it can be turned into sludge ash by igniting it to 800 °C for 2 h. This sludge ash can be used in concrete.

8.8 Factors Affecting the Recycling of Wastewater from Textile Industry

Factors influencing recycling of wastewater performance can be listed down as below:

8.8.1 User Opinions and Satisfaction

Water recycling process is indirectly associated with user opinion and satisfaction because user is always aware with the quality of water. Water Supply Corporation (WSC) of the particular area is responsible to ensure the quality of the water, track record of all operation and maintenance done. Thus, indirectly the complaints from the user have direct bearing on the performance of the water treatment plant.

8.8.2 Community Management

The community management is responsible to ensure that the wastewater recycling plant is well managed, under control and efficiently operated to produce high quality water. The water recycling plants requires vigorous monitoring by operator because it is based on machine and automatic run. The operator must be full time working for controlling and operating the wastewater recycling machine.

8.8.3 Level of Service

Water quality is defined in terms of its chemical, physical, and biological characteristics. The level at which wastewater recycling is performed is an important factor for recycling.

8.8.4 Materials and Equipment

The machinery and equipment involved in processing the wastewater must be highly efficient, so that it can be used for drinking, farming and industrial purposes. The machinery must be for a long term use and blended with new technology to give a better performance towards water recycling.

8.8.5 Financial Status

The water recycling processes needs lots of expenditure on the machinery, building, workers, dams and chemical treatment. The cost of recycling is very high to make it operative. Because of this reason, the government has allocated a lot of money to enable the water recycling function well. Thus, the user will get the benefit from this investment and can use the water safely.

8.8.6 Personnel

One of the important factors which influence the wastewater recycling process is the technician or staff availability and training because clean water is essential for good health, fisheries, wildlife and industries. Water recycling plant operators recycle wastewater upto an extent where it is safe for drinking. A skilled operator will have much influence on to the performance of the water recycling system.

8.8.7 Working conditions

The operators working in wastewater recycling plant works from both indoors and outdoors, and might be exposed to noise from machinery and nasty smells of wastewater. They should give careful consideration to security methods because they may face hazardous conditions, such as slippery walkways, risky gases and malfunctioning equipment. Treatment plants generally operates 24 h every day, 7 days a week, hence, working conditions largely influence the water treatment performance.

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Chapter 9
Treatment and Recycling of Wastewater from Pharmaceutical Industry

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Abstract Pharmaceutical compounds are used for many beneficial purposes in the modern society, but they also contaminate surrounding environment during their exposure. They may enter the environment through numerous routes e.g. treated wastewater discharge, sewage from landfills, sewer lines, runoff from animal wastes and land application of manure fertilizers. The pharmaceutical wastewater consists of high concentration of organic matter, microbial toxicants, high salt concentration and non-biodegradable compounds. Due to limited water resources, it is essential to understand and develop the methodologies for treatment of pharmaceutical wastewater. Trace amounts of suspended solids and dissolved organic matter still persist even after secondary treatment, therefore, advanced treatment is prerequisite in order to improve the quality of pharmaceutical wastewater. In this chapter, the emphasis is mostly on best available technologies to remove and recycle the pharmaceutical wastewater. Effluents arising from different sectors of active pharmaceutical ingredients (API), bulk drugs and related pharmaceutics, consuming a bulk amount of water are evaluated and the strategies are destined to recover valuable compounds upto a larger extent, and finally wastewater treatment is discussed. The complete removal of pharmaceutics from wastewater is not feasible with a single technology. The hybrid wastewater treatment appears to be the best comprising conventional treatment plans in conjunction with biological and advanced post-treatment methods. The recommendations provided in this analysis will be useful for the treatment of wastewater resulting from the pharmaceutical industry.

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R. L. Singh, R. P. Singh (eds.), *Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future*, Applied Environmental Science and Engineering for a Sustainable Future, https://doi.org/10.1007/978-981-13-1468-1_9

Keywords Pharmaceutical drugs · Active pharmaceutical ingredients · Organic pollutants · Bioremediation · Phytoremediation · Hybrid wastewater treatment

9.1 Introduction

Pharmaceuticals are a large and diverse group of synthetic and natural compounds designed to prevent, cure and treat acute and chronic diseases to improve health prospects. A large amount of wastes from pharmaceutical industries are dispensed and consumed annually worldwide. The usage and consumption are increasing constantly due to the discoveries of new drugs. After intake, these active ingredients undergo metabolic processes in organisms. Significant fractions of the parent compound are excreted in unmetabolized form into wastewater treatment systems. Therefore, body metabolization and excretion followed by the wastewater treatment are considered to be the primary route of discharge of pharmaceuticals in the environment.

Pharmaceuticals and their metabolites in the surface water and aquatic sediment is subject of numerous studies concerning pharmaceuticals in the environment (Kadam et al. 2016; Patneedi and Prasadu 2015). Several studies have reported the occurrence and distribution of pharmaceuticals in soil irrigated with reclaimed water (Sui et al. 2015; Ebele et al. 2017) and soil consisting of biosolids from urban sewage treatment plants (Gao et al. 2016). Studies indicated present treatment processes are not sufficient to reduce these micropollutants from the pharmaceutical wastewater, so they find their way into the environment. Once they enter the environment, micropollutants can produce harmful effects on aquatic and terrestrial organisms. Pharmaceutical active compounds are of emerging concern because they are biologically active compound and display toxic effects during exposure on organisms. Various examples of negative effects of pharmaceutical products have been reported in form of development of antibiotic resistance in microbes, reduction in microbial ability of nitric oxidation and methanogenesis, feminization in fish or alligators, migratory behaviour of Salmon and extinction of vulture from India.

9.2 Classification of Pharmaceutical Wastes

Pharmaceutical wastes are classified in three different categories: Hazardous, Non-hazardous and Chemo waste.

9.2.1 Hazardous Waste

Hazardous wastes are of two types: listed and characteristic wastes. Listed wastes appear in one of four lists F, K, P and U. Pharmaceuticals are listed in either P or U category. Characteristic wastes are regulated because they exhibit certain hazardous properties such as ignitability, corrosivity, reactivity and toxicity.

Table 9.1 P-listed pharmaceutical wastes

Active constituent	Waste code
Arsenic trioxide	P012
Epinephrine	P042
Nicotine	P075
Nitroglycerin	P081
Phentermine (CIV)	P046
Physostigmine	P204
Physostigmine salicylate	P188
Warfarin >0.3%	P001

To determining which pharmaceutical waste is hazardous, Resource Conservation and Recovery Act (RCRA) definitions must be considered. Hazardous drugs are categorized as P and U list or chemical characteristic (D-list) by federal Environmental protection Agency (EPA) regulations.

9.2.1.1 P-Listed Pharmaceutical Waste

Acutely hazardous wastes are listed in P category; those are considered harmful even in small quantities. One of the primary criteria for including a drug in the P-list is their lethal dose (LD_{50}). LD_{50} is the amount of drug which causes the death of 50% of a group of test animals. Eight chemicals in the P-list are used as pharmaceuticals (Table 9.1).

9.2.1.2 U-Listed Pharmaceutical Wastes

This group includes such common compounds e.g. acetone, phenol, lindane, choralhydrate and selected anti-neoplastic waste. There are 21 drugs in the U-list (Table 9.2). These chemicals are listed primarily for their toxicity. Similar to a P-listed waste, when a drug waste containing one of these chemicals is discarded, it must be managed as hazardous waste if two conditions are satisfied: (1) The discarded drug waste contains a sole active ingredient that appears in the U list, and (2) It has not been used for its intended purpose.

9.2.1.3 Chemical Characteristics of Pharmaceutical Wastes

In addition to the P- and U- listed wastes, a waste is considered hazardous under RCRA if it possesses at least one of the four unique and measurable characteristics:

1. **Ignitability (D001):** Wastes that can easily catch on fire and sustain combustion.

Table 9.2 U-listed pharmaceutical wastes

Active constituents	Waste code
Chloral hydrate (CIV)	U034
Chlorambucil	U035
Cyclophosphamide	U058
Daunomycin	U059
Dichlorodifluoromethane	U089
Hexachlorophene	U132
Lindane	U129
Melphalan	U150
Mercury	U151
Mitomycin C	U010
Paraldehyde (CIV)	U182
Phenol	U188
Reserpine	U200
Resorcinol	U201
Saccharin	U202
Selenium sulphide	U205
Streptozotocin	U206
Trichloromonoflurومethane	U121
Uracil mustard	U237
Warfarin	U248

Table 9.3 D-listed chemicals used in drug formulations

Ingredient	Waste code
Arsenic	D004
Barium	D005
Cadmium	D006
Chloroform	D022
Chromium	D007
Lindane	D013
M-cresol	D024
Mercury	D009
Selenium	D010
Silver	D011

2. **Corrosivity (D002):** Corrosive wastes corrode metals or other materials or burn the skin.
3. **Reactivity (D003):** Reactive wastes are unstable under normal conditions. They may cause explosions, toxic fumes, gases, or vapours when heated, compressed, or mixed with water.
4. **Toxicity (Multiple D Codes):** Toxic wastes are harmful or fatal when ingested or absorbed (e.g., containing mercury, lead, etc.). Toxic D-listed chemicals used in drug formulation are listed in Table 9.3.

9.2.2 Nonhazardous Pharmaceutical Waste

It is a general consideration that once the manufacturer's packaging is opened, any unused or partially used product is nonhazardous pharmaceutical waste e.g. vials, bottles, intravenous (i.v.) therapy bags, tubing containing drugs and expired medicines have been dropped or spit out by a patient. Leftover medications are also considered as pharmaceutical waste those should be disposed of in accordance with EPA and Drug Enforcement Administration (DEA) regulations. When permitted by both state regulations and RCRA, this waste can be solidified and placed in a landfill. However, a better management practice is to have nonhazardous pharmaceutical waste processed by a medical waste incinerator or a properly permitted municipal waste incinerator. Disposal of devices used to administer (such as inhalers) nonhazardous medications, is another consideration. In addition to RCRA requirements, some states have regulations specific to the device and propellant used to deliver drugs, those must be considered in establishing waste streams. For example, in Nebraska, hospitals are required to either segregate inhaler devices from the normal waste stream or puncture and triple rinse the container before disposal in the nonhazardous waste stream (Smith 2002).

9.2.3 Chemo Pharmaceutical Waste

There is some confusion in chemotherapy, antineoplastic and cytotoxic terms. Chemotherapy is a chemical treatment, commonly used for cancer treatment. Antineoplastic refers specifically to inhibiting or preventing the growth or development of cancerous cells. Cytotoxic is referring to any chemical that is toxic to cells. One chemotherapy agent is a P-listed constituent of concern and eight chemotherapy agents are U-listed (Table 9.4).

Table 9.4 P and U listed chemotherapy agents

Constituents of concern	Product name	Waste code
Arsenic trioxide	Trisenox	P012
Chlorambucil	Leukeran	U035
Cyclophosphamide	Cytoxan, neosar	U058
Daunomycin	Daunorubicin, cerubidin, DaunoXome, rubidomycin	U059
Diethystilbestrol	DES, stilphostrol	U089
Melphalan	Alkeran, L-PAM	U150
Mitomycin C	Mitomycin, mutamycin	U010
Streptozotocin	Streptozocin, zanosar	U206
Uracil Mustard	No longer in active use	U237

9.3 Active Pharmaceutical Ingredients (APIs) and Biopharmaceuticals

APIs are complex molecules with different functions including physico-chemical and biological properties. These are polar in nature and their molecular weight typically ranges from 200 to 1000 Dalton (Da). APIs are part of micropollutants because they are often found in the μg/l or ng/l range in the aquatic environment.

Genetically modified pharmaceuticals are known as biopharmaceuticals. The first and best-known example was recombinant human insulin. The environmental relevance of biopharmaceuticals is not yet clear. They are not closely related to natural products and therefore expected to be quickly biodegraded or denatured.

9.4 Characteristics of Pharmaceutical Wastewater

Wastewater characteristics play a key role in the selection of treatment process (Deegan et al. 2011). The wastewater characteristics generated during the manufacturing of pharmaceuticals depending on the raw materials, equipments, manufacturing compounds as well as formulation processes (Mayabhate et al. 1988). Kavitha et al. (2012) studied the physicochemical analysis of pharmaceutical wastes and treatment plant's efficiency and found the variation in characteristics from the inlet to outlet point of septic tanks. They observed reduction in BOD COD, TSS, TDS, chlorides, sulphates and pH. Das et al. (2012) studied the control of pharmaceutical effluent parameters through bioremediation. They collected the samples from nine different points situated in the industry and observed the range of sulphates (44–1527), TDS (484–1452), TSS (24–84) and COD (1257.9–1542.9) mg/l. Madukasi et al. (2010) characterized the pharmaceutical wastewater and observed the TSS (425), TDS (1600), BOD (146.7), N_2 (533.7), Zn (0.056), Fe (2.1), Mn (0.605), Cu (0.022), acetic acid (422.7), propionic acid (201.3) and butyric acid (304.5) mg/l. A suitable range of various parameters of pharmaceutical wastewater has shown in Table 9.5.

9.5 Factors Affecting the Rate of Biodegradation of Pharmaceutical Wastes

The cleaning up of pharmaceutical wastes in the environment is a real world problem. Better understanding of the factors which affect biodegradation is of great ecological significance, since the choice of bioremediation strategy depends on it. Biodegradation of the pharmaceutical wastes depends on a number of factors such as:

1. Stereochemistry of the compound
2. Compound toxicity

Table 9.5 Characteristics of pharmaceutical wastewater

Characteristics	Rang of parameters
pH	3.7–8.5
TSS (mg/l)	48–1113
TDS (mg/l)	600–1770
Total solids	880–4934
BOD (mg/l)	20–1800
COD (mg/l)	128–3500
BOD/COD	0.15–0.51
Alkalinity (mg/l)	90–564
Total nitrogen (mg/l)	80–164
Ammonium nitrogen (mg/l)	74–116
Total phosphate (mg/l)	18–47
Turbidity (NTU)	2.2–138
Chloride (mg/l)	205–261
Oil and grease (mg/l)	0.5–2.9
Phenol (mg/l)	95–125
Conductivity (μS/cm)	157–1673
Temperature (°C)	32–46

3. Compound concentration
4. Microbial strain efficiency
5. Degradation conditions
6. Sludge retention time
7. Environmental factors
8. Contact efficiency between bacterial biomass and organic matter

9.6 Sources of Pharmaceutical Wastewater

The introduction of pharmaceuticals products into the environment after use is a typical concern. They are recognized as being an important part of the chemicals those are present in low concentrations in the environment (Schwarzenbach et al. 2006). If the drugs and their transformation products are not eliminated during sewage treatment, they may enter to the aquatic environment and eventually contaminate drinking water. The concentrations of pharmaceuticals in surface water and effluent from sewage treatment plants (STPs) have been shown to lie in range of ng/l to mg/l.

The consumption and application of pharmaceuticals may vary from country to country (Goossens et al. 2007; Schuster et al. 2008). The heavy usage of streptomycin in fruits is reason for the high resistance of pathogenic bacteria against these compounds in USA. In Germany, the use of these antibiotics for this purpose has been banned. If, governmental regulations are imposed on the health system it may happen that some compounds are not used any more or others gain more importance, e.g. for economical reasons. Some antibiotics such as streptomycin are used in the cultivation of fruits (pomology) while others are used in bee-keeping. Pharmaceutical wastes produced by many different sources as follows:

9.6.1 Manufacturers

Because of high cost of pharmaceuticals, the amount of emissions occurring during manufacturing has been thought to be negligible. In Asian countries concentrations of a single compound in water may reach up to mg/l in the effluents (Li et al. 2008).

9.6.2 Hospitals

The effluent of pharmaceuticals in hospital wastewater is higher than other. However, the total substance flow is much lower due to less share of effluent from hospitals in municipal effluent (Schuster et al. 2008).

9.6.3 Private Households

Expired medicines are sometimes disposed of down household drains. In accordance with European Union (EU) prescription, the discarding of unused drugs through household waste has been permitted since 1994.

9.6.4 Landfills

Landfill is a site for the disposal of waste materials. If there is no collection of the effluent, this may be a source for contamination of surface water or groundwater.

9.7 Effects of Pharmaceutical Wastewater

9.7.1 On Human

The extent of human exposure to pharmaceuticals active agents (PAA) from the environment is a complex function of many factors. These factors include the type, distribution, concentrations, pharmacokinetics, structural transformation and the potential bioaccumulation of the diverse pharmaceuticals in the environment. The growing concerns about health risks via environmental exposures, many researchers have speculated about the potential for inducing an antibiotic resistance. Some microbiologists believe that if antibiotic concentrations are higher than the minimum inhibitory concentrations (MICs) of a pathogenic bacterial species, a selective pressure would be exerted and, as a result, antibiotic resistance would be selectively promoted (Segura et al. 2009).

9.7.2 On Environment

Due to high solubility of most PAA, aquatic organisms are exposed to their effects. Researchers have found that a class of antidepressants may be found in frogs and can significantly slow their development. The increased presence of estrogen and other synthetic hormones in wastewater due to birth control and hormonal therapies has been linked to increased feminization of exposed fishes and other aquatic organisms. The chemicals within these PAA could either affect the feminization of different fishes, therefore affecting their reproductive rates (Siegrist et al. 2004). In addition to being found only in waterways, some PAA can also be found in the soil. Since these substances take a long time or cannot be degraded biologically, they make their way up to the food chain. Information pertaining to the transport and fate of these hormones and their metabolites in dairy waste disposal is still being investigated (Zhang et al. 2010). The pollution resulting from PAA not only affects marine ecosystems, but it also affects those habitats depending on this polluted water.

9.8 Biological Methods for Treatment of Pharmaceutical Wastewater

The pharmaceutical industry has adopted different strategies and processes to treat the wastewater and its reuse to control the environmental pollution. The oldest methods employed for wastewater treatment include physical, chemical and thermal treatment methods. But these treatment methods have several disadvantages including huge labour requirement, high maintenance cost, low efficiency, and huge equipments etc. In order to attain maximum efficiency in wastewater treatment and water reuse, an advanced technology has been developed and further research is going on for better results also known as bioremediation and phytoremediation (Chelliapan et al. 2011). Bioremediation (use of microorganisms) and phytoremediation (use of plants) have been adopted to clean up harmful chemicals from the environment.

Biological treatment methods have been widely used in the management of pharmaceutical wastewater treatment due to their low cost and effectiveness. They may be subdivided into aerobic and anaerobic processes (Suman Raj and Anjaneyulu 2005). Aerobic applications include activated sludge, membrane batch reactors and sequence batch reactors (Chang et al. 2008; Chen et al. 2008). Anaerobic methods include anaerobic sludge reactors, anaerobic film reactors and anaerobic filters (Oktem et al. 2007; Sreekanth et al. 2009). Biological methods are also classified as either attached growth or suspended growth according to the living status of the microorganisms. Activated sludge method is effective aerobic process for the treatment of some kinds of low strength pharmaceuticals in wastewater. This process has the disadvantage of slow sludge settling. Activated sludge treatment is also unsuitable for the treatment of wastewater where the COD levels are greater than 4000 mg/l (Suman Raj and Anjaneyulu 2005). The wastewater characteristics such as solvents, APIs intermediates and raw materials play an important role in the selection of biological treatment methods. These characteristics represent recalcitrant substances which affect the efficiency of biological treatment processes (Helmig et al. 2007).

9.8.1 Aerobic Methods

Aerobic condition is speeding up biodegradation process at a faster rate and to a greater extent compared to anaerobic conditions in a given time period (Murphy et al. 1995). Moreover, biological reactors have less construction cost, easy operational and maintenance procedures. An air injection is applied to the biological wastewater treatment plant and access the performance. The treatment process of the bioreactors depends on aeration rate and retention time. The aerobic digestion process consists of two reaction steps (Ros and Zupancic 2002) as follows:

$$\text{Organic matter} + NH_4^{+} + O_2 \rightarrow \text{cellular material} + CO_2 + H_2O$$

$$\text{Cellular material} + O_2 \rightarrow \text{digested sludge} + CO_2 + H_2O + NO_3^{-}$$

There are various aerobic pharmaceutical wastewater treatment methods which are mentioned below.

9.8.1.1 Conventional Activated Sludge Process (CASP)

CASP is oldest industrial wastewater bio-treatment process. The wastewater after primary treatment (suspended impurities removal) is treated in a CASP that comprises aeration tank followed by secondary clarifier. The aeration tank is completely mixed with air where specific concentration of biomass is maintained along with sufficient concentration of dissolved oxygen (2 mg/l) to affect biodegradation of soluble organic impurities measured as BOD or COD. The aerated mixed liquor from the aeration tank overflows to secondary clarifier unit to separate out the biomass, treated water to the downstream filtration system for finer removal of suspended solids (Fig. 9.1).

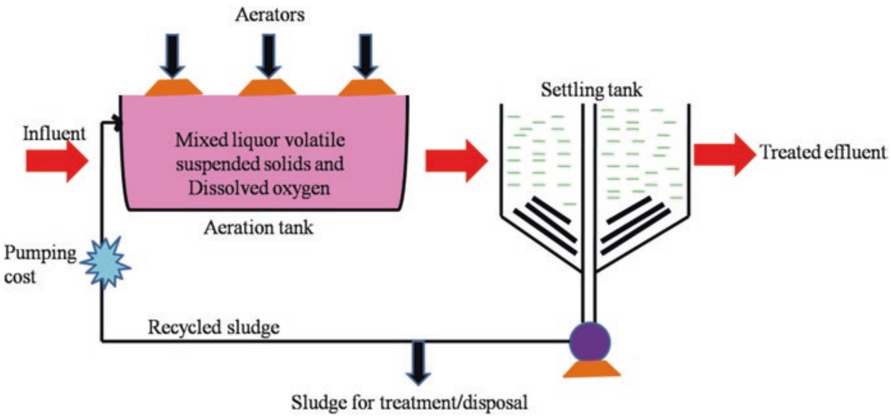

Fig. 9.1 Conventional activated sludge process

9.8.1.2 Cyclic Activated Sludge System (CASS) or Sequence Batch Reactor (SBR)

SBR is a real time batch process, belongs to the broad category of an unsteady-state activated sludge system (Irvine et al. 1979). The difference between SBR and CASP is that SBR carries out equalization, aeration and sedimentation in time manner rather in a space sequence (Fig. 9.2). In CASP, the relative tank volume is fixed and cannot be redistributed as easily as in SBR. The operational flexibility also allows designers to use the SBR to meet many different treatment objectives at a single time such as BOD reduction along with nitrification/denitrification. The basic configuration and mode of operation permit combined nitrogen and phosphorous removal mechanisms to take place through a simple one shot control of the aeration. SBR utilizes a simple time-based sequence which incorporates: Aeration (for biological reactions), Settle (for solids-liquid separation) and Decant (to remove treated effluent).

The CASS-SBR process maximizes operational simplicity, reliability and flexibility. Important reasons for choosing CASS-SBR over conventional constant volume activated sludge aeration and clarifier process include:

1. Operates under continuous reduced loading through simple cycle adjustment.
2. Operates with feed-starve selectivity, limiting substrate to microorganism ratio, and aeration intensity.
3. Tolerates shock load.
4. Reduced land requirement.
5. Easy plant expansion.
6. No adjustments to the return sludge flow rate are necessary.

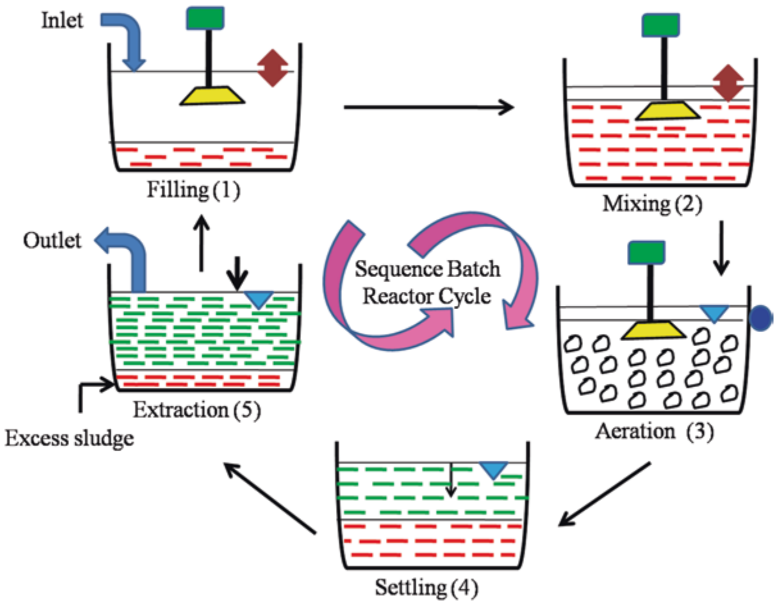

Fig. 9.2 Sequence batch reactor cycle

9.8.1.3 Integrated Fixed Film Activated Sludge (IFAS) System

It is a latest technology that incorporates an attached growth media within the suspended growth reactor (Fig. 9.3) (U.S. EPA 2010). It provides additional biomass growth within a reactor in order to meet more efficient treatment process. Due to more bacterial population on a fixed surface IFAR system eliminate the need to increase the suspended growth. IFAS configuration is similar to an activated sludge plant, with biomass carriers introduced into carefully selected zones within the activated sludge process. This system allows two different biological populations to act synergistically, with the mixed liquor suspended solids (MLSS) degrading most of the organic load (BOD) and the biofilm creating a strongly nitrifying population for oxidation of the nitrogenous load (NH_4^+). The common advantages of all of the above described configurations are as follows:

1. The fixed biomass combines aerobic, anaerobic and anoxic zones and increases the sludge retention time, promoting better nitrification compared to simple suspended growth systems.
2. Fixed film media provides additional surface area for biofilm to grow on it and degrade the organic impurities that are resistant to biodegradation or may even be toxic to some extent.
3. System nitrification is also restored faster since a large mass of nitrifiers is retained on the fixed-film.

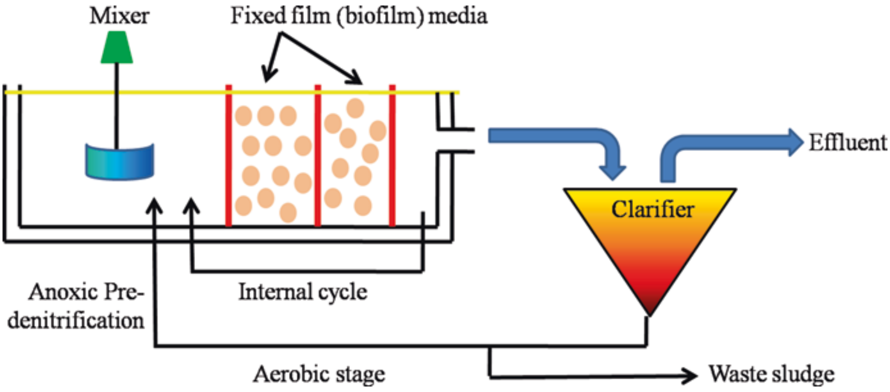

Fig. 9.3 Integrated fixed film activated sludge (IFAS) system

4. Reduced sludge production: due to less sludge wastage, the sludge handling and dewatering facility is smaller compared to the activated sludge process.
5. Improved process stability
6. It can be easily incorporated in the existing activated sludge system to meet additional processing capacity requirement and/or stricter discharge regulations without the need of additional concrete tanks
7. For new installations, IFAS systems will generally require less volume and therefore have less capital cost than a CASP system

9.8.1.4 Membrane Bioreactor (MBR)

MBR combines conventional biological treatment (e.g. activated sludge) processes with membrane filtration to provide an advanced level of organic and suspended solids removal. In MBR, the bio-solids are separated by a polymeric membrane based on micro or ultra-filtration unit against gravity in the secondary clarifier as in CASP. When designed accordingly, these systems can also provide an advanced level of nutrient removal (BOD). In an MBR system, the membranes with pore size in a range of 0.035–0.4 μ are submerged in an aerated biological reactor (Fig. 9.4). MBR allows high quality effluent to be drawn and eliminates the sedimentation and filtration processes typically used for pharmaceutical wastewater treatment. Since, sedimentation is not required the biological process operates at a much higher mixed liquor concentration. This reduces the requirement of tanks and allows many existing plants to be upgraded without adding new tanks. To provide optimal aeration and scour around the membranes, the mixed liquor is typically kept in 1.0–1.2% solids range, which is ~4 times that of a conventional plant. Therefore, the advantages of MBR system over CASP system are obvious as listed below:

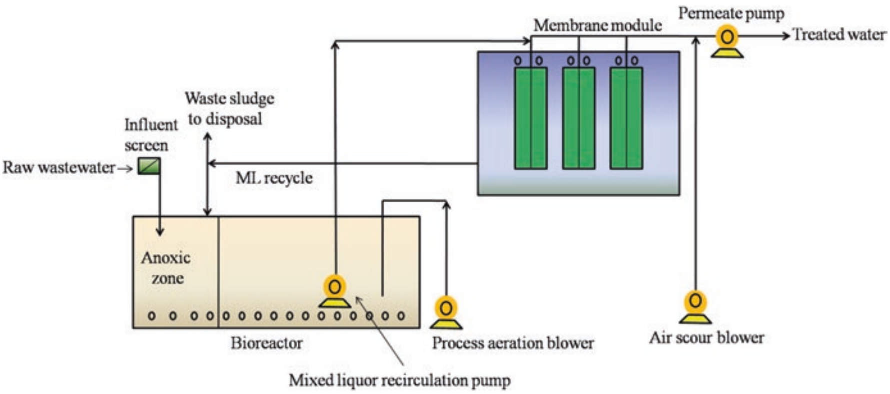

Fig. 9.4 Membrane bioreactor

1. MBR maintained MLSS/MLVSS (mixed liquor suspended solids and mixed liquor volatile suspended solids) ratio 3–4 (~10,000 mg/l) times higher than CASP (~2500 mg/l).
2. MBR requires only 40–60% of the space compared to CASP, therefore significantly reducing the physical workload.
3. Due to micro/ultrafiltration, MBR system has superior effluent quality compared to CASP, so the treated effluent can be directly reused as cooling tower make-up or for gardening
4. High effluent quality
5. High loading rate capability

9.8.1.5 Aquatech Enhanced Membrane Bioreactor (Aqua-EMBR)

It is non-submerged and external type MBR for industrial applications especially in petrochemical and pharmaceutical wastewater applications. The ultrafiltration membrane (UM) is positioned outside the bioreactor tank, rather than submerging in the bioreactor tank or the downstream membrane tank (Fig. 9.5). UM modules are arranged vertically and are aerated continuously at the bottom. Continuous air injection is applied to sustain the design permeate flux and also to drive the mixed liquor recirculating flow back to the aeration tank. Mixed liquor is thus transported via an air lift pump through the module, while the membrane feed/recirculation pump is only used to overcome the hydraulic losses and maintain a relatively constant flow of mixed liquor through the membrane. This innovative design reduces much of the feed pumping energy requirement and enables Aqua-EMBR system to consume lower energy than other MBR systems. The advantages of Aqua-EMBR over submerged MBR systems include:

1. Aqua-EMBR has no membrane tank, it can be built much quicker.
2. Offers friendly working environment.

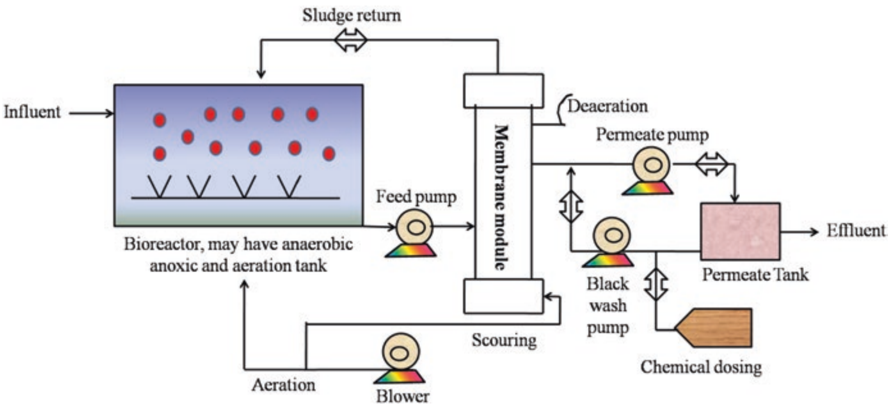

Fig. 9.5 Aquatech enhanced membrane bioreactor

3. Fifty percent less surface area of membrane needed per unit volume permeate production.
4. Electrical power consumption is 10–15% lower.
5. Contain tightest membrane pore size of 30–40 nm, good turbidity of permeate <0.2 NTU and TSS levels <0.5 mg/l.
6. Highest effluent quality.

9.8.2 Anaerobic Methods

In anaerobic treatment, organic content decomposes into methane and CO_2 in the presence of microorganisms. Anaerobic pharmaceutical wastewater treatment process has many advantages such as little sludge production, less energy requirement, high organic loading rate, low nutrient requirement and production of low biogas (Shi et al. 2017). Source of inoculum and feed pre-treatment can affect the treatment efficiency. However, low pH and slow growth rate results into a longer hydraulic retention time (HRT). A high-rate configuration was designed to treat industrial wastewater at relatively shorter HRT to overcome this problem (Patel and Madamwar 2000). Enright et al. (2005) reported anaerobic biological treatment of pharmaceutical wastewater and achieved 60–70% COD removal efficiency.

The biological conversion of organic matter occurs in three steps: hydrolysis, acidogenesis and methanogenesis. (i) Hydrolysis: higher molecular-mass compounds converted into compounds suitable for use as a source of energy (ii) Acidogenesis: bacterial conversion of the compounds into lower-molecular-mass intermediate compounds (iii) Methanogenesis: bacterial conversion of the intermediate compounds into simpler end products, such as CH_4 and CO_2.

According to trophic requirements, used bacteria can be divided into three groups:

1. **Hydrolytic bacteria (acidogens):** hydrolyzes the long chain organic compounds into short-chain acids and molecules e.g., carbohydrates are converted into low-chain fatty acids, alcohols, hydrogen and CO_2 under anaerobic condition. The generation time of these bacteria is 2–3 h. The distribution of final product depends on the bacterial species and on the environmental factors such as temperature and pH.
2. **Obligate hydrogen producing acetogens:** This group converts compound formed in the first stage into acetic acid and hydrogen. Low hydrogen pressure favours these reactions (Harper and Pohland 1986).

$$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2$$

3. **Methanogens (obligate anaerobes):** These bacteria produce methane. The doubling time of these bacteria is 2–10 days. These are further divided into two groups as:

(a) Hydrogen utilisers (lithotrophs)

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \text{ convert ADP to ATP}$$

(b) Acetic acid users (acetotrophs)

$$CH_3COOH \rightarrow CH_4 + CO_2 \text{ produce } 0.25 \text{ mole of ATP}$$

The methane producing bacteria are strict anaerobes which are extremely sensitive to changes in temperature and pH. These bacteria are active in two different temperature zones, namely, mesophilic (30–35 °C) and thermophilic (50–60 °C). However, anaerobic processes have been operated at 15 °C successfully when sufficient residence time for these bacteria was provided.

Upflow anaerobic sludge blanket (UASB) reactors and anaerobic fixed film reactor (AFFR) are anaerobic process. Both processes are used for pharmaceutical wastewater treatment (Fang et al. 1995). The success of UASB depends on the formation of active granules. These granules consist of self-immobilized, compact form of aggregate of organisms and lead to an effective retention of organisms in the reactor (Akunna and Clark 2000). UASB reactor is independent from mechanical mixing and recycling of sludge biomass. Researchers have utilized UASB reactor for the treatment of chemical synthesis-based pharmaceutical wastewater (Oktem et al. 2007). In 2009, hybrid UASB reactor was reported to treat bulk drug industrial wastewater utilizing thermophilic strain (Sreekanth et al. 2009). Toth et al. (2011) studied the performance of a laboratory-scale UASB reactor for the treatment of a pharmaceutical wastewater, under different operating conditions.

AFFR has a biofilm support for biomass attachment. This reactor has advantages like construction simplicity, elimination of mechanical mixing, better stability and capability to withstand toxic shock load. This type of reactor can recover very quickly after a period of starvation (Rajeshwari et al. 2000). In this reactor, glass bead, corrugated plastic coconut coir, charcoal and nylon fibre can be used as support media, which enhances the reactor performance (Acharya et al. 2008). Gangagni Rao et al. (2005) studied the treatment of wastewater with high suspended solids from a bulk pharmaceutical industry using AFFR and concluded that the AFFR could be used efficiently for the treatment of bulk pharmaceutical wastewater having high COD (60–70% removal), TDS, TSS and BOD (80–90% removal). It has been recognized that the anaerobic treatment is in many ways ideal for wastewater treatment and has several advantages mentioned as below:

1. A high degree of waste stabilization
2. A low production of excess biological sludge
3. Low nutrient requirements
4. No oxygen requirement
5. Production of valuable by-product e.g. methane gas
6. Organic loading is not limited to oxygen supply
7. Less land required as compared to many aerobic process
8. For few months, non-feed conditions do not affect adversely to the system and this makes it attractive option for seasonal industrial wastewater treatment

9.9 Biological Sources of Pharmaceutical Wastewater Treatment

9.9.1 Bacteria

Some bacterial strains like *Pseudomonas, Enterobactor, Streptomonas, Aeromonas, Acinetobactor* and *Klebsiella* showed up to 44% COD reduction of pharmaceutical wastewater (Ghosh et al. 2004). Chaturvedi et al. (2006) isolated 15 rhizosphere bacteria, those show 76% color reduction and 85–86% BOD and COD reduction within 30 days. The bacterial community is required to provide all metabolic capabilities for complete mineralization of toxic organic compounds, which is essential for degradation of pharmaceutical pollutants (Tewari and Malviya 2002). *Arthrobacter, Comamonas, Rhodococcus, Pseudomonas* and *Ralstonia* are known to degrade phenolic and complex organic compounds. Some fermenting bacteria such as *Clostridium* species are able to degrade m-dihydroxybenzene (Kavitha and Beebi 2003). Duffner et al. (2000) proposed phenol/cresol degradation by the thermophilic *Bacillus thermoglucosidasius* A7.

Kumar et al. (2005) and Agarry and Solomon (2008), reported the biodegradation kinetics of phenol, catechol and chlorophenol using *P. putida* MTCC 1194 and *P. fluorescence*. The *Rhodobacter sphaeroides* was found to be effective in ameliorating hazardous pollutants found in pharmaceutical wastewater with over 80% COD reduction (Madukasi et al. 2010). Researchers also achieved a significant COD removal (62% at 30 °C and 38% at 60 °C) in pharmaceutical wastewater by using mixed bacterial culture (Lapara et al. 2001). Long-term accumulation of persistent antibiotics and their metabolites in agro-ecosystems can result in toxicity to crops and soil ecosystem as well as on the quality of groundwater (Du and Liu 2012). Pharmaceuticals have been shown to affect plant growth and yields (Goss et al. 2013). The most common pharmaceutical wastes and antibiotic degrading bacteria are summarised in Table 9.6.

Table 9.6 Bacterial cultures involved in pharmaceutical wastes and antibiotic degradation

Name of bacterial culture	Pharmaceutical wastes degradation	References
Acidovorax delafieldii	Dgradation of organic pollutants and biosorbent of toxic heavy metal Cr(VI) over 90% COD reduction	Rozitis and Strade (2015)
Aeromonas caviae	Degradation of organic pollutants and biosorbent of toxic heavy metal Cr(VI) over 90% COD reduction	Rozitis and Strade (2015)
Arthrobacter	Degradation of the pharmaceutical mixture diclofenac, ibuprofen, and sulfamethoxazole	Aissaoui et al. (2017)
Aspergillus niger	Degradation of organic pollutants and reduction of COD, TSS, TDS, sulphates over 75%	Das et al. (2012)
Brevibacterium epidermidis	Degradation of sulfonamide antibiotics	Levine (2016)
Bacteroides fragilis	Degradation of tetracycline	Park and Levy (1988)
Bacillus licheniformis,	Degradation of organic pollutants and reduction of COD, TSS, TDS, sulphates over 75%	Das et al. (2012)
Bacillus megatherium	Degradation of organic pollutants and reduction of COD, TSS, TDS, sulphates over 75%	Das et al. (2012)
Bacillus pumilis	Degradation of organic pollutants and reduction of COD, TSS, TDS, sulphates over 75%	Das et al. (2012)
Bacillus subtilis	Degradation of organic pollutants and reduction of COD, TSS, TDS, sulphates over 75%	Das et al. (2012)
Castellaniella denitrificans	Degradation of sulfonamide antibiotics	Levine (2016)
Candidatus microthrix	Removal of phosphorus removal	Kristiansen et al. (2013)
Citrobacter youngae	Degradation of the pharmaceutical mixture diclofenac, ibuprofen, and sulfamethoxazole	Aissaoui et al. (2017)
Enterobacter hormaechei	Degradation of the pharmaceutical mixture diclofenac, ibuprofen, and sulfamethoxazole	Aissaoui et al. (2017)
Flavobacterium johnsoniae	Degradation of organic pollutants and biosorbent of toxic heavy metal Cr(VI) over 90% COD reduction	Rozitis and Strade (2015)
Hyphomicrobium facilis	Removal of phosphorus removal	Kristiansen et al. (2013)
Microbacterium sp. strain C448	Degradation of sulfamethazine	Hirth et al. (2016)
Moraxella osloensis	Degradation of organic pollutants and biosorbent of toxic heavy metal Cr(VI) over 90% COD reduction	Rozitis and Strade (2015)
Nitrobacter	Degradation of organic pollutants and reduction of COD, TSS, TDS, sulphates over 75%	Das et al. (2012)

(continued)

Table 9.6 (continued)

Name of bacterial culture	Pharmaceutical wastes degradation	References
Nitrosomonas	Degradation of organic pollutants and reduction of COD, TSS, TDS, sulphates over 75%	Das et al. (2012)
Nocardia	Modification of rifampin and efficient degradation of erythromycin	Morisaki et al. (1993) and Tanaka et al. (1996)
Pseudomonas aeruginosa, Pseudomonas aeruginosa 3011	Degradation of organic pollutants and biosorbent of toxic heavy metal Cr(VI) over 90% COD reduction and efficient degradation of fosfomycin	Rozitis and Strade (2015), Šabić, et al. (2015), and Llaneza et al. (1985)
Psuedomonas fluorescens	Degradation of organic pollutants and reduction of COD, TSS, TDS, sulphates over 75%	Das et al. (2012)
Pseudomonas pseudoalcaligenes	Degradation of organic pollutants and biosorbent of toxic heavy metal Cr(VI) over 90% COD reduction	Rozitis and Strade (2015)
Pseudomonas sp.	Degradation of the pharmaceutical mixture diclofenac, ibuprofen, and sulfamethoxazole	Aissaoui et al. (2017)
Pseudomonas putida	Degradation of organic pollutants and reduction of COD, TSS, TDS, sulphates over 75%	Das et al. (2012)
Paracoccus versutus	Degradation of organic pollutants and biosorbent of toxic heavy metal Cr(VI) over 90% COD reduction	Rozitis and Strade (2015)
Rhodobacter sphaeroides	Removal of phosphorus removal and efficient degradation of phenol and other organic solvents over 80% COD reduction	Kristiansen et al. (2013) and Madukasi et al. (2010)
Rhodococcus sp.; *Rhodococcus equi*	Degradation of organic pollutants and reduction of COD, TSS, TDS, Sulphates over 75% and efficient degradation of the pharmaceutical mixture diclofenac, ibuprofen, and sulfamethoxazole, rifampin	Das et al. (2012), Aissaoui et al. (2017), Morisaki et al. (1993), and Tanaka et al. (1996)
Rhodoferax ferrireducens	Removal of phosphorus removal	Kristiansen et al. (2013)
Sphingobacterium thalpophilum	Degradation of organic pollutants and biosorbent of toxic heavy metal Cr(VI) over 90% COD reduction	Rozitis and Strade (2015)
Streptomyces lividans	Degradation of erythromycin and other macrolides	Wright (2005)
Tetrasphaera elongate	Removal of phosphorus removal	Kristiansen et al. (2013)
Trichococcus collinsii	Removal of phosphorus removal	Kristiansen et al. (2013)
Tsukamurella inchonensis	Degradation of organic pollutants and biosorbent of toxic heavy metal Cr(VI) over 90% COD reduction	Rozitis and Strade (2015)

9.9.2 Fungi

Fungal strains have some limitations due to the presence of a long growth cycle and spore formation for treatment of pharmaceutical wastewater treatment (Table 9.7). Spina et al. (2012) used *Bjerkandera adusta* MUT 2295, a fungal strain, to compare fungal treatment process with activated sludge treatment process. Through fungal treatment they achieved 91% COD reduction compared to activated sludge, which reduced 78% COD. A group of fungi known as Ascomycetes also play an important role in the treatment of pharmaceutical wastewater, e.g. *Penicillium decumbens* and *Penicillium lignorum* have shown significant reduction in COD, phenol and color (Mohammad et al. 2006; Angayarkanni et al. 2003).

9.9.3 Algae

Treatment of pharmaceutical industry wastewater using algae has been studied over 50 years (Nandy et al. 1998; Oswald and Gotaas 1957). Microalgae have a potential to reduce the contaminants such as metals in aquatic systems (Fulke et al. 2010, 2013; Wang et al. 2013; Park et al. 2011). First of all, the metal ions are adsorbed over the algal cell surfaces rapidly, thereafter removed slowly into the cytoplasm (Omar 2002). The biomass of microalgae rises during wastewater treatment and has the potential to remove inorganic pollutants especially nitrogen and phosphorus from wastewater resulting from pharmaceutical industries. However, nutrients are removed from wastewater through a direct uptake by the algal cells (Hoffman 1998). Algal treatment of pharmaceutical wastewater, mediated through a combination of nutrient uptake, elevated pH and high dissolved oxygen concentration, can offer an ecologically secure, cheap and efficient way to remove metals and nutrients

Table 9.7 Fungal cultures involved in treatment of pharmaceutical wastes

Name of fungi	Pharmaceutical wastes degradation	References
Candida inconspicua	Degradation of organic pollutant and reduction of COD over 76.6%	Rozitis and Strade (2015)
Fusarium solani, Fusarium udum	Degradation of organic pollutant and reduction of COD over 89.4%	Rozitis and Strade (2015)
Galactomyces pseudocandidum	Degradation of organic pollutant and reduction of COD over 76.6%	Rozitis and Strade (2015)
Phaerochaete chrysosporium	Degradation of organic pollutant and reduction of COD over 90%	Aissaoui et al. (2017)
Pseudallescheria boydii	Reduction of COD over 95%	Rozitis and Strade (2015)
Rhodotorula mucilaginosa	Removal of organic pollutant and reduction of COD over 76.6%	Rozitis and Strade (2015)
Trichosporon asahii, Trichosporon domesticum	Degradation of organic pollutant and reduction of COD over 76.6%	Rozitis and Strade (2015)

compared to conventional treatment procedures (Brennan and Owende 2010; Fulke et al. 2013; Nijhawan et al. 2013). Several researchers have established that metals are sequestered in polyphosphate bodies in green algae. These polyphosphate bodies serve as a storage pool for metals and also act as detoxification agents. Studies have revealed that the alga *Scenedesmus obliquus* can accumulate Cd and Zn by increasing the amount of phosphorus in the media (Yu and Wang 2004). Physiochemical characteristics like pH, COD, BOD, total solids, sodium, potassium and heavy metals have been analysed for the evaluation of toxicity of pharmaceutical wastewater after its treatment with micro green algae *Scenedesmus quadricauda* (Vanerkar et al. 2015).

9.9.4 Plants

Phytoremediation of wastewater is an emerging low-cost technique for removal of hazardous metal ions from pharmaceutical wastewater and is still in an experimental stage. Heavy metals such as cadmium and lead are not easily absorbed by microorganisms. In such case, phytoremediation is proved as a better tool for bio-treatment because natural or transgenic plants are able to bioaccumulate these toxins (Amin et al. 2013). Aquatic plants have an excellent capacity to reduce the level of toxic metals, BOD and total solids from the pharmaceutical wastewater (Table 9.8). *Typha latipholia* and *Phragmitis karka* used for treatment of pharmaceutical effluent (Billore et al. 2001) by different mechanism such as nitrification and denitrification. Some physicochemical processes such as the fixation of phosphate by iron and aluminium in the soil filter are also used by plant for remediation of wastes. Researchers also reported the phytoremediation of phenol by peroxidases of tomato hairy root cultures in wastewater from pharma industries (González et al. 2006). Moreover, plants are able to tolerate high concentrations of antibiotics, nutrients and heavy metals (Table 9.8) and in some cases even to accumulate them in their tissues. Plant contains various metabolites to degrade pharmaceutical wastes, for example in the case of *Lemna gibba*, phenyl-beta-D-glucopyranoside was identified as a metabolite resulting from phenol degradation (Barber et al. 1995).

9.10 Water Recycling and Reuse Technologies

Water recycling is a way to reuse treated water for beneficial purposes such as agricultural and landscape irrigation, industrial processes, toilet flushing and replenishing a ground water basin. Water recycling technologies offers resources and financial savings. Wastewater treatment can be tailored to meet the water quality requirements of a planned reuse. Recycled water for landscape irrigation requires less treatment than recycled water for drinking water. Various technologies are using for recycling of pharmaceutical wastewater such as:

Table 9.8 List of plants involved in phytoremediation of pharmaceutical wastes

Plant name	Pharmaceutical wastes	References
Brassica rapa	Salinomycin, sacox	Furtula et al. (2012)
Cucumis sativus	Enrofloxacin, sulfamethoxazole	Liu et al. (2009)
Dacus carota	Tylosin, sildenafil, atorvastatin, diazinon, phenylbutazone, roxithromycin	Hillis et al. (2011) and Jones-Lepp et al. (2010)
Eichhornia crassipes	Uptake of phenol, Cu, Pb, Zn, Cr, Ni, Mn, Cd, Fe	Wolverton and McKown (1976), Saha et al. (2017), and Mishra et al. (2013)
Euphorbia prostrata	Cd, Cr, Pb	Husnain et al. (2013)
Eleocharis cellulose	Zn and Cu	Cortes-Esquivel et al. (2012)
Hordeum vulgare	Ibuprofen, acetaminophen	Kotyza et al. (2010)
Lactuca sativa	Enrofloxacin, gemfibrozil, diazinon, phenylbutazone	Hillis et al. (2011)
Lemna gibba	Efficient degradation of acetaminophen, diclofenac, progesterone, Sulfamethoxazole and phenol	Brain et al. (2008), Allam et al. (2016), and Barber et al. (1995)
Lemna minor	Chlorides and sulphates	Saha et al. (2015)
Lens esculenta	Sulfamethazine	Piotrowicz-Cieślak et al. (2010)
Linum usitatissimum	Ibuprofen, diclofenac, acetaminophen	Kotyza et al. (2010)
Lycopersicon esculentum	Gemfibrozil, sildenafil	D'Abrosca et al. (2008)
Medicago sativa	Oxytetracycline, levofloxacin, tylosin, trimethoprim	Kong et al. (2007)
Marsilea quadrifolia	Chlorides and sulphates	Saha et al. (2015)
Nelumbo lute	Chlorides and sulphates	Saha et al. (2015)
Oryza sativa	Trimethoprim, sulfamethazine, chlortetracycline	Liu et al. (2009)
Panicum miliaceum	Sulphadimethoxine	Migliore et al. (1995)
Phragmites autralis	Ciprofloxacin, oxytetracycline	Liu et al. (2013)
Pistia stratiotes	Efficient degradation of organic pollutants and reduction of COD over 20% and removal of chlorides and sulphates	Di Luca et al. (2014) and Saha et al. (2015)
Ralstonia eutropha	4-chlorophenol	Hill et al. (1996)
Raphanus sativus	Enrofloxacin	Migliore et al. (1995)
Spinacia oleracea	Azithromycin, roxithromycin	Jones-Lepp et al. (2010)
Trapa natans	Cu, Hg	Mishra et al. (2013)
Typha domingensis Pers.	Zn and Cu	Cortes-Esquivel et al. (2012)
Vigna angularis	Sulfamethazine	Piotrowicz-Cieślak et al. (2010)

1. Membrane filtration system
2. Nanotechnology
3. Microbial fuel cells
4. Natural treatment system
5. Dry urine diverting toilets

9.10.1 Membrane Filtration System (MFS)

A membrane is a thin layer of semi-permeable material that separates substances when a driving force is applied across the membrane. MFS is used for removal of microorganisms and natural organic material, which can impart color, tastes, and odors to water and react with disinfectants to form disinfection byproducts. In Pharmaceutical industry MFS is used for cold sterilisation. Cold sterilization is a method of sterilization that requires the reusable semi-critical items to be immersed in EPA-approved liquid chemicals. These chemicals can include glutaraldehydes, peracetic acid, and hydrogen peroxide-based solutions. As advancements are made in membrane production and module design, capital and operating costs continue to decline. The membrane filtration processes includes microfiltration (0.03–10 μ), ultrafiltration (0.002–0.1 μ), nanofiltration (0.001 μ) and reverse osmosis.

9.10.2 Nanotechnology

Nanotechnology encompasses the creation of new materials and devices from nano-sized building blocks (Hu and Shaw 1998). Building blocks that are used to make nano molecules are arranged with dimensions of 1–100 nm. For improving the wastewater treatment and recycling processes, the use of nanomaterials is being researched to construct separation process (Bellona and Drewes 2007). Additionally, the use of nanomaterials for bioremediation and disinfection of wastewater is gaining popularity (Hu et al. 2005; Mohan and Pittman 2007). For instance, nanomaterials metal oxide (TiO_2) is tested successfully for their antimicrobial activity. Fullerenes (C60) as pollution tracers are being used to provide contaminant-fate information to assist in developing water remediation strategies. Magnetic nanoparticles are being developed to adsorb metals and organic compounds (Hillie et al. 2006). Various pharmaceutical pollutants such as phthalates, alkylphenols, bisphenol-A and many others could be removed by using nanofiltration membranes.

Table 9.9 List of nanomembranes and their processes

Membranes	Process
Nanofiltration membranes	It is a pressure-driven process wherein molecules and particles less than 0.5–1 nm are rejected by the membrane. It is characterized by a unique charge-based repulsion mechanism allowing the separation of various ions
Nanocomposite membranes	It comprises mixed matrix and surface-functionalized membranes. Mixed matrix use nanofillers that are embedded in a polymeric or inorganic oxide matrix. Nanofillers provides higher surface-to-mass ratio. Al_2O_3 and TiO_2 can help to increase the mechanical and thermal stability as well as permeate flux of polymeric membranes. The incorporation of zeolites improves the hydrophilicity of membranes resulting in raised water permeability. Antimicrobial nanoparticles (nanosilver, CNTs) and (photo)catalytic nanomaterials (bimetallic nanoparticles, TiO_2) are mainly used to increase resistance to fouling
Self-assembling membranes	It is an autonomous organization without human intervention. High-density cylindrical nanopores can be formed that way to be useful not only for nanofluidic devices but also for water filtration. Such membranes belonging to the category of ultrafiltration provide enhanced selectivity and permeate efficiency
Aquaporin-based nanomembranes	Aquaporins are pore-forming proteins and ubiquitous in living cells. Under certain conditions, they form highly selective water channels that are able to reject most ionic molecules. The combination of high water permeability and selective rejection make them an ideal material for creating novel high flux biomimetic membranes. This kind of membrane is able to withstand pressures up to 10 bar and allow a water flux >100 L

Nanofiltration membranes are used to produce effluent with low concentrations of pharmaceutical pollutants (Bruggen et al. 2008). Table 9.9 summarizes various nanomembranes and their processes.

9.10.3 Microbial Fuel Cells

Microbial fuel cells (MFCs) are promising technology for the treatment of pharmaceutical wastewaters (Mahendra and Mahavarkar 2013). It is a green approach for the utilization of wastewater for the generation of bioelectricity. Its great advantage is the direct conversion of organic waste into electricity. They have capability to recover bioenergy out of the wastewater, while limiting both the energy input and the excess sludge production (Rabaey and Verstraete 2005). MFC is just like a unique kind of battery or electrochemical cell, which contains two electrodes anode and cathode, separated by an ion exchange membrane (Fig. 9.6). On the anode side, bacteria grow and proliferate, forming biofilm (a dense cell aggregate) that adheres to the MFC's anode. During their microbial metabolism the bacteria act as catalysts for converting the organic substrate into CO_2 and H^+/e^-. Normally many bacteria

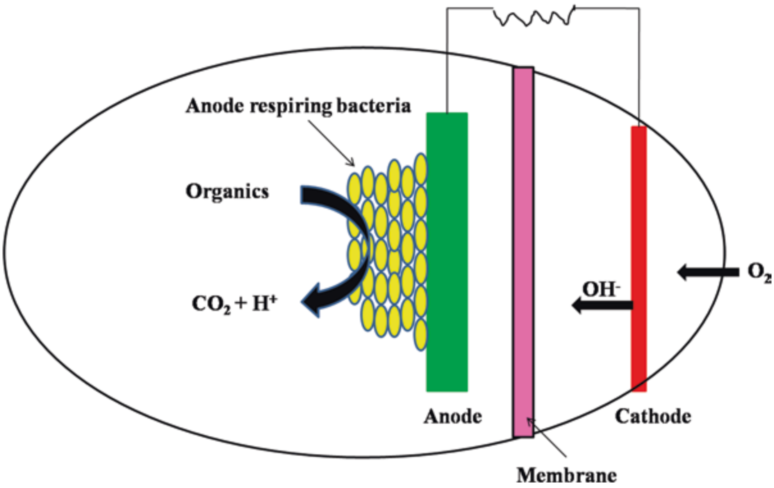

Fig. 9.6 Microbial fuel cell

use oxygen as a final electron acceptor, but in the anaerobic environment of the MFC, specialized bacteria that send the electrons to an insoluble electron acceptor means to MFC's anode. The anode-respiring bacteria are able to oxidize organic pollutants found in pharmaceutical wastewater and transfer the electrons to the anode. The scavenged electrons then flow through an electrical circuit and terminate at cathode of MFC, thus generating electricity. Ions are transported through the fuel cell's ion membrane, to maintain electroneutrality, although the membrane is often excluded. Therefore, MFC may perform double duty, targeting electrons from waste streams and converting them into useful energy. The performance of MFCs decreased with a decrease in the wastewater concentration. If electricity generation in these systems can be increased, MFC technology may provide a new method to counteract wastewater treatment plant operating cost, making wastewater treatment more affordable for both developing and developed nations. Thus, wastewater treatment along with production of electricity may help in saving money.

9.10.4 Natural Wastewater Treatment System

Natural treatment systems (NTS) are engineered system that has a minimal dependence on mechanical elements to support the wastewater treatment and recycling processes, instead using microorganism, plants, soil and other natural processes to degrade pharmaceutical wastewater pollutants. NTS cleans pharmaceutical wastewater in a sustainable form at low cost, low input manner and can be designed to have a long life. NTS are intended to treat wastewater that has already gone through primary or secondary treatment for providing further treatment, polishing and recycling. Some important processes that play a role in the NTS include bacterial decomposition, natural aeration, natural cooling (especially in night), nutrient uptake by plants, metal reduction through sedimentation, adsorption of metals to soils and filtration through gravel or other media. Five major types of NTS are commonly used:

1. Wetland treatment
2. Phytotreatment
3. Water quality trading
4. Indirect discharge
5. Wastewater pond systems

9.10.4.1 Wetland Treatment

Wetland treatment involves utilizing existing wetlands or constructing engineered wetlands to treat pharmaceutical wastewater. Many natural processes such as water uptake, microbial breakdown, passive cooling, sedimentation etc occur in wetlands can help to reduce common pollutants (TSS, BOD, COD, metals and temperature). Wetland used for wastewater treatment typically has a capacity to control flow direction, detention time, water level and rely totally on natural processes. There are two basic types of wetland treatment systems: free water surface (FWS) (Fig. 9.7) and vegetated submerged bed (VSB) wetlands (Fig. 9.8).

FWS visually resemble wetland that contains aquatic plants that grow in soil layer on bottom of wetland and water flow through the stems and leaves of plants. VSB do not resemble natural wetlands because they have no visible water instead they consist of a bed of media (crushed rock, small stones, sand or soil) which has been planted with aquatic plants. Wetland treatment may also provide additional community benefits including the creation and preservation of wildlife habitat, environmental education and recreation opportunities for hiking and bird watching.

9.10.4.2 Phytotreatment

Treatment of wastewater by using plants (rooted plants, floating aquatic plants and algae) is known as phytoremediation. In this treatment system effluent passes through a vegetated medium, allowing for further recycling of effluent. N and P in the wastewater are utilised as nutrients by plants. The plants uptake the treated wastewater and absorb the nutrients along with other pollutants such as metals. Further polishing occurs as the effluent filters through the soil medium in which the plants grow before flowing to ground or surface water. There are two major phototreatment systems: water recycling and tree farms.

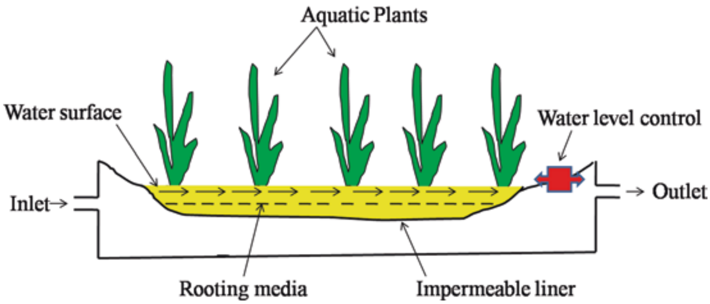

Fig. 9.7 Free water surface (FWS) wetland system

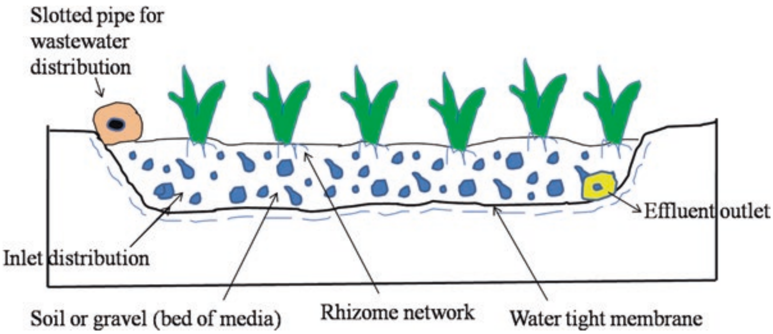

Fig. 9.8 Vegetated submerged bed (VSB) wetland system

Recycled treated wastewater can be used for:

- Irrigation on animal pasture, parks and playgrounds.
- Irrigation on orchards and vineyards.
- Industrial uses such as cooling, rock crushing, street sweeping, commercial car washing and dust control.

Tree farms treatment systems can be used to grow trees, such as poplars to absorb nutrients, reuse biosolids and grow woods.

9.10.4.3 Water Quality Trading (WQT)

WQT is a flexible approach to achieve water quality goals in cost effective manner with great environmental benefits. It can be used to balance a variety of pharmaceutical wastewater pollutants parameters such as temperature, nutrients etc. Sponsored committee can obtain pollution reduction credits by taking action to create or restore wetlands, streamside riparian areas, floodplains, aquatic habitat or other stream related areas. Thus, WQT can provide supplementary environmental benefits such as flood retention, riparian improvement and habitat.

9.10.4.4 Indirect Discharge (ID)

ID involve physical, chemical and biological treatment processes for further treatment of groundwater through the soil matrix before it reaches to the surface water. The soil matrix may be saturated all the time by infiltration, and the soil and associated microbial and chemical/physical activity further treats the wastewater. Systems that could be used for ID of treated pharmaceutical wastewater include:

- Rapid and moderate rate infiltration systems
- Constructed wetlands for evaporation/transpiration and minimal seepage
- Surface spray irrigation applied at greater than agronomic rates
- Exfiltration galleries, drainfields, mounds and bottomless sand filters
- Evaporation ponds with infiltration components
- Injection wells discharging above the water table

9.10.4.5 Wastewater Pond Systems (WPS)

Wastewater ponds are large ponds where wastewater is held for days or months. These ponds are designed to reproduce a natural pond, encouraging the growth of aerobic and anaerobic bacteria those may reduce BOD, TSS and pathogens levels. There are two main types of WPS:

1. **Facultative wastewater ponds:** This is used to treat raw industrial wastewater at primary or secondary treatment level (Fig. 9.9). They contain an aerobic layer of water overlaying an anaerobic layer. Aerobic bacteria provide odor control along with nutrient and BOD removal, while anaerobic bacteria aid in sludge digestion, denitrification and some BOD removal. The system relies on oxygen production by photosynthetic algae and/or reaeration at the surface to maintain the aerobic processes.
2. **Aerobic pond systems:** These are shallower ponds that maximize aerobic processes. Aerobic ponds are often adopted to improve effluent treatment High light penetration and good aeration at the surface allow aerobic bacteria to biochemically stabilize the wastewater (Fig. 9.10). Advantage of this system includes short detention time with low land and energy requirements. The disadvantage of this pond system is more complexity and the effluent may contain high levels of TSS if the algae are not removed prior to discharge.

9.10.5 Dry Urine-Diverting Toilets

Dry urine-diverting toilets neither pollute nor waste the water. The human waste is diverted, sanitised and recycled in a safer way. This approach is also called ecological sanitation or ecosan. For an adequate functioning of these kinds of toilets, system does not require a constant source of water. The design of a toilet makes it

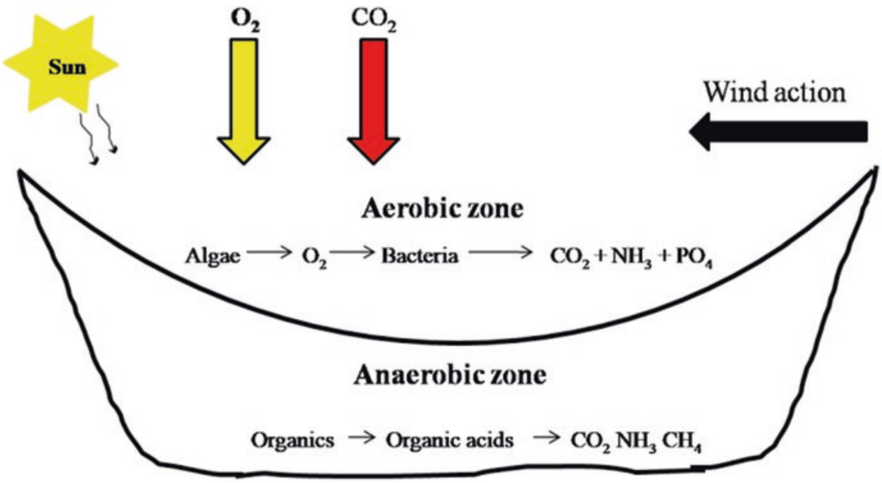

Fig. 9.9 Facultative wastewater ponds

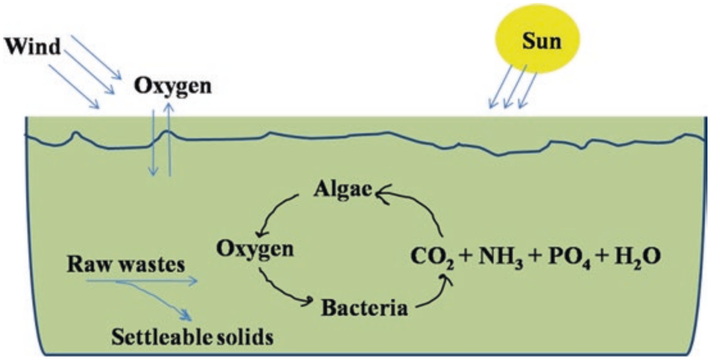

Fig. 9.10 Aerobic pond system

easily adaptable to different types of communities and can be assembled with cheap and locally produced materials.

Special toilets don't mix the urine and faeces (Fig. 9.11). Dry urine diverting toilets separate, collect, store and treat these two flows. Well-constructed and well-maintained urine-diverting toilets don't develop bad odors, nor attract flies. After sanitising the urine and faeces, these nutrients rich products are reused in agriculture or garden.

For better activity of dry urine diverting toilet, four things must be keep in mind that will assure that there will be no smell and the products can be adequate sanitised:

Fig. 9.11 Dry urine-diverting toilets

- The design of the toilet-slap assures urine does not touch the faeces.
- The faeces are led into a faeces chamber and are covered with prepared soil, ashes, lime and/or wood-flints.
- The chambers must be kept completely dry.
- Urine and faeces are always treated separately.

9.11 Environmental Benefits of Water Recycling

Water recycling decreases the diversion of water from responsive ecosystems. Other advantages of waste recycling include decreasing wastewater discharges and reducing pollution. Recycled water can also be used to create or enhance wetlands and riparian habitats. Some most important benefits of wastewater recycling are as:

9.11.1 Decrease Diversion of Freshwater from Sensitive Ecosystems

Plants, wildlife and fish depend on sufficient water flow to their habitats to live and reproduce. The lack of adequate flow, as a result of diversion for agricultural, urban, and industrial purposes, may cause drop of water quality and ecosystem health.

People who reuse water have demand of using recycled water for the environment and ecosystems health.

9.11.2 Decrease Wastewater Discharge to Active Water Bodies

In some cases, a driving force for water recycling does not come from water supply requirement but from a need to eliminate or decrease wastewater discharge to the ocean or a stream. By avoiding such conversion of salt water marsh to brackish marsh, the habitat for two endangered species can be protected.

9.11.3 Used to Create or Enhance Wetlands and Riparian Habitats

Wetlands provide many benefits including wildlife habitat, water quality improvement, flood diminishment and fisheries breeding grounds.

9.11.4 Reduce and Prevent Pollution

When pollutant discharge to water bodies is reduced, the pollutant loadings to these bodies are decreased. Application of recycled water for agricultural and landscape irrigation can provide an additional source of nutrients and natural sources of fertilizers.

9.11.5 Save Energy

As the demand for water increases, more water is treated and transported over large distances which can require a lot of energy. Recycling water reduces the energy need to move water longer distances or pump water from deep within an aquifer.

9.12 Future of Water Recycling

Water recycling has proven to be effective, essential and successful process in creating a reliable water supply without compromising public health. Nonpotable reuse is a widely acceptable practice that will continue to grow. However, in many parts of the developed countries, the usage of recycled water is increasing to accommodate environmental need and water supply demand. Recycling of wastewater requires far less energy than treating salt water using a desalination system.

While water recycling is vary cost effective and environmental sustainable approach, the wastewater treatment for reuse and the installation of distribution systems at centralized facilities can be initially expensive compared to such water supply alternatives as imported water, ground water or the use of gray water. Institutional barriers, as well as varying agency priorities and public misperception, can make it difficult to implement water recycling projects. Finally, early in the planning process, agencies must reach out to the public to address any concerns and to keep the public informed and involved in the planning processes. As water energy demand and environmental need grow, water recycling will play a big role to insure proper water supply. By working together to overcome problems, water recycling with its conservation can help us to sustainably manage our vital water resources. Communities and businesses are working together to meet the need of water supply locally in a way to expand the resources, support the environment and strengthen the economy.

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Chapter 10
Treatment and Recycling of Wastewater from Oil Refinery/Petroleum Industry

Shailja Singh and Shikha

Abstract Petroleum refinery effluents (PRE) are generally the wastes generated from industries primarily engaged in refining crude oil, manufacturing fuels, lubricants and petrochemical intermediates. These effluents or wastewater, generated, are considered as a major source of aquatic environmental pollution. The effluents are mainly composed of oil, grease and many other toxic organic compounds. The process of crude oil refining consumes large volume of water. Consequently, significant volume of wastewater is generated. The requirement of water depends upon on the size, crude products and complexity of operation. Petroleum refining units need water for distillation, desalting, thermal cracking, catalytic and treatment processes in order to produce useful products such as LPG (Liquefied Petroleum Gas), gasoline, asphalt, diesel, jet fuel, petroleum feedstock etc. Wastewater generated through petroleum refineries contains various hydrocarbons. It has been estimated that the demand for world oil is expected to rise to 107 mbpd (million barrels per day) in the next two decades. By 2030 oil will account for 32% of the world's energy supply. The increasing demand of oil clearly shows that effluents produced from the oil industry will continue to be produced and discharged into the water bodies. The pollutants found in the effluent are seriously toxic and hazardous to the environment. Techniques used for effluent treatment include adsorption, coagulation, chemical oxidation, biological techniques as well as contemporary technologies like membranes and microwave-assisted catalytic wet air oxidation and Advanced oxidation processes (AOP) like heterogeneous photo-catalytic degradation which is based on its potential to completely mineralize the organic effluents beside being cost effective, readily available and the catalyst used itself is non-toxic in nature. The review provides a detailed description on nature of effluent or wastewater produced from the oil refinery units, its discharge into the water bodies, toxicological effects of the effluent on terrestrial and aquatic ecosystem and the various treatment technologies designed for the treatment and recycling of wastewater generated during operation.

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R. L. Singh, R. P. Singh (eds.), *Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future*, Applied Environmental Science and Engineering for a Sustainable Future,
https://doi.org/10.1007/978-981-13-1468-1_10

Keywords Oil refinery · Petroleum industry · Petrochemical intermediates · Advanced oxidation processes (AOP) · Crude oil refining

10.1 Introduction

PRE commonly known, as the petroleum refinery effluents are the wastes that are originated primarily from the industries engaged in crude oil refining and fuel manufacturing, lubricants and other petrochemical based products (Harry 1995). These effluents are considered as one of the most prominent source of aquatic environmental pollution (Wake 2005). Oil and grease along with the other toxic organic compounds are the main components of effluent. However, efforts have been done to replace the fossil fuels with alternatives, yet the crude oil remained to be the most important raw material for various processes. The need to satisfy the increasing demand of global energy, which is expected to increase by 44% over the next two decades (Doggett and Rascoe 2009), has made the crude oil processing and the PRE generation, a major global problem.

The process involved in crude oil refining requires large amount of water. Consequently, the wastewater is generated in higher volume (Coelho et al. 2006). Coelho et al. (2006) investigated that the volume of PRE generated during processing is 0.4–1.6 times the amount of the crude oil that is being processed. On the basis of the present yield of 84 mbpd (million barrels per day) of crude oil, the total of 33.6 mbpd of effluent reported to be generated globally (Doggett and Rascoe 2009). Over the next two decades, the demand for the world oil is expected to increase to 107 mbpd, and oil will account for 32% of the world's energy supply by 2030. The biofuels such as ethanol and biodiesel are expected to account for 5.9 mbpd by 2030. The contribution from other form of renewable energy sources viz., wind and solar power have been estimated to be 4–15% (Doggett and Rascoe 2009; Marcilly 2003). The data clearly revealed that effluents produced from the oil industry will continue to be produced and discharged into the main water bodies. Pollutants that are found in the effluent are known to cause serious toxic hazards to the environment. Petroleum refinery effluents vary depending upon the oil type being processed, the plant's configuration, and procedures followed during the operation (Saien and Nejati 2007). It enters into waterways system and adversely affects the water quality.

The present chapter gives a detailed analysis for the composition and characteristics of petroleum refinery effluent or wastewater, environmental damage caused by the PRE, methods and steps involved in the treatment of the wastewater being discharged from the oil refinery and certain new techniques developed to deal with wastewater for improved treatment.

10.2 Refinery Water Overview

Oil refineries are the complicated system of many operations, which depends upon the crude types and the products that are desired. All the refineries are not alike because of the different procedure followed and the type of crude being processed. Petroleum refineries are the large consumer of water, in comparison to other industries depending upon the basis of size, crude, products and complexity of operations. Within a refinery, the water network is unique system like its processes.

10.3 Overall Refinery Water Balance

Water is used in many processes of petroleum refinery. However, not every process needs raw or treated water. Water can be reused in many places (Fig. 10.1). In petroleum refinery water in large proportion can be continually recycled. Some amount of water gets lost in the atmosphere, including steam losses and cooling tower evaporation and drift. Water in smaller quantity can also leave with the products. Some specific process requires a continuous supply of water to the operation such as steam generating systems or cooling water systems. The knowledge of water balance and requirement for a refinery is an important step towards optimizing usage of water recycle and reuse as well as optimizing performance of water and wastewater treatment systems.

Different sources of water for oil refinery are as follows (IPIECA 2010):

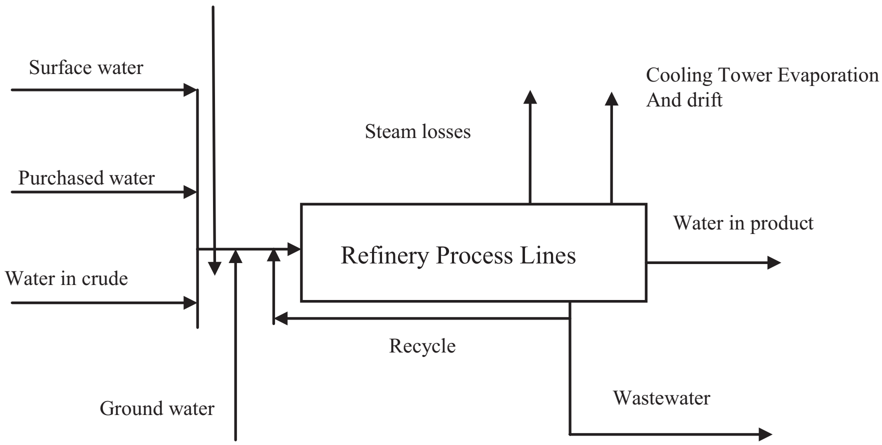

Fig. 10.1 Refinery water balance

10.3.1 Surface Water

Surface water is termed as water required for the refinery that can be supplied from various surface water sources like rivers or lakes. Sometimes the water may be supplied from sea or any other brackish water sources.

10.3.2 Purchased Water

It includes water, which is supplied by municipality. They usually provide potable water but they could also offer treated effluent for industrial purpose.

10.3.3 Water in Crude

When the crude is brought to the refinery it possesses some entrained water that has been remained from the oil well extraction process or pickup during transshipment. The water is removed from the crude as storage tank bottom sediment and water and then it is transferred for wastewater treatment.

10.4 Characteristics of Wastewater from Refineries

Various chemical processes like distillation, cracking, polymerization, alkylation, coking and hydro treating are being used in refining process of crude oil in petroleum refineries in order to convert oil unto many products. In each and every process wastewater is generated per day in the refinery. Based upon generation of polluted wastewater, it is divided into two types: process and non-process wastewater.

The process wastewater are basically produced during refining step where the hydrocarbons have been in direct contact with itself while that of non-process wastewater is generated from equipment flushing, cooling tower (Benyahia et al. 2006). Usually, the stream of the process and non-process wastewater are separated for accomplishing the treatment in the best way and to prevent the contamination of large amount of water with that of dangerous pollutants.

Water that is present in the crude oil is responsible for the production of process wastewater during the refining process of crude oil. Water could be present in emulsified form with the oil in the well from where it is extracted (Valles et al. 2013). The production of process wastewater is also due to water vapor, which is used as stripping medium or like diluents in processes such as distillation. The other reason is that liquid water is being used in units of desalting (IPIECA 2010). The composition of process wastewater includes inorganic substances, oil and some other toxic organic compounds. Among these pollutant oil and grease are considered as group of organic compounds and it is a source of several other toxic compounds found in refinery wastewater like phenols, polyaromatic hydrocarbons (PAH) and benzene. Oil is considered hydrophobic but its nature of phase depends upon the various conditions of the environment, for example, under anaerobic conditions oil gets hydrolyzed into acetate. The pollutants that are present in the wastewater generally depend on type of oil used for refining, plant's configuration and the other processes being used in the installation steps (Saien and Nejati 2007). For example, in distillation or cracking units water vapor is required, so in these units water vapor gets condensed in environment which contain hydrocarbons like hydrogen sulphide and ammonia, so the produced wastewater possess such compounds in high concentration. When cokes are utilized in installation it generates wastewater, which has high concentration of phenols and cyanides. Various refineries' processes and their possible pollutants found in wastewater are as follows:

Isomerization – Isomerization process generate caustic wash water, which is calcium chloride and Sour water, which contain ammonia and hydrogen sulfide.

Fluid catalytic cracking – Fluid catalytic process produces sour water (ammonia, cyanides, hydrogen sulfide, oil, phenols suspended solids).

Alkylation – In alkylation process spent potassium hydroxide stream (hydrofluoric acid) are produced.

Crude desalting – Crude salting generates desalting wastewater, which contains ammonia, hydrogen sulfide, metals, phenol salts and solids

Catalytic hydrocracking – Sour water, which consists of ammonia, suspended solids and hydrogen sulfide, are produced.

Coking – It produces sour water which possess hydrogen sulfide, ammonia and suspended solids.

Distillation – Distillation produces sour water (ammonia, chlorides, phenol, hydrogen sulfide, mercaptans and suspended solids.

Catalytic hydro treating – Catalytic hydro treating produces sour water that contains suspended solids, hydrogen sulfide and phenol.

Lubricating oil manufacture – Steam stripping wastewater (oil and solvents) and solvent recovery wastewater (oil and propane) are produced while lubricating oil manufacture.

Sulfur removal – Removal of sulfur produces sour water, which has ammonia and hydrogen sulfide)

Catalytic reforming – Catalytic reforming generates sour water (ammonia, hydrogen sulfide, mercaptans, oil, suspended solids,)

Thermal cracking – Thermal cracking generates sour water, which primarily contains dissolved solids, hydrogen sulfide, ammonia, phenol and suspended solids.

10.5 Effects on the Environment

The area surrounding the oil refinery is generally have a low diversity and abundance of fauna owing to the reason that several species are unable to survive near the effluent producing source (McLusky and Martins 1998). The effluent discharged from the refinery contains many toxic inorganic and organic compounds among which phenols are very toxic for humans. Phenols if consumed in small concentrations could harm greatly. Chronic toxicity occurs due to phenols. They are known to cause diarrhea, mouth souring, vision impairment and dark urine problem in human. It also shows its toxic effects over aquatic fauna (Kulkarni and Kaware 2013). The effluent discharged contains such compounds, which easily get soluble in water and act as precursors for the formation of many other compounds that are toxic in nature (El-Naas et al. 2010). Benzene, toluene, ethylbenzene and xylenes (BTEX) are the compounds, which are commonly the part of crude oil. Such compounds get absorbed via skin when person is exposed to showering with water polluted or ingested with the contaminated water. Certain other effects that occur due to benzene consumption in drinking water for long time are anemia, decrement in blood platelets and even it could cause cancer. If ethyl benzene is consumed, liver or kidney failure could occur. The health effects that are caused by toluene are same as ethyl benzene but it is also responsible for affecting the nervous system of a person. Also, the consumption of xylene causes damage to the nervous system (USEPA 2013).

Field surveys have revealed that the effluents exert impact on growth of organisms, which live in proximation to refinery outlets for effluent discharge. The organisms are smaller than others that are further away from the oil refinery unit. Many studies conducted have clearly shown the toxic effect of the effluent, which could be observed as impoverished area that surrounds the refinery discharge. In such area no fauna is found or if some of the pollution tolerant species are present, they are low in diversity. Size of impact area varies on the basis of effluent and the site from where it is discharged. The density of invertebrate normally increases with the distance from the site of discharge. The enrichment effect could be seen as rise in biomass or its abundance. The reason behind high biomass is presence of one species that is commonly found in proximation to the impoverished area. It confirms the species, abundance and biomass (SAB) relationship where the peak of opportunistic species is found within a few hundred meters of the source (Pearson and Rosenberg 1978).

10.6 Effects on Aquatic Ecosystem

Wastewater discharged into aquatic bodies is harmful for aquatic life because it contains oil and grease. The formation of layer of oil over the surface of water decreases the penetration of light and results in reduction of photosynthetic activity and oxygen production. Due to this layer dissolution of oxygen decreases from atmosphere into the water, thus influencing the amount of dissolved oxygen present and affects the number of species that survive under such conditions. Environmental health is disturbed because of the compounds present in water contaminated with oil. They show detrimental effect for aquatic life. Moreover, they are carcinogenic and mutagenic (Alade et al. 2011). The contaminants present in wastewater being discharged from refineries, which are hazardous for life, are: suspended solids, phenols, benzene, ethyl benzene, xylenes, sulphides, ammonia, poly aromatic hydrocarbons and chemical oxygen demand (IPIECA 2010; Ishak et al. 2012). Polycyclic aromatic hydrocarbons (PAH) are normally found in crude oil. PAH undergo biodegradation slowly under the aerobic conditions in aquatic environments. Degradation process of the compounds decreases with increase in number of aromatic ring. PAH persist in the environment from 100 days to a couple of years. If all such compounds are discharged continuously in the water body, they could deteriorate the health of the ecosystem. These compounds are lipid soluble, so they easily get stored in fat of certain animals, which are then consumed by humans. Some PAH had shown to have carcinogenic and genotoxic effects in mice (WHO 2003).

Ammonia found in surface water in high concentrations can cause dangerous effects on the aquatic life, like reduction of oxygen in fish's blood. The toxicity effects on animals vary depending upon the various parameters like temperature and pH as this would help to alter the molecule's oxidation state (USEPA 2013). Exposure to nitrates and nitrites for long period of time causes hemorrhage of spleen and encourage the oxygen's displacement in blood (USEPA 2006). Hydrogen sulfide is known as corrosive gas, which is toxic in nature. It is formed in aqueous environment that have sulphate as well as organic matter. This gas is considered highly toxic for the aquatic life, even when it is present in very small concentrations, and causes obnoxious odors, which in turn affect the surrounding atmosphere (Altas and Buyukgungor 2008).

Wake (2005) had reported that the refinery effluents at different concentrations are toxic for invertebrates, fish and algae. The area around the refinery where the effluents were being discharged had shown a low diversity of fauna because of the harsh environment created by these discharges. The increase in the organic chemicals, like ammonia in the water can lead to enrichment of algae and biomass. The pollutant content of refinery effluent depends on the operations that are performed and the crude oil being treated. Effects of these pollutants to the environment are different for each case.

10.7 Selection of Oil/Water Separation Technologies

Wastewater stream of petroleum industry contains oil in various forms:

Free oil: The oil is in the form of separate oil globules of sufficient size and referred to as floating oil (Mohr et al. 1998). Free oil can be removed either by skimming the surface in the skim tank or by performing gravity separation (Yokogawa Corporation of America 2008).

Emulsified oil: Such type of oil is found in form of very small droplets or globules, having diameter of approx. 20 mm or less. In water it can form stable suspension. According to the API, gravity cannot separate a true emulsion. According to Mohr et al. (1998), designing of enhanced gravity separators is possible in order to treat waters containing such type of oil for small flow rates. The oil from the wastewater can be separated by the addition of chemicals to reduce the pH followed by incorporation of dissolved oxygen or nitrogen to eliminate the emulsified oil (Yokogawa Corporation of America 2008).

Dissolved oil: Such type of oil is not found in the form of droplets. It occurs in the form true molecular solution within water, which cannot be eliminated by gravity separation method. Dissolved oil can be removed by using biological treatment methods, adsorption technique by utilizing activated carbon or other adsorbents, or absorbents (Mohr et al. 1998; Yokogawa Corporation of America 2008).

It is crucial to know information about the distribution of oil-droplet size in petroleum industry wastewater in order to determine the proper oil water separation system and its efficiency. According to Benyahia et al. (2006) certain technologies like API separator, corrugated plate interceptor (CPI) separator, upflow sandfilters, induced gas flotation (IGF), dissolved air flotation (DAF), and filters have been proved effective in removing oil-droplet of size approximately larger than 150, 40–270, 2–270, 10–100, 5–100 and 5–30 mm, respectively. According to Arthur et al. (2005), particles or droplets of minimum size 150, 40, 25, 3–5, 10–15, 5, 5, 2, and 0.01 mm could be removed by API separator, CPI separator, IGF (no flocculants), IGF (with flocculants), hydrocyclone, mesh coalescer, media filter, centrifuge, and membrane filter, respectively.

The factors that are considered for the proper selection and designing of oil-water separation systems are as follows:

- Sources of oil in wastewater
- Characteristics of the oil
- Concentration of the suspended solids and oil in the raw wastewater
- Presence and concentration of oil-wetted solids
- Temperature that affects the size and type of selected oil-water separator,
- Temperature and pH that influence the material selection for oil-water separation equipment
- The impact of oil on the equipment of downstream-treatment

The selection of oil-water separation system is based on the parameters such as BOD, COD, TSS, TKN, ammonia, etc., and on the ultimate wastewater-treatment discharge requirements for oil concentration. For example, if effluent requires the removal of BOD or COD and installation of a biological-treatment system then this could impact the selection of the oil-water (Schultz 2007).

10.8 Treatment Technology

Treatment of oily wastewater is important before discharging it into the environment because its high organic and mineral content may severely pollute the coastal waters, rivers, estuaries, the seashore, soil and groundwater (Uan 2013). Wastewater, which comes out from refineries, cannot be directly discharged into aquatic bodies. It requires primary, secondary and tertiary treatment process in order to remove the pollutant load present in it (Fig. 10.2).

With the help of primary treatment process, the settleable and floating material present in the wastewater like suspended solids and oil can be removed using physical and chemical operations. During secondary treatment process all the dissolved pollutants are removed from water by chemical/biological processes. By tertiary treatment the effluent is subjected to various processes so that it can meet the different final discharge standards (Bagajewicz 2000). Oily wastewater treatment is classified as follows (Benyahia et al. 2006; European Commission and Joint Research Center 2013; U.S. EPA 1995; IPIECA 2010; Jafarinejad 2015; Goldblatt et al. 2014):

- Process wastewater pretreatment
- Primary treatment
- Secondary treatment
- Tertiary treatment or polishing

10.8.1 Process Wastewater Pretreatment

In certain cases the wastewater generation from some units of the petroleum industry requires pretreatment before discharging it for wastewater treatment (IPIECA 2010). Certain practices that are being used in the petroleum industry as pretreatment are as follows:

- Neutralization is done to maintain the pH of the wastewater to meet the desired range for discharge and to establish the proper conditions before oxidation-

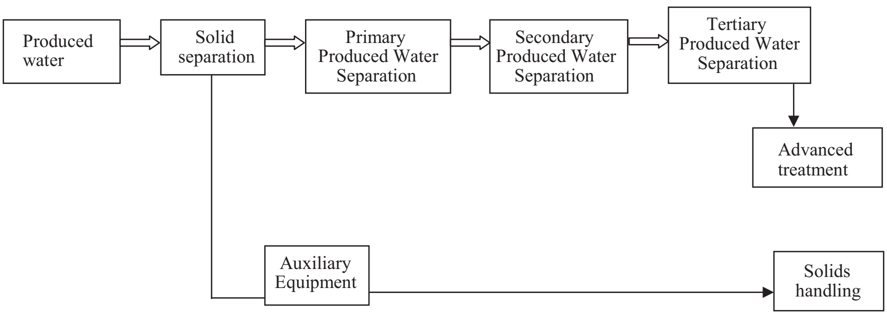

Fig. 10.2 Different treatment stages of wastewater

reduction chemical reaction, better adsorption, precipitation of heavy metals as hydroxides and at last for proper clarification.

- Emulsion breaking is done for some oil-water mixtures using chemicals like wetting agents in a tank with agitator(s), coagulants, skimmers, flocculants.
- Desalter oil-water separation is done using a separation tank and sending the oil which is in skimmed form to refinery slopes and solids to the sludge treatment plant or the coker unit (IPIECA 2010).
- Recovery and reduction of hydrocarbons from the wastewater at different source like at nitrogen or air stripping process for benzene recovery from wastewater, high pressure wet air oxidation process (>20 barg) to convert sulfur-containing substances into sulfates, and amines and nitriles to molecular nitrogen, low-pressure oxidation (<20 barg), liquid-liquid extraction from wastewaters for extraction of phenol from wastewater (European Commission and Joint Research Center 2013).
- Stripping of sourwater (European Commission and Joint Research Center 2013; IPIECA 2010).

10.8.2 Primary Treatment

The primary treatment of wastewater is a important step as it allows the effective and prolong use of secondary treatment unit. In this step the heterogeneous components found in the effluent like suspended solids (SS), solid particles, suspended solid and immiscible liquids, are reduced significantly (Renault et al. 2009). This is basically done mechanically by using gravity in API separators or separation tanks. If the primary treatment of wastewater is not performed then the presence of salts and sulphide can greatly interrupt the subsequent biological operation (Demirci et al. 1997; Altas and Buyukgungor 2008). Colloids as well as dispersion also generate problem and damage the equipment during the preceding stage (Renault et al. 2009). The mechanical step is generally followed by the physiochemical step, where heavy metal concentration is reduced and small-sized suspended solids are further decreased by agglomeration into large-sized particles so that removal could occur easily by sedimentation, filtration or floatation (El-Naas et al. 2009). The primary treatment process basically consists of oil/water separator where oil, water and solids are separated from each other. This process is followed by secondary separation process in which dissolved air flotation (DAF) or induced air flotation (IAF) unit is used.

10.8.2.1 First Stage: Separation (Oil/Water Separators, API Separators)

In API separators refinery wastewater is treated, which possess oil and oil-bearing sludge. In separators due to difference specific gravity heavier material settled below the lighter liquids. Hydrocarbons are skimmed off that float over the surface, while the sludge is periodically removed that settles to the bottom of the separator. In API separator, firstly wastewater is collected in the pretreatment chamber, which allows the removal of sludge. A diffusion barrier present in it allows the wastewater to run down the separator towards the outlet while the lighter fractions of oil are skimmed off. Sometimes flights and scrapers are used to remove heavier solids. For preventing the oil from escaping into outlet section, underflow baffle plates are generally used. Parts that form API separators are as follows:

1. Chain and flight scraper
2. Adjustable overflow weir
3. Flow distributors (vertical rods)
4. Oil layer
5. Slotted pipe skimmer
6. Oil retention baffles
7. Sludge sump
8. Trash trap (inclined rods)

API separators are effective in separating three phases (oil, solids and water) that are normally present in wastewater of oil refineries. There are some of the refineries that make use of CPI (corrugated plate interceptors) or PPI (parallel plate separators). Both PPI and CPI separators are smaller in size than a comparable API. They both require less plot space. Such devices are very useful as two-phase separators (water and oil) but they are not much effective when a third phase (solids) is present. The solids that are found in refinery wastewater foul and plug the equipment so it require frequent maintenance and cleaning (IPIECA 2010).

10.8.2.2 Secondary Oil/Water Separation

The refinery effluent from the primary separation step is then further sent for the removal of fine solids and oil either to DAF unit or an IAF unit. The choice of opting DAF or an IAF unit is specific to refineries. It needs to be evaluated on the basis of influent conditions and the required outlet conditions.

Dissolved Air Flotation (DAF)

In a DAF system the first step is flocculation/coagulation. Stabilization of the dispersed particles (oil/solids) is done by negative electric charges on their surfaces, which cause them to repel each other. Since this prevents the collision of charged particles to form larger masses, called as flocs. They do not settle. Chemical coagulation and flocculation techniques are being used for assisting the removal of colloidal particles from suspension. These processes, which are done usually in sequence, are the combination of chemical and physical procedures. Chemicals are usually mixed with wastewater to encourage the aggregation of the suspended solids into large particles that are enough to settle down or be removed easily. A part of the effluent is recycled in a DAF system, which is then pressurized and saturated with air and then mixed with incoming feed. During the depressurization of recycled stream the air bubbles are released, which attach themselves to any free oil/solids present in the feed and float them on the surface of the vessel. The floating material is then skimmed off and transferred to the refinery slops after further dewatering. Some solids are settled down to the bottom of the DAF where they are periodically removed (Schultz 2007).

Induced Air Flotation (IAF)
In induced air flotation unit, using a rotor-disperser mechanism encourages the air. The spinning rotor acts like a pump and it forces the fluid through the disperser opening, which then generate vacuum in the standpipe. Vacuum that is generated in the standpipe draws the air and merges it with the liquid. The liquid then move past the series of cells before it leaves the unit and the float passes over the weir on one or both sides of the unit. Merits of the IAF technique is due to its compact size, low capital cost and effective removal of free oil and suspended materials (Schultz 2007). IAF unit include the following parts:

1. Motor
2. Agitator mechanism
3. Froth Crowder
4. Radial Launder
5. Single Concentrate Launder
6. Mixing Baffle
7. Semi circular feed box
8. Disperser hood
9. Disperser
10. Rotor
11. Tank bevels
12. Hybrid draft tube
13. False bottom

10.8.3 Secondary Treatment

In this treatment process, dissolved oil and other for of organic pollutants are consumed by microorganisms which then oxidize organic matter into simpler products such as H_2O, CH_4 and CO_2 under aerobic, semi aerobic or anaerobic conditions (U.S. EPA 1995). The carbon, nitrogen and phosphorus (C:N:P) ratio of 100:5:1 is sufficient for the growth of microorganisms (Ishak et al. 2012). Biological treatment is widely accepted as a wastewater treatment technology for the removal of dissolved organic compounds in the oil refining industry. Generally, the biological treatment is classified into two categories:

- Suspended growth processes
- Attached growth processes

10.8.3.1 Suspended Growth Processes

Suspended growth process is a biological treatment process where the microorganisms are mixed thoroughly with organics in the liquid, and then it is maintained as suspension in the liquid. Microorganisms use organic part as food for their growth and metabolism and clump together to form an active biomass. Activated sludge process is the most commonly practiced suspended growth process that is used in the treatment of oil refinery wastewater.

Activated Sludge

Activated sludge process is known as the most effective technique of all the biological systems available (Fig. 10.3). It is utilized in many oil refineries across the globe and is considered as one of the reliable method under biological treatment process. Activated sludge is a continuous suspension of aerobic biological growths in a wastewater containing entrapped suspended colloidal, dissolved organic and inorganic materials. The microorganisms use the organic material as a carbon source and energy for the microbial growth, and convert the food into cell tissue, water and oxidized products (mainly CO_2) (IPIECA 2010; Ishak et al. 2012).

In activated sludge process, the refinery wastewater enters the aeration tank where the microorganisms are brought in direct contact with organic pollutants of the wastewater. Injection of air is done continuously into the system in order to keep the sludge in aerobic condition and to maintain the concentration of solids in suspension. The mixture of sludge and wastewater in the aeration tank is termed as the 'mixed liquor'. The biomass present in the mixed liquor is referred to as MLSS (mixed liquor suspended solids). In a typical refinery wastewater treatment system, the MLSS is composed of 70–90% active MLVSS and 10–30% inert solids. The incoming refinery wastewater enters into the aeration tank where it comes in contact with microorganisms and air. From the aeration tank the effluent is transferred to the

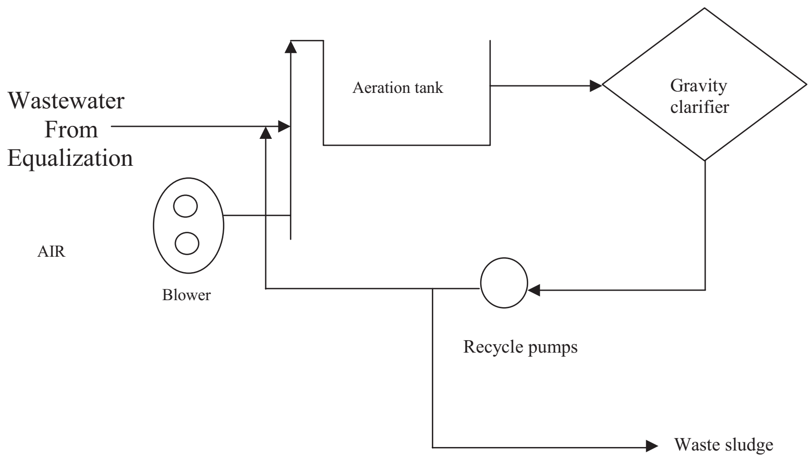

Fig. 10.3 Activated sludge process

clarifier. The organic pollutant found in the wastewater gets transformed into the biomass and then it gets separated in the clarifier. A small portion of the concentrated sludge, which is referred to as 'return activated sludge (RAS), from the clarifier is recycled back and then mixed with the incoming wastewater, and the remaining of the sludge is released as 'waste activated sludge (WAS) (Ishak et al. 2012).

Activated Sludge Treatment with Powdered Activated Carbon

Both for of activated carbon that is, powdered activated carbon (PAC) and granular activated carbon (GAC) has been utilized for a longer period of time for water and wastewater treatment because it has large surface area for adsorption (Jafarinejad 2015). The diameter of powdered activated carbon is less than 200mesh (Tri 2002). Treatment of activated sludge with PAC resembles the conventional activated sludge process, but in this process, PAC is added to the aeration tank or mixed liquor. The removal of contaminants is achieved and enhanced by a combining the biodegradation and adsorption technique (IPIECA 2010; Tri 2002). The PACT process is generally used for those petroleum industries where strict standards for wastewater must be met for certain contaminants (IPIECA 2010). According to Tri (2002), the PACT process can generally remove organic pollutants more efficiently than the biodegradation or adsorption process alone.

Sequencing Batch Reactor

The sequencing batch reactor (SBR) is known as an alternative semi-batch biological treatment method that makes use of aeration, sedimentation as well as clarification in a single reactor. The unit processes like aeration and sedimentation are same for both the SBR and activated sludge systems. In activated sludge systems different basins are used for the unit operations, while in the SBR a common basin is used for the operations in a sequential order. SBR technology has limited usage in refinery wastewater treatment (Metcalf and Eddy 1991; Gurtekin 2014; U.S. EPA 1999).

The various steps of operation are described below (Metcalf and Eddy 1991):

Fill: During this step, wastewater along with the substrate is transferred to the reactor. The aeration system is not activated because the reactor is filled with wastewater from the equalization tank.

React: During this step, aeration of wastewater is done in the same way as performed in the activated sludge system. Biological activity is started in this phase of operation.

Settle: In this step, aeration is discontinued and MLSS is allowed to settle down. The settling is completed under quiescent conditions. During the settle period no flow nor enters or withdraw from the reactor.

Decant: During decant process; the treated supernatant effluent is withdrawn out from the upper portion of reactor. At the bottom of the reactor the sludge blanket is maintained so that it is easily available as seed sludge for the next cycle.

Idle: This is not important step and is generally not performed for the wastewater treatment system of oil refineries. The idle period can be defined as the time between draw and fill; it can be zero or can be days. Normally, this process is used in multi-tank systems, so that enough time could be provided to one reactor in order to complete its fill phase before getting switched over to another unit.

Membrane Bioreactor Technology
Membrane bioreactors (MBRs) are defined as a suspended growth biological treatment process (Fig. 10.4). Membrane bioreactor combines the membrane process (e.g. microfiltration) with that of a suspended growth bioreactor, so that secondary clarification can be eliminated which is used in an activated sludge system.

Aerated Lagoons
In this system, wastewater is treated in earthen in-ground basin, which is used for both the aeration and settling functions. To promote the biological treatment air is injected through mechanical or diffused aeration units in the lagoon. Aerated lagoons are of usually two types:

Aerobic lagoons In aerobic lagoons, the basic criterion is to maintain the dissolved oxygen throughout the basins. For such system, settling can take place at a portion of the pond, which is separated by baffles. Separate settling of sludge and disposal facilities might be required. The settled sludge is periodically removed.

Aerobic-anaerobic/facultative lagoons In such types of lagoons, maintenance of oxygen is required in the upper layer of the liquid in basin and the rest of the lagoon remains in anaerobic condition. A small portion of suspended solids is transferred to the downstream part of the lagoon where its settling takes place and finally undergoes anaerobic decomposition.

Aerated lagoons generally require much larger area of plot than other treatment methods. They are commonly used where land area is not much expensive or when discharge standards are not very restrictive. With the current strict effluent standards faced by the oil refining industry, aerated lagoons are not used frequently for treatment of wastewater in refineries because they could not produce the comparable quality of effluent to activated sludge systems.

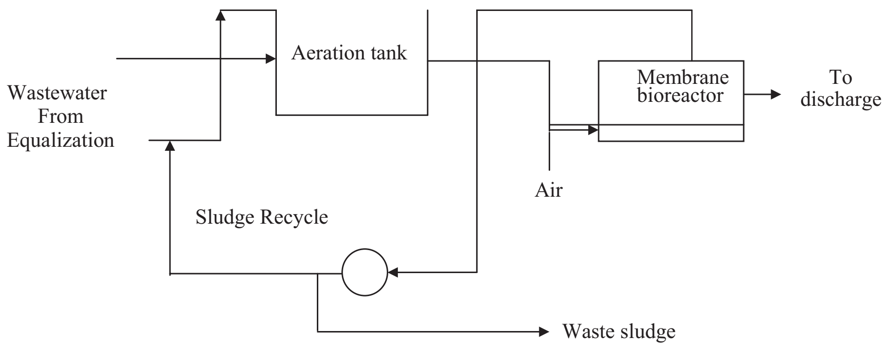

Fig. 10.4 Membrane bioreactor system

10.8.3.2 Attached Growth Process

In attached growth process, microorganisms grow over the packing material that is kept into the reactor. This material is basically made up of plastic, rock, gravel or other synthetic material. Examples of such type of process are trickling filters and rotating biological contactors (IPIECA 2010).

(a) **Trickling filter system**

The trickling filter system includes:

- a bed of packed material like rock or plastic packing on which, the continuous distribution of wastewater can be done.
- under drain system for carrying the treated water to different units
- distributors for the distribution of influent wastewater to the surface of filter bed

A layer of microorganisms develops over the packing in trickling filter. As wastewater is passed through the trickling filter bed, the microorganisms biodegrade the organic matter, which is to be removed from the liquid that is flowing over the packing material. Final clarifier, which is located immediately downstream of the filter, serves to eliminate microbial growths that is periodically shed from the filter media (IPIECA 2010).

(b) **Rotating biological contactor**

In this system the microorganisms are attached to form a layer of biological mass on large diameter discs where a central horizontal shaft rotates the discs, thereby exposing the biofilm to the wastewater and to the atmosphere sequentially. The basic element of the rotating biological contactor (RBC) is composed of closely spaced plastic discs, which is mounted on a horizontal shaft. The disc material is made up of polystyrene or polyvinyl chloride. The plastic discs are submerged in wastewater and the horizontal shaft through an air driven motor rotates them continuously. Microorganisms adhere themselves to the plastic surface and a layer is formed of biological mass (slime) over the discs. Over time, the excess of sludge is shed from the discs. As the discs rotate, the adhered microorganisms react with the pollutants in the wastewater and convert them into the biomass and CO_2 (Suzuki and Yamaya 2005; EPA 1997; Ishak et al. 2012). Relatively low consumption of energy, simple maintenance and operation, and successive treatment of influent contaminants are some of the merits of RBC systems (Suzuki and Yamaya 2005). Moreover, the need for additional aerators is eliminated due to oxygen-transfer facilitation in the system by the rotating discs (Chavan and Mukherji 2008).

Suzuki and Yamaya (2005) had designed a single-stage RBC consisting of biodrum to remove hydrocarbons present in wastewater coming from industrial discharges at 25 °C and at pH 7.0 in a batch mode. The biodrum is a cylindrical mesh drum, which is filled with random packing of polyurethane foam cubes that retain petroleum-degrading achlorophyllous microalga *Prototheca zopfii* cells. The amount of algal cells, immobilized in the 1 cm^3 pieces, was greater than the pieces of smaller pore size under the experimental conditions studied. They concluded that the rate of removal for n-alkanes (C_{14}, C_{15}, and C_{16}) in the RBC with biodrum system was significantly higher as compared to those RBC systems with polycarbonate biodisk. The RBC's efficiency to treat the wastewater from a petrochemical industry that produced acrylonitrile in a laboratory scale was investigated. At hydraulic loading of 0.011 m^3/m^2/day, the removal efficiencies for cyanide, COD, BOD_5, and NH_4OH were greater than 99%, 95.2%, 99.1%, and 77%, respectively. They also reported that the COD/nitrogen (N) ratio did not affect removal of cyanide, whereas the substrate/cyanide ratio affected the performance of the process, with more than 99% cyanide removal achieved at a ratio of 20/1.

Chavan and Mukherji (2008) performed an investigation on the consortium of phototrophic microorganisms and a bacterium that developed over the discs of an RBC for treatment of wastewater that contained diesel oil. Oil-degrading bacterium, *Burkholderia cepacia*, and oil-tolerant phototrophic microorganisms was fed to the reactor. The residual diesel in the effluent was found to be 0.003%. They reported the advantages of this system, which include Total petroleum hydrocarbon (TPH) removal, good settleability of biosolids and no soluble-carbon source requirement. The nitrogen/phosphorus (N/P) ratio influenced the relative dominance of the phototrophic microorganisms and bacterial culture, which was a key factor in determining the efficient performance of the reactor. The studies suggested that the RBC system could be the feasible technology for the treatment of oily wastewater from the oil/petroleum industry. The feasibility of coupling RBC with PBSS (porous biomass support system) using polyurethane foam as a porous supporting media to biodegrade oil/petroleum refinery wastewater on a laboratory scale has also been reported. For all of the hydraulic loadings, the removal efficiency of total COD and oil were above 80%. Ammonia nitrogen and phenol removal were above 90% and 80%, respectively. They concluded that this system could be used effectively for practical purposes with moderate hydraulic loading rates.

(c) **Nitrification, or nitrification with denitrification**

At some refinery site the wastewater is required to meet the ammonia or nitrogen limits. Then the biological treatment system includes either nitrification (by the use of nitrifying bacteria) or a combination of nitrification/denitrification step. Avoiding the discharges of spent amines and proper removal of ammonia in the sour water stripper can control the concentration of nitrogen compounds in refinery wastewater. If the level of nitrogen compounds is still high to meet regulatory limits, then nitrification or nitrification/denitrification should be performed in the biological treatment system. Nitrification is the term, which is used to describe the two-step biological process where ammonia is oxidized to nitrite and then the nitrite is oxidized to nitrate. Nitrification is basically the biological oxidation of ammonia to nitrite (e.g., with Nitrosomonas bacteria), which is then followed, by oxidation of the nitrite to nitrate (e.g., with Nitrobacter).

$$2NH_4^+ + 3O_2 \xrightarrow{\text{Nitrifying bacteria such as Nitrosomonas}} 2NO_2^- + 2H_2O + 4H^+$$

$$2NO_2^- + O_2 \xrightarrow{\text{Nitrifying bacteria such as Nitrobacter}} 2NO_3^-$$

In denitrification process, the nitrate is reduced to form nitric oxide, nitrous oxide and nitrogen gas. Two types of arrangement system are used in this process. In the first system, an anoxic tank where denitrification occurs follows the aeration/nitrification tank. A food source (typically methanol) is added to this tank to help the process. In the second system, the aeration/nitrification tank follows the anoxic tank. In this case, the food source for the anoxic tank is the BOD of the incoming wastewater. A portion of treated wastewater from the aeration tank is recycled back so that the nitrates reduction in the effluent could occur (EPA 1997; European Commission and Joint Research Center 2013).

10.8.4 Recent Research Approaches in Biological Treatment of Oily Wastewater

10.8.4.1 Treatment of Oil Refinery Wastewater by Bacteria

The usage of microorganisms for the treatment of oily wastewater has shown some good and effective results recently. In many cases microbial consortia has been utilized to remove hazardous contaminants in oily wastewater. The biological treatment of oily wastewater has not been very much well developed because of the diverse nature and behavior of microbes under various environmental conditions. The recent research activities in this particular area have shown notable removal of contaminants from oily wastewater. Song et al. (2011) made the combination of the whole-cell lipase with *Yarrowia lipolytica* and a fungal lipase for treating oily wastewater. Results showed that during whole-cell treatment for 72 h, 96.9% of oil and 97.6% of COD was removed. However, when only *Y. lipolytica* was added, 87.1% of oil and 91.8% of COD was removed. In addition to this, in the control system where no cells were incorporated, 45.1% of oil and 67.5% of COD was removed in 72 h.

Immobilized triacylglycerin lipase has been utilized for the removing oil and grease from synthetic oily wastewater. It has been shown that around 48% of oil and grease and 47% of COD were removed by using 0.3 g/L of immobilized triacylglycerin lipase (Dumore and Mukhopadhyay 2012). According to Tang et al. (2012) Bio-Amp may be used for the treatment of grease trap wastewater, which contained fat, oil and grease. The results revealed the 40% removal of fat, oil and grease after the adding commercial bio-additive. In addition to this COD, total nitrogen, total phosphorous and total fatty acids were found to be decreased by 39%, 33%, 56%, and 59% respectively.

Pseudixanthomonas sp. RN402 has been reported to degrade crude oil, diesel oil, n-hexadecane and n-tetradecane by Nopcharoenkul et al. (2013). The results demonstrated that RN402 strain was efficient in degrading approximately 89% of diesel oil, 65% of n-hexadecane and 92% of n-tetradecane 83% of crude oil. Co-digestion of pig manure and residues for the pretreatment of waste vegetable oil was investigated by Hidalgo et al. (2013). It was revealed that oily vegetable waste could be treated by co-digestion of substrates that contained high levels of ammonium-nitrogen and alkalinity without any addition of chemicals. Polyurethane foam (PUF)-immobilized *Gordonia* sp. JC11 has been utilized by Chanthamalee et al. (2013) for treating bilge water. PUF-immobilized bacteria worked more efficiently in removing oil than indigenous bacteria and were able to remove 40–50% of boat lubricant. Shokrollahzadeh et al. (2008) investigated the treatment of petrochemical wastewater by using an activated sludge treatment which contained 67 aerobic bacteria like *Pseudomonas*, *Comamonas*, *Acidovorax*, *Flovobacterium*, *Cytophaga*, *Sphingomonas* and *Acinetobacter* genera. The results obtained revealed that the activated sludge treatment removed 80% of total hydrocarbons 89% of COD, 99% of ethylene dichloride, and 92% of vinyl chloride. It has been found that pretreatment of for oily wastewater by utilizing a group of immobilized microorganisms; B350M and B350, in a pair of biological aerated filter (BAF) reactors may ease the degradation process. The biodegradation process was operated for a period of 142 days with 4 h hydraulic retention time (HRT). The results indicated that B350 and B350M were efficient in treatment of oily wastewater. They demonstrated that the reactor with immobilized B350M showed a mean degradation efficiency of 78% for total organic carbon and 95% for oil. In addition, B350 degraded 64% of total organic carbon and 86% of oil (Zhao et al. 2006).

The comparison of biodegradation of crude oil by aerobic microbiota from the Pampo Sul Oil Field (sample P1) to the natural biodegraded oil (sample P2) was performed by Da-Cruz et al. (2008). Use of ion chromatograms was made to monitor the biodegradation of sample P1 for 60 days. The results showed the degradation of C_8–C_{12} n-alkanes and isoprenoids, including pristine and phytane, by the day 60. Khondee et al. (2012) made use of an internal loop airlift bioreactor which contained chitosan immobilized-*Sphingobium* sp. P2 for the treatment of oily lubricants in wastewater. The chitosan-immobilized bacteria showed great efficiency in removing automotive lubricants from synthetic and carwash wastewater. In semi-continuous batch experiments, they removed 80–90% of the 200 mg/L total hydrocarbons from both synthetic as well as carwash wastewater. Biological aerated filter (BAF) process was used by Xie et al. (2007) to treat polluted oily wastewater under optimal conditions of 1 h HRT, 5:1 volume flow ratio of air/water, and with a backwashing cycle of 4–7 days. The results revealed that the average removal efficiency of COD, oil pollutants, and suspended solids was found to be 84.5%, 94%, and 83.4%, respectively. Santo et al. (2013) treated petroleum refinery wastewaters using biological treatment by activated sludge. The results indicated the removal of 94–95% COD, 85–87% total organic carbon, and 98–99% total suspended solids. An upflow anaerobic sludge blanket bioreactor was designed by Rastegar et al. (2011) for the optimization of petroleum refinery effluent treatment. The results obtained indicated that when the system was operating at HRT of 48 h, the removal of COD was 81%. The rate of biogas production increased with the increase of HRT. Batch adsorption tests were performed by Ibrahim et al. (2012) for petroleum wastewater using biosorbents. They investigated the effect of contact time and pH on the removal of emulsified oil in wastewater. Their results revealed that the percentage of oil removal reached its maximum removal of more than 90% at pH 6–8.

10.8.4.2 Treatment of Oil Refinery Wastewater by Algae

The usage of algae for treatment of waste water is a known idea. Many researchers have developed the techniques for exploiting the fast growth of algae and its capacity for removing nutrient. The removal of nutrient is basically an effect of assimilation of nutrients as the algae grow, but other nutrient stripping phenomena also occur e.g. ammonia volatization and phosphorous precipitation as a result of high pH induced by the algae (Hammouda and Raouf 1994). Some reports revealed that a large part approximately 90% of the phosphorous removal is due to this effect (Doran and Boyle 1979; Mesple et al. 1996; Proulx et al. 1994). The researchers are taking advantage of the algae's appetite for chemical nutrients to clean the waste water from the refinery water, removing noxious chemicals – including 90% of the ammonia nitrogen and 97% of the phosphorus. At a Chevron oil refinery in Hawaii, researchers have grown microalgae in a 5000l photobioreactor, flowing wastewater from the refinery through the reactor. The researchers have successfully removed noxious chemicals, including 90% of the ammonianitrogen and 97% of the phosphorus. As the microbes feed, they grow and multiply, providing a wealth of algal-based biomass for the production of bioenergy and high value biobased chemicals and special products. The bioreactor contains a mixed microbial consortium that is enriched for *Scenedesmus* algal species. The authors have also described the experiments evaluating the ability of *Chlorella* and *Scenedesmus* to degrade some of the pollutants from petroleum based industries.

10.8.4.3 Treatment of Oil Refinery Wastewater by Fungi

Biodegradation by microorganisms shows one of the primary mechanisms by which petroleum wastewater and other hydrocarbon pollutants can be removed from the environment (Okoh 2003). In bioremediation, degradation of toxic pollutants is carried out either by intracellular accumulation or via the enzymatic transformation to less or nontoxic compounds (Brar et al. 2006). However, it has been experimented that single cultures of fungi are better than the mixed cultures (Okerentugba and Ezeronye 2003) and more recently, fungi have been found to be better degraders of petroleum than traditional bioremediation techniques including bacteria (Batelle 2000). Diverse fungal cultures have been investigated recently for bioremediation processes. Filamentous fungi play an major role in degrading petroleum hydrocarbons by producing capable enzymes because of their aggressive growth, greater production of biomass and extensive growth of hyphae in the soil, fungi offer potential for biodegradation technology (Saadoun 2002) The high surface -to-cell ratio of filamentous fungi makes them better degraders under certain niches. It is fungi that can especially handle breaking down some of the largest molecules present in nature (Fernández-Luqueño et al. 2010). Some fungi exude extracellular enzymes which allow for digestion of energy sources in their surroundings and further towards the fungus (Mai et al. 2004). *Aspergillus niger* is a haploid filamentous fungi and is a very essential microorganism in the field of biology. The fungi is most commonly found in mesophilic environments such as decaying vegetation or soil, plants and enclosed air environment (Wu et al. 2000).

10.8.5 Tertiary Treatment

Tertiary treatment or polishing refers to any treatment that takes place downstream of the secondary treatment plant for obtaining a very high-quality effluent to meet discharge limits (U.S. EPA 1995; Goldblatt et al. 2014). Tertiary treatment needs to be considered if the refinery needs to meet stringent limits for different contaminants such as (U.S. EPA 1995; Goldblatt et al. 2014):

- Trace organics such Polyaromatic hydrocarbons (PAHs)
- Dissolved and suspended metals
- Chemical oxygen demand (COD)
- Total suspended solids (TSS)

Tertiary treatment consists of techniques that help in meeting discharge standards and remove all the remaining compounds that could not be eliminated through primary and secondary treatment. Examples of tertiary techniques include activated carbon filters, oxidation processes, granular filtration and membrane filtration. With these units, total suspended solids, chemical oxygen demand and other non- biodegradable compounds such as dissolved metals and PAH can be removed from the wastewater (IPIECA 2010).

10.8.5.1 Sand Filtration

The effluent after biological treatment system still contains about 25–80 mg/l of suspended solids depending upon the operation conditions in the clarifier. Refineries at various locations need to meet the limits as low as 15 mg/l on a consistent basis. Under such condition, one option for the effluent treatment is using sand filters. This process involves passing the wastewater through a filter bed that is composed of filter media. Dual media filters are also used which comprise of a layer of anthracite over sand. The anthracite traps the larger particles and the finer solids are held up in the sand. The forward flow is stopped and the filter is backwashed to eliminate the trapped solids periodically (Bush 1980).

10.8.5.2 Activated Carbon

Dissolved organic constituents from the refinery wastewater can be removed by carbon adsorption. The activated carbon is basically applied as effluent ‘polishing’ step (removal of residual organics) for wastewater that has been processed in a biological treatment system. This is because the use of carbon will be prohibitively high if it is applied to the refinery wastewater. In this process wastewater is passed though the bed of granular activated carbon (GAC) where the organics present in the wastewater are adsorbed by the carbon. The carbon bed is regenerated periodically to remove the organics from the exhausted carbon (Bush 1980; Pombo et al. 2011; Okiel et al. 2011).

10.8.5.3 Chemical Oxidation

Chemical oxidation process in a refinery is normally used for reducing residual COD, trace organic compounds and non-biodegradable compounds. It is not commonly found in a refinery wastewater treatment plant. The following oxidation reagents are generally used in a chemical oxidation system (IPIECA 2010):

- Ozone
- Hydrogen peroxide
- Chlorine dioxide

Chemical oxidation could be enhanced in some cases by the utilizing UV light as a catalyst, but this needs evaluation on a case-by-case basis.

The overall process which involves primary, secondary and tertiary treatment is done for the treatment of wastewater generated from oil refinery industry. Various agencies such as Central pollution control board (CPCB), India, European protection agency (EPA), World Bank have defined standards for discharging the treated wastewater into the aquatic water bodies. The industries follow guidelines according to the standards provided. In Indian CPCB standard is followed for discharging the effluent (Table 10.1).

Table 10.1 Standard according to CPCB

Parameter	Standard
$BOD_{3\ days\ 27\ °C}$	15.0 mg/l
COD	125.0 mg/l
pH	6.0–8.5
Phenols	0.35 mg/l
Ammonia	15 mg/l
Sulphides	0.5 mg/l
Phosphorus	3.0 mg/l
Oil and grease	5.0 mg/l
Chromium (hexavalent)	0.1 mg/l
Chromium (total)	2.0 mg/l
Lead	0.1 mg/l
Zinc	5.0 mg/l
Nickel	1.0 mg/l

10.9 Emerging Technologies in Treatment of Wastewater

10.9.1 Treatment via Hybrid Technologies

The integration of different oily wastewater treatment technologies, with the purpose of observing the overall impact of the combined technologies on the removal efficiencies of pollutants, has also been investigated. The removal of oily compound of Pars Oil Refinery wastewater was done using dissolved air floatation (DAF) system and active sludge reactor and clarifier (ASR). It was analyzed that the physical treatment and DAF, removed 27.8%, 49% and 29.7%, of BOD, COD and oil respectively. In addition to this, the biological treatment, ASR, removed 73.4% and 84.7% of COD and BOD respectively. This suggested that the biological methods of treatment had great efficiency in the removal of COD and BOD (Otadi et al. 2011). DAF treatment technology was further improved by the application of acidification and coagulation for the treatment of biodiesel wastewater. It was found that DAF alone or DAF with acidification were not efficient in the treatment of biodiesel wastewater, yet the DAF technology improved with acidification and coagulation achieved additional removal of oil and grease by 10%, giving total removal of 85–95% (Rattanapan et al. 2011). The combination of acidification, electrocoagulation, and biomethanization were found to be more efficient than acidification, coagulation, flocculation, and biomethanization for the treatment of biodiesel wastewater. The results obtained revealed that the combination of acidification, electrocoagulation, and biomethanization removed 99% of COD, however, acidification, coagulation, flocculation, and biomethanization removed 94% of COD.

10.9.2 Treatment via Adsorption and Ultraviolet Radiation

For the treatment of oily wastewater certain innovative technologies using adsorption technique and ultraviolet radiation have been developed. The crude oil with an initial concentration of 0.5–30 g/l was adsorbed by the hydrogel of chitosan based polyacrylamide which was prepared by radiation induced graft polymerization. A new technology of cotton-based hydrogel nanocomposite prepared by free-radical graft copolymerization of acrylamide and acrylonitrile onto fabric followed by insertion of Ag nanoparticles was developed. The nanocomposite displayed super hydrophilic and superhydrophobic properties. The ultrasound dispersed nanoscale zerovalent iron (NZVI) had been developed for the treatment of petroleum refinery wastewater. The influence of NZVI dosage and initial pH on COD removal percentage was studied. The optimum initial pH was found to be 5 and the optimum dosage of NZVI was 0.15 g/L (Rasheed et al. 2011). A new pretreatment system that was based on TiO_2 and vacuum ultraviolet irradiation (185 nm) for the treatment of oily wastewater had been discovered. The best conditions for the system were found to be 10 min irradiation at pH 7, flow rate of air 40 L/h, initial COD 3981 mg/L, and TiO2 150 mg/L. Natural minerals were also used to destabilize emulsions. The natural minerals that were used for the study consisted of artificial zeolite, bentonite, natural zeolite, diatomite, and natural soil. It was reported that at pH 1 and 60 °C emulsions were destabilized to form floating oils after the addition of natural minerals, and could be recycled easily. In addition the removal percent of COD was over 90% (Yuan et al. 2011). The catalytic ozonation of heavy oil refining wastewater (HORW) over activated carbon supported iron oxides catalysts using activated carbon (AC) as the reference has been investigated. The catalyst was characterized by chemical analysis, XRD, N_2 adsorption–desorption and SEM. A significant increase in COD removal efficiency was observed in FAC^+ ozone compared with AC $^+$ ozone due to more hydroxyl radicals, identified by tert-butyl alcohol (TBA). The composition analysis of organic pollutant in HORW by FT-ICR MS discovered organic pollutants chain scission and oxidation process during the treatment. A great improvement of biodegradability for treated HORW had been obtained. The investigation revealed the catalytic potential of FAC catalysts for ozonation of HORW (Chen et al. 2013). The performance of employing Fenton's reagent in the solar photo-catalyst of TiO_2 to treat petroleum wastewater from Sohar oil Refinery, Oman had been investigating. A central composite design (CCD) with response surface methodology (RSM) is applied to evaluate the relationships between operating variables, such as TiO_2 and Fenton dosage, pH, and reaction time, to identify the optimum operating conditions. Quadratic models for the following three responses prove to be significant with very low probabilities (<0.0001): chemical oxygen demand (COD), total organic carbon (TOC) and residual iron (Fe). The obtained optimum conditions included a reaction time of 90 min, 0.66 g/L TiO_2, 0.5 g/L H_2O_2, 0.01 g/L $Fe^{2+,}$ and pH 4.18. TOC and COD removal rates are 62% and 50%, respectively, and 0.8 ppm residual iron was obtained. The predictions correspond well with experimental results (TOC and COD removal rates of 64%, and 48%, respectively, and 0.5 ppm residual iron). The solar photo-Fenton process has well efficient for petroleum wastewater treatment in acidic conditions pH <7 and more economic by free energy (Aljuboury et al. 2015).

10.9.3 Electrocoagulation

Electrocoagulation is a simple and efficient treatment method involving the electro dissolution of sacrificial anodes and formation of hydroxo-metal products as coagulants, while the simultaneous production of hydrogen at the cathode facilitates the pollutant removal by flotation. Electrocoagulation treatment is particularly effective for destabilization of oil-in-water emulsions by neutralizing charges and bonding oil pollutants to generated flocs and hydrogen bubbles. The development of electro coagulation technologies provided a promising alternative for oil removal from wastewater (An et al. 2016).

10.9.4 Treatment via New Hollow Fiber Membrane

A new hollow fiber membrane was fabricated for the treatment of industrial wastewater in Al-Daura refinery in Baghdad using the submerged membrane bioreactor (MBR) technique with a new membrane-type module. The hollow fiber characterization seems to be within the range of ultrafiltration membranes, and the fabricated hollow fibers have a skinless porous outer surface. The effects of mixed liquor suspended solids (MLSS) concentration (i.e., 500 and 1000 mg/l) and preheating temperatures of the effluent wastewater (i.e., 25, 45, and 55 °C) at different preheating periods (i.e., 15, 30, and 45 min) on the performance of MBR and removal efficiency of COD, BOD, oil content, phenol, and turbidity were investigated. It was found that the removal efficiency of COD, BOD, oil content, phenol, and turbidity were enhanced by increasing of MLSS concentration. This efficiency was significantly enlarged by applying different preheating temperatures and times. For example, at 45 min preheating time, the removal efficiency of COD, BOD, oil content, and phenol at 1000 mg/l, and 55 °C were measured to be 71%, 60% and 100%, respectively. In fact, the obtained results confirmed that the initial wastewater preheating followed by the submerged MBR can be offered a possibility of alternative process for oily wastewater treatment, especially when reuse of oily wastewater is taken into account (Alsalhy et al. 2016).

10.10 Comparative Analysis of Different Oily Wastewater Treatment Methods

Several oily wastewater treatment methods are being used currently but the percent of oil removal varies among them. The assessment of the most efficient technology depends on number of considerations including the quality of influent, the treatment cost, the environmental footprint, and the energy consumption. According to Al-Ani (2012), a combined technology that consists of flotation and filtration-adsorption units is the most effective method in the treatment of oily wastewater from an old processing plant of the North Oil Company. The Overall removal efficiencies of oil and grease, TDS, COD, and TSS were found to be 99.9%, 89.4%, 99.2%, and 99.5% respectively. Fakhru'l-Razi et al. (2009) advised that the biological pretreatment of oily wastewater can be cost effective and environmentally friendly, and it is appropriate to combine it with a physical treatment, like membrane filtration for better treatment. Zhu et al. (2014) proved that the most efficient treatment for oily wastewater treatment is membrane technology, including polymer-dominated membranes, nanomaterial-based advanced membranes, and ceramic membranes, because of their greater separation efficiency and easy operation. Energy consumption is another parameter used to assess the efficiency of oily wastewater treatment technologies. The better option for lowering energy consumption is to combine the oily wastewater technologies with the use of renewable energy. According to Ho et al.

(2014), renewable energy technologies are energy-saving techniques that can reduce the consumption of energy by 20% in wastewater treatment. Ho et al. (2014) indicated that solar energy and biogas are applicable in treatment of wastewater. The solar energy source may have capacity to cover 40% of electricity consumption and biogas can produce 40% of the electricity required. Renewable energy sources could help in reduction of carbon dioxide emission with lower treatment cost. Ho et al. (2014) also indicated that an annual CO_2 emission reduction of 7000–9100 tons could be achieved with a flow capacity of 100,000 m^3/day, leading to reduction of adverse impacts on the environment.

10.11 Recycling and Reuse of Wastewater

The water is important aspect of life. The wastewater generated from oil refineries could be used after treatment for several other purposes. There are opportunities for reusing oily wastewater in steam boilers or recycling it in injection wells for the enhancement of crude oil exploitation. There are also the opportunities for the sale of the oil concentrate from oily water treatment to oil recycling companies. A great amount of oily wastewater is discharged into the environment by industries. Now days, there has been a continuous review of regulatory limits for oily wastewater discharge into the environment in many countries. In China, for example, with a population of 1.36 billion people, the maximum allowable limit for recycling wastewater, as required by the China Department of Petroleum, is 2 mg/L oil and suspended solids for reuse in boiler inlets, and 10 mg/L of oil and 5 mg/L of suspended solids for recycling into injection wells (Zeng et al. 2007). Thus, efforts toward achieving optimal treatment in terms of the quality of treated oily wastewater for reuse or recycling remain a challenging task (Tir and Moulai-Mostefa 2008; Zouboulis and Avranas 2000). The work is being done in this field for exploring better ways of recycling and reusing wastewater generated from oil refineries.

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Chapter 11
Treatment and Recycling of Wastewater from Beverages/The Soft Drink Bottling Industry

Minal Garg

Abstract Water being the essential natural resources on earth is primarily required in domestic, agricultural and industrial sectors. Soft drink/beverage industries consume huge amount of fresh water as one of the essential ingredients and therefore, lead to waste water generation in large quantity. Major contributors for freshwater loss in beverage industry include washing of bottles, cleaning of machines and equipment, production line losses, filtration wastes and raw material wastes. These activities contaminate the discharged water with phosphates, nitrates, sodium, organic substances, suspended particles, increased BOD (biological oxygen demand), COD (chemical oxygen demand), high pH, thereby make it unfit for its reuse. Improved waste management is an hour of need for sustainable future and is based on the principle of 3Rs: reduce, reuse and recycle. The current chapter provides an overview on the major waste water generating activities in soft drink industries/breweries. Cost effective waste water treatment/management practices/strategies to reutilize and save fresh water resource thereby reduce pollution loads are some of the major challenges that require detailed investigation.

Keywords Beverages · Brewery industry · Waste water · Waste water treatment · Water management

11.1 Introduction

Water is one of the essential natural resources on earth and almost all the spheres of life including agricultural, domestic and industrial sectors are heavily dependent on it. Deterioration in its quality and its scarcity are posing global threat to aquatic and terrestrial life, sustainable human livelihoods, livestocks and environment. Growing urban population particularly in developing countries put lot of pressure to land and water resources. Some of the other important factors responsible for its depletion

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R. L. Singh, R. P. Singh (eds.), *Advances in Biological Treatment of Industrial Waste Water and their Recycling for a Sustainable Future*, Applied Environmental Science and Engineering for a Sustainable Future,
https://doi.org/10.1007/978-981-13-1468-1_11

and deterioration include drastic climate changes and the developing economy of nation. Moreover, these factors result in growing volumes of waste water. Judicial use of water, reutilization and recycling of waste water is highly recommended in order to prevent our earth from heading towards water stress condition. Moreover, processes and systems which are heavily dependent on fresh water use should be subjected to strict environmental legislations in order to meet the growing needs for fresh water (Alam et al. 2007).

Significant industrial growth over few decades is not only putting lot of pressure on water resources but also contributing environmental pollution by discharging contaminated effluents directly into rivers and drains. Increased consumers' demand for beverages revolutionize brewery industry and led the manufacturers produce and develop an ever – increasing wide variety of drinks/beverages. Preservation of flavor and nutritional value of the beverages became possible due to advancements in the pasteurization/sterilization and refrigeration techniques and this took the production of beverages to newer heights year by year. Major revolution in terms of beverages consumption was realized in twentieth century. Better transport system allowed the wide distribution and thereby drastically increased the global sale of drinks.

Beverage industries (wineries, distilleries, breweries and soft drink manufactures) supply variety of beverages ranging from alcoholic (molasses, winery, spirits) to non-alcoholic (fruit juices, soft drinks, diet soft drinks, vegetable juices, mineral water, flavored water, coffee, tea). Production processes consume large amount of fresh water globally. Beverage industries are recently being emerged as one of the leading contributors to produce waste water in large quantity. Increased activities in beverage industries result in not only the discharge of high strength/contaminated water but also lead to the depletion of natural water resource and thereby pose serious threat to the environment (Daufin et al. 2006).

Lack of finances, space, technical assistance and trained skill are few of the constraints being faced by the industries which deprive them from installing the functional waste water treatment plants. This makes implementation of efficient treatment strategies and appropriate waste water management some of the biggest challenges in today's world. Better water management, cleaner production processes and waste water minimization under stringent environmental regulations may help in maximizing the economical and ecological benefits.

This chapter discusses the generation and discharge of waste water during various production processes in beverage industries and its quality characteristics. This chapter further provides an in-depth knowledge on the various possible effective strategies to treat, reutilize and recycle the beverage industry waste water under stringent international discharge standards framed by regulatory bodies.

11.2 Beverage Industries

Global analysis of beverages intake for 187 countries reveal significant consumption trends. As per survey, sweetened beverages' consumption has been found to be highest in Caribbean population and lowest in East Asia with the highest average intake of 3.4 servings per day (Singh et al. 2015).

According to Chicago based Euromonitor International, the recent global sale of soft drink as a major non- alcoholic beverage has increased from 3% in 2014 to 6% to reach $867.4 billion. Although America is still the world's largest market in soft drink sale, but China, Mexico and Brazil are also growing strong in terms of values and volumes. Asia Pacific and Middle East Africa are the other two leaders who continue to drive overall volume growth. According to Technavio's market research investigation and analysis, the global market of alcoholic beverages is expected to grow at a CAGR (compound annual growth rate) of above 2% by 2020. One of the primary drivers of this market is identified as the increased demand for premium alcoholic beverages and its use is considered to be more of a status symbol. Beer dominates the alcoholic drinks and accounts of the 75% market share. Research analysts estimate that the market of alcoholic drinks would be dominated by Europe, the Middle East and Africa and the total market share is expected to reach 48% by 2020. Figure 11.1 provides an estimate on percent distribution of global sales of beverages (alcoholic and non-alcoholic) by region in the past 5 years.

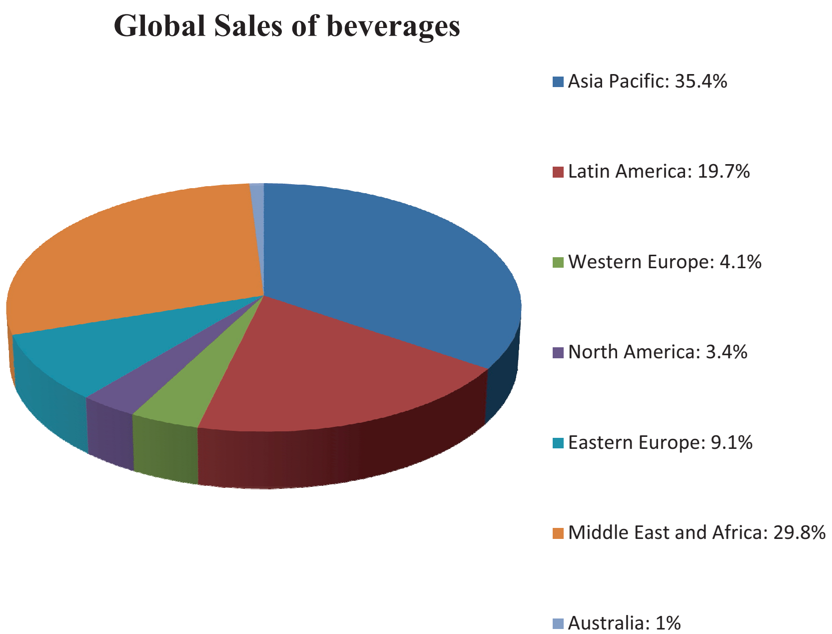

Fig. 11.1 Worldwide global sales of beverages

Market survey analysis observes increasing trends for the worldwide per capita consumption of beverages. However, according to executives and business experts, the beverage industry is heading towards biggest changes in the upcoming years. Companies are moving towards some of the dramatic changes in the world of beverages and these include:

- Instead of solely focusing on regular carbonated soft drinks, big companies are keener to develop more healthy beverages.
- Substantial investment on Research and Development sector by the companies which will facilitate bringing the new products in the market.
- Production of healthy beverages: Healthy beverages will take the center stage. Products like an organic Gatorade and new Aquafina flavored waters emphasize more on positive health benefits are more likely to be launched.
- Recipe revamp: Reformulations of recipe for the existing drinks, for example, removal of aspartame from Diet Coke is in pipeline.
- Cutting down Calories: American Beverage Association (ABA) pledged in 2014 to cut calories by 20% by 2025 by serving smaller cans/bottles and switching consumers to low – calorie drinks. This target can be achieved without cutting necessarily sugar from the recipe.

Demonization of sugar is considered as one of biggest enemies of beverage industries. Owing to the poor health effects of traditional beverages, brewery is eager to humanize itself by launching vintage – inspired sodas like 1893 and Dewshine, non-GMO (genetically modified) labeled Tropicana etc. The rise in such craft beverages not only provides companies a big chance to cash in but also confer ripple effect on the pricing as well as significance of acquisitions in case of non – alcoholic beverages. Naturally sweetened, herb infused, gluten-free alcoholic drinks with the drastic decrease in calorie (less than one-third amount of calories compared to the regular ones) are in high demand and are likely to hit the market in the years to come. Government regulatory bodies are encouraging the promotion of customized, unique, healthier foods and beverage options especially for children and the effort in this area by the brewery sector is a welcome move (Jean 2017).

Due to presence of local and international vendors, rise in consumption of drinks, increased demand for new flavors and health conscious drinks, the beverage market has become highly competitive and constantly experiencing the competition in terms of product type and its price. The statistics for the global beverage sales share during the past 5 years worldwide according to beverage type is shown in Fig. 11.2. The site https://www.statista.com/statistics/232773/forecast-for-global-beverage-sales-by-beverage-type can be referred for the present statistics.

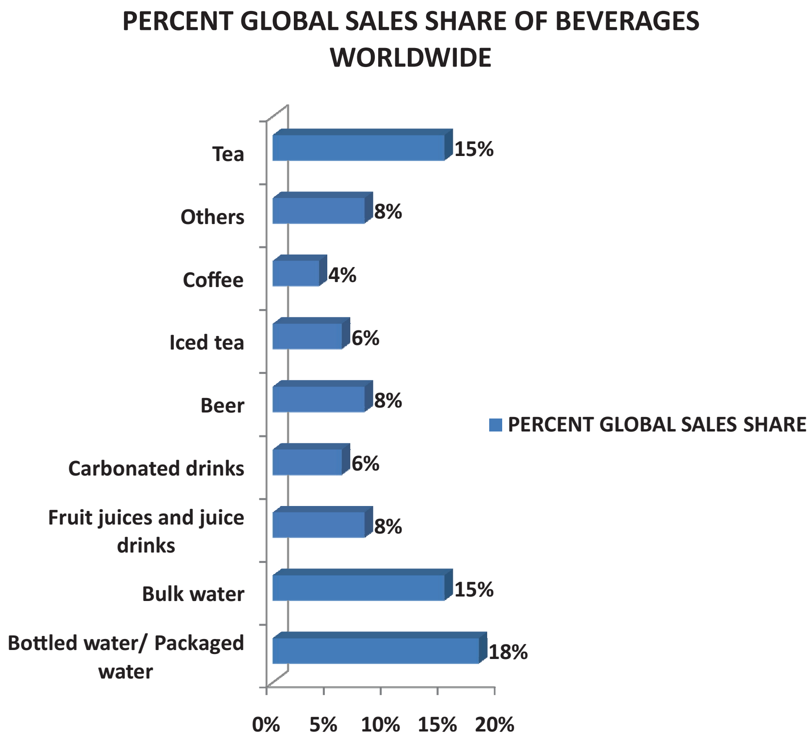

Fig. 11.2 Global sales share of alcoholic and non-alcoholic beverages

11.3 Production Processes and Waste Water Generation in Breweries

Food processing industry especially beverage industry has undergone a drastic change over the past few decades. Instead of large manufacturing facilities, efficient production lines accommodating wide varieties of drinks, minimal cost and no environmental pollution are gaining popularity. Basic production processes employed in beverage industry are same, nevertheless, certain peculiarities are associated with specific drink and these are discussed in detail.

11.3.1 Production Processes of Alcoholic and Non-alcoholic Beverages

Alcoholic beverages (distilled spirits, wine and brewing) and non-alcoholic beverages (soft drinks, fruits and vegetable juices, flavored water, tea, coffee) are very popular among population and its business has been expanding considerably day by day globally. Some of these beverages (tea, beer, wine) have been in great demand in the market since thousands of years, nevertheless, commercialized industries were developed only in the past few centuries. These industries have evolved from regional firms to corporate giants. These giants are making and selling brewery products in international markets. Advancements in the technology for mass production, product packaging, and refrigeration not only increase the shelf life of the product but also prevent them from losing flavor, taste and color.

Breweries produce not only traditional drinks but also fortified/functional drinks containing amino acids, vitamins, fruits and vegetables' extracts, herbs and minerals (Brouns and Kovacs 1997; Siró et al. 2008). They claim to be health friendly, improve digestion, boost immunity and provide lot of energy. Owing to different tastes and preferences of the consumers, certain other ingredients like carbon dioxide (CO_2), caffeine, sweeteners, aromatic substances, acids are also added in small quantities. Water is the primary requirement in breweries. Water content in different drinks varies from 90% to 99%. Since pure and tasteless water is required, hence sometimes pretreatment of water is recommended using various techniques like coagulation – flocculation, adsorption, filtration and ion-exchange. Carbonated drinks are impregnated with carbon dioxide gas. It imparts acidic flavor, biting taste by stimulating mouth's mucous membranes, enhances aroma as the gas bubbles drag the aromatic components during their rise to the surface of soft drinks and increases the shelf life of the product by inhibiting microbiological growth. Caffeine is another natural aromatic substance which is extracted from 60 different plants including coffee beans and kola nuts. It is added in small amounts and imparts classic bitter taste and enhances the flavor of the drink. Non-diet soft drinks, fruit juices (pineapple, oranges) contain about 7–14% of different sweeteners mostly glucose and fructose. Since fructose is 50% sweeter than glucose and has low calorie value, hence addition of high fructose corn syrup is practiced. Diet or low calorie soft drinks are added with the approved artificial sweeteners like aspartame, saccharin, suralose, and acesulfame K (acesulfame potassium). To keep the balance of sweetness in drinks, acids like citric acid (extracted from citrus fruits, blackcurrants, strawberries, and raspberries), phosphoric acid and malic acid (extracted from apples, cherries, plums, peaches) are added. These acids act as preservatives, enhance the flavor, keep the drink fresh and thirst – quenching. Colorants, antioxidants, emulsifying agents and stabilizing agents to improve the taste, color and shelf life are also added.

11.3.1.1 Production Process of Fruit Juices

Fruit juices are extracted from wide variety of fruits including pineapple, apple, grapes, citrus fruits, mangoes etc. Sometimes, different fruit juices are blended and processed into a frozen concentrate with the help of evaporators to remove water by using heat and vacuum followed by chilling it. Concentrates are taken for dilution with filtered water, pasteurization and packaging under sterile conditions.

11.3.1.2 Production Process of Soft Drinks

Concentrates, treated water, liquid and solid ingredients including sweeteners/flavorants/additives are piped into a filling room using clean and sanitized filling machines. Carbon dioxide stored in liquid state, piped into carbonation units and allows the different beverages to absorb CO_2 differentially (15–75 psi of CO_2). Product is finally taken for bottling and canning.

11.3.1.3 Production Process of Coffee

Coffee as a beverage was introduced in Europe during sixteenth century. It gained worldwide approval and possess high commercial value. Production of coffee starts with cleaning and removal of pulp surrounding the beans by natural fermentation with bacteria, yeast and fungi, which is important for full flavor and aroma development. This is followed by roasting, grinding of coffee beans and its packaging under sterile conditions. To produce instant coffee with increased shelf life, its extracts are exposed to hot air blow, evaporation, cooling and lyophilization (freeze drying).

11.3.1.4 Production Process of Tea

Tea is consumed worldwide and majorly contributes to the economic development of multinational companies/nations. Production process of tea, the second most popular drink, consists of blending of various cut and dried tea leaves with hot water. The liquid concentrates/extracts are clarified, stabilized and added with natural sweeteners, sugar or sugar substitutes, flavoring agents like lemon or other fruit flavors prior to packaging. Figure 11.3a provides an overview of the industrial production processes of non-alcoholic beverages.

11.3.1.5 Production Process of Alcoholic Beverages

The mode of preparation of alcoholic beverages classifies them into fermented beverages or non-distilled (wine, beer etc.) and distilled beverages (brandy, whisky etc.). The type of beverages produced in any specific geographical region depends

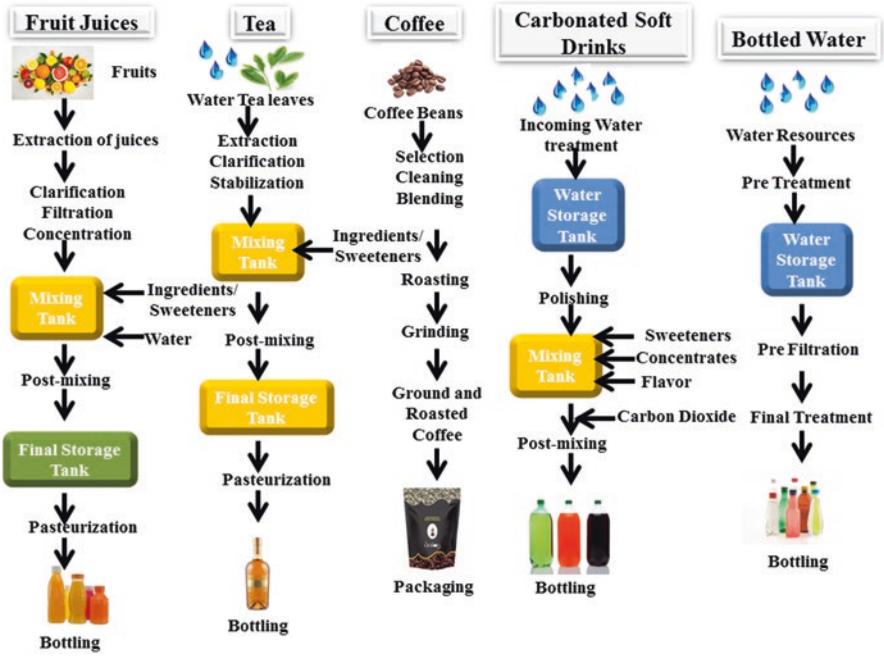

Fig. 11.3a Production processes of non-alcoholic beverages

on the particular crop grown. Cooler regions of Europe, Poland, Russia largely produce beer and lagers from barley while Southern regions with warm climate including Greece, Italy, France, Spain mainly produce wines from grapes. The starting materials/extracts/fermented mashes comprise of either starchy materials (cereal grains or roots) or sugary materials (fruit juices, grapes, sugarcane juice, molasses, potatoes, sugar beets, honey, cactus juice, nuts, plant sap or other food products) are used to prepare liquors. These raw materials are processed, crushed/ground and the mash is taken for starch solubilization using steam-jet cooking. Enzymes are added to slurry to facilitate starch saccharification, reduce mash viscosity and thus hydrolysed to simple sugars. The resulting mash after cooling is now taken for fermentation process where sugars are allowed to convert into alcohol and carbon dioxide with the help of yeast/microbial activities under sterile conditions. Downstream processing is done to clarify, refine the product to make it suitable for human consumption. These alcoholic beverages can be either drunk fresh or requires storage/aging. Aging/maturation, blending with additives to improve organoleptic properties followed by filtration and distillation is done to increase alcohol strength. This is followed by the final bottling/canning of the finished product. Figure 11.3b describes the key production stages in the industrial production of alcoholic beverages.

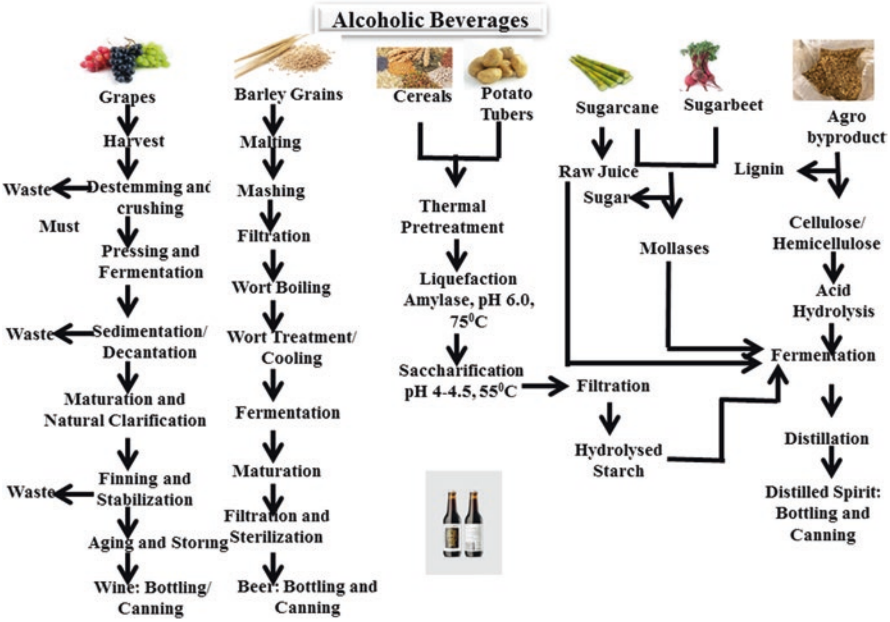

Fig. 11.3b Production processes of alcoholic beverages

11.4 Waste Water Generation

Beverages industry requires lot of water during various production processes of alcoholic and non alcoholic drinks. Water is one of the essential raw materials in beer/soft drink production with the consumption of 2.5–3.5 l of fresh water per liter of the drink produced. Its consumption varies and the waste water generation during the production processes of different products is influenced by various factors which include:

- Number of operational hours
- Age of facility
- Incentives to employee to minimize water usage, raw material and production loss
- Frequency of product changes
- Type of production whether batch or continuous production process
- Cost incurred for waste water and solid wastes disposal
- Cost per kilo liter (KL) of water

Beverage industries generate wastes and release into environment. Raw material wastes, production line losses (spilled product and broken packaging), filtration wastes, packaging on incoming products (on site) as well as on outgoing products and waste water as discharged effluents are generated during different production stages.

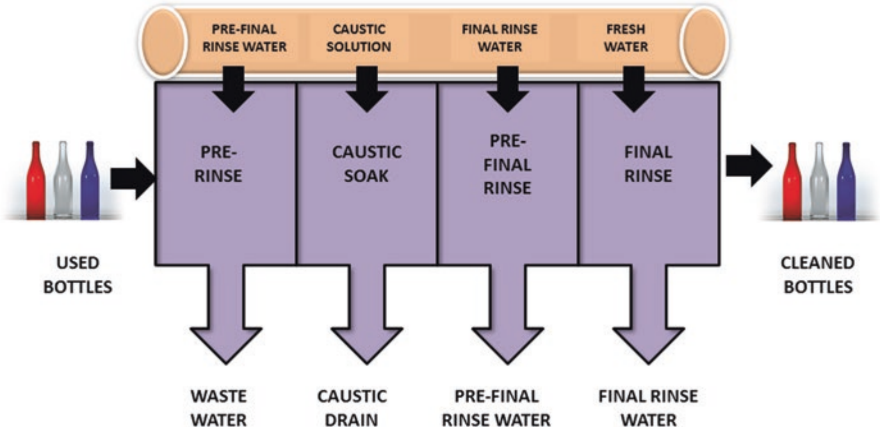

Fig. 11.4 Stages of bottle washing process

Huge quantity of fresh water is required for plant wash down, floor washing and general work area, boiled feed water, coolants in cooling towers, bottle washing, cleaning of bottling machines, equipment, filter backwashing, filter and pipe work during product/flavor change (Fillaudeau et al. 2006). Bottle washing contributes to the 50% of total waste water generation during production with an average of 1.25 l of waste water produced per liter of soft drink produced (Ramirez et al. 2004). Purpose of bottle washing is to remove microorganisms, debris, suspended solids, residual contaminants and chemicals including detergents, sodium hydroxide, salts of phosphates, nitrates and chlorine solution from its surfaces to render the bottled drink safe for human consumption.

Equipment and machines used for washing the bottles operate different wash cycles of pre-rinse, pre-wash, caustic wash, pre-final rinse and final rinse. Figure 11.4 describes various stages of bottle washing process.

Number of reagents including chlorine, detergent and 3% solution of sodium hydroxide are required for washing.

- **Pre-rinse:** Washing starts with pre-cleaning the bottles in inverted position with used pre-final water to remove solid/liquid foreign contaminants and warm the bottles.
- **Caustic soak/bath:** Several soak and rinse baths of the bottles followed by main cleansing in caustic soda bath which contains 2–3% of sodium hydroxide at the temperature of 60–80 °C to eliminate bacteria/microorganisms and remove dirt particles.
- **Caustic drain:** Bottles are inverted to facilitate the draining off the caustic solution.

- **Pre-final rinse:** Rinsing of bottles is done with used/recycled water from obtained from final rinse.
- **Final rinse:** Final rinse is done in cool water bath (28 °C) and used water as waste water is drained to sewage or recycled for fresh/another cycle of bottle washing during pre-rinse.

11.5 Characteristics of Waste Water

Tracking system to monitor the amount and type of waste water generated is required to assess the adequacy of the disposal facilities and the management of discharge water. The discharged waste water after final bottle wash is observed to be gray in color. Due to presence of high caustic soda in discharge effluent, its pH was measured as 10. Waste water generated during processing in breweries is normally highly biodegradable with high organic carbon content and caustic soda (Tebai and Hadjivassilis 1992). Discharged water from washing of cans and bottles is rich in detergents and lubricants used in the machinery. High sugar content (60–150 g/L) contributes to high chemical oxygen demand (COD) in the effluents which can reach upto 15,000 mg of oxygen per liter (O_2/L). Other pollutants include total suspended solids, 5 day biochemical oxygen demand (BOD5), salts of chlorides, phosphate, sulfates, sodium, potassium and calcium (Imoobe and Okoye 2011). Large amount of nitrogen and phosphorous are present in waste water produced in alcoholic beverage facilities due to the chemicals used in CIP (clean-in-place) units (Acharya et al. 2008; Mohana et al. 2009). Wastes obtained from citrus-processing plants primarily consist of liquid or aqueous wastes. Irrespective of its source, waste stream is mainly contaminated with suspended solids (sac material, juice, pulp and waxes); soluble organics (sugar, and acids), inorganics (caustic soda) and volatile organics (d-limonene from peel oils) with a BOD:COD ratio of 0.6 (El-Kamah et al. 2010).Chemical composition of the contaminated water discharged from different breweries is listed in Table 11.1.

Other than concentration of chemical and biological contaminants, strength of waste water is also characterized by change in physical properties. Major physical properties of pre-treated waste water discharge in breweries include high pH/alkalinity, color, odor, turbidity, temperature, electrical conductivity (varies from 2300 to 4700 μS/cm), fixed or volatile mineral solids and hardness. Analysis of water and waste water is done under well-established standard procedure (Arnold et al. 1992; Gupta 2004).

The probable sources/areas and major contributors to waste water in a typical soft drink plant are listed in Table 11.2.

Table 11.1 Composition of the waste water discharged from various breweries

Major constituents	Brewing industry				References
Chemical oxygen demand (COD): mg/L	Fruit juice	Winery: red and white: 3112–3997	Soft drinks	Distillery	Akunna and Clark (2000), Vlyssides et al. (2005), Parawira et al. (2005), Ozbas et al. (2006), Oktay et al. (2007), Sreethawonga and Chavadej (2008), Sangave and Pandit (2006), El-Kamah et al. (2010), and Haroon et al. (2013)
	Sour cherry 1000–8000	Brewery: Opaque	Bottle washing: 25–125	Grain: 16,500–22,520	
	Apple: 1600–2500	Beer: 8240–20,000	Energy drink: 33,000	Molasses: 106,500	
				Whisky: 16,600–58,000	
Biochemical oxygen demand (BOD): mg/L	Fruit juice: 1650–6900	Winery: red and white: 1740–1970	Soft drinks	Distillery	
	Sour cherry	Brewery: Opaque	Bottle washing	Grain	
	Apple	Beer	Energy Drink	Molasses: 31,600	
				Whisky: 8900–30,000	
Total suspended solids (TSS): mg/L	Fruit juice: 112–1534	Winery: red and white	Soft drinks	Distillery	
	Sour cherry	Brewery: Opaque	Bottle washing: 26–90	Grain	
	Apple	Beer: 2901–3000	Energy drink	Molasses	
				Whisky	
Total dissolved solids (TDS): mg/L	Fruit juice: 2304–17,918	Winery: red and white: 3112–3997	Soft drinks	Distillery	
	Sour cherry	Brewery: Opaque	Bottle washing: 750–1200	Grain	
	Apple	Beer: 8240–20,000	Energy drink	Molasses: 74000	
				Whisky: 6080–17,750	

(continued)

Table 11.1 (continued)

Major constituents	Brewing industry				References
pH	Fruit juice: 5.9	Winery: red and white: 6.0–6.2	Soft drinks	Distillery	
	Sour cherry	Brewery: Opaque	Bottle washing: 9–11	Grain: 3.3–4.3	
	Apple	Beer: 3.3–6.3	Energy drink: 5.4	Molasses: 5.7	
				Whisky: 3.8	
Total nitrogen: mg/L	Fruit juice	Winery: red and white	Soft drinks	Distillery	
	Sour cherry	Brewery: Opaque	Bottle washing	Grain: 120–150	
	Apple	Beer: 0.034	Energy drink: 20–1180	Molasses: 1900	
				Whisky	
Total phosphorous: mg/L	Fruit juice: 4.6–20.8	Winery: red and white: 7.0–8.5	Soft drinks	Distillery	
	Sour cherry	Brewery: Opaque	Bottle washing	Grain: 15–18	
	Apple	Beer: 16–24	Energy drink: 2.5	Molasses: 300	
				Whisky: 150–600	

Table 11.2 Probable sources of contaminants and areas in a typical soft drink plant

Probable areas	Water treatment plant	Sugar syrup area/ room	Bottle – washing plant	Bottling/canning
Type of contaminants	Water treatment chemicals, solids	Sucrose/fructose/ glucose, cleansing chemicals, flavorants	Caustic solution and other cleansing chemicals, solids	Solids, Sucrose/ fructose/glucose, flavorants

11.6 Waste Water Management Strategies

Owing to increased demand from civilization and industrialization and competition for diminished water supply/availability, optimum and sustainable water utilization is an hour of need. Owing to huge amount of water consumption in beverage sector, it is highly needed for the breweries to make decisions for recycle and reuse of water and treatment of waste water generated during various stages of production processes. Disposal of untreated waste water is considered as serious environmental hazard as it can result in salination and eutrophication of fresh water resources (Gonzalez-Garcia et al. 2013). To assure the public about the better quality of treated water than municipal drinking water is one of the biggest challenges being faced by the industry. Almost all the beverage industries of any significant size are concentrating on (i) using measured water ratios; (ii) regularly monitoring the water consumption;(iii) designing plans/goals and developing strategies to minimize water intake/loss; and (iv) its recycle.

Brewing industries are doing lot of efforts towards better water management and waste water minimization. This section discusses the various strategies being adopted by the breweries to minimize fresh water loss.

11.6.1 Water Intake Management

Water intake in beverage sector varies and depends on the differences in type of products, production processes and bottling/packaging/canning of the finished product. Industries are heading towards advanced technologies to maximize water saving approach. Every single effort is made to reduce water intake without compromising the production quality and quantity. A flow chart describes the possible stages of water recycling in the production of beverages before it is taken for treatment (Fig. 11.5).

Below mentioned are the probable and possible areas where water saving and its judicial consumption can be realized:

- Selection of equipment
- Utilization and modification of equipment

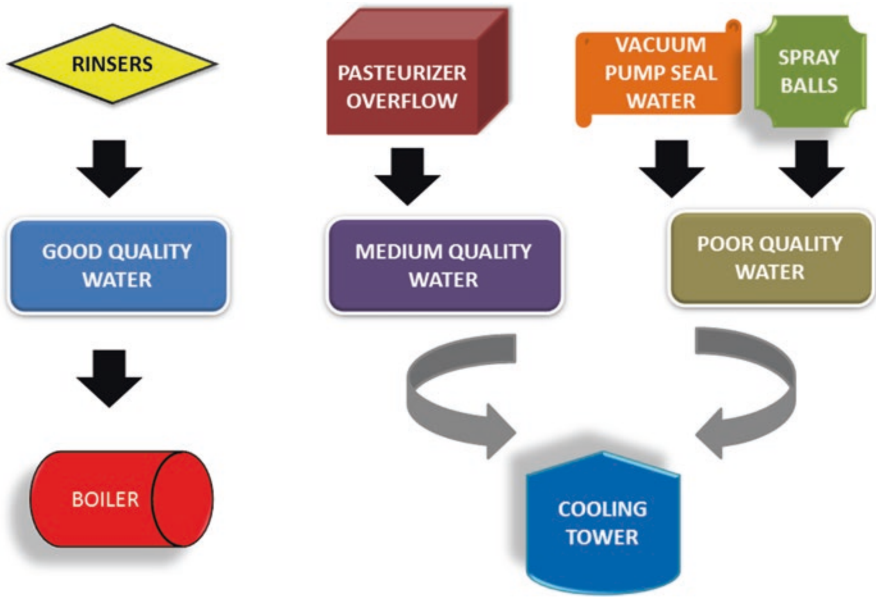

Fig. 11.5 Water recycling in brewery before treatment

- Techniques for water saving and reclamation
- Regular surveys for water monitoring
- Water management

11.6.2 Selection of Equipment

Proper water usage and minimal waste water production are the important factors to be considered while purchasing the major equipment like bottling lines and type of sprays placed in bottle washers as they are responsible for large share of water intake. High pressure, low volume jets, automatic ON/OFF valves in the pipe lines/hose pipes are some of the other effective measures that can result restricted consumption of water. Future advancements in the technology should be based on the use of oil in place of water in heat transfer systems and radiators as a substitute in traditional cooling towers.

11.6.3 Utilization and Modification of Equipment

Use of technology to make modifications in equipments and the processes for proper utilization of nature resources is highly needed.

(A) **Bottle washers:** Use of high jet pressures, pulsating jets, correct nozzle sprays can influence the rinsing and make it more effective in terms of water usage. Regular watch on bottle washers is required and the older bottle washers are modified to ensure the discontinuation of bottle spraying system once the machine is shut off.

(B) **Hose pipes:** They should be regularly checked for any wear and tear loss and must be replaced if they are damaged.

(C) **Water treatment plants:** Operations of over capacity water treatment plants should be avoided as due to backwashing of sand and carbon filters, they many times result in huge water wastage.

(D) **Equipment modification:** Older equipment should be replaced with the new and advanced ones. They should be modified to include water recycling. Water used in compressors and vacuum pump should be collected and reused.

11.6.4 Regular Surveys for Water Monitoring

Water meters should be selectively installed in water- intensive areas. These areas are continuously monitored. They should be isolated if they are consuming unnecessarily large amount of water and control it. Water meters should be calibrated regularly for their high performance efficiency. Simple water surveys are devised to monitor water consumption and keep check against water supply information in water – intense areas like taps, pipes and valves.

To manage the pollution loads, it is highly required to accurately monitor the flow volumes in the effluent stream. Skilled trained personnel are desired to implement the system for regular follow up of the effluent – related matters as the quality and quantity of the effluent depends on the size of the system and varies enormously with respect to the production stage/process.

11.7 Reducing Pollution/Contamination Load

Reduced water intake although concentrates the effluent better, however it may not necessarily cut down the pollution load. Number of measures required to adopt in order to minimize the contamination load are described below.

- Minimization of product loss
- Minimization of use of chemicals
- Reduction of solid content

11.7.1 Minimization of Product Loss

Product loss is normally realized during production process especially during product change – overs. Careful forward planning can be helpful in minimizing number of change overs. Extraction and collection of remnant syrup for later usage, careful transfer of bottles and cans to the conveyors and accurate monitoring of filling heights in bottling and canning plants to reduce spillage are few necessary steps required towards minimization of product loss and hence pollution load.

11.7.2 Minimization of Use of Chemicals

Use of harsh cleansing agents/chemicals should be avoided. Caustic soda is one of the important chemicals essentially required in bottle wash plant and significantly contributes to water contamination. Its use in high dilution and lower strength in combination with high temperature is recommended. Techniques are available to reclaim and recycle caustic soda from the effluent. Carry – over of caustic soda to final rinse section during bottle washing should be prevented by ensuring sufficient drip times. Its neutralization before discharging it into final effluent drain ensures minimal pollution load.

11.7.3 Reduction of Solid Content

Returnable bottles/recycled bottles containing durable tapes/paper labels and adhesives should be treated separately and thereby prevent fibers from paper labels and strong adhesive tape entering into the effluent stream.

11.8 Effluent/Waste Water Treatment

It is a moral obligation for the beverage industry to treat waste water before it is released to municipal sewage or water stream. This practice although increases the cost of production process but at the same time facilitates preservation of fresh water resources, reduces pollution load in the environment and serves to improve general public relations. Degree of effluent or waste water treatment varies from simple screening techniques to very extensive and complete waste water treatment system. An ideal waste water treatment plant in breweries should incorporate facilities and operate under the compliance with the world health organization (WHO) standard guidelines and the ministry of health parameters. Figure 11.6 provides a flow chart of the components and treatment process in an ideal waste water treatment plant in breweries.

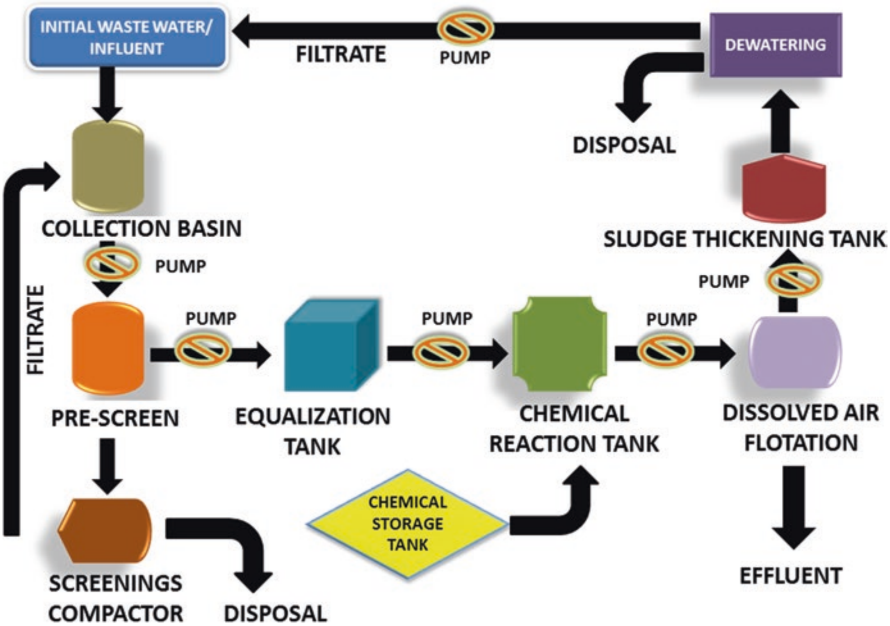

Fig. 11.6 Waste water treatment plant in beverage industry

The waste water treatment specialists/decision makers examine and scale the problem in accordance with their requirements and on the basis of certain criteria, the waste water treatment process is selected and executed (Isiklar and Buyukozkan 2006). Some of the important factors that remarkably influence the selection process are grouped into three categories.

Technical/Administrative criteria

(A) **Applicability:** Data from large -scale treatment plants, pilot- scale treatment plants and already published data evaluate the applicability of the treatment process.
(B) **Performance:** It is usually defined in terms of quality of the effluent and its variability, which is expected to be consistent with the effluent discharge requirements. Quality of the effluents can also be judged by the percent removal of BOD, COD, total suspended solids, total nitrogen and phosphorous.
(C) **Reliability:** Long-term reliability of the processes is required.
(D) **Resistance to hydraulic shocks:** The ability of processes and their efficiencies with respect to wide range of flow rates is evaluated.
(E) **Resistance to organic loading shocks:** The characteristics of the influents/waste water influence the type of process and therefore, their ability with respect to high organic loads is evaluated.
(F) **Coordination with local climate:** Climatic conditions such as temperature affect the treatment process by altering the rate of reaction of many biological processes. High temperatures affect metabolic processes and may accelerate the generation of odor as well as limit atmospheric dispersion.
(G) **Flexibility in operation:** Ability of the process to operate in varying physical and chemical conditions.
(H) **Simple operation and maintenance:** Simple operation and regular maintenance of the treatment plant is required.

Economic criteria

(A) **Capitol cost:** It includes the cost for mechanical and civil works.
(B) **Land requirement:** Sufficient space for accommodating required facilities and scope for future expansion is considered.
(C) **Operation and maintenance cost:** This includes maintenance, repair cost, personnel and energy input cost.
(D) **Sludge disposal cost:** It includes the cost incurred during sludge production and treatment.

Environmental criteria

(A) **Degree of treatment:** As per the requirements of standard effluent, process efficiency is determined.
(B) **Odour generation:** Odour generation from the treatment plant has become a major concern among the public and therefore, its control is must under the compliance with standard guidelines.

(C) **Risk:** Safety of workers/operators/trained personnel is an important issue and therefore, risk involved in production process needs to be evaluated.
(D) **Amount of sludge generation:** Amount of sludge generated during various stages of production process should not be discharged into environment; however, it should be properly treated.

Waste water treatment plant should be equipped with modern treatment facilities including SCADA (supervisory control and data acquisition system) which speeds up the remote operations and helps in:

- Real-time monitoring
- Performance of water treatment plant
- Quality of water and its distribution processes
- Comparisons of measured parameters based on real and historical data
- Archiving the historical data
- Regular generation of daily and monthly reports

Manufacturing facilities in waste water treatment plant are challenged by number of factors. Some of the important and deciding factors are mentioned below.

- Variations in influent conditions caused by load shocks
- Change in temperature
- Increase in production
- Change in manufacturing operations
- Degree of spillage
- Washwater surges
- Operational malfunction
- Limited equalization capacity

11.8.1 Waste Water Treatment

Effective waste water treatment is often difficult to achieve for numerous and varied reasons (Chen et al. 2006). Nevertheless, atypical waste water treatment plant for waste water generated during production process in beverage industry comprises of:

- Screening
- Neutralization/Equalization
- Chemical treatment
- Anaerobic and aerobic treatment
- Sludge separation or dissolved air floatation
- Sludge disposal

11.8.1.1 Screening

Influent drawn from the processing plant undergoes preliminary treatment where it is physically screened for the removal of big floating matters including labels, cans and bottle lids, and other large/solids/debris. Rotary drum screen is one the effective and efficient methods to remove organic waste from beverage waste water. Screening out of organic matter can result in substantial reduction of BOD5 levels in the waste stream and enhance the treatment processes. Separated solid debris can be disposed off and taken to sludge digester for its treatment. The end products of sludge digestion can be used as landfill and gases produced during this process can be used to generate power/electricity.

11.8.1.2 Neutralization/Equalization

Equalization or neutralization mixing tank stores waste water before it is further processed. Equalization/neutralization is required for maintaining proper pH balance, adequate dampening of organic fluctuations and prevention of shock loading of biological systems to control or minimize the fluctuations in waste water properties in order to provide optimal conditions for subsequent treatment process. The pH equalization mixers can be designed to allow the constant suspension of the particles. This will facilitate less chemical consumption, uniform mixing inside the tank using less energy, reduce cost and eliminate the problems associated with high torque mechanical mixers mainly used for constant mixing, operational maintenance inside the tank.

Balancing is highly recommended in case of soft drink industry where variations are more prevalent due to sudden high concentrations of syrup or detergents. It facilitates controlled discharge of an effluent with consistent pollution load. Water attains alkaline pH due to continuous dumping of caustic and increased levels of inorganic constituents. Hence neutralization is carried out, using addition of carbon dioxide or acid solution (hydrochloric acid or sulphuric acid). Low cost and on site ready availability of carbon dioxide makes it one of the most convenient reagents for neutralization in the soft drink industry.

11.8.1.3 Chemical Treatment

Following screening and other pretreatment process, waste water is pumped into chemical reaction tank where chemicals are added to bring about flocculation and coagulation. Coagulation consists of series of chemical and mechanical operations and is designed to convert stable/unsticky particles to unstable/sticky particles. Coagulants are added into water being treated with violent agitation to disperse it, followed by addition of flocculating agents to agglomerate small particles into well-defined flocks. Water containing flocks now move to the sedimentation tank to remove settleable solids by gravity. The purpose of chemical treatment is to reduce the organic content before waste water enters the biological treatment process. Since the high sugar content in waste water can promote the immense growth of bacteria with lower density, therefore, instead of sedimentation, dissolved air flotation may be used.

11.8.1.4 Anaerobic and Aerobic Treatment

Soft drink waste water is normally treated biologically due to presence of high organic content. Anaerobic or aerobic treatments are selected depending upon the growth of microbial mass. Slow rate of reaction and lack of scientific knowledge are associated with anaerobic processes, nevertheless they generate less sludge and biogas. Anaerobic digestion method is the choice of method for the treatment of industrial effluents containing large amount of soluble/insoluble forms of organic matter (Wang et al. 2004).

(A) **Aerobic treatment**

If the waste stream is not contaminated with high biomass/organic matter, aerobic treatment is the process of choice because of its ease in operation. Number of aerobic treatment processes including suspended or attached (fixed film) growth treatment processes can be employed. However, sufficient contact time between the waste water and microorganisms and sufficient levels of dissolved oxygen (DO) as well as nutrients are important for good treatment results. Aerobic suspended growth treatment processes comprises of activated sludge processes, aerated lagoons, or sequencing batch reactors (SBR).Extended aeration, higher hydraulic retention time (HRT) and solids retention time (SRT) are recommended to use.

Trickling filter and rotating biological contactor (RBC) processes are used for aerobic attached growth treatment of waste water. Microorganisms are fixed to an inert material (rock, gravel, slag, sand, redwood, plastic and other synthetic materials) to form a biofilm. Aeration facilitates oxidation of organic wastes as water flows over the aerobic microorganisms and thereby removal ofBOD5, COD and color. Series of closely positioned circular discs of polystyrene or polyvinyl chloride (PVC) rotate while being submerged and overlaid with waste water. This aerobic biological treatment process involves the production of activated mass of organisms including bacteria, protozoa for effective stabilization of organic wastes in presence of oxygen via series of metabolic reactions carried out by microorganisms.

Broad range of fungal species including soil fungi (*Fusarium* sp.), white-rot fungi (*Trametes, Polaria*), soft-rot fungi (*Chaetomium*sp.), *Saccharomyces cerevisiae*, *Rhodotorula*sp, *Klyveromyces marxianus*; bacterial species including *Pseudomonas* strains, *Nocardia corralina*, *Actinomycetes*, filamentous bacteria like *Thiothrix* sp., *Haliscomenobacter hydrossis*; and mixed microbial cultures from wide variety of habitats can degrade chlorinated aromatic hydrocarbons, synthetic high polymers and heterocyclic aromatic hydrocarbons and remove the color. Activated sludge comprises of 95% of bacteria and 5% of higher organisms. Depending on the type of bacterial communities present in the settling tank, it forms flocs or conglomerates, sink to bottom, forms dense sludge and leave the effluent clear. Trickling filters comprise of rock, redwood media filters (3–10 ft in depth) where the bacterial culture feeds on organic wastes that percolate through the media in thin films. These bacteria metabolize and degrade/reduce organic wastes to stable compounds of nitrogen and carbon. Design of reactors is based on either suspended microbial growth or use of biofilm on solid support medium like plastic spheres, granulated charcoal, diatomaceous earth, glass beads to provide large surface area for microbial growth.

Biodegradation is carried out by dehalogenases, oxygenases, dioxygenases where oxygen serves as an external electron acceptor. Complex organic compounds are broken down into relatively stable products such as carbon dioxide, water, mineralized sludge and oxidized volatile solids. This leads to substantial lowering down the levels of COD to 50–90% and BOD5 to 99%. Low capital cost; ease of removal of color, odour (volatile organic compounds) and refractory organics (non-biodegradable CODs); and improved sludge settling properties are few advantages of aerobic treatment process (Kasmi et al. 2016).

(B) **Anaerobic treatment**

Anaerobic process is another biological treatment method that suits to both waste water treatment and sludge digestion. It is not limited by the efficiency of the oxygen transfer and therefore, it is capable of treating number of organic wastes especially high organic strength waste water (≥5 g COD/L).Microorganisms involved are facultative and anaerobic which convert organic materials into carbon dioxide and methane in the absence of oxygen and traces of hydrogen sulphide. Some of the limitations of this process include slow startup, production of undesirable odors from hydrogen sulfide and mercaptans, high degree of operational difficulties and longer retention time.

Anaerobic process involves three groups of microorganisms (1) hydrolytic microorganisms (facultative and obligate anaerobes); (2) acidogenic microorganisms (facultative and obligate anaerobes); (3) methanogenic microorganisms (strict/obligate anaerobes). Although these bacteria are distantly related to each other, nevertheless, they depend on each other for the supply of nutrients and maintenance of suitable environment. Anaerobic treatment involves two distinct stages of acid fermentation and methane formation. Acidic fermentation stage merely converts complex organic molecules into simpler molecules without lowering BOD5 or COD. This stage is marked by the conversion of complex organic waste (biomolecules like proteins, lipids, carbohydrates) to small soluble molecules like triglycerides, fatty acids, amino acids and sugars through hydrolysis which occurs mainly by fermentative bacteria. The conversion is facilitated by the catalytic action of extracellular enzymes present in heterogeneous and anaerobic bacteria. Degradation of complex organic wastes depends on substrate composition, temperature, particle size and retention time (Matovic 2013). Metabolic products undergo fermentation, beta-oxidations etc. and further metabolized to simple organic compounds such as short-chain volatile acids and alcohols. Microbial organisms are tolerant to low pH/acidic condition.

The second stage or methane formation stage utilizes methane forming bacteria which perform acetogenesis and convert short-chain fatty acids to acetate, hydrogen gas, and carbon dioxide. Acetogensis is followed by methanogenesis where several species of strictly anaerobic bacteria produce methane from acetate, carbon dioxide and hydrogen. pH control is necessary for this stage as fermentation remains constant at alkaline/high pH. Operational conditions which include temperature, organic loading rate (OLR), alkalinity and pH, hydraulic retention time (HRT), feedstock characteristics, and reactor design are essential parameters which affect the complexity of bioconversion processes thereby performance of anaerobic digestion.

Anaerobic treatment makes use of number of different bioreactors. The biological phase can be in either attached, suspended or in immobilized forms. Many times, immobilization is preferred despite of additional material costs because of higher growth rate of methanogens and their diminished loss in the effluent. Depending upon the arrangement/forms of biological phases, mainly three types of anaerobic treatment processes are employed.

1. **Anaerobic suspended growth processes:** It comprises of anaerobic contactors; complete mixed processes; and anaerobic sequencing bath reactors.
2. **Anaerobic sludge blanket processes:** It includes anaerobic baffled reactor (ABR); upflow anaerobic sludge blanket (UASB) reactor; and anaerobic migrating blanket reactor (AMBR).
3. **Attached growth anaerobic processes:** It typically comprises of the processes of upflow packed bed attached growth reactors; attached growth anaerobic fluidized-bed reactors; upflow attached growth anaerobic expanded-bed reactors; and down flow attached growth processes.
4. **Covered anaerobic lagoon processes and membrane separation anaerobic treatment processes** are also used sometimes.

The total cost incurred to dispose the sludge produced by anaerobic process is 10% to that produced by aerobic process. Anaerobic plants demand 5–20% less cost compared to aerobic plants in terms of nutritional requirements. Other than these advantages, absence of aeration does not lead to the volatilization of organic contaminants and thus avoids possibility of air pollution.

11.8.1.5 Sludge Separation or Dissolved Air Flotation

This process is used to separate solids, oil, chemicals, grease from the waste water that can impart an unpleasant odor and taste to water. This system removes total suspended solids (TSS) and particulate BOD, highly resilient to process alterations and requires minimal operator intervention. It starts with the saturation of pressurized water with dissolved air before its discharge into a flotation vessel. Solid particles, chemicals and other impurities will adsorb onto the surface of microscopic air bubbles, thereby allow it to float on the surface and form a sludge blanket. The sludge is skimmed off the surface of water by scrapper assembly and then taken to sump/sludge thickening tank. Due to high transportation and storage costs, large volumes of effluent can be reduced. It is pumped to dewatering tank for its further treatment process. Number of different pumping or filtering processes are employed to separate water from solids. Belt filter presses and centrifuges are the principal methods in separation of sludge into liquid and bio-solids. Approximately 12–35% of solids/dewatered products are separated from the liquid. Water can be circulated back and the bio-solids can be discharged and used as landfill. These systems are not cost efficient and require high degree of maintenance, supervision and trained skilled personnel.

11.8.1.6 Tertiary Treatment Processes for Recycling Treated/Purified Water

(A) **Chemical precipitation:** Lime or soda ash is added in water to remove or reduce its hardness, converts the soluble salts into insoluble ones followed by flocculation and sedimentation to make it potable.

(B) **Adsorption:** This technique employs the use of adsorbents with high specific surface area. Some examples of adsorbents include activated alumina, clay colloids, activated carbon and hydroxides. It helps in reducing water pollution by decolorizing dyes and removing impurities by adsorbing it on the surface of adsorbents.

(C) **Membrane filtration:** Range of synthetic polymeric membranes with small pores are available to physically separate particles of size down to 10^{-7} mm including viruses and some ions under pressure from water. Ultrafiltration/microfiltration/nanofiltration are pressure-driven membrane based filtration processes and are capable of physical sieving and diffusion controlled transport. This process efficiently separates microbes, viruses, small molecules, organic components, salts, dyes etc. from the waste water. Resistance to microbial attack/damage, adverse chemical environment and high temperature are few special features of membranes, nevertheless, possibility of membrane clogging and therefore, its time to time replacement, high capital cost and disposal problem of concentrated residues left after separation restrict the frequent use of this process in water-reuse/recycle.

11.9 Recycling of Waste Water from Beverages/Soft Drink Bottling Industry

Large amount of fresh water is required for rinsing and cleansing operations especially during the reuse of glass bottles before they are refilled. Approximately 25 m^3 of water per hour is consumed for washing an average sized bottle- washer. Machines wash the empty bottles and cans repeatedly unless they are thoroughly cleaned. This activity produces huge quantity of waste water rich in sugar and caustic soda. This is followed by their strict inspection for the presence of any physical, chemical damage and residual contamination.

To minimize fresh water consumption and volume of waste water, water used for last bottle washing rinse must be recycled/reutilized during the pre-rinse and pre-washing cycles. Caustic solution is also many times recycled to maximize its use. Fresh water intake and resource input can again be minimized by allowing the washing cycles to take place in closed circuits, thereby reduce pollution of finite fresh water resource (Haroon et al. 2013). Besides this, number of other practices like use of floating media filtration and nano-filtration system can reduce the consumption of tap water by 60% (Miyaki et al. 2002). A microfiltration–reverse system and dual filter media – ion exchange system purify the rinse water for reuse in bottle washing and thereby reduce the consumption of soft water by 58% and 57%, respectively (Visvinathan and Hufemia 1997).

11.9.1 Techniques for Water Saving and Reclamation

(A) **Bottle-washer rinse reclamation:** Two important reclamation systems namely ion exchange and carbon dioxide reclamation systems are successfully developed and implemented in operation in large number of bottling plants. Efficiency of ion exchange system in terms of percent water reclaiming is 90% while that of carbon dioxide is 75%. Despite the fact that ion exchange system is capable of handling large quantity of water, nevertheless, owing to its high cost, difficulty in operation and its contribution of salts to effluent, carbon dioxide reclamation system is gaining popularity.

Large intake of rinse water during bottle washing operations recommends the use and necessitates the implementation of at least one of the available water reclamation systems.

(B) **Filter backwash recovery:** Large quantity of filter backwash water is produced which can be removed and recycled for the services which require low quality water including floor washing. After discharging the waste water containing high solid content into drain, the remaining water from backwashing operations can be reclaimed/recycled/reused for the services which do not require high grade/pure water.

(C) **Rinse water:** Pre-final and final rinse water from bottle washing plants can be collected for its recycle to pre-rinse the bottles/cans which do not require high quality water. If water is found to be contaminated, it is pumped to treatment plant for its purification.

(D) **Counter- current flow:** Bottle- washing plants are based on counter- current flow systems and thereby optimally utilize water use. Water is recycled for the pre-rinse purpose and also can be used in cooling towers and boilers.

(E) **Cascading:** It is the technique where the used water (less contaminated) instead of discharging it into sewage, is rather cascaded to low service washing operations as these services do not require good quality water. One of the good examples for this is the recycling of used water in bottle – washing plants.

Although the principal outcome of reducing water intake is the minimization of the amount of waste water generation, nevertheless, it also leads to increased concentration of effluents due to poor dilution effects and thereby results in less pollution loads in the environment.

11.10 Performance of Waste Water Treatment Plant

Performance of water treatment plant depends on number of factors.

(A) **Water quality:** Following the treatment procedures, rigorous tests are conducted to determine the quality of water. Water quality is defined by the chemical, physical and biological content of water. The quality of water should be checked by conducting various tests to meet drinking water guidelines.

(B) **Financial status:** An efficient treatment plant involves lot of expenditure on machinery, and energy resources to run the plant.

(C) **Trained and skilled personnel:** Availability of technician/staff/operators influences the performance of water treatment plant. Operators need mechanical aptitude and should be enough competent in basic mathematics, chemistry, and biology. Basic familiarity with computer is needed as the modern treatment plants are designed with computer-controlled equipment and more sophisticated instrumentation. This will help monitoring the equipment, store sampling data, make process control decisions, record maintenance activities, and generate reports. Operators should be trained to control important processes during operation which include controlling pumps, valves, and other processing equipments. They should be trained to read, interpret, adjust meters and gauges, perform sampling and laboratory analyses to check water quality, keep records, handle complaints, and do the repairs and maintenance in case of breakdown.

(D) **Proper control and monitoring of the treatment plant**
Owing to variations in water chemistry plant operating conditions, new environmental laws and proper monitoring is required to achieve satisfactory results. Some of the benefits of proper monitoring are:

Minimization of risks associated with chemical underfeeds or overfeeds;

Compliance with environmental regulations and national discharge consents;

Substantial saving of water and energy resources; and

Improved plant productivity and performance

General assessment methodology proposed by Balkema et al. 2002 is built on multi-objective optimization and sustainability indicators for sustainable water treatment systems. The sustainability indicators are mentioned below:

(A) **Functional Indicators –** These indicators define the minimal technical requirements in water treatment system. These include:

- Minimal required effluent quality;
- Adaptability: Possibility to extend the capacity of the system and incorporation of additional treatment, if required;
- Durability: Life period;
- Robustness: Availability to cope with the fluctuations in influent during the production process;
- Reliability: Sensitivity of the system to equipment malfunction and instrumentation; and
- Maintenance.

(B) **Economic Indicators –** These include:

- Total investment cost including cost incurred during operation and maintenance.
- Affordability and cost effectiveness, and
- Requirement of labor.

(C) **Environmental Indicators –** These include:

- Accumulation of contaminants;
- Input energy resources;
- Emissions BOD/COD; and
- Sludge/waste production.

(D) **Technical Indicators –** These include:

- Durability and performance of the treatment plant;
- Reliability and small scale solution.

11.11 Regulations for Waste Water Management

Strengthening of legislation and regulation enforcement is required to eliminate the accumulation or dumping of hazardous substances/pollutants in environment. Beverages are produced under strict sanitary guidelines. These guidelines focus not only on the production process but also handling of hazardous wastes, proper disposal of wastes, procedures for safe storage of product and its transportation. Equipment used in breweries are properly cleaned and disinfected with harsh cleansing agents. Nevertheless, workers exposed to caustic cleaners may develop allergies/dermatitis. Sometimes, inhalation of fumes by the cleansers may cause damage to lungs, throat, mouth and nose. Glass containers, overhead conveyors, high-speed fillers and electrical systems are potential sources of causing injury. However, modern plants are more mechanized and safe to work with.

Environmental regulatory agencies frame essential disposal guidelines which are mandatory for the beverage industries to comply with for the sustainable water use. General discharge standards for waste water released by the breweries are based on biological, physical and chemical quality which includes suspended particles, odor, color, pH, BOD, COD, nitrogen, phosphorous and other elements etc. (http://www.cpcb.nic.in/Industry_Specific_Standards.php). Regulatory guidelines to define water quality provide scientific information about various quality parameters as well as ecologically relevant toxicological threshold values to protect and restrict specific water uses. Water used for drinking may be good for irrigation purpose but water used in irrigation may not meet drinking water guidelines.

Coordination between different levels of government organizations that are involved in law enforcement activities related to waste management is must. Regulatory bodies have been instrumental in improving waste water management practices and treatment performances by the industries. Spreading environmental awareness among industrialists and general population; accurate monitoring mechanisms; incentives to industries for decreasing pollutant discharges; market based system of fines/levies to the industries based on the amount of effluent discharges; and shutting down the industries for extreme non-compliance are some of the necessary measures/actions should be implemented by the policy analysts.

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