The Handbook of Environmental Chemistry 117
Series Editors: Damià Barceló · Andrey G. Kostianoy

Mahmoud Nasr
Abdelazim M. Negm *Editors*

Cost-efficient Wastewater Treatment Technologies

Natural Systems

Springer

The Handbook of Environmental Chemistry

Volume 117

Founding Editor: Otto Hutzinger

Series Editors: Damià Barceló • Andrey G. Kostianoy

In over four decades, *The Handbook of Environmental Chemistry* has established itself as the premier reference source, providing sound and solid knowledge about environmental topics from a chemical perspective. Written by leading experts with practical experience in the field, the series continues to be essential reading for environmental scientists as well as for environmental managers and decision-makers in industry, government, agencies and public-interest groups.

Two distinguished Series Editors, internationally renowned volume editors as well as a prestigious Editorial Board safeguard publication of volumes according to high scientific standards.

Presenting a wide spectrum of viewpoints and approaches in topical volumes, the scope of the series covers topics such as

- local and global changes of natural environment and climate
- anthropogenic impact on the environment
- water, air and soil pollution
- remediation and waste characterization
- environmental contaminants
- biogeochemistry and geoecology
- chemical reactions and processes
- chemical and biological transformations as well as physical transport of chemicals in the environment
- environmental modeling

A particular focus of the series lies on methodological advances in environmental analytical chemistry.

The Handbook of Environmental Chemistry is available both in print and online via https://link.springer.com/bookseries/698. Articles are published online as soon as they have been reviewed and approved for publication.

Meeting the needs of the scientific community, publication of volumes in subseries has been discontinued to achieve a broader scope for the series as a whole.

Cost-efficient Wastewater Treatment Technologies

Natural Systems

Volume Editors: Mahmoud Nasr · Abdelazim M. Negm

With contributions by

O. Alizadeh · T. Alshaal · S. Barbagallo · R. N. Bharagava · M. A. Di Berardino · S. E. Di Berardino · R. Bhateria · M. Bilal · G. L. Cirelli · L. A. Daniel · L. de S. Leite · H. Elbasiouny · F. Elbehiry · N. Elhawat · M. G. Eltarabily · A. M. Folami · M. Govarthanan · S. K. Gupta · D. Hamidi · G. J. Heckrath · B. V. Iversen · S. A. Iwarere · S. U. T. Kadri · H. Kallali · N. Kapoor · L. Kumar · F. Licciardello · O. Mahjoub · R. Malisa-van der Walt · A. Mohamed · S. Mona · S. I. Mulla · R. Nagesh Babu · M. Nasr · A. M. Negm · L. Pugliese · M. A. Savanur · Y. Sharma · B. Singh · M. Sokáč · S. Straface · F. M. Swalaha · A. Taigbenu · A. N. Tavanappanavar · A. Tiwari · Y. Velísková · D. Ventura

Springer

Editors
Mahmoud Nasr
Environmental Engineering Department
Egypt-Japan University of Science
and Technology (E-JUST)
Alexandria, Egypt

Abdelazim M. Negm
Water and Water Structures Engineering
Department
Faculty of Engineering, Zagazig University
Zagazig, Egypt

ISSN 1867-979X ISSN 1616-864X (electronic)
The Handbook of Environmental Chemistry
ISBN 978-3-031-12917-9 ISBN 978-3-031-12918-6 (eBook)
https://doi.org/10.1007/978-3-031-12918-6

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Series Preface

With remarkable vision, Prof. Otto Hutzinger initiated *The Handbook of Environmental Chemistry* in 1980 and became the founding Editor-in-Chief. At that time, environmental chemistry was an emerging field, aiming at a complete description of the Earth's environment, encompassing the physical, chemical, biological, and geological transformations of chemical substances occurring on a local as well as a global scale. Environmental chemistry was intended to provide an account of the impact of man's activities on the natural environment by describing observed changes.

While a considerable amount of knowledge has been accumulated over the last four decades, as reflected in the more than 150 volumes of *The Handbook of Environmental Chemistry*, there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

In recent years, there has been a growing tendency to include subject matter of societal relevance in the broad view of environmental chemistry. Topics include life cycle analysis, environmental management, sustainable development, and socio-economic, legal and even political problems, among others. While these topics are of great importance for the development and acceptance of *The Handbook of Environmental Chemistry*, the publisher and Editors-in-Chief have decided to keep the handbook essentially a source of information on "hard sciences" with a particular emphasis on chemistry, but also covering biology, geology, hydrology and engineering as applied to environmental sciences.

The volumes of the series are written at an advanced level, addressing the needs of both researchers and graduate students, as well as of people outside the field of "pure" chemistry, including those in industry, business, government, research establishments, and public interest groups. It would be very satisfying to see these volumes used as a basis for graduate courses in environmental chemistry. With its high standards of scientific quality and clarity, *The Handbook of Environmental Chemistry* provides a solid basis from which scientists can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The Handbook of Environmental Chemistry is available both in print and online via https://link.springer.com/bookseries/698. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of *The Handbook of Environmental Chemistry* by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló
Andrey G. Kostianoy
Series Editors

Preface

This is the first of two volumes that together provide a comprehensive overview of the current reliable, practical, and cost-efficient wastewater treatment technologies applied in several developed and developing countries. The two volumes support the sustainable development goals (SDGs) and green economy of the contributing countries, concerning high-efficiency treatment of wastewater to ensure safe and applicable solutions to increase the availability of water resources for various uses. Therefore, we have included in the book the latest experiences from developed countries such as the USA, China, and Denmark to raise the benefits of the book for audiences and stakeholders. The book also gives valuable information to several communities that lack financial and technical support/resources necessary for attaining an environment-economic-health nexus.

This volume is divided into 5 main themes: Part I: Introduction; Part II: Concepts and Knowledge of Natural-Based Wastewater Treatment; Part III: Natural Wastewater Treatment Technologies; Part IV: Wastewater Management and Sustainability; and Part V: Conclusions and Recommendations. It consists of 15 chapters written by researchers, scientists, and experts from more than 10 countries, including Slovak Republic, Italy, Denmark, India, China, Republic of Korea, South Africa, Portugal, USA, and other countries from the Middle East/North Africa (MENA) region, representing about 20 institutions worldwide. The book gives essential information on the natural (non-mechanized) wastewater treatment technologies and demonstrates the current challenges in wastewater management and pathways toward sustainability, offering valuable guidelines to ensure sustainable and innovative solutions for wastewater treatment in the light of climate change, resource, demand, and funding challenges. The editors would like to thank all contributors to this volume. Without their hard work during all stages of the book, it was not possible for this volume to see the light. Great thanks to them for their patience during various revision phases of the chapters. Also, thanks to all the team of "The Handbook of Environmental Chemistry" for their help and support during all stages from the moment of receiving the proposal until the book gets published. It was a long journey during a difficult time of the COVID-19 pandemic. Although the editors and the authors of the chapters did their best to produce a unique and high-quality volume for the benefits of academia and stakeholders worldwide, they are still willing to improve the volume contents based on constructive comments from audiences.

Last but not least, the editor Mahmoud Nasr acknowledges Nasr Academy for Sustainable Environment (NASE). The editor Abdelazim M. Negm acknowledges the support of the Science, Technology, and Innovation Authority (STIFA) of Egypt in the framework of the grant no. 30771 for the project titled "A Novel Standalone Solar-driven Agriculture Greenhouse – Desalination System: That Grows its Energy and Irrigation Water" via the Newton-Mosharafa Funding Scheme Call 4.

Alexandria, Egypt Mahmoud Nasr
Zagazig, Egypt Abdelazim M. Negm

Contents

Part I
Introduction

Introduction to "Cost-efficient Wastewater Treatment Technologies: Natural Systems"

Mahmoud Nasr and Abdelazim M. Negm

Contents

Abstract Recently, the exponential increase in population number, industrialization, urbanization, and agricultural practices has been accompanied by the generation of huge volumes of wastewater. This wastewater contains various organic and inorganic pollutants that might cause severe human risks if disposed of in the environment without proper treatment. Hence, appropriate wastewater treatment technologies should be well defined, following strict and controlled national and

M. Nasr (✉)
Environmental Engineering Department, Egypt-Japan University of Science and Technology (E-JUST), Alexandria, Egypt

Sanitary Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, Egypt
e-mail: mahmoud-nasr@alexu.edu.eg; mahmoud.nasr@ejust.edu.eg

A. M. Negm
Water and Water Structures Engineering Department, Faculty of Engineering, Zagazig University, Zagazig, Egypt

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 3–16, DOI 10.1007/698_2022_909,

international regulations. Wastewater treatment facilities could be designed, implemented, and operated by either natural- or engineered-based processes. This chapter highlights the basic concepts of the non-mechanical wastewater treatment facilities contained in the book volume "Cost-efficient Wastewater Treatment Technologies: Natural Systems." These approaches cover information on waste stabilization ponds (WSPs), microalgae for phycoremediation, anaerobic treatment of sewage, adsorption technology in wastewater treatment, green nanomaterial for environmental remediation, deactivation of waterborne pathogens in natural eco-systems, treated wastewater reuse for irrigation, and agricultural drainage water (ADW) management. Some case studies supporting the concept of wastewater treatment by natural systems are presented.

Keywords Ecological wastewater treatment, Environmental-friendly approach, Non-mechanical units, Phytoremediation, Reuse in irrigation, Water quality standards

1 Introduction

Recently, an exponential growth of population has been associated with a rapid expansion of industrial and agricultural activities [1]. These practices generate large quantities of wastewater that contain various contaminants such as organic compounds, heavy metals, nitrogen and phosphorus, and persistent elements [2]. The release of these substances into the environment leads to various human health risks such as severe vomiting, nausea, liver toxicity, damage to the nervous system, anemia, destruction of blood cells, and eventually death [3]. Hence, experts, scientists, and researchers are exerting significant efforts to find appropriate wastewater treatment technologies that could be cost-efficient, reliable, and practical.

The wastewater treatment plants (WWTPs) can be designed, implemented, and operated using natural input attributes such as plant biomass, (micro)algae, atmospheric oxygen, and algae/bacteria interactions [4]. These elements are included in simple ecological treatment units such as constructed wetlands [5], stabilization ponds [6], and infiltration land [7], where the biological pathways to remove pollutants occur naturally (with no or low contribution from human operators) [8]. Contaminants' removal in the natural treatment systems is also ensured by physical filtration, sedimentation, adsorption, and sunlight disinfection [8]. These non-mechanized systems could also be used to recover resources via water reuse in the agricultural and aquacultural sectors [9]. Because these ecological treatment systems utilize minimum quantities of fossil fuel with achieving good performance, they tend to overcome the high costs of the most conventional wastewater treatment processes [10]. However, the decision of the best natural treatment system depends on various criteria such as influent/effluent wastewater quality, land, and open space availability, capital and operation costs, and seasonal variation [11]. Hence, more types of research are required to understand these natural/ecological systems and address the emerging challenges associated with pollution control and resource recovery.

To address the aforementioned idea, the next sections briefly present the main technical elements of each chapter contained in the book volume titled "Cost-efficient Wastewater Treatment Technologies: Natural Systems." These topics are related to the natural wastewater treatment systems such as simplified and low-energy ecological treatment facilities, bioremediation and biotechnology for a green future, environmental impact assessment of wastewater reuse, wastewater management and sustainability for irrigation, high-performance and cost-effective biosorbents for heavy metals removal, and eco-friendly nanomaterials for wastewater environmental management.

2 Waste Stabilization Ponds (WSPs)

Waste stabilization ponds (WSPs) represent low-cost natural systems that could provide treatment performances (e.g., biochemical oxygen demand, BOD, and pathogen removals) comparable to the conventional WWTPs [12]. With proper design and operation, WSPs would be able to maintain a final effluent complying with the reuse regulations and guidelines [13]. WSPs could work appropriately in warm climates, giving a reliable and cost-effective wastewater treatment technology in developing countries [8]. WSPs are notably flexible in terms of their designed shape, influent loading rates, and applications to different wastewater types; thus, gaining popularity worldwide [6]. In particular, most developing countries implement the WSP technology because it is inexpensive in terms of construction cost and energy utilization [14].

This book volume gives an overview of various types of WSPs, highlighting the related design criteria, function, and disinfection processes. Essential information on the operation and maintenance of WSPs, with the strategies and methods used to enhance the treatment performance, is revealed. The main points covered by this topic include:

- The common three types of WSPs (i.e., anaerobic, facultative, and maturation), connected in either series or parallel, experience different design criteria, organic loading, and biological and chemical pathways.
- Although WSPs are recognized for their simple design and operation, and low construction cost, the included microorganisms (e.g., algae and bacteria) should be periodically monitored and assessed to avoid system failure.
- WSPs could reduce nutrients (nitrogen and phosphorus), giving a final effluent applicable for reuse in agriculture and aquaculture.
- With the adequate design, construction, monitoring, and planning, WSPs could remarkably remove various pathogenic microorganisms and organic and

inorganic contaminants. In particular, the sunlight disinfection of the maturation ponds is used to eliminate bacteria, viruses, protozoan, and helminth parasites.
- The economic benefits obtained from WSPs by-products (e.g., suitable quantities of algal biomass) should be defined.
- More studies are required to investigate the applicability of WSPs to remove heavy metals and micropollutants (e.g., microplastic) from wastewater.

3 Microalgae for Phycoremediation

Microalgae biomass is a source of biofuels and high value-added products, maintaining various commercial and industrial applications [15]. The application of synthetic aqueous solutions for microalgae cultivation might be expensive and raise the biomass production cost. Alternatively, wastewater is used as a low-cost growth medium, providing microalgae with suitable amounts of nutrients (N and P) [16]. This approach is employed to maintain the dual benefit of pollution reduction and energy generation, making the entire biomass production process economically feasible [17].

In this context, this book volume displays an overview of microalgae production integrated with wastewater treatment, highlighting essential case studies in Brazil as one of the most biodiesel producing countries. The main points covered by this theme include:

- Microalgae production is an important approach to fulfill the needs of energy, food, and raw materials.
- Microalgae production requires no intensive fossil energy consumption or arable land resources, and the derived high-value compounds have numerous applications.
- Efforts have been exerted to reduce the costs of biomass cultivation and harvesting because the production cost at a large scale is still expensive.
- Microalgal biomass is utilized as a biological resource for the dual benefit of bioenergy production and pollution control.
- Wastewater treatment using microalgae-based systems is a promising strategy to overcome the prices involved in microalgae cultivation.
- Detailed information on the main factors affecting microalgae cultivation and the related operational conditions is given.
- Different wastewater types have been tested for elevating microalgae cultivation performance, with the tangential benefit of promoting safe effluent disposal.
- Microalgae harvesting is performed by various methods, including flotation, filtration, centrifugation, and sedimentation; hence, choosing the optimum harvesting technique at a large scale is still a limiting step.
- The profitability of wastewater-derived algal biodiesel should include the costs of the carbon market, wastewater treatment, cell disruption, and lipid extraction, as well as an evaluation of the benefits to human health and eco-systems.

- It is essential to investigate the applicability of reducing the dissolved inorganic nutrient species (NO_2^--N, NO_3^--N, NH_4^+-N, and PO_4^{3-}-P) during long-term cultivation and operation.

4 Anaerobic Treatment of Sewage

The anaerobic-based systems of wastewater treatment are robust, economic, efficient, and easy to operate [18, 19]. This book volume demonstrates the state-of-the-art of main anaerobic reactors used in wastewater treatment by focusing on their advantages, limitations, and challenges. The volume also gives information on the design requirement and operational conditions of each anaerobic unit.

A case study of a full-scale wastewater treatment system was designed to serve 7,500 inhabitants and composed of an Imhoff tank, two trickling filters, and one settling tank. This system was upgraded by transforming the Imhoff tank into an anaerobic hybrid filter (AHF) reactor. The new project was robust, easy to operate, and consuming a lower amount of energy, attempting to meet the standard and strict legislation for discharge in water bodies. Moreover, the reactors' performance in treating municipal wastewater under different temperature conditions (i.e., 15, 20, 25, and 35) and hydraulic retention times (HRTs) ranging from 10 to 48 h was investigated. The results of this system include:

- The anaerobic hybrid filter (AHF) system has potential benefits for the pre-treatment/treatment of municipal wastewater under subtropical–temperature conditions.
- The application of AHF with two-packing media could retain the active biomass inside the interstices, develop a specific and stable biological community, and perform solid/gas/liquid separation higher than the one-packing module [11].
- Overall treatment performance for COD and nitrogen removal efficiencies was adequately maintained.
- Biogas generated under anaerobic degradation was methane-rich (about 80%) with a small fraction of hydrogen sulfide.
- The upgraded system was feasible for treating municipal wastewater under subtropical or Mediterranean temperature conditions.
- Imhoff tanks that are old and out of service could be upgraded and converted to AHF systems.

5 Adsorption Technology in Wastewater Treatment

Recently, industrial development and population growth have increased the release of pollution into the environment, encouraging researchers, scientists, and stakeholders to find cost-effective wastewater treatment strategies [20]. One of the most common solutions to this objective is adsorption, which refers to the accumulation of compounds on the adsorbent via physical adsorption and/or chemisorption [21]. The adsorption process could be performed via two different methods, namely mixing (batch) and fixed-bed column [22]. Mixing adsorption systems are rarely used for large-scale industrial applications because they experience higher operational costs and potential problems under real conditions than continuous fixed-bed processes. Different mechanisms such as ion exchange, precipitation, complexation, pore-filling, and oxidation-reduction are involved in the adsorption process [23].

Natural material such as agricultural residuals and food wastes could be utilized to prepare a cost-effective adsorbent, making the entire adsorption project inexpensive [24]. Hence, synthesizing low-cost adsorbents has recently attracted the attention of industries and researchers [25]. This book volume reviews the mechanisms, effective factors, and operational conditions of adsorption processes for removing various organic and inorganic pollutants from wastewater. In particular, the volume evaluates the effects of process factors such as pH, contact time, initial concentration of pollutant, adsorbent dosage, temperature, and particle size on the adsorption process. It also provides essential information on scaling up the adsorption systems, with a description of the process modeling and engineering techniques. The reactivation, desorption, and regeneration methods in the adsorption-related studies were summarized. Different types of low-cost adsorbents, such as natural/bio materials, agricultural wastes, and industrial by-products and the required pre-treatment methods are reviewed and demonstrated.

The book volume illustrates several important points for the adsorption technology in wastewater treatment as follows:

- Affordable wastes (e.g., agricultural residues) have been broadly utilized to reduce the costs of the adsorption processes for wastewater treatment [26].
- Thermal, chemical, and biochemical pre-treatment transformations can enhance the adsorbent performance by altering the surface characteristics/functional groups.
- The application of several treatment cycles tends to reduce the adsorption capacity of some material, requiring the replacement of new material and/or employing specific regeneration methods [27].
- While natural-based adsorbents are environmentally friendly and cost-effective in uptake wastewater pollutants, further research on their management beyond long-term use is important.

6 Green Nanomaterial for Environmental Remediation

Nanotechnology has found broad applications in remediating and improving the environment, viz., heavy metal and dye removals, detection of pesticide contamination, and degradation of complex pollutants. The integration of green chemistry and nanotechnology further assists and enhances these environmental-related applications [28]. This green approach for nanoparticles' preparation saves a huge amount of energy utilization by reducing the manufacturing procedures. Nanomaterial (e.g., iron nanoparticles) prepared from green material retain various advantages such as novelty, cost-effectiveness, eco-friendliness, and broad applicability [9]. Hence, the greener approaches involved in preparing iron nanoparticles have attracted more attention worldwide because they are low-cost and environment-friendly. The main points covered by this topic comprise:

- Green synthesized nanoparticles can be easily produced using simple technical methods with cheap resource requirements, supporting their possible application in large-scale industrial environments.
- Fabricating metal-based nanoparticles via green routes offers multiple positive merits over the conventional (e.g., chemical) methods.
- Offering rapid, simple, and much easier synthesis methods of iron nanoparticles at the atomic scale level could maintain supreme versatility for achieving the desired catalytic properties.
- Practically, plant biomass is one of the best alternatives for establishing stable metal nanoparticles. As such, selecting the suitable plant species for the synthesis of iron nanoparticles is a greener approach that relies on the plant's natural composition and reducing agents.
- Due to their biocompatibility and lower toxicity, nanoparticles originated from biomass enjoy biodegradation, and biomedical and biotechnology applications.
- This greener technique could be further used to reduce the toxic effects associated with chemical utilization in inorganic nanoparticles' preparation.

7 Deactivation of Waterborne Pathogens in Natural Eco-Systems

Rising demand for water resources, due to the increase in population growth and human activities, has recently resulted in the generation of large amounts of wastewater [29]. Wastewater containing a wide range of organic and inorganic contaminants passes through the WWTPs before being discharged into the water bodies [30]. Conventional WWTPs could partially eliminate the emerging contaminants of concern (CEC), including specific classes of pharmaceutical drugs, antibiotic-resistant bacteria, and pathogenic organisms. Recently, emerging technologies in wastewater treatment, including the deactivation of pathogenic microorganisms, have gained worldwide attention [31]. For example, plasma technology is one of the common emerging applications used for inactivating waterborne pathogens, especially those found in drinking water [32].

This book volume represents some of the advantages of the plasma emerging technology for water treatment processes, while highlighting perspectives for its future development. In particular, the thermal, non-thermal, and electrohydraulic plasma generation strategies, with the associated benefits and current challenges in water research, were given. The main points covered by this theme include:

- Because specific groups of contaminants are ineffectively removed from wastewater, emerging applications (e.g., plasma technologies) have gained great attention in environmental-related research.
- The application of plasma technology has observed a large extension in multiple fields of science, such as agriculture, medicine, biomedical, and biotechnology.
- The different approaches used to generate this plasma method, especially the non-thermal technology form, are represented.
- The benefits and current challenges associated with plasma applications in the environmental-related studies (e.g., in microbial inactivation) are highlighted.

8 Treated Wastewater Reuse for Irrigation

Three fundamental resources (i.e., water, nutrients, and energy) could be obtained from various wastewater treatment processes [33]. The theme of "Treated Wastewater Reuse for Irrigation" represents the utilization of these resources in the irrigation of agricultural land fields. The theme provides essential information on the main stages of wastewater treatment, viz., primary or mechanical, secondary (e.g., biological-based process), and tertiary or advanced stages [34]. The book volume also highlights the use of algal biomass to remove the nitrogen and phosphorus species at the tertiary stage of wastewater treatment [35]. The generated biodiesel, proteins, and dry biomass from the algal systems could be used in several industrial and agricultural applications. Decisions regarding the irrigation scheme with treated wastewater are based on specific features of the soil and crops [36], which should comply with the national and international regulations [10]. The current challenges and recommendations in wastewater remediation for the irrigation application were discussed.

9 Agricultural Drainage Water (ADW) Management

Currently, the gap between water supply and demand is progressively widening because of the exponential growth in the world population [37]. The non-conventional practices of water conservation, sustainability, and management are highly supported by the reuse of treated wastewater for agriculture [38]. Because water scarcity is a critical environmental issue worldwide, it is considered the main motivation for agricultural drainage reuse.

Hence, the main objective of agricultural drainage water (ADW) management is to minimize the volume of freshwater applied for irrigation while maintaining sufficient crop production [39]. This aim is supported by the recycling of ADW, which should be subjected to proper analysis, assessment, and evaluation to comply with wastewater reuse standards for irrigation.

Accordingly, this book volume illustrates essential points as follows:

- ADW is characterized by high loads of organic matter (expressed by biological oxygen demand, BOD) and nutrients (nitrogen and phosphorus).
- The application of treated ADW in improving the soil’s organic and nutrient contents, cation exchange capacity, and moisture-holding properties greatly benefits the farmers’ community.
- The management of high volumes of ADW is challenging because specific crops could be cultivated in reclaimed water reuse condition. The selection of these crops depends on several parameters, including irrigation method (furrow, sprinkler, or drip), growth stage (initial, developmental, and mid- and late- season phases), and arrangement of soil layers (sand, clay, and sand-clay mixtures).
- Increasing the amounts of heavy metals and salinity in ADW is a challenging issue that requires accurate treatment and reuse decisions.
- The successful application of practical ADW reuse strategies depends on the wastewater reclamation techniques, irrigation water quality, crop selection, and leaching of toxic elements through the soil to groundwater.
- It’s recommended to employ salt-tolerant crops in the final phase of the ADW reuse system because the water quality becomes poorer after irrigating different and successive fields.

10 Treated Wastewater Reuse for Irrigation: A Case Study in Mediterranean Rim

Reclaimed water use in the agricultural sector is an essential strategy for sustainable water resource management in the Mediterranean Rim. This book volume assigns the main approaches to handle the common and significant obstacles that restrain the broad application of reclaimed water in agriculture. First of all, technical, regulatory, and social aspects, with the environmental risks, linked to the reclaimed water use in agriculture (focusing on South-Italy and Nord-African) were analyzed. The volume also demonstrates the design, installation, implementation, and operation, as well as performance efficiencies, for the possibilities of nature-based solutions for reclaimed water reuse. Case studies over the past two decades concerning the reclaimed water use in agriculture in the Mediterranean regions were analyzed. Recommendations for future application of nature-based techniques (e.g., phytoremediation by constructed wetlands) to mitigate surface soil and water losses, supporting the farming system and agricultural productivity are given. More studies are required to solve the most significant barriers affecting the development of an integrated reclaimed water use scheme in the Mediterranean region.

11 Agricultural Drainage Water (ADW) Management: A Danish Case Study

Edge-of-field technologies for the treatment of agricultural drainage water could reduce nutrient concentrations and loads in surface water bodies [40]. Agriculture runoff and drainage are major sources of the nutrient load to surface waters. A substantial reduction in this load is essentially required for compliance with the regulations of the European Water Framework Directive. Denmark is a European country that depends on groundwater for drinking purposes, while other water resources such as the reuse of drainage water could be used in irrigation. The book volume represents some Danish case studies attempting to protect the aquatic environment from a high nutrient load of drainage waters. In Denmark, a large percentage of the tile-drained agricultural catchments contributes to the total losses of both nitrogen (N) and phosphorus (P) [41]. Because these catchments exhibit large variability in geology, soil class, climate, and agricultural practices, the associated nutrient load should be assessed and evaluated. Different edge-of-field technologies for treating agricultural drainage water are tested in Denmark, considering the large spatiotemporal variation in nutrient losses. These technologies (installed in a tile-drained agricultural field) include constructed wetlands, woodchip bioreactors, and filter systems. Depending on the technical design, these technologies are expected to offer high nutrient removal, promote biodiversity, and maintain flood protection and control [42]. The results from a long-term monitoring campaign and assessment of data related to the investigated edge-of-field technologies would assist in determining the optimum drainage water management schemes.

12 Surface Water Quality: A Case Study of Hron River

Pollution concentration in the river system is partially reduced by the self-purification phenomenon, with a high possibility of the hydrology aspects and the river hydraulics, where the dilution, mixing, and dispersion processes are incorporated. To take into account the complexity of all these processes, a comprehensive modeling approach with the use of advanced computational and numerical models is recommended. Hence, the book volume provides numerical modeling methods used to analyze the effects of discontinuous sources of contamination on the quality of receiving water bodies. Moreover, it deals with the possibilities, challenges, and limitations of numerical simulation model applications for stormwater management in the urban catchments. The model MIKE11 was successfully used for numerical simulations of water quality, providing various strategies and management practices for water quality evaluation and improvement.

The modeled case study demonstrates the impacts of transport and discharge of combined sewer overflows (CSOs) on the receiving water body (e.g., an example of the Hron River, Slovakia). This objective was maintained by conducting the following steps: (1) create a model of the stormwater runoff from the Banská Bystrica town by its sewer network, (2) develop a model of CSOs to the Hron River (with the MOUSE model), (3) simulate the water quality in the Hron River with the MIKE 11 model, (4) estimate and assess re-aeration, degradation of organic substances, oxygen depletion, nitrification, and denitrification, and (5) lastly, evaluate the outflow of discharged wastewater from the CSOs structures in the Banská Bystrica town and its impacts on the receiving water.

13 Conclusions

This book volume intends to improve and address the main topics related to wastewater treatment by the natural and non-mechanical systems. As such, the volume succeeded in reviewing the current low-cost, eco-friendly, and effective ecological remediation technologies comprehensively. It offers a global perspective of sustainable and innovative solutions for wastewater treatment in light of climate change, resource, demand, and funding challenges. Moreover, it appeals to environmental managers, scientists, and policymakers alike.

Acknowledgments The editors who wrote this chapter would like to thank the authors of the chapters for their efforts during the different phases of the book including their inputs in this chapter. The first author acknowledges Nasr Academy for Sustainable Environment (NASE). The second author acknowledges the support of the Science, Technology, and Innovation Authority (STIFA) of Egypt in the framework of the grant no. 30771 for the project titled "A Novel Standalone Solar-driven Agriculture Greenhouse—Desalination System: That Grows its Energy and Irrigation Water" via the Newton-Mosharafa Funding Scheme Call 4.

References

1. Ansari F, Ravindran B, Gupta S, Nasr M, Rawat I, Bux F (2019) Techno-economic estimation of wastewater phycoremediation and environmental benefits using Scenedesmus obliquus microalgae. J Environ Manage 240:293–302
2. Fawzy M, Nasr M, Helmi S, Nagy H (2016) Experimental and theoretical approaches for Cd (II) biosorption from aqueous solution using Oryza sativa biomass. Int J Phytoremediation 18(11):1096–1103
3. USEPA (2009) Targeted National Sewage Sludge Survey Sampling and Analysis Technical Report. United States Environmental Protection Agency, Washington
4. Ahmad Ansari F, Nasr M, Guldhe A, Kumar Gupta S, Rawat I, Bux F (2020) Techno-economic feasibility of algal aquaculture via fish and biodiesel production pathways: a commercial-scale application. Sci Total Environ 704:135259
5. Nasr M, Ismail S (2015) Performance evaluation of sedimentation followed by constructed wetlands for drainage water treatment. Sustain Environ Res 25(3):141–150
6. Achag B, Mouhanni H, Bendou A (2021) Improving the performance of waste stabilization ponds in an arid climate. J Water Clim Change 12(8):3634–3647

7. Nasr M (2019) Environmental perspectives of plant-microbe nexus for soil and water remediation. In: Kumar V, Prasad R, Kumar M, Choudhary D (eds) Microbiome in plant health and disease. Springer, Singapore, pp 403–419. https://doi.org/10.1007/978-981-13-8495-0_18
8. Mahapatra S, Samal K, Dash R (2022) Waste stabilization pond (WSP) for wastewater treatment: a review on factors, modelling and cost analysis. J Environ Manage 308:114668
9. Nakum J, Bhattacharya D (2022) Various green nanomaterials used for wastewater and soil treatment: a mini-review. Front Environ Sci 9:724814
10. Partyka M, Bond R (2022) Wastewater reuse for irrigation of produce: a review of research, regulations, and risks. Sci Total Environ 828:154385
11. Jin L, Sun X, Ren H, Huang H (2023) Hotspots and trends of biological water treatment based on bibliometric review and patents analysis. J Environ Sci (China) 125:774–785
12. Passos R, Dias D, von Sperling M (2022) Simple mid-depth transverse baffles to improve bacterial disinfection in a shallow maturation pond–performance evaluation and CFD simulation. Environ Technol 43(10):1437–1445
13. Omidinia-Anarkoli T, Shayannejad M (2021) Improving the quality of stabilization pond effluents using hybrid constructed wetlands. Sci Total Environ 801:149615
14. Vagheei R (2021) Upgrading of waste stabilization ponds using a low-cost small-scale fine bubble diffused aeration system. Water Sci Technol 84(10–11):3104–3121
15. Ansari F, Nasr M, Rawat I, Bux F (2021) Artificial neural network and techno-economic estimation with algae-based tertiary wastewater treatment. J Water Process Eng 40:101761. https://doi.org/10.1016/j.jwpe.2020.101761
16. Ansari F, Singh P, Guldhe A, Bux F (2017) Microalgal cultivation using aquaculture wastewater: integrated biomass generation and nutrient remediation. Algal Res 21:169–177
17. Deepnarain N, Nasr M, Kumari S, Stenström T, Reddy P, Pillay K, Bux F (2020) Artificial intelligence and multivariate statistics for comprehensive assessment of filamentous bacteria in wastewater treatment plants experiencing sludge bulking. Environ Technol Innov 19:100853. https://doi.org/10.1016/j.eti.2020.100853
18. Long S, Liu X, Chen J, Zhao L, Pavlostathis S (2022) Effect of tetracycline on bio-electrochemically assisted anaerobic methanogenic systems: process performance, microbial community structure, and functional genes. Sci Total Environ 837:155756
19. Ezz H, Ibrahim M, Fujii M, Nasr M (2021) Dual biogas and biochar production from rice straw biomass: a techno-economic and sustainable development approach. Biomass Convers Biorefin
20. İlyasoglu G, Kose-Mutlu B, Mutlu-Salmanli O, Koyuncu I (2022) Removal of organic micropollutans by adsorptive membrane. Chemosphere 302:134775
21. Tee G, Gok X, Yong W (2022) Adsorption of pollutants in wastewater via biosorbents, nanoparticles and magnetic biosorbents: a review. Environ Res 212:113248
22. Fito J, Kefeni K, Nkambule T (2022) The potential of biochar-photocatalytic nanocomposites for removal of organic micropollutants from wastewater. Sci Total Environ 829:154648
23. Raza A, Altaf S, Ali S, Ikram M, Li G (2022) Recent advances in carbonaceous sustainable nanomaterials for wastewater treatments. Sustain Mater Technol 32:e00406
24. Fawzy M, Nasr M, Nagy H, Helmi S (2018) Artificial intelligence and regression analysis for Cd(II) ion biosorption from aqueous solution by Gossypium barbadense waste. Environ Sci Pollut Res 25(6):5875–5888
25. Fawzy M, Nasr M, Abdel-Rahman A, Hosny G, Odhafa B (2019) Techno-economic and environmental approaches of Cd2+ adsorption by olive leaves (Olea europaea L.) waste. Int J Phytoremediation 21(12):1205–1214
26. Fawzy M, Nasr M, Adel S, Helmi S (2018) Regression model, artificial neural network, and cost estimation for biosorption of Ni(II)-ions from aqueous solutions by Potamogeton pectinatus. Int J Phytoremediation 20(4):321–329
27. Kumi A, Ibrahim M, Fujii M, Nasr M (2020) Synthesis of sludge-derived biochar modified with eggshell waste for monoethylene glycol removal from aqueous solutions. SN Appl Sci 2(10):1696

28. Omran B, Baek K-H (2022) Valorization of agro-industrial biowaste to green nanomaterials for wastewater treatment: approaching green chemistry and circular economy principles. J Environ Manage 311:114806
29. Pilevar M, Kim K, Lee W (2021) Recent advances in biosensors for detecting viruses in water and wastewater. J Hazard Mater 410:124656
30. Wang M, Zhu J, Mao X (2021) Removal of pathogens in onsite wastewater treatment systems: a review of design considerations and influencing factors. Water 13(9):1190
31. Bayat F, Didar T, Hosseinidoust Z (2021) Emerging investigator series: bacteriophages as nano engineering tools for quality monitoring and pathogen detection in water and wastewater. Environ Sci Nano 8(2):367–389
32. Gururani P, Bhatnagar P, Bisht B, Kumar V, Joshi N, Tomar M, Pathak B (2021) Cold plasma technology: advanced and sustainable approach for wastewater treatment. Environ Sci Pollut Res 28(46):65062–65082
33. Abdulla H, El-Shatoury S, El-Shahawy A, Ghorab S, Nasr M, Trujillo M (2019) An integrated bioaugmentation/electrocoagulation concept for olive mill wastewater management and the reuse in irrigation of biofuel plants: a pilot study. Environ Sci Pollut Res 26(16):15803–15815
34. Khairy S, Shaban M, Negm A, Eldeen O, Ramadan E (2022) Drainage water reuse strategies: case of El-bats drain, Fayoum governorate, Egypt. Ain Shams Eng J 13(5):101681
35. Gupta S, Kumar N, Guldhe A, Ansari F, Rawat I, Nasr M, Bux F (2018) Wastewater to biofuels: comprehensive evaluation of various flocculants on biochemical composition and yield of microalgae. Ecol Eng 117:62–68
36. Jaiswal M, Hussain J, Gupta S, Nasr M, Nema A (2019) Comprehensive evaluation of water quality status for entire stretch of Yamuna River, India. Environ Monit Assess 191(4):208
37. Kumi A, Ibrahim M, Nasr M, Fujii M (2020) Biochar synthesis for industrial wastewater treatment: a critical review. Mater Sci Forum 1008:202–212
38. Shaaban N (2022) Water quality and trophic status of Lake Mariut in Egypt and its drainage water after 8-year diversion. Environ Monit Assess 194(6):392
39. Jorge C, Almeida M, Brito R, Covas D (2022) Water, energy, and emissions nexus: effect of inflows in urban drainage systems. Water 14(6):868
40. Kumi A, Ibrahim M, Fujii M, Nasr M (2022) Petrochemical wastewater treatment by eggshell modified biochar as adsorbent: a techno-economic and sustainable approach. Adsorpt Sci Technol 2022:2323836
41. Schneider R, Stisen S, Højberg A (2022) Hunting for information in streamflow signatures to improve modelled drainage. Water 14(1):110
42. Nasr M, Shmroukh A (2020) Gray-to-green infrastructure for stormwater management: an applicable approach in Alexandria City, Egypt. In: Negm A (ed) Flash floods in Egypt. Advances in science, technology & innovation (IEREK interdisciplinary series for sustainable development). Springer, Cham, pp 369–379. https://doi.org/10.1007/978-3-030-29635-3_16

Part II
Concepts and Knowledge of Natural-Based Wastewater Treatment

Nature-Based Treatment Systems for Reclaimed Water Use in Agriculture in Mediterranean Countries

Feliciana Licciardello, Olfa Mahjoub, Delia Ventura, Hamadi Kallali, Annabi Mohamed, Salvatore Barbagallo, and Giuseppe L. Cirelli

Contents

Abstract The Mediterranean region is one of the most vulnerable areas to climate change. This area is affected by severe water scarcity, which is expected to prevail by the upcoming years. The use of reclaimed water (RW) in agriculture is a way to reduce water scarcity, alleviate pressures on groundwater and other freshwater

F. Licciardello (✉), D. Ventura, S. Barbagallo, and G. L. Cirelli
Dipartimento di Agricoltura, Alimentazione e Ambiente, Università degli Studi di Catania, Catania, Italy
e-mail: flicciar@unict.it

O. Mahjoub
Institut National de Recherche en Génie Rural, Eaux et Forêts, Ariana/Nabeul, Tunisia

H. Kallali
Centre de Recherches et des Technologies des Eaux, Nabeul, Tunisia

A. Mohamed
Institut National de la Recherche Agronomique de Tunisie, Ariana, Tunisia

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 19–44, DOI 10.1007/698_2021_783,

resources, and improve irrigated crop productivity and environmental sustainability. RW is already being used, directly or indirectly, in many semi-arid areas of the world (e.g. Africa, Central America, Southern Europe, and Southern Asia).

In the last decades, Nature-Based Solution (NBS) systems such as constructed wetlands (CWs) or waste stabilization ponds (WSPs) have been proven to be a convenient solution for the decentralized treatment of wastewater (WW) of various origins and for their high landscape integration and low maintenance costs. In particular, NBS systems have rapidly evolved through the use of various design and operational modes or other adjustment (i.e. aeration in subsurface, recirculation rates, etc.) so as to improve effluent water quality with respects to various pollutants removal. Notwithstanding the numerous advantages, several barriers still limit the agricultural RW use practices in both developed and developing countries around the Mediterranean rim. From the technical viewpoint, the poor quality of RW can dissuade farmers from reuse as it could allow only cultivating low revenue crops. A low-cost natural treatment of municipal WW could alleviate restrictions for the agricultural irrigation and save the use of organic and mineral fertilizers.

This chapter reports various aspects linked to the use of RW in agriculture in Mediterranean countries, namely Southern Italy and Nord-African countries. Case studies of the last two decades concerning the RW use in agriculture in South Mediterranean regions were analysed to highlight technical, regulatory, and environmental aspects. Also, use-related risks in agriculture of RW produced by NBS systems in Mediterranean countries are discussed.

Keywords Constructed wetlands, Effluents, Reclaimed water, Volatilization

1 Introduction

The Mediterranean region is one of the most vulnerable areas to climate change [1]. Water shortages are expected to continue [2] due to the increasing degradation of water resources (overuse, pollution, salinization, etc.) and water demand in agriculture, as also in the urban, industry, and energy sectors. As an effect of climate change, the frequency and intensity of droughts and their environmental and economic damages have drastically increased over the past 30 years. The droughts of the summer of 2017 may illustrate the dimensions of economic loss; the Italian farming sector alone was predicting losses of EUR 2 billion [3]. Agriculture is in fact the largest water user. The 2017 World Development Report [4] evidenced a water consumption in terms of crop irrigation reaching 70%, on average, of the world water requirements.

When conventional water resources are insufficient, reclaimed water (RW) is one of the most available, constantly produced and relatively unaffected water resource by climatic conditions [5]. RW is already being used, directly or indirectly, in many semi-arid areas of the world [6]. In particular, RW is becoming an increasingly important source of irrigation, since agriculture sector is often the most penalized among others. In Southern Europe, agriculture is consuming more than 50% of the total available water resources [7]. In North African countries, this figure is exceeding 80% in a country like Tunisia. Tunisia is one of the most vulnerable countries to water shortage in the region with a water share of than 450 m^3/capita/year. In Northern Africa, water shortage is one of the main issues faced by the agricultural sector in this dry area with unevenly distributed water resources. Climatic conditions are putting high pressure on freshwater resources in addition to population growth. By 2020, half of the countries in the region are expected to be applying Best Available Technologies (BAT) and Best Environmental Practices (BEP) in non-conventional water projects. Besides, in order to increase the technological awareness on water reuse in the North Africa, a regional programme has been planned. Tunisia has made steps forward in integrating WW reuse in its water management strategy since the early years 90s. Currently, secondary treated WW is produced by 122 WWTP, out of them 112 are treating urban effluents.

In general, there is great potential of RW in irrigation of agricultural fields close to urban centres, also providing a considerable input of required nutrients for plants and reducing their net discharge on sensitive surface waters [8].

In the last decades, Nature-Based Solution (NBS) systems such as Constructed Wetlands (CWs) or waste stabilization ponds (WSPs) have been proven to be a convenient solution for the decentralized treatment of wastewater (WW) of various origins and for their high landscape integration and low maintenance costs. In particular, NBS systems have rapidly evolved through the use of various designs and operational modes or other adjustment (i.e. aeration in subsurface CWs, recirculation rates, etc.) so as to improve effluent water quality with respects to various pollutants. CWs can effectively treat raw, primary, secondary or tertiary treated sewage and many types of agricultural and industrial WW.

Notwithstanding all the numerous positive impacts, several barriers still limit the spreading of the agricultural RW use practice in both developed and developing countries around the Mediterranean rim. From the technical viewpoint, in some cases the poor quality of RW has dissuaded farmers from its reuse as it could only be reused for cultivating low revenue crops. A low-cost natural treatment of municipal WW could alleviate restrictions for the agricultural irrigation and could save on the use of organic and mineral fertilizers. Moreover, as reported by Salgot et al. [9], among institutional and socioeconomic causes, a key drawback for diffusing agricultural use of RW and its public acceptance is the absence of an adequate international legislation. This fact leading in many cases to homogeneous quality standards and fairness issue. On this regard, Tran et al. [8] mentioned how "the suitability of reclaimed water for specific applications depends on its quality and usage requirements". Generally, in irrigation practice the main quality factors to control possible adverse effects on human, plant, and soils integrity, for eligible recycled water are salinity, heavy metals, and pathogens.

In the attempt to develop their own recycling and reuse criteria, usually proceeding by the most advanced ones (i.e. California and Australia), Southern Europe states, like Italy, Greece, and Spain, enforced "semi-scientific" and too stringent regulations to be really applied [9]. At the light of that, EU (European Union) recognized the need to implement a common water reuse regulatory instrument at international level and is working towards both, minimum quality requirements and health and environmental risk-based policies [10]. On 25th May 2020 the European Parliament and of Council approved the “Regulation on minimum requirements for water reuse” [11]. This Regulation lays down minimum requirements for water quality and monitoring, as well as provisions for risk management, for the safe use of reclaimed water in the context of integrated water management. The purpose of this Regulation is to guarantee that reclaimed water is safe for agricultural irrigation, thereby ensuring a high level of protection of human and animal health and the environment, promoting the circular economy, and supporting adaptation to climate change. Then this will contribute to the Directive 2000/60/EC targets by addressing water scarcity and the resulting pressure on water resources, in a coordinated way throughout the Union, thus also prompting the efficient functioning of the internal market.

However, in the perspective to adopt the new EU guidelines for reclaimed water use at national level, many constrains will probably remain for a long time, mostly referring to physical and economic ones.

This chapter reports various aspects linked to the RW use in agriculture in South-Italy and Nord-African countries. In particular, case studies of the last two decades concerning the RW use in agriculture in South Mediterranean regions are resumed to highlight technical, regulatory, and environmental aspects. Also, use-related risks in agriculture of RW produced by NBS systems in Mediterranean countries are discussed.

2 Reclaimed Water Use in Agriculture in Med Region

2.1 State of Play

The use of municipal RW in agricultural and other sectors has been proposed since the 1970s as an opportunity to cover water shortage, save freshwater resources of high quality and contribute to the protection of environment from pollution also in the Mediterranean rim.

The use of RW for crop irrigation is an alternative to the scarcity of water quality and quantity, suffered in many countries of the Mediterranean basin. RW can provide an important saving of fertilizers (i.e. nitrogen and phosphorus) as well as benefits for the environment, by avoiding the discharge of contaminants into waterways [12] and providing consistent available water throughout the year.

Possible uses of RW include irrigation of food or non-food crops, irrigation of green or leisure zones (with or without direct contact), aquaculture, industry (water for refrigeration, cleaning), municipal use and aquifer recharge, among others [13].

The use of RW for crop irrigation is a common practice for some years now. The agricultural use has been tested on crops such as forage [14], alfalfa and radish [15], wheat and maize [16], trees [17], and vegetable crops [18]. Moreover, different practices involving RW use, in terms of irrigation techniques (surface and subsurface drip irrigation) [5], cultivation systems [19], and treatments technologies, [6, 20] have been tested.

One of the most economically feasible agricultural uses of RW is the irrigation of high-value horticultural crops, which typically has high returns per volume of water invested in [21]. However, this practice has been approached with trepidation, owing primarily to concerns about risks to human health via contamination of food with pathogenic microorganisms [22].

The effects of treated WW by CWs on irrigated vegetable crops (i.e. tomato, lettuce, zucchini, and eggplants) from physical, chemical, microbiological, and production perspectives were investigated in Sicily for several years [5, 18, 23, 24]. Experiments were conducted in open fields near the CW system of San Michele di Ganzaria (Eastern Sicily).

On the other side of the Mediterranean, in Tunisia, the use of RW in agricultural irrigation was a very prosperous activity that started in the early years 1980s. Treated effluents used for irrigation were mainly deriving from secondary biological treatment process operating in intensive treatment plants. The latter is widely recognized as a relatively efficient process based on the quality of the influents and the treatment efficiency that relies on energy. Irrigated areas have been abandoned due to the low quality of the effluents alongside the low acceptability of the end users, despite the low pricing. Hence, from economic perspective, the reuse of reclaimed water cannot be deemed as successful in the whole country; success stories are closely related to local initiatives launched by skilled operators, i.e. farmers. Overall, cost recovery is generally not achieved representing one of the main obstacles to improving the quality of the effluents and to be solved throughout the adoption of low-cost technologies.

2.2 Technical and Regulatory Aspects

WW treatment technologies are ever evolving with a wide range of processes. The latter are encompassing from the simplest to the most complicated and from the smallest size of decentralized, on-site, treatment systems dedicated to process domestic effluents from a household to the largest centralized treatment plants to treat (a mix of) hundred thousands of cubic metres of effluents collected from various types of establishments and origins. This is regardless of the countless combinations of various types of treatments to remedy to their respective shortcomings. Regulations have to do so through update and review throughout the years, generally on regular basis.

The relation between treatment technologies and regulation is not straightforward even though they are closely connected: water regulators require proves and references to set threshold limits for the quality parameters that fit with the capacities of the treatment plants and their efficiencies. Regulations and guidelines are meant to protect the environment and human health therefore they have to take into consideration not only the affordable technologies but they also foresee future improvements and innovations. It was forecasted that by 2020, half of the countries in the Mediterranean region are expected to be applying the Best Available Technologies (BAT) and the Best Environmental Practices (BEP) to treat non-conventional water. CWs dates back to the years 80's. However, few countries in the Med Basin did regulate its use for WW treatment.

In France, the majority of the CWs are Vertical Flow (VF) systems; Horizontal Flow (HF) are rather part of hybrid systems [25]. HF was also reported to be used to treat cheese dairy farm effluent [26].

In Italy, CW existed since the mid-1980s but it was not considered a treatment technology by the Italian legal framework before 1999 [27]. In 1999, CW was "officially" recognized as treatment technology by EC Directive 91/271 of the municipal WW treatment and around 90 CWs were constructed in 3 years between 1999 and 2001 [27]. The D.Lgs. n.152 of 1999 law enforcement has largely facilitated the spread of this technology across the country with very specific instructions for its implementation based on the volume of effluent discharges by the area. Urban centres discharging in freshwater bodies were the most targeted.

In Spain as well, CWs were introduced in the mid-1990s and prospered in the 2000s [28].

CWs are relatively simply technologies characterized by few mechanical and electrical parts, so, main technical problems for the use of RW for irrigation can be related to their effects on the irrigation system itself. In the following paragraphs, effects of RW on technological system management highlighted in Sicily during last decades will be described; moreover, some technical problems related to CWs themselves were highlighted.

2.2.1 Technical Aspects

Compared to the northern Mediterranean side, especially in Sicily, CW is a relatively new treatment process introduced for the treatment of municipal effluents. The very first CW have seen the light in 2001. The CW was located in San Michele di Ganzaria, a rural community of about 5,000 inhabitants, located 90 km southwest of Catania [29]. The whole project, included a tertiary system with four HF reed beds followed by three stabilization reservoirs, as detailed in Sect. 3.2.1. In this study site, effects of irrigation with RW on technological system management were investigated in Sicily during some experimental campaigns [23, 24]. In every experiment, a plot irrigated with fresh water (FW, from an agricultural reservoir) was used. The experimental plots were equipped with drip irrigation systems, consisting of surface (DI) and subsurface (SDI) laterals, buried at a depth of 0.05 m.

During the experimental irrigation system used in Castorina et al. [24] irrigation plots were covered by black/white plastic mulching. Mulch provides a better soil environment, moderates soil temperature, reduces splash effects, and increases water infiltration during intensive rains, and controls weeds [30]. Lettuce (*Lactuca sativa*

L.) (cultivar *Canasta*), zucchini (*Cucurbita pepo L.*; cultivar *President*), and eggplant (*Solanum melongena L.*) (two cultivars *Dalia – DA* and *Birga – BI*) were transplanted and cultivated.

The emission uniformity (EU, %) of DI and SDI laterals evaluated during the study indicated reductions of 12% (from 90% to 78%) in RW and 18% (from 93% to 75%) in FW pipelines. Microbial biofilm growth within the pipelines and/or the emitters may have caused these reductions, as confirmed by literature [31, 32]. In particular, the presence of the microbial biofilm (i.e., a heterogeneous and functional aggregation containing microbial community) was confirmed in the study (i.e., colonies of *Streptococcus Faecalis* and *Serratia marcescens*) by laboratory analyses. No significant variation in the EU was observed between the two micro-irrigation techniques (DI versus SDI).

In the experimental irrigation system used in Aiello et al. [23] subsurface light pipe P1 Rootguard (P1 RTG) was used together with other pipe in order to test the reduction of the microbial biofilm formation. In this case, EU was excellent or good for all plots (according to the classification of [33]) throughout the tests. In particular, mean EU data were in the order of 91% for P1 RTG.

In Tunisia, CW was never meant to be a treatment process to treat effluents because WW collection has always been centralized in treatment plants to be processed using intensive biological treatment. Up-to-date, WW treatments in Tunisia encompass 122 treatment plants including nine treatment plants in rural area; the rest are dedicated for the treatment of urban or industrial effluents. Consequently, CW is recognized neither by the WW treatment utility nor by the water/environmental regulators as an official treatment process. Unlike in Italy where CW have been built since the mid-1980s [27] and 175 CW were built in <15 years with 75% of the systems were located in central and northern Italy (provinces Veneto, Emilia-Romagna and Toscana) with a majority of HF systems [34]. More than 1,000 systems are in operation and around 300 systems exist in the public sector.

The first functional constructed wetland in Tunisia was built in 2004. It was meant to treat primarily WW of a community of 750 inhabitants. The design consisted in two VF beds covering 121 m^2) and HF bed covering 207 m^2. Ponds were planted with *Phragmites australis* and *Typha latifolia* in addition to mint (*Mentha sp.*). The substrate was composed of gravels with various sizes.

The treatment system has produced an effluent that was complying with the former standard of discharge 106.02 (1989) for the parameters BOD, COD, and TSS; the latter were not supposed not to exceed 30, 90, and 30, respectively. Nevertheless, the load of nitrogen as Kjeldahl total nitrogen and phosphorus were not met which may represent a constraint [35].

2.2.2 Regulatory Aspects

On the international level, the two benchmark guidelines for RW use are the California regulations (State of California 1978) and the World Health Organization (WHO) guidelines [36]. The first one is very strict, following a “zero risk” approach that adopts the "best available technology" [37]. The "zero risk" approach is based upon the fact that pathogenic micro-organism could survive for days, weeks, and at times months in the soil and on crops, so, detection in any of these environments is sufficient to indicate that a public health problem exists. Therefore, for example, recycled water used for the surface irrigation of food crops, should be tertiary or at least secondary disinfected if RW comes into contact the edible portion of the crop or does not, respectively [38].

For many years, the California state regulations were the only legal valid reference for recycling and reuse [9]. WHO [36] recognized that the extremely strict California standard for RW use, adopted by many countries, was not justified by the available epidemiological evidence nor was it likely that many countries, especially developing countries, could meet this strict standard. The WHO guideline was more flexible and it was established in order to be applicable in developing countries with lower economic possibilities [39]. The WHO guidelines followed a "calculated risk" approach, based on existing epidemiological evidence and they considered irrigation as an additional treatment stage. This approach proposes the "unrestricted irrigation" scenario [40] and suggests a median design risk for rotavirus infection of 10^{-3} pppy (per patient per year), considering feasible a 2–3 log unit reduction of *E. coli* in RW, due to rotavirus die-off between last irrigation and consumption. The success of the implementation of some post-treatment health protection measures for the reuse in agriculture was already reported for case studies in Ghana, Senegal, Vietnam, and India [41].

The differences between the two approaches and among the different guidelines and regulations, may raise doubts about their capability to protect end users; in particular, the countries that do not yet have guidelines or experience may decide not to deal with RW use [42, 43]. Most comprehensive standards developed specifically for RW use practices and issued by European States were, until today, either derived from the California guidelines (e.g., Greece, Cyprus, and Italy) or from the Australian guidelines and revised WHO criteria (e.g., France) [44] or from a combination of the above (e.g. Spain and Portugal). Fawell et al. [45] stated that the non-existence of the common standard is the biggest obstruction for the expansion of the RW use sector.

Even if the main European standards include additional preventive measures following the multiple-barrier approach, Italian standards are not aligned to those preventive measures. Ventura et al. [46] discussed various normative, economic physical barriers to the RW use practise spread in Italy. The actual Italian normative (Italian Ministry Decree 185/2003) derived, in fact, from the most restrictive approach. Thus, there is a lack of quality guidelines for diversified agricultural reuse sectors and a microbiological risk assessment, as promoted by the WHO [40]. Moreover, this normative presents a list of overabundant water quality parameters (e.g., chemical and microbiological compounds) to be analysed [47], with consequent high monitoring costs, mainly for small treatment facilities. Additionally, total costs for developing RW use in agriculture are not sustainable and user-friendly when considering the construction, operation, and maintenance of "additional" processes for tertiary and disinfection treatments and RW distribution networks [46, 48]. Following the Sustainable Sanitation Alliance [49, 50], it is key to implement sanitation systems which are sustainable. In order to be sustainable a sanitation system has to be not only economically viable, socially acceptable, and technically and institutionally appropriate, it should also protect the environment and the natural resources.

For example, waste biological ponds are recommended by the WHO, because of their effectiveness in removing nematodes eggs and helminths eggs, a pathogen endemic within developing countries. Biological ponds have an advantage that they are very efficient and inexpensive (both in terms of capital investment and O&M costs) [51]. A recent overview on different studies on natural and conventional disinfection technologies (among others chlorine-based disinfectants and UV radiation) showed that even if the latter represent the most used treatments, natural disinfection processes could represent valuable solutions, due in particular to the absence of chemical reagents [52].

In Europe, a common strategy on RW use was issued on January 2020 and approved on 25th May 2020. Based on the proposal of "Minimum quality requirements for water reuse in agricultural irrigation and aquifer recharge" [10], the European Parliament and the Council approved the "Regulation on minimum requirements for water reuse" [11].

The purpose of this legal instrument is to facilitate the uptake of water reuse whenever it is appropriate and cost-efficient and differentiate its application, thereby creating an enabling framework for those Member States who would continue or introduce the practice of water reuse.

2.3 Social Aspects

Social and cultural acceptance are key factors to successful projects of reuse in agriculture [53]. The quick development of the technologies associated with WW treatment has tremendously facilitated the acceptance to use this resource instead of fresh water. However, the lack of social acceptance has been considered as one of the major obstacles to not only the adoption of the technologies but also to the reuse, especially in agriculture. Social acceptance is rather related to the negative perception which may result in the reluctance to the reuse [54]. Hence, the acceptance of a treatment process depends largely of how it integrates into the environment and how its products are perceived by the end users. There is a strong need to gain trust because the society that is likely to change its behaviour may also influence its entourage [55].

In most advanced countries, CW is deemed to have several features. For example, Germany which is the cradle of HF CWs. Since the 1980', guidelines were established for that purpose which has largely facilitated the way CW is nowadays well integrated into the landscape and the way WW is treated and reused.

In Tunisia, CW was tested in several studies for the treatment of domestic and rural effluents. However, it is not fully adopted yet even for small communities; it is still practiced at pilot scale. The removal of chemical, physical, and biological pollutants are still on the learning curve and the technology is not well mastered in spite of the interesting results. The outcomes of the experiments carried out up to now are certainly encouraging and highly promising. Meanwhile, they are scattered, focusing on the technical parameters and do not yet bring to the society a prototype that could be adopted at full scale while assuring the release of a securely treated effluent that can be safely used for agricultural irrigation or else.

As a consequence, studies investigating the social acceptance of CW and social impact are still lacking because up-to-date the CW was only applied at lab-scale as pilot to treat a limited amount of water and for a short period of time. Therefore, the sensitization of the society to the features and the advantages of CW are not seriously considered by the scientists as part of the strategy of treatment and reuse. The establishment of regulation for the use of CW and its application at large scale requires that scientists capitalize on the available knowledge and success stories to come up with a design that meets threshold values that can be applied at least for the basic parameters, in a first stage.

2.4 Environmental Aspects

Environmental health problems may result from insufficient provision of sanitation and WW disposal facilities. The application of CW for the treatment of WW for agricultural irrigation has much potential, especially when incorporating the reuse of nutrients like nitrogen and phosphorous, essential for plant production. Among the current treatment technologies applied in urban wastewater reuse for irrigation, wetlands were concluded to be the one of the most suitable ones in terms of pollutant removal and have advantages due to both low maintenance costs and required energy [56]. CW use plants that can cope with pollutants in water [57] and support microbial community that biodegrade different types of contaminants. Besides, contaminants can be eliminated through physical process, chemical transformations of the compounds (reduction, oxidation, volatilization, and precipitation). The ultimate process is uptake by plants [58].

CW are promoted as the most environmental and human friendly technology and the less harmful because it complete harmony with the ecological system. However, health and environmental risks may derive mainly from the low removal of nitrogen and phosphorus that may end up with eutrophication in addition to the removal efficiency of some other classes of pollutants, mainly microbiological parameters; this may justify the recourse to disinfection step to guarantee the innocuousness of the exposed products.

CW is effective in removing organics and suspended solids. The relatively low removal of nitrogen could be improved by the combination of various types of CW. The removal of phosphorus is also usually low, requiring media with high sorption capacity. Meanwhile, pathogen removal is a challenge, requiring lagoons or hybrid wetland systems or a final disinfection step.

In general, organic and inorganic materials like nutrients, pathogenic microorganisms, and suspended solids are the main components that are meant to be removed from WW when applying CW. Biodegradable substances can be easily degraded and removed through bacterial metabolism. However, inorganic substances including phosphorus needs to be removed through more sophisticated processes like chemical co-precipitation with iron, aluminium, or calcium [59] in order to preserve the quality of the environment.

The use of CW for the treatment of industrial effluents aims at removing harmful components released from various types of factories. Minimum requirement need to be met like pH (6.0–8.5) and temperature (around 30 °C). The application of CW for industrial treatment is not very common in the Mediterranean countries. However, CW can address a large variety of treatments to achieve several goals like pH adjustment, BOD degradation, removal of nitrogen (ammonia), and removal of heavy metals. An example of the role of plants in the uptake of industrial heavy metals in treatment wetlands is phytoremediation. It was described also as the solution to the removal of contaminated soils with hydrophilic contaminants.

2.5 *Health Risks*

Faecal coliforms are the best overall indicators of water faecal pollution [60]. CWs are engineered systems, designed to remove nutrients, contaminants, and pathogens. CW was reported to be efficient for the removal of pathogens and bacterial indicators. Removal rates up to 99% were registered. Several factors contribute to the variability parameter like the initial load, the season, the type of CW, and the residence time. In general, HF are more efficient than VF because of the higher residence time [61].

In Italy, the removal rate of coliforms in 4 CW (Moscheta, Gorgona, Spannocchia, and Pentolina) using HF for tertiary treatment was comprised between 1 and 4 log10 units [62].

In Tunisia, duckweed-microalgae constructed wetland was not efficient in removing total and faecal coliforms with rates down to 68.5 and 47.16%, respectively. Noemi et al. [63] reported higher removal for faecal coliform (95%) using a duckweed based pond. Antibiotics [64] and heavy metals [65] may accumulate in wetland plants.

2.5.1 Heavy Metals

The removal of heavy metals within constructed wetlands is performed generally by rhizosphere and soil-based stabilization processes, adsorption onto sediments through solubilization and reprecipitation (e.g. Fe, Cu, Zn, Mn, and Al), and partially by plant uptake (Cr, Zn, Pb) [66]. The most common sorption models are Langmuir and Freundlich isotherms. Several models describe the sorption process of the charged species into soil particles from the solution where wetland bottom sediments attract the ionic forms of contaminants from WW.

2.5.2 Emerging Contaminant

New knowledge is required on the presence of contaminants of emerging concern in treated WW because of their potential risks for the environment and humans when treated WW is applied for irrigation purposes. More research on pharmaceuticals and their uptake by crops irrigated with reclaimed water is recommended. These crops are used for human consumption and/or animal forage and could potentially be harmful. Compounds of emerging concern can also be stress factors for crops irrigated with reclaimed water and should also be assessed together with conventional water quality parameters such as organic strength, nutrients, and solids in the future [56].

2.5.3 Microbial Parameters

With the aim to investigate the risks associated with the use of RW for the irrigation of vegetable crops in Sicily by using the system mentioned on Sect. 2.2.1 and detailed on Sect. 3.2.1, different experiments were carried out in Sicily during last decades.

For example, in Castorina et al. [24] RW samples were collected along the treatment line, at the inlet (RW0) and outlet (RW1) of one (H-SSF2) of the four CWs-based system (located in S. Michele di Ganzaria and described in the Sect. 3.2) and downstream to the stabilization reservoir and shallow tank, before (RW2) and after (RW3) the sand filter and then analysed.

FW samples were collected at the agricultural reservoir. Main microbiological parameters, *Escherichia coli* (*E. coli*) and *Salmonella*, in FW and RW were monitored and measured (Standard Methods, [67]) during the irrigation season at intervals of approximately 30 days. Results are reported in Table 1.

Table 1 Microbiological parameters in RW at the different sampling points. Mean value and standard deviation (in brackets) (data source: [24])

Parameter	RW sampling point 0	RW sampling point 1	RW sampling point 2	RW sampling point 3	FW	Italian RW use limits (MD 185/2003)
E. coli (CFU/100 mL)	2×10^5 (1×10^5)	8×10^3 (6×10^3)	7×10^3 (6×10^3)	5×10^3 (4×10^3)	0	50[a]
Salmonella (CFU/100 mL)	Absent	Absent	Absent	Absent	Absent	Absent[b]

RW Reclaimed WW, *FW* Fresh Water, *E. coli* Escherichia coli
[a]Limit value for 80% of samples; a maximum of 200 CFU/100 mL is allowed in 20% of samples
[b]100% of samples

Soil contamination analysis assessed *E. coli* and *Salmonella* concentrations within soil columns (from 0.1 to 0.3 m of depth beneath soil surface) near the emitters. Laboratory processing for soil microbial and constituent analyses were performed as outlined in APHA [67]. Soil samples (about 100 g) microbial levels (CFU 100 mL^{-1}), in 100 g soil samples, were enumerated using membrane filtration techniques. Microbiological results of RW and FW used for irrigation of vegetable crops in Castorina et al. [24] are summarized in Table 1.

Annual means and standard deviations (in brackets) were compared with Italian recommended limits [68]. Water contamination by *E. coli* varied considerably during the trials at the different sampling points from 10^3 to 10^5 CFU/100 mL. None of the RW samples analysed in 2013 had *E. coli* concentrations below the mandatory limit of 50 CFU/100 mL. For 92% of the samples, concentration values were higher (up to 1.7×10^5 CFU/100 mL) than the permitted upper threshold (200 CFU/100 mL). *Salmonella* was not detected in the RW samples. In 15% of samples, *E. coli* contamination was above the value of 10^4 CFU/100 mL fixed by the World Health Organization in 2006 for the "unrestricted irrigation" scenario, in order to reach a median design risk for rotavirus infection of 10^{-3} pppy (per patient per year), considering a 2–3 log unit reduction due to rotavirus die-off between last irrigation and consumption. In particular, according to WHO Guidelines [40], WW treated by the CW system could be used for vegetable crop irrigation by implementing some post-treatment health protection control measures.

Analyses on soil sampled at different depths within the experimental field revealed the presence of *E. coli*, with a maximum concentration of $2{\cdot}10^1$ CFU g^{-1} at 0.10 m beneath soil surface. In this study, and as confirmed in the literature [5, 69], a certain microbial persistence was individuated along the investigated soil profile. No *Salmonella* contamination was detected in soil samples. ANOVA analysis did not reveal significant differences in contamination values along the soil profile between what RW and FW. On vegetable products, ANOVA revealed a significant microbial contamination, both in terms of *E. coli* and *Total Coliform*. In particular, among the different vegetable crops irrigated by RW, lettuce revealed the worst microbiological quality related to the low quality water supplied. Anyway, *Salmonella* was not detected in all RW irrigated products.

Similar results were found by Aiello et al. [23], that based on a 6-year monitoring programme, showed that municipal RW (coming from the same CW located in S. Michele di Ganzaria) may be successfully used, under specific experimental conditions, to irrigate and grow tomato crops. In particular, the risk assessment analysis, carried out by applying the Quantitative Microbial Risk Analysis model (QMRA) according to WHO [40] procedures, highlighted that by applying the post-treatment health protection control measures (such as product washing, disinfection, peeling and/or the natural pathogen die-off after last irrigation), the acceptable rotavirus infection risk was generally preserved, although *E. coli* content of RW was often over the limits set by the Italian law.

For further contribution to the argument on the "zero risk" and "calculated risk" currently followed worldwide, Licciardello et al. [18] analysed removal efficiency (physical-chemical and microbial) of two different tertiary treatment options for RW use in agriculture. The first option included in series horizontal subsurface constructed wetland system, biological pond (i.e., lagooning), storage reservoir (i.e., tank), sand and disk filters, while the second included in series horizontal subsurface constructed wetland system, sand and disk filters, and ultraviolet (UV) systems. Details of both tertiary treatment systems using RW coming from the same CW reed bed are provided in the Sect. 3.2.1. RW were used to irrigate Tomato (*Solanum licopersycum L.*, Cv *Missouri*) and eggplant (*Solanum melongena L.*). The results of this study, showed that natural treatment system, recommended by the WHO for using RW in agriculture, together with sand and disk filters, can represent a reliable alternative to the high intensive disinfection treatment based on UV.

3 Natural Based Treatment Systems in Med Countries

3.1 Design, Construction, and Operation

In general Med countries are in warm-climate areas. The climatic factor needs to be taken into account in the design of treatment wetlands (TWs) in these regions. In general, the working principles of the treatment system will be the same, but specific characteristics need to be considered. Among the others, developing countries or regions have generally limited resources for infrastructure implementation, operation, and maintenance. Several developing countries show high regional economic contrasts, with technically developed areas coexisting with poor regions, but the focus here remains only on those with limited financial resources. Again, there are several aspects that should be taken into account in the planning, design, and operation, and maintenance (O&M) of the treatment systems [70] in developing countries.

The fact that in warm-climate regions, with higher WW temperatures, biochemical reactions and some physical processes take place at a faster rate is still a debating problem. Some studies reported that, for a given effluent quality and surface area allocated for TW, removal efficiencies are expected to be higher at more elevated temperatures and land requirements are likely to be smaller [71]. However, other authors highlighted how it could be uneasy identifying clear temperature effects on TW performance. In fact, Kadlec and Wallace [72] reported a certain variability for temperature correction factor (θ) values when applying the *P-k-C** model. For COD and BOD removal in horizontal sub-superficial flow (HSSF) wetlands (#34) this factor ranged from 0.891 to 1.140 (corresponding $\theta < 0$ to worse efficiency with increasing temperature, $\theta > 0$ to better efficiency with increasing temperature, and $\theta = 1$ to no temperature effects on removal) and highlighted some lacking debate in literature. Nevertheless, evidence mostly suggests that “TW BOD removal is not improved at higher wetland temperature". This consideration reinforced the previous conclusion on the absence of temperature dependence on TW BOD data [73, 74].

Moreover, hydrological behaviour of TWs may be influenced by rainfall regime. In arid areas, evapotranspiration is likely to play an important role, leading to water losses and concentration of constituents in the effluent. Also, in arid areas, it is common to have a wide amplitude of temperature variations between day and night [71].

Most of the wetland literature emanates from developed countries under temperate or cold climate, in which there is a considerable accumulated experience as a result of thousands of units in operation. There should be a strong incentive to develop regional design guidelines for treatment wetlands based on actual experience in low-income and warm areas, so that future designs are really well suited to the local conditions [71].

In regions with limited financial resources, it is essential that construction costs are small, so that the implementation of the treatment systems becomes viable. Additionally, operation and maintenance (O&M) costs must also be low, in order to guarantee the plant sustainability in the long run, and to contrast probable neglect due to lack of funds. Frequently, in developing countries funding for the WW treatment plant (WWTP) implementation comes from a state or international agency (frequently with financing at low interest rates), but O&M costs are taken over by the operator or service provider, and this may be affected by the tariff structure (if at all existent), which must be sufficient to cover all costs related to the good functioning. CWs are very competitive in terms of construction costs and are frequently very advantageous in terms of O&M costs, compared with other treatment systems. Thus, it is important to guarantee adequate routine O&M, since wetlands are systems which are very robust for a long time until they fail completely, needing large sums to recover the efficiency [71].

Moreover, in most applications in developing regions, lack of skilled manpower for undertaking even basic operational duties is frequent, and this reinforces the suitability of natural systems such as CWs. So, the level of mechanization should be kept to a minimum. Anyway, the fact that CWs are very simple systems to operate must not become an excuse to neglect the basic duties associated with the running of the treatment plant. It is observed that there is a tendency in many developing countries to abandon maintenance and operation rather than undertaking routine basic low-cost maintenance and operation. It is important to note that every system fails without proper O&M, and this is also the case with wetlands [71]. Main failures in the performance of wetlands due to inadequate O&M are:

- Failure of the pre-treatment stage (e.g., septic tanks) due to lack of desludging, which may cause overflow of sludge to the wetlands.
- Failure of the distribution system, especially in vertical flow wetlands, where there is a need for a uniform distribution of the liquid over the whole surface of the bed.

3.2 Efficiencies

Most of domestic WW hybrid-CWs have been constructed and evaluated in cold climate regions of central and northern Europe [75] and only a few examples of these type of treatment systems in Mediterranean regions have been reported [76]. In sight of the water scarcity scenario and stringent regulations, the enlargement of knowledge on this matter may only enhance their acceptance and future implementation of this eco-technology in small communities of warm regions.

In order to evaluate the treatment capacity of CWs in warm regions some examples are reported below.

3.2.1 CW Located in San Michele di Ganzaria in Sicily

The whole plant included a tertiary system made of four HF reed beds followed by three stabilization reservoirs [29]. The monitored reed bed is used for tertiary treatment of about 1,100 p.e., with a design flow rate of 1.75 L/s. The bed is 78 m long, 25 m wide, and the surface area is 1,950 m^2 (about 1.7 m^2/p.e.) corresponding to a hydraulic loading rate of 0.077 m/d. The filtering bed (8–10 mm gravel with a porosity of 0.38) is 0.6 m deep and the average water depth is 0.4 m. The wetland was planted in January 2001 with *Phragmites* sp. at a density of four rhizomes/m^2; the complete plant cover was reached in October 2001. From March 2001 to September 2005, samples of WWTP influent, CW influent, and effluent were collected and physical–chemical and microbiological characteristics of WW were analysed.

The average concentrations of TSS, BOD_5, and COD detected in the rough WW can be classified as medium to strong [77]. The chemical–physical and microbiological parameters show a significant temporal variability (CV $>$ 50%). During the 5-year monitoring period the HF has shown a satisfactory treatment performance with medium to high levels of removal of TSS, BOD_5, COD, TN, and TP with an effluent average quality compatible with the limits imposed by the Italian regulation for WW discharge in water bodies and for WW reuse. An average removal of 2–3 log units of FC and *E. coli* was achieved, with a maximum of 4–5 log units observed in the 5th year of monitoring; however, only 15% of total samples matched *E. coli* limits ($<$50 CFU/100 mL) for WW reuse fixed by Italian legislation in the case of natural treatment systems' effluents. The CW unit was very effective ($E = 100\%$) in the removal of *Salmonella* and helminth eggs and it provided high buffer capacity also during periods with lower WWTP efficiencies. The overall efficiency of CW is significantly high, if we consider that the CW actual residence time, estimated by tracer tests, was about 20 h.

The CW pilot plant, located close to the municipal WW treatment plant (WWTP), is made of 2 parallel lines, each one consisting of 6 HF functioning in parallel [78].

In each line, five beds are planted with different macrophyte species, while one bed is unvegetated. In particular, *Cyperus papyrus*, *Vetiveria zizanioides*, *Miscanthus x giganteus*, *Arundo donax*, *Phragmites australis* were used. Results showed that vegetated beds have showed a better performance in the removal process for all the investigated parameters than unvegetated beds, underlining the active role of macrophytes in the WW treatment. The best removal performances obtained in the beds planted with Phragmites australis, confirmed that this is the most suitable plant species to be used in constructed wetlands for wastewater treatment. About the capability to treat WW for reuse purposes, *E. coli* concentration in the CW effluents was not always under the maximum limit for wastewater reuse fixed by Italian legislation but ensured that health-based targets proposed by the WHO guidelines [40] can easily achievable by combining CW systems with some post-treatment health protection control measures. Finally, during the monitoring period, *Phragmites australis showed the highest evapotranspiration rates.*

3.2.2 Hybrid-CW Located at the IKEA Store in Sicily

The hybrid-CW system of the IKEA store of Catania (Eastern Sicily, Italy) (Latitude 37° 26' N, Longitude 15° 01' E, altitude 11 m asl) is the newest component of the WW treatment plant of the store, which also include a sequential batch reactor (SBR) and a screening unit. The plant is located in a semi-arid climate area, characterized by an average annual precipitation of about 500 mm, and values of air temperature in summer reaching 40 °C. The SBR was designed for treating WW produced by toilets and the food area of the store; SBR was designed for a maximum flow rate of 30 m^3 day^{-1} (2 batch phases every 12 h) and Total Nitrogen (TN) load of 135 mg L^{-1}.

The first bed (first stage) of the hybrid-CW is a HF, covering a surface area of about 400 m^2 (12 × 34 m) and filled with 10–15 mm volcanic gravel for a depth of 0.60 m. HF was planted with two different aquatic species; *Phragmites australis* (i.e. highly tolerant specie to pollutant concentrations) occupies 2/3 of the HF surface area, and *Iris pseudacorus* cover the remaining surface area, close to the HF outlet. The second bed (second stage) of the hybrid-CW is a vertical subsurface flow treatment wetland (VF1), designed to further remove the WW organic matter and SS and to nitrify ammonia to nitrate. VF1 is 24 m long, 24 m wide, with a surface area of about 580 m^2; it is planted with *Cyperus Papyrus var. Siculu*s and *Canna indica*. The porous substrate of VF1 was realized for the first 0.45 m with volcanic sand (5–15 mm), while the remaining 0.30 m till the bottom were filled with coarse gravel (25–40 mm).

The third bed (third stage) of the hybrid-CW is a vertical subsurface beds (VF2), which has the same design characteristic of VF1 (size, area, porous medium), but is planted with *Typha latifolia* and *Iris pseudacorus*. Macrophytes were transplanted in the month of July 2014, with a density of 3, 2, and 4 plants m^{-2} in HF, VF1, and VF2, respectively. About the hybrid-CW operation, the HF is discontinuously fed. It was designed to receive 30 m^3 daily effluent from SBR (two discharges of 15 m^3 each one) and 20 m^3 effluent from the screening unit, that by pass SBR, when the WW produced in the IKEA exceeds SBR design flow rate. The hydraulic loading rate (HLR) of HF varies between 75 and 125 L m^{-2} d^{-1}.

The HF unit experiences frequent overloading peaks due to the extreme variability in the number of visitors at the store, and after 2 years of operation it showed signals of partial clogging at the inlet area. The hydraulics of the HF unit has been monitored through measurements of hydraulic conductivity at saturation (Ks), tracer tests, and geophysical (i.e. electrical resistivity tomography – ERT) measurements carried out during the years 2016 and 2017 [79].

Tables 2 and 3 show the physical-chemical and bacteriological concentrations of the hybrid-CW system for April–June 2016 and December–February 2017 (periods I and II) and March–April 2017 And May–July 2017 (periods III and IV). Each period has 6–9 WW samples. These tables also show the limits imposed by Italian regulations for RW discharge into water bodies (LD 152/06) and for agricultural reuse (MD 185/03). Table 4 shows the removal efficiency (RE) of the whole hybrid-CW. The high variability of pollutant concentrations at the inlet of the hybrid-CW reflects the large number of customers who visit the IKEA® store and produce WW, which can be three-fold greater on weekends and holidays. In particular, on these busy times, the hybrid-CW often receives WW directly from the screening unit, without passing through the SBR, due to its frequent overload, and therefore has lower quality.

The hybrid-CW units provided efficient reduction of TSS (up to 99.3% $\pm$ 0.4), COD (up to 92.7% $\pm$ 6.8), and BOD_5 (up to 96.6% $\pm$ 3). The major parts of TSS, COD, and BOD_5 reduction took place in HF (first stage) (Tables 2 and 3) thus reducing the clogging problem in the other stages. Vertical units contributed (data not showed) to further decrease of organics and TSS, producing a final effluent usually complied with the reuse and discharge standards. The hybrid-CW system had a high rate of total nitrogen reduction (up to 69.5% $\pm$ 17, Table 4), confirming its efficient ammonification and denitrification. Ammonia was oxidized to nitrate at the vertical stages (data not showed), thus quite high amount of nitrate was found at the outlet, generally over the discharge limit. This could be reduced recirculating the effluent to the primary treatment. These measurements of effluent suggest an inversion in the HF unit. The removal efficiency of total phosphorous (TP) concentration was low during periods I and II, but increased up to 54.4% $\pm$ 1 during periods III and IV (Table 3).

A considerable improvement in microbiological water quality was achieved at the hybrid-CW. In fact, the influent *E. coli* concentration was reduced meanly of 2–3 log unit in the HF and other 1–4 in the VF1 and VF2 (data not showed), obtaining an overall *E. coli* reduction of 4–6 log unit, from CW influent to CW effluent. The microbiological reduction rates were 1.7–4 log units (Table 4), and the *E. coli* concentrations were generally acceptable, according to the stringent limits of Italian legislation for RW agricultural use (MD 185/03). The RE values of the whole hybrid-CW system provide evidence of the important role of the HF unit for reduction of pollutants (Table 4). This high Removal Efficiency may be due to the higher physical-chemical and microbiological concentrations of the influent entering the system, as well as the performance of the HF unit.

So, the results of the study carried out by Marzo et al. [79] show that partial clogging did not reduce the capacity for removal of organic matter and suspended

Table 2 Mean (standard deviation) of physical-chemical (mg L^{-1}) and bacteriological (CFU/100 mL) concentrations at the hybrid-CW inlet, outlet, and at the HF unit during monitoring periods I (April–June 2016) and II (December 2016–January 2017) (source [79])

	April–June 2016 (Period I)			December 2016–January 2017 (Period II)				
	Hybrid-CW influent	HF outlet	Hybrid-CW outlet	Hybrid-CW influent	HF outlet	Hybrid-CW outlet	Italian RW discharge limit[a]	Italian RW use limit[b]
TSS	81.9	11.5	3	162.6	15.5	1.2	80	10
	(±14)	(±0.7)	(±1.4)	(±25)	(±0.7)	(±0.1)		
BOD_5	226.5	9.8	14	321.9	57.5	31.6	40	20
	(±66)	(±3.2)	(±5.5)	(±152)	(±2.8)	(±8.8)		
COD	430.6	46.6	30	643.7	115	62.5	160	100
	(±144)	(±44.0)	(±25)	(±304)	(±5.7)	(±18)		
TN	85	38.3	28.9	140	72.5	44		15
	(±33)	(±1.7)	(±3.2)	(±30)	(±7.8)	(±0.3)		
N-$(NH_4)^+$	27.6	20.4	0.6	77.7	44.5	4.2	15[c]	2
	(±33)	(±8.9)	(±0.3)	(±18)	(±13.4)	(±5)		
N-$(NO_3)^-$	23.1	1.8	17.9	46	0.2	39	20[c]	–
	(±10)	(±1.6)	(±7.8)	(±7)	(±0.1)	(±0.2)		
TP	8.3	14.8	8.5	22.1	29	21	10	10
	(±3)	(±5.4)	(±1.2)	(±0.1)	(±9.9)	(±2.8)		
E. coli	4.7×10^5	1.9×10^3	35×10^{-1}	3.1×10^6	6.7×10^3	2.5×10^2	5.0×10^3[d]	100[e]

[a]Ministerial Decree 185 [68]
[b]Legislative Decree 152 [80]
[c]Limit for discharge into surface water bodies
[d]Maximum value in 80% of samples
[e]Recommended value for P.E. N 2000

Table 3 Mean (standard deviation) of physical-chemical (mg L^{-1}) and bacteriological (CFU/100 mL) concentrations at the hybrid-CW inlet, outlet, and at the HF unit during monitoring periods III (March–April 2017) and IV (May–July 2017) (from [79])

	March–April 2017 (Period III)			May–July 2017 (Period IV)			Italian RW discharge limit[a]	Italian RW use limit[b]
	Hybrid-CW influent	HF outlet	Hybrid-CW outlet	Hybrid-CW influent	HF outlet	Hybrid-CW outlet		
TSS	63	32	17.5	37.8	14.5	8.1	80	10
	(±37)	(±8.5)	(±3.5)	(±16)	(±13)	(±7.1)		
BOD_5	83.8	12.9	3.2	87.4	42.4	37.2	40	20
	(±28)	(±1.2)	(±3.1)	(±66)	(±69.1)	(±69)		
COD	161.6	27	14	187.7	79	66.5	160	100
	(±3)	(±1.4)	(±6.4)	(±129.8)	(±125)	(±120)		
TN	108	60.7	35.5	80.3	43.5	30.8		15
	(±30)	(±48.5)	(±27.5)	(±6)	(±21)	(±2.5)		
N-$(NH_4)^+$	26.7	1.8	0.5	14.8	0.6	0.3	15[c]	2
	(±14)	(±1.8)	(±0.2)	(±6)	(±0.6)	(±0.2)		
N-$(NO_3)^-$	65.9	45	30	57.9	21.4	28.1	20[c]	–
	(±41)	(±42.4)	(±25.5)	(±10)	(±17.6)	(±3)		
TP	12.9	3.2	5.9	9.3	5.7	4.9	10	2
	(±1.9)	(±3)	(±0.9)	(±2)	(±0.6)	(±0.5)		
E. coli	1.03×10^6	6.7×10^3	1.26×10^2	4.6×10^5	5.2×10^3	2×10^1	5.0×10^3[d]	100[e]

[a]Ministerial Decree 185 [68]
[b]Legislative Decree 152 [80]
[c]Maximum value in 80% of samples
[d]Limit for discharge into surface water bodies
[e]Recommended value for P.E. N 2000

Table 4 Mean removal efficiencies (RE, % for chemical parameters and as $\log_{10}$ reduction of CFUs for *E. coli*) ± standard deviations of the HF stage and the total hybrid-CW during the four monitoring periods (from [79])

	April–June 2016 (Period I)		December 2016–January 2017 (Period II)		March–April 2017 (Period III)		May–July 2017 (Period IV)	
	HF outlet	Hybrid-CW outlet	HF outlet	Hybrid-CW outlet	HF outlet	Hybrid-CW outlet	HF outlet	Hybrid-CW outlet
TSS	93.2	95.8	90.3	99.3	43.3	68.4	49.4	73.1
	(±9	(±1.4)	(±2)	(±0.4)	(±20)	(±13)	(±6)	(±33)
BOD_5	92.3	93.2	79.7	88.3	84	96.6	66.9	72.9
	(±2)	(±3.6)	(±11)	(±8)	(±4)	(±3)	(±35)	(±38)
COD	88.4	92.7	79.2	89	83.3	91.6	69.7	76.4
	(±13)	(±6.8)	(±10)	(±6)	(±1)	(±4)	(±32)	(±32)
TN	40.3	55.1	47.6	67.8	48	69.5	45.5	61.4
	(±10)	(±7.1)	(±6)	(±7)	(±30)	(±17)	(±52)	(±6)
N-$(NH_4)^+$	n.s.[a]	78.2	38.9	95.3	94.3	98.3	95.2	96.9
		(±30.8)	(±32)	(±5)	(±4)	(±0.1)	(±3)	(±3)
N-$(NO_3)^-$	93.6	20.7	99.6	14.3	40.2	58.5	64.8	50.2
	(±5)	(±8.3)	(±0.2)	(±13)	(±28)	(±13)	(±25)	(±11)
TP	n.s.[a]	26.7	n.s.[a]	5.1	76.4	54.4	37.9	46.3
		(±11.2)		(±14)	(±20)	(±1)	(±10)	(±9)
E. coli	1.4	4	1.6	2.9	1.2	2.9	1.6	1.7
	(±1)	(±0.7)	(±1)	(±1)	(±0.1)	(±0.3)	(±2)	(±2)

[a]Not significant

solids of the HF system under study, in agreement with the results of Vymazal [81]. The severity and extent of clogging depend on inflow loading, and when the system is not overloaded, the clogging is slow and is restricted to the inflow zone.

4 Conclusions and Recommendations

Studies and experiences reported in this chapter showed the suitability and the great potential of the agricultural RW use practice, reporting some approaches to solve the most common barriers still limiting its diffusion in the Mediterranean rim.

The use of municipal RW in agricultural and other sectors has been proposed since the 1970s as an opportunity to cover water shortage, save freshwater resources of high quality, and contribute to the protection of environment from pollution.

Problems related to technical aspects of treatment technologies and reuse practice have been progressively solved during last decades, especially in Mediterranean countries that have longer experience with this practice, like Sicily and Tunisia. However, in Tunisia, CW is still not considered an official treatment process.

Legislation is another aspect that still need to be fully addressed. The recently approved "Regulation on minimum requirements for water reuse" [11] in Europe is still not adopted. So, most of the existing regulations are based on semi-scientific criteria and have little or no direct relationship to public health protection. Also, their practicality is very limited. Indeed, some are very complicated and others (e.g., Italian and Hellenic) too stringent to be applied. On the other hand, Mediterranean countries still did not regulate use of RW.

Moreover, social acceptance is still not adequately investigated probably because the sensitization of the society to the features and the advantages of the use of RW in agriculture are not seriously considered by the scientists as part of the strategy of treatment and reuse.

On the other hand, as the experiences reported here highlighted, environmental and health risks can be addressed by a comprehensive monitoring of the soil-plant system when WW reuse is practiced in the agricultural context, ending with human consumption of the produced crop.

Additionally, total costs for the developing of RW use in agriculture are not sustainable and user-friendly when considering the construction, operation, maintenance, and monitoring of "additional" processes for tertiary and disinfection treatments and RW distribution networks.

Another aspect that needs to be addressed is related to costs. In particular, it is necessary to set a clear rule for sharing the total costs of treatment between the users of municipal service, who pay the part of the treatment required by discharge standards, and the users in agriculture, who should support the supplementary costs related to the treatment for achieving quality standards for reuse; this should take into account that farmers, in relation to the low profitability of Mediterranean agriculture, cannot pay the extra costs for treatment and monitoring by themselves, otherwise they would be discouraged from using them.

References

1. Collet L, Denis R, Borrell Estupina V et al (2015) Water supply sustainability and adaptation strategies under anthropogenic and climatic changes of a meso-scale Mediterranean catchment. Sci Total Environ 536:589–602
2. La Jeunesse I, Cirelli C, Aubin D et al (2016) Is climate change a threat for water uses in the Mediterranean region? Results from a survey at local scale. Sci Total Environ 543:981–996
3. EC (2018) Proposal for a regulation of the European Parliament and of the council on minimum requirements for water reuse. European Commission, p 337
4. UNWWDR (2017) UN-world water development report wastewater the untapped resource. http://www.unesco.org/new/en/naturalsciences/environment/water/wwap/wwdr/. Accessed 6 Jun 2018
5. Cirelli GL, Consoli S, Licciardello F et al (2012) Treated municipal wastewater reuse in vegetable production. Agric Water Manag 104:163–170
6. Pedrero F, Kalavrouziotis I, Alarcón JJ et al (2010) Use of treated municipal wastewater in irrigated agriculture – review of some practices in Spain and Greece. Agric Water Manag 97 (9):1233–1241

7. EEA (2009) Water resources across Europe – confronting water scarcity and drought European Environmental Agency report no 2/2009 ISSN 1725-9177
8. Tran QK, Schwabe KA, Jassby D (2016) Wastewater reuse for agriculture: development of a regional water 356 reuse decision-support model (RWRM) for cost-effective irrigation sources. Environ Sci Technol 50(17):9390–9399
9. Salgot M, Oron G, Cirelli GL et al (2017) Criteria for wastewater treatment and reuse under water scarcity (chapter 14). In: Handbook of drought and water scarcity: environmental impacts and analysis of drought and water scarcity. CRC Press, New York, pp 263–282
10. Alcalde-Sanz L, Gawlik B (2017) Minimum quality requirements for water reuse in agricultural irrigation and aquifer recharge – Towards a water reuse regulatory instrument at EU level Réédition, EUR 28962 EN, Publications Office of the European Union, Luxembourg. ISBN 978-92-79-77176-7 (print), 978-92-79-77175-0 (pdf), https://doi.org/10.2760/804116 (online), https://doi.org/10.2760/887727 (print), JRC109291
11. UE 741 (2020) Regulation on minimum requirements for water reuse
12. Ait-Mouheb N, Bahri A, Thayer BB et al (2018) The reuse of reclaimed water for irrigation around the Mediterranean Rim: a step towards a more virtuous cycle? Reg Environ Chang 8 (3):693–705
13. Cirelli GL, Consoli S, Juanicò M (2009) Moelling *Escherichia coli* concentration in a wastewater reservoir using an operational parameter MRT%FE and first order kinetics. J Environ Manag 90:604–614
14. Bole JB, Bell RG (1978) Land application of municipal sewage wastewater: yield and chemical composition of forage crops. J Environ Qual 7(2):222–226
15. Rosas I, Báez A, Coutiño M (1984) Bacteriological quality of crops irrigated with wastewater in the Xochimilco plots Mexico city Mexico. Appl Environ Microbiol 47(5):1074–1079
16. Al-Jaloud A, Hussain G, Al-Saati AJ et al (1993) Effect of wastewaters on plant growth and soil properties. Arid Soil Res Rehabil 7:173–179
17. Tzanakis VE, Paranychianakis NV, Kyritsis S, Angelakis AN (2003) Wastewater treatment and biomass production by slow rate systems using different plants species. Water Sci Technol 3 (4):185–192
18. Licciardello F, Milani M, Consoli S et al (2018) Wastewater tertiary treatment options to match reuse standards in agriculture. Agric Water Manag 210:232–242
19. Pedrero F, Alarc'on JJ (2009) Effects of treated wastewater irrigation on lemon trees. Desalination 246:631–639
20. Barbagallo S, Cirelli GL, Consoli S et al (2003) Wastewater quality improvement through storage: a case study in Sicily. Water Sci Technol 47(7-8):169–176
21. Hamilton AJ, Stagnitti F, Premier R et al (2006) Quantitative microbial risk assessment modelling for the use of reclaimed water in irrigated horticulture. In: Brebbia CA, Popov V, Fayzieva D (eds) The sustainable world series vol 13 environmental health risk III. Wessex Institute of Technology, Ashurst, pp 71–81
22. Toze S (2006) Reuse of effluent water-benefits and risks. Agric Water Manag 80:147–159
23. Aiello R, Cirelli GL, Consoli S et al (2013) Risk assessment of treated municipal wastewater reuse in Sicily Water. Sci Technol 67(1):89–98
24. Castorina A, Consoli S, Barbagallo S et al (2016) Assessing environmental impacts of constructed wetland effluents for vegetable crop irrigation international. J Phytoremediat 18 (6):626–633
25. Merlin G, Pajean JL, Lissolo T (2002) Performances of constructed wetlands for municipal wastewater treatment in rural mountainous area. Hydrobiologia 469:87–98
26. Khalil A, Prudent P, Bettaieb MM et al (2005) Pilot treatment plant: constructed soil reed bed for a cheese dairy farm effluent. In: Book of the internat symp wetland pollutant dynamics and control, Ghent University, Belgium, pp 77–78
27. Masi F, Bendoricchio G, Conte G et al (2000) Constructed wetlands for wastewater treatment in Italy: state-of-the-art and obtained results. In: Proceedings of the 7th IWA international conference on wetland systems for water pollution control, Orlando, pp 979–985

28. Puigagut J, Villaseñor J, Salas JJ et al (2007) Subsurface-flow constructed wetlands in Spain for the sanitation of small communities: a comparative study. Ecol Eng 30:312–319
29. Cirelli GL, Consoli S, Grande D et al (2007) Subsurface constructed wetlands for wastewater treatment and reuse in agriculture – five years of experience in Sicily Italy. Water Sci Technol 56(3):183–191
30. Rashidi M, Gholami M (2011) Interactive effect of plastic mulch and tillage method on yield, yield components and quality of tomato. Am Eurasian J Agric Environ Sci 4:6–12
31. Gamri S, Soric A, Tomas S et al (2014) Biofilm development in micro-irrigation emitters for wastewater reuse irrigation. Science 32(1):77–85
32. Hiskakis M, Babou E, Briassoulis D (2011) Experimental processing of biodegradable drip irrigation systems – possibilities and limitations. J Polym Environ 19:887–907
33. Rodrìguez C (1990) Evaluacion de instalaciones de microirrigacion IV Curso de Tecnologia del Riego (Evaluation of the microirrigation system IV Course on Irrigation technology) ETSIA Universidad Politecnica de Catalunia Lleida Spain
34. Pucci B, Masi F, Conte G et al (2004) Linee giuida per la progettazione e gestione di zone umide artificiali per la depurazione dei reflui civili. IRIDRA Srl, Firenze
35. M'hiri F, Kouki MS, Hanchi B (2005) Performance of constructed wetland treating domestic wastewaters in Tunisia: first experience. In: Book of abstracts of the international symposium on wetland pollutant dynamics and control, Ghent University, Belgium, pp 114–115
36. WHO (1989) Health guidelines for the use of wastewater in agriculture and aquaculture. World Health Organization
37. US EPA, Guidelines for Water Reuse AR-1530 EPA/600/R-12/618 (2012) US Environmental Protection Agency National Environmental Research Center
38. State of California (2001) "The purple book" (excerpts from the health and safety code water code and titles 22 and 17 of the California Code of Regulations). Department of Health Services, Sacramento
39. Bixio D, Thoeye C, Wintgens T et al (2008) Water reclamation and reuse: implementation and management issues. Desalination 218:13–23
40. WHO (2006) Guidelines for the safe use of wastewater excreta and greywater. World Health Organization, Geneva
41. Bastian R, Murray D (2012) Guidelines for water reuse US EPA Office of Research and Development Washington DC EPA/600/R-12/618 2012
42. Hernandez V, Bellver-Domingo Á, Hernández-Sancho F (2018) Efficiency of wastewater treatment facilities: the influence of scale economies. J Environ Manag 228:77–84
43. Qadir M, Sato T (2016) Water reuse in arid zones. In: Urban water reuse handbook. CRC Press, Boca Raton, pp 867–874
44. WHO (2014) Meeting the MDG drinking water and sanitation target: the urban and rural challenge of the decade. http://www.who.int/water_sanitation_health/monitoring/jmpfinal.pdf. Accessed Aug 2017
45. Fawell J, Le Corre K, Jeffrey P (2016) Common or independent? The debate over regulations and standards for water reuse in Europe. Int J Water Resour Dev 32:559–572
46. Ventura D, Barbagallo S, Consoli S et al (2019) On the performance of a pilot hybrid constructed wetland for stormwater recovery in Mediterranean climate. Water Sci Technol 79 (6):1051–1059
47. Cirelli GL, Consoli S, Di Grande V (2008) Long term storage of reclaimed water: the case studies in Sicily (Italy). Desalination 218:62–73
48. Rossi G, Cirelli GL (2020) Assessment of non-conventional water resources. In: Rossi G, Benedini M (eds) Water resources of Italy. World water resources, vol vol 5. Springer, Cham
49. Andersson K, Dickin S, Rosemarin A (2016) Towards "sustainable" sanitation: challenges and opportunities. Urban Areas Sustain 8(12):1289
50. SuSanA (2018) Towards more sustainable sanitation solutions – sustainable sanitation alliance vision document. http://www.waterandmegacities.org/wastewater-treatment-in-hyderabad/. Accessed 22 May 2018

51. Salama Y, Chennaoui M, Sylla A et al (2014) Review of wastewater treatment and reuse in the Morocco: aspects and perspectives international. J Environ Pollut Res 2(1):9–25
52. Collivignarelli C, Abbà A, Benigna I et al (2018) Overview of the main disinfection processes for wastewater and drinking water treatment plants. Sustainability 10:86
53. Mahjoub O, Jemai A, Gharbi N et al (2017) Public acceptance of wastewater use in agriculture: Tunisian experience. In: Hettiarachchi H, Ardakanian R (eds) Safe use of wastewater in agriculture: from concept to implementation. UNU-FLORES. Springer, Cham
54. Baumann DD (1983) Social acceptance of water reuse. Appl Geogr 3:79–84
55. Drechsel P, Mahjoub O, Keraita B (2015) Social and cultural dimensions in wastewater use. In: Drechsel P, Qadir M, Wichelns D (eds) Wastewater: an economic asset in an urbanizing world geographical focus: low- and middle-income countries part 3 the enabling environment for use. Springer, pp 75–92
56. Almuktar SAAAN, Abed SN, Scholz M (2018) Wetlands for wastewater treatment and subsequent recycling of treated effluent: a review. Environ Sci Pollut Res 25:23595–23623
57. Borkar RP, Mahatme PS (2011) Wastewater treatment with vertical flow constructed wetland. Int J Environ Sci 2(2)
58. Scholz M, Hedmark Å (2010) Constructed wetlands treating runoff contaminated with nutrients. Water Air Soil Pollut 205:323–332. https://doi.org/10.1007/s11270-009-0076-y
59. Hammer D (1989) Constructed wetlands for wastewater treatment: municipal industrial and agricultural. Lewis Publishers, Chelsea
60. Edberg SC, Rice EW, Karlin RJ, Allen MJ (2000) Escherichia Coli: the best biological drinking water Indicator for public health protection. J Appl Microbiol 88:1068–1168
61. Khatiwada N, Polprasert C (1999) Kinetics of faecal coliform removal in constructed wetlands. Water Sci Technol 40(5):109–116
62. Conte G, Matinuzzi N, Giovannelli L, Pucci B, Masi F (2001) Constructed wetlands for wastewater. Water Sci Technol 44 (11-12):339–343. https://doi.org/10.2166/wst.2001.0849
63. Noemi R, Moshe A, Gideon O (2004) A pilot study of constructed wetlands using duckweed (Lemna gibba L.) for treatment of domestic primary effluent in Israel. Water Res 38:2241–2248
64. Liu Y, Imlay JA (2013) Cell death from antibiotics without the involvement of reactive oxygen species. Science 339(6124):1210–1213. https://doi.org/10.1126/science.1232751
65. Ha NTH, Sakakibara M, Sano S (2011) Accumulation of Indium and other heavy metals by Eleocharis acicularis: an option for phytoremediation and phytomining. Biores Technol 102:2228–2234
66. Ventura D, Ferrante M, Copat C, Grasso A, Milani M, Sacco A, Licciardello F, Cirelli GL (2021) Metal removal processes in a pilot hybrid constructed wetland for the treatment of semi-synthetic stormwater. Sci Total Environ 754:142221. https://doi.org/10.1016/j.scitotenv.2020.142221
67. APHA (2005) Clesceri LS, Greenberg AE, Eaton AD (eds) Standard methods for the examination of water and wastewater20th edn. American Public Health Association the American Water Works Association and the Water Environment Federation, Washington
68. Ministerial Decree 185 (2003) "Norme tecniche per il riutilizzo delle acque reflue" ("Technical standards for wastewater reuse") GU n169 del 23-07-2003
69. Aiello R, Cirelli GL, Consoli S (2007) Effects of reclaimed wastewater irrigation on soil and tomato fruits: a case study in Sicily (Italy). Agric Water Manag 93:65–72
70. IWA (2020) Assessment of treatment plant performance and water quality data – a guide for students, researchers and practitioners. Von Sperling M, Verbyla ME, Oliveira SM (eds). IWA Publishing
71. IWA (2019) Wetland technology: practical information on the design and application of treatment wetlands. In: Langergraber G, Dotro G, Nivala J, Rizzo A, Stein OR (eds). IWA Publishing. https://doi.org/10.2166/9781789060171
72. Kadlec RH, Wallace SD (2009) Treatment wetlands.2nd edn. CRC Press, Boca Raton
73. Kadlec RH, Knight RL (1996) Treatment wetlands. Lewis Publishers, Boca Raton, 893

74. Brix H (1998) Denmark. In: Constructed wetlands for wastewater treatment in Europe, In: Vymazal J, Brix H, Cooper PF, Green MB, Haberl R (eds). Backhuys Publisher, Leiden, p 123
75. Vymazal J, Kröpfelová L (2011) A three-stage experimental constructed wetland for treatment of domestic sewage: first 2 years of operation. Ecol Eng 37(1):90–98
76. Ávila C, Garfí M, García (2013) Three-stage hybrid constructed wetland system for wastewater treatment and reuse in warm climate regions. Ecol Eng 61A:43–49
77. Metcalf and Eddy, Inc (1991) Wastewater engineering treatment disposal and reuse.3rd edn. McGraw-Hill Book Company, New York
78. Barbagallo S, Cirelli GL, Marzo A et al (2013) Effect of different plant species in pilot constructed wetlands for wastewater reuse in agriculture. J Agric Eng 44:796–802
79. Marzo A, Ventura D, Cirelli GL et al (2018) Hydraulic reliability of a horizontal wetland for wastewater treatment in Sicily. Sci Total Environ 636:94–106
80. Legislative Decree 152 (2006) “Norme in materia ambientale” (“Standards on the environment”) GU n 88 del 14 aprile 2006 - Supplemento Ordinario n 96
81. Vymazal J (2018) Does clogging affect long-term removal of organics and suspended solids in gravel-based horizontal subsurface flow constructed wetlands? Chem Eng J 331:663–674

Treatment Systems for Agricultural Drainage Water and Farmyard Runoff in Denmark: Case Studies

Lorenzo Pugliese, Goswin J. Heckrath, Bo V. Iversen, and Salvatore Straface

Contents

Abstract Nutrient losses from agricultural lands are responsible for degrading water quality and accelerating eutrophication at local and regional scale. Subsurface tile drainage is an agricultural water management measure extensively used in some Northwestern European countries to improve poor internal field drainage and crop production. However, drains constitute artificial and direct conduits responsible for

L. Pugliese (✉), G. J. Heckrath, and B. V. Iversen
Department of Agroecology, Aarhus University, Tjele, Denmark
e-mail: lorenzo.pugliese@agro.au.dk; goswin.heckrath@agro.au.dk; bo.v.iversen@agro.au.dk

S. Straface
Department of Environmental Engineering, University of Calabria, Arcavacata di Rende, Italy
e-mail: salvatore.straface@unical.it

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 45–66, DOI 10.1007/698_2021_784,

shortening the residence time and accelerating nutrient transport through the hydrological system. Thus, they put the aquatic ecosystems at risk since they promote rapid drainage water transport and reduce the possibility for natural nutrient removal.

Edge-of-field technologies have been developed and implemented in the last decades to reduce diffuse pollution caused by nitrogen (N) and phosphorus (P) losses. These technologies are primarily used in critical source areas, where measures at farm-scale appear insufficient to meet the removal targets. They are placed at the edge of agricultural fields and connected to the main drainage pipe. Widely recognized technologies include constructed wetlands, woodchips bioreactors, and filter systems. This chapter presents the results obtained in Denmark from three different and currently investigated edge-of-field technologies treating agricultural drainage water.

Keywords Agricultural drainage water, Constructed wetland, Edge-of-field technologies, Filter system, Nutrient losses, Woodchip bioreactor

1 Introduction

1.1 Agriculture Challenges in Northwestern Europe

Increasing nutrient load to coastal waters has been documented in the last decades on a global scale. More severe effects have been observed in regional seas having certain hydrographic characteristics and surrounded by high densely populated coasts. In Europe, the North and Baltic Seas are receiving increasing nutrient loads due to anthropogenic inputs of nitrogen (N) and phosphorus (P) being responsible for point source and diffuse pollution. The North Sea is a shelf see covering an area of 570.000 km^2 and extending from Great Britain to Denmark. The water residence time ranges between 365 and 500 days [1]. The Baltic Sea in one of the largest blackish-water basin in the world with an area of 377.000 km^2. The semi-enclosed shape is responsible for water residence time of about 30–40 years [2].

Regional seas receive nutrients loads from inland waters such as lakes, rivers, and streams, resulting in adverse effects of structure and functionality for regional and local ecosystems. The overly nutrient enrichment of water bodies is responsible for eutrophication which causes biodiversity reduction by excessive blue-green algae growth.

The protection of water bodies has been on the EU agenda since 1980. Several directives were enacted and implemented over the last four decades to tackle the problem of eutrophication. Among the most important there are the Water Framework Directive 2000/60/EC, the Urban Wastewater Treatment Directive 91/271/EEC, and the Nitrates Directive 91/676/EEC. This resulted in a substantial reduction of point source pollution in the North and Baltic Sea area. However, diffuse

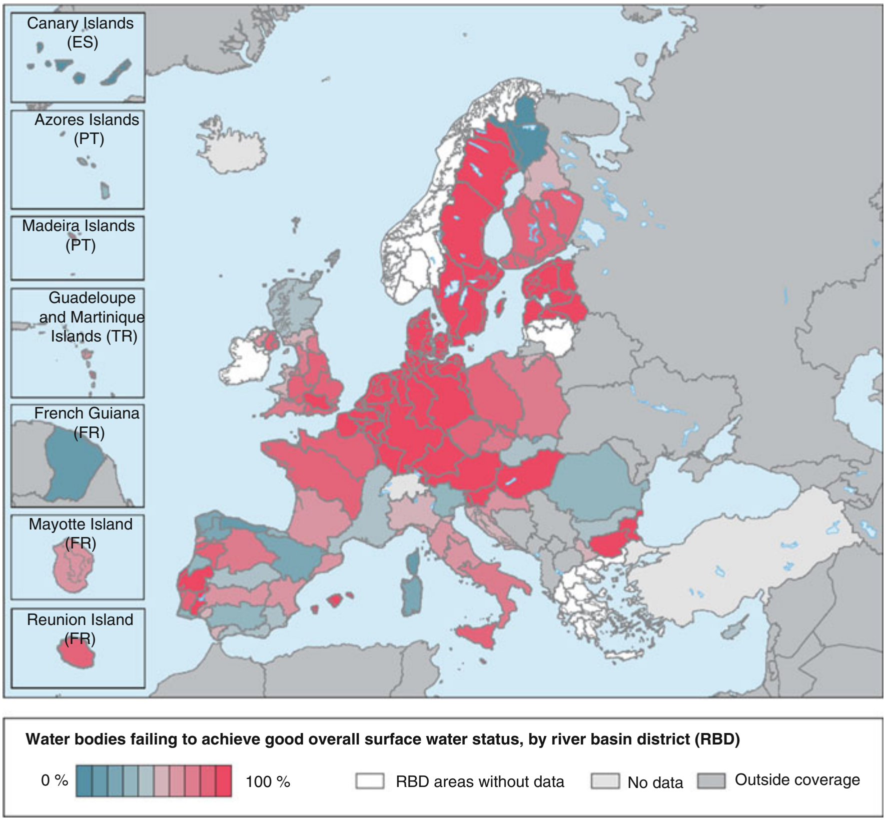


Fig. 1 Percentage of water bodies in Europe's river basin districts that are not in good ecological status/potential: second river basin management plan [3]

pollution primarily caused by intensive agriculture remains a serious problem for meeting the EU's minimum target of good status (Fig. 1).

1.2 Tile Drainage Water

Subsurface tile drainage is extensively used in order to improve water conditions in soils and thus soil cultivation and crop production. Artificial drainage is primarily used in low-lying areas characterized by (1) a relatively high groundwater table, (2) low permeable soil, and (3) wetlands with organic soils. Under these circumstances, artificial tile drainage effectively lowers the groundwater table, removes excess water, and improves soil porosity and structure. Dry soils warm up faster than wet soils, thus increasing soil temperatures in spring which favor earlier sowing and germination of seeds. Tile drainage also improves soil trafficability and reduces the risk of soil compaction due to use of heavy machinery and tillage on wet soils. This is particularly important for climatic regions characterized by limited growing seasons. Additional positive effects include more water infiltration and less surface runoff, which decreases soil and nutrient losses. Finally tile drainage reduces pick flows and the water volumes lost from the watershed. The main drawbacks of this practice is the great impact on the water and nutrient balance of a landscape. Tail drains are direct pathways for the transport of nutrients, which are not filtered by contact with soil particles. Additionally, this management practice changes the hydrology of the landscape, reducing its overall water storage capacity.

Depending on soil/crop type and costs, drainage pipes are generally installed at a depth of 0.6–1.2 m and spaced 10–100 apart [4]. Relatively high presence of tile drains in agricultural areas is found in some Northwestern European countries, including the UK (30%), the Netherlands (34%), in the Scandinavian countries (40%) and Finland (91%) [5, 6]. In Denmark, tile drains cover 50% of the agricultural area primarily constituted of glacially derived clayey soils and located in the eastern part of the country [7]. Subsurface geology has proved to be a key factor governing drain flow dynamics, with higher drainage in stream valleys and wetlands and lower drainage in hilly catchment areas. Regarding soil type, heavy clay soils show an initial slow drainage response followed by a rapid increase, while other soil types have a more constant response. A statistically significant correlation was found between the sand percentage in the subsurface geology and the drain flow volume [8]. Moreover, results from a study on the clay till from the Norsminde catchment in Denmark revealed that the geology below 3 m has a large impact on drain flow. Deeper geology must thus be considered when modeling tile-drained agricultural fields to be able of capturing the transient dynamics, unless an impermeable layer is found at a shallow depth [9].

Tile drainage discharge is generally seasonally dependent and increases in response to precipitation/snowmelt while it decreases during drought periods. A study investigating the effect of tile drains on flow in a Danish Weichsel till area showed a piezometer head variation up to nearly 3 m between summer and winter [8]. The decrease in head occurred in spring–summer during 5–5.5 months, while a rapid increase was documented when autumn water surplus started. A relatively high average tile drain discharge contribution (83%) was measured in the Netherlands in response to some major rainfall events characterizing the winter and spring seasons [10]. Thus, a strong seasonal pattern can be identified for tile drainage with greater discharges occurring during the winter and spring seasons and very small or absent discharges across the summer season.

1.3 Nutrient Losses in Tile Drains

Natural flow routes for water and nutrient transport are partially dismissed by subsurface tile drains. These artificial and direct conduits shorten the residence time and cause a rapid nutrient transfer through the hydrologic system.

Tile drains facilitate N transport primarily in soluble forms. Factors facilitating the loss of N are local climate, soil and crop type, length of growing season, options of winter cover crops and catch crops, tillage and soil management practices. Certain factors are field specific and cannot be changed, while others may be adjusted to reduce N losses [11]. A study in the UK investigated the risk of nutrient transfer through tile drains for biosolids amended soils [12]. Significant concentration of nitrate varying between 3 and 34 mg/L was found before amendment. An experimental field study in the Netherlands estimated a 91% contribution from tile drains of the total nitrate load [10].

The major factors influencing P and sediment transport from tile drains are soil characteristics including preferential flow paths, P sorption capacity and redox conditions, drainage depth and spacing of the drains, surface inlets, management practices such as tillage, cropping systems, P application rate and timing, hydrology, and climate [13]. Total P (TP), dissolved P, and particulate P (PP) are the most commonly investigated P forms. In England, annual losses of TP and dissolved P through field tile drains were estimated to be 0.37–2.64 and 0.037–0.74 kg/ha/yr, respectively [14]. In the Netherlands, loads of TP from sandy soils to tile drains accounted for 0.14–0.31 kg/ha/year. [15]. The concentration of the different P forms in tile drains depends on the drain capacity and on the operating frequency, thus, varying with flow and season. Export of P is often characterized by an early pulse caused by preferential transport of surface water through macropores and tiles during precipitation, irrigation, and/or snowmelt events [16]. In Sweden, a number of multi-event, seasonal, and annual studies evaluated the TP load to tile drains to vary between 0.02 and 4.63 kg/ha/year [17, 18]. Heckrath et al. [19] found a larger fraction of dissolved P (66–68%) in UK tile drainage water in comparison to PP (8–35%). However, PP may represent a large fraction of TP under high-flow conditions. A six time greater P loss was measured in England during stormflow in comparison with baseflow from a grassland catchment. Dissolved P accounted for 70% of the total losses during baseflow conditions, while predominantly PP loss occurred during stormflow [20]. Dominant PP concentrations were also reported from studies in Sweden and Finland [21, 22]. The non-growing season (from December to March) was reported to account for 35–40% of annual P losses in Denmark [21]. A series of field experiments investigating subsurface P transport in Denmark reported a minimum and maximum TP concentration of 0.5 and 2 mg/L, respectively, with temporary maximum of 4.8 mg/L [23].

2 State of the Art

Nutrient losses through drainage discharge can be mitigated at farm-scale. Measures include better control in the application of mineral fertilizers and the use of agricultural management practices. Among the most common practices there are cover/

catch crops, controlled trafficking, subsoiling, vegetated buffer strips. Cover/catch crops protect soils from erosion, reduce the amount of runoff, and ensure that nutrients stay in the root zone. Controlled trafficking preserves soil structure and reduces runoff and erosion by restricting compaction to specific traffic lines. Indirect benefits of this measure include reduced waterlogging and enhanced soil biological activity due to improved levels of organic matter. Vegetated buffer strips are strips of land located between agricultural fields and watercourses, aiming at trapping sediments and immobilizing soluble nutrients through plant uptake or microbial degradation. However, measures at farm-scale may be insufficient, especially in critical source areas of nutrient losses.

Edge-of-field technologies are recognized as non-point and economically feasible nutrient mitigation solutions. Despite the higher cost in comparison to farm-scale measures, these technologies provide high nutrient removal, promote biodiversity, and increase flood control. They are generally used for critical source areas and installed at the edge of tile-drained agricultural fields. Constructed wetlands, woodchips bioreactors, and filter systems are among the edge-of-field technologies tested in Denmark to tackle nutrient losses from drainage discharge.

2.1 Constructed Wetlands

Constructed wetlands (CWs) are ecologically engineered systems ameliorating water quality through natural processes involving wetland vegetation, soil, and their associated microbial assemblages [24]. The primary treatments include sedimentation, filtration, oxidation, reduction, adsorption, and precipitation. The growing popularity in the last decades is due to low operational costs and energy consumption.

The classification of CWs generally depends on three main factors: water level in the system, water flow movement, type of macrophytes (emergent, submerged, floating-leaved, free-floating) [25, 26]. Surface flow (SF)/free water surface CWs and subsurface flow (SSF)-CWs are considered the main two types. The former (SF-CW) is similar in appearance to natural marshes and it is constituted of basins naturally or artificially waterproofed. In this system, the water surface is kept above the substrate at a depth which typically ranges between 0.3 and 1 m. Aerobic conditions characterize the near-surface layer of water, while anaerobic conditions are found in the deeper layers. Shallow areas favor emergent plant growth and homogenize the water flow through the formation of small channels simulating a plug-flow reactor behavior. Organic removal occurs via settling and filtration of suspended particles and microbial degradation and settling of colloidal particles. An artificially waterproofed basin entirely filled with inert material of appropriate particle size characterizes the SSF-CWs. According to the water flow movement in the system, SSF-CW can have a horizontal (HSSF-CW) or vertical (VSSF-CW) flow configuration. Anoxic conditions are predominant for both configurations as the water flow level is continuously kept below the inert material. However, continuous flow from the inlet is generally found in HSSF-CWs, whereas discontinuous flow from the inlet occurs in VSSF-CWs, which resemble more batch reactors [27]. The construction cost of SF-CWs is lower in comparison to SSF-CWs. Additionally, the former offers greater flow control and more diverse wildlife habitat. However, nutrient removal per unit of land is lower. Thus, larger agricultural areas are needed to achieve comparable results. The SSF-CWs perform better under cold climate due to the insulation effect of the unsaturated surface layer [28].

The removal of N in SF-CWs is highly variable and primarily controlled by the inflow load and the ratio between the CW and the drained catchment (W/C) surface area [29]. Results from agricultural wetlands in Finland, Sweden, and the USA demonstrated that for W/C of at least 2%, a N removal of 20% can be obtained, while for W/C $> 7\%$ a N removal of 50% can be reached [30]. Removal of N equal to 40% was reported for a W/C ratio of 5% by Tanner et al. [31]. A more recent review [32] on SF-CWs revealed that W/C $> 1\%$ does not result in any substantial increase of N removal. However, the W/C ratio does not account for the system volume defined by the water depth and may lead to inaccurate evaluation of the CW effectiveness. Several studies indicated that SF-CWs work as P sinks. Nevertheless, other studies demonstrated that these systems can release P when receiving event-driven drainage discharge peaks. Retention of P occurs through (i) deposition of PP on the basin soil surface, (ii) sorption of dissolved reactive P (DRP) onto the reactive soil sites, (iii) DRP precipitation with Fe and Al oxides and Ca in the water column to the top sediments, and (iv) biological uptake by plants, phytoplankton, and bacteria of bioavailable forms [33]. The contribution by deposition generally constitutes the main retention mechanism. The DRP retention by sorption sites is variable and depends on geochemical characteristics, pH, redox conditions, and P concentrations at the soil–water interface. Calcium is the major P sorbent for mineral alkaline soils, while Fe and Al oxides are the most common sorbents for mineral acidic soils. Retention by plant uptake increases during the growing season and it is normally low.

2.2 *Denitrifying Bioreactors*

Carbon-based SSF-CWs are optimized engineered systems, targeting primarily N losses via subsurface tile drainage. The failure or success of these systems largely depends on the hydraulic retention time (HRT), temperature, and microbiology [34]. The HRT is defined by the system design, the flow rate, and the filter media porosity. Different design methods have been proposed in the last decades to cope with variable flow rates. Denitrification processes are affected by temperature and thus follow seasonal variations. Better performances are generally achieved at higher temperature. The carbon (C) media represents the source supporting denitrification under anaerobic conditions. The choice of the bioreactor carbon media depends upon cost, porosity, C: N ratio, and longevity. The most commonly used media include cobs, corn stalks, wheat and barley straw, pine and almond shells, and woodchips media [35]. All these media are characterized by dual porosity structure which promotes diffuse mass exchange into immobile domains. However, woodchips media are generally preferred due to the relatively low cost, hydraulic conductivity, longevity, and high C:N ratio.

Bruun et al. [36] investigated the N removal efficiency in different hydraulic designed woodchip-based SSF-CW. The aspect ratio (width-to-height ratio) appeared to be an important parameter defining the cross sectional area and the flow pathway length. Initial results showed that the horizontal flow design had better N removal efficiency compared with vertical upward and downward flow designs. However, a later tracer test and modeling investigation revealed that the vertical downward design had the largest N removal rate (67% under low flow conditions), which was primarily attributed to the longer residence time. In contrary, the vertical upward design showed the most pronounced non-equilibrium and lowest N removal [37]. Field studies reported N reductions varying from 2 to 22 g/m^3/d in woodchips bioreactor (WB) having a size of <1 to >1,000 m^3 with lower rates often associated with N limitations [34]. A practice-oriented review carried out by Christianson et al. [35] showed that the removal rate for SSF-CWs varied between 12 and 76%. Chun et al. [38] demonstrated the ability of these systems to effectively reduce N pulses at high concentrations.

Studies on P retention by woodchip-based bioreactors treating agricultural drainage water are limited. However, comparable studies can be found in the literature. Robertson et al. [39] investigated WB treating septic effluent and found a <30% reduction of soluble P concentration. On the contrary, no significant change was found by Schipper et al. [40] in P concentrations for dairy shed and treated domestic effluent after treatment in large-scale (80–300 m^3) WBs. Gottschall et al. [41] demonstrated that WBs can also retain P (30%). Finally, Choudhury et al. [42] investigated a treatment system for vegetable wash water constituted of a sedimentation tank and woodchip filter installed in a subsurface trench. Results showed that P removal was mostly associated with PP (91%), while DRP in the outflow was only affected to a minor extent.

2.3 Filter Systems

Filter systems or simply removal structures have been widely tested in the last decades to tackle primarily DRP losses to surface waters. Effective filters have a sufficient size and hydraulic conductivity and an effective P sorption capacity. The system is placed in hot spots and hydrologically active areas receiving DRP concentration preferably larger than 0.2 mg/L [43]. The unconsolidated P sorbing material (PSM) is the core of the system. Besides, having a strong sorption capacity, the PSM should be physically stable, operate under natural pH, and must not produce pollution by releasing toxic contaminants. A natural, synthetic, or industrial by-product PSM characterized by a strong P sorption capacity is generally used. These materials can be grouped in iron (Fe)/aluminum (Al) based and calcium

(Ca)/magnesium (Mg) based PSM [44]. The DRP retention occurs by chemisorption or ligand exchange onto the sorption sites surface for the Fe/Al based PMs, while it occurs through precipitation for Ca/Mg based PSM [45].

Results from laboratory experiments revealed that Fe-oxide based PSM presents higher sorption capacity, reactivity, and stability in comparison to Ca-based PSM [46]. High P removal efficiency (>95%) in solution up to 100 mg/L was also found by Allred and Racharaks [47] who tested Fe-based PSM including zero-valent Fe, porous Fe composite, sulfur modified Fe and Fe oxide/hydroxide. Further experiments confirmed good P retention and hydraulic conductivity in treating agricultural drainage waters with porous Fe composite [48]. Studies investigating P retention from agricultural drainage discharge at field scale are limited. Performances are expected to be lower due to hydrological factors, which are not taken into account at laboratory scale. The P retention of two on-site filters located in southwestern Finland was monitored in a long-term field-scale experiment [49]. The sand filters were enhanced with a layer of Fosfilt-s, a side product of titanium dioxide production. Results showed that the system was able to remove 37% of TP and 45% of DRP. Small scale field filters containing iron coated sand were successfully installed and tested by Vandermoere et al. [50]. During the 10 week field trials, the authors reported a P removal efficiency between 70 and 90%.

3 Case Studies

In Denmark, a number of edge-of-field technologies have been developed and investigated following the national regulation in order to reduce nutrient losses from agricultural land to surface waters. Despite the positive results, a continuous effort is put in place in order to find more suitable and cost-effective solutions contributing to long-term and stable nutrient removal from drainage waters. Below are presented three case studies and their corresponding results obtained during long-term monitoring campaigns.

3.1 Surface-Flow Constructed Wetland: Fillerup

The SF-CW is located in Fillerup, within the Norsminde Fjord catchment – Denmark (55°57′34”N 10°05′30″E) [50]. The system was constructed in 2010 and placed at the outlet of the main discharge pipe receiving tile drainage water from a 45 ha sandy clay loam morainic agricultural field. The system occupied a total surface area of 0.28 ha (0.6% of the drainage area). Three main components could be identified: (1) a sedimentation basin, (2) deep zones, and (3) shallow zones (Fig. 2). The 1-m deep sedimentation basin allowed removal of coarse particles and facilitated even flow across the entire system. Deep zones (1-m deep) increased the HRT and provided flow redistribution. Shallow zones (0.3-m deep) promoted vegetation

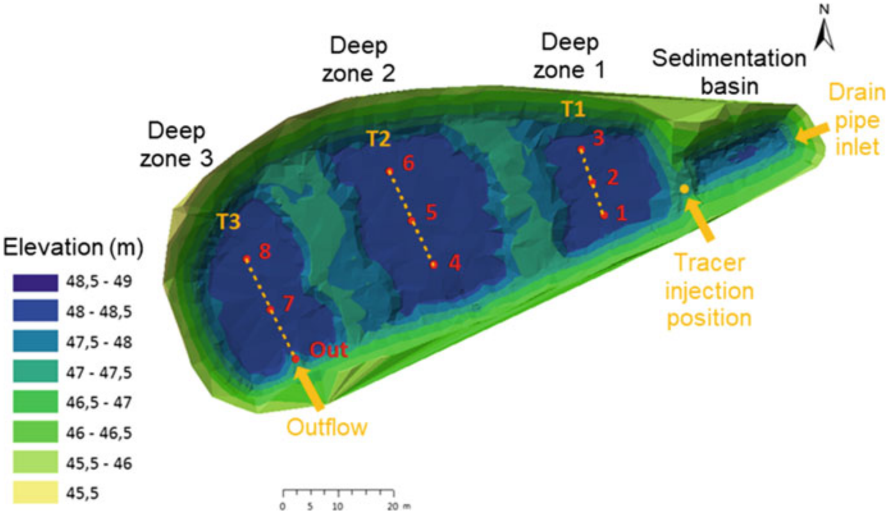


Fig. 2 Schematic of the surface-flow constructed wetland (SF-CW) in Fillerup. The main system components are also indicated (modified from [51])

growth and limited flow dispersion. Typha sp., Phragmites australis, Epilobium sp. were the dominant emerging plants, while Characeae was the dominant submerged species.

The monitoring program ran from January 2013 to May 2017 under the iDRAIN project (https://idraen.dk/). Values of tile drainage discharge (Q) were measured by an electromagnetic flow meter and continuously logged by a pulse data logger having a 10 s resolution. Daily water samples were collected automatically at the inlet and outlet of the system for the determination of the nutrient concentration. Chemical analysis of the water samples was carried out either individually or as a composite sample according to the Q hydrograph. In particular, individual analysis was carried out during periods characterized by highly variable drainage discharge, while composite samples were analyzed during periods with steady and low drainage discharge. Analysis for TN was carried out on unfiltered samples, which were initially autoclaved for 30 min at 121 °C in an alkaline peroxydisulfate solution. Subsequently, the digested samples were acidified and moved to an autoanalyzer for measuring their adsorbance. Analysis for TP was carried out using a spectrophotometer at 890 nm with ascorbic acid (5%) after 30 min acid persulfate (5%) digestion in autoclave at 121 °C [52, 53].

Values of Q across two entire hydrological years (from August to end of July) were highly variable with distinct peaks caused by heavy precipitation events (Fig. 3a). A number of two periods, corresponding to the autumn–winter season characterized by highly variable Q values and peaks up to 24 L/s, can be identified. On the contrary, lower Q values were generally recorded during the spring–summer seasons. Daily TN inlet concentrations varied between 0.0 and 18.6 mg/L, while

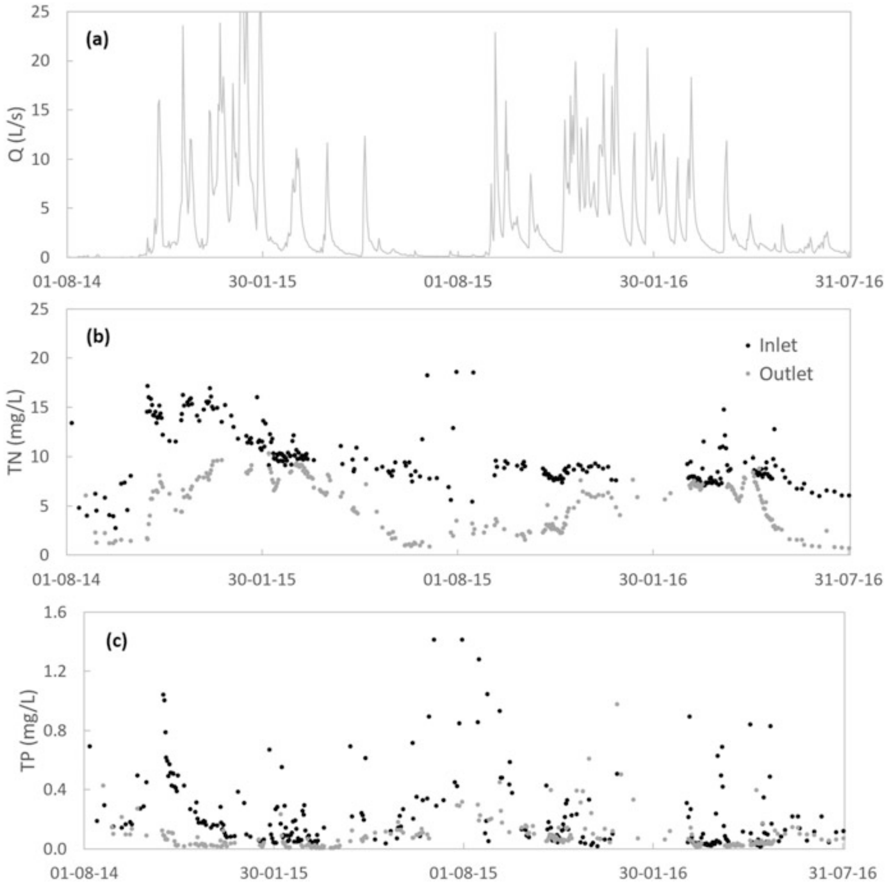


Fig. 3 Daily (**a**) drainage discharge (Q), (**b**) inlet and outlet concentration of total nitrogen (TN), and (**c**) total phosphorus (TP) for the SF CW in Fillerup

outlet concentrations ranged from 0.7 to 15.7 mg/L (Fig. 3b). Major differences between inlet and outlet TN concentrations can be identified especially across spring–summer seasons. The yearly TN removal efficiency of the system varied between 37 and 42% (Table 1). Discharge-weighted TP inlet concentrations varied between 0.01 and 1.42 mg/L, while outlet concentrations ranged from 0.0 to 1.0 mg/L (Fig. 3c). In contrast to TN, differences between inlet and outlet TP concentrations do not follow a clear seasonal trend. The yearly TP removal efficiency was higher in comparison with TN and ranged between 43 and 73% (Table 1).

Table 1 Yearly drainage discharge (Q), total nitrogen (TN), and total phosphorus (TP) at the inlet, outlet, and removed (%) in Fillerup

Case study	Hydrological (year)	Q (m^3)	TNin (kg/ha)	TNout (kg/ha)	TNremoval (%)	TPin (kg/ha)	TPout (kg/ha)	TPremoval (%)
Fillerup[a]	2014/2015	103,291	35	22	37	0.565	0.151	73
	2015/2016	120,197	27	16	42	0.875	0.497	43

[a]Kjærgaard et al. in preparation

3.2 *Surface-Flow Constructed Wetland Paired with Woodchip Bioreactor: Ryaa*

The SF-CW + WB was located in Ryaa, within the Limfjorden catchment – Denmark (57°13′05.8”N, 9°44′19.7″E) [54]. This design concept pairs a SF-CW and a WB in one system to ensure significant reduction of both P and N. Limited retention of P was in fact documented in WBs, while a similar effect for N was reported in CWs [41, 55]. The additional advantage is the smaller agricultural area needed for construction (0.1% to 0.2% of the catchment area) compared with standalone and currently used SF-CWs (~1%) [54]. The SF-CW + WB was established in 2011 and received through a pumping system tile drainage water from 85 ha of freshwater peat agricultural fields. The system occupied a total surface area of 0.19 ha (0.1% of the drainage area). The main system components were (i) a sedimentation basin, (ii) the WB, and (iii) a clarification basin, all being 1-m deep (Fig. 4). The sedimentation basin promoted sedimentation of suspended particles and PP. Denitrification was activated in the WB, which also allowed P immobilization and deposition. The clarification basin finalized the process by oxygenating the anoxic effluent leaving the system. Phragmites australis was the dominant emerging plants.

The monitoring program ran from August 2016 to June 2019 under the Future Cropping project (https://futurecropping.dk/). The procedure for Q sampling and TN and TP analysis is described in details for the previous field case.

During three entire hydrological years (from August to end of July), a number of three high Q periods can be identified with peak flows >28 L/s (Fig. 5a). These periods correspond to the autumn–winter season. On the contrary, lower Q values were generally recorded during the spring–summer seasons. However, this trend in 2017/18 was less pronounced. Daily TN inlet concentrations varied between 1.3 and 17.5 mg/L, while outlet concentrations ranged from 0.6 to 14.1 mg/L (Fig. 5b). Inlet

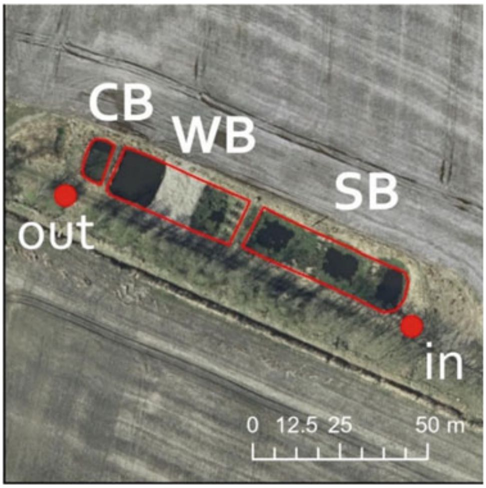


Fig. 4 Orthophoto of the surface-flow constructed wetland (SF-CW) paired with the woodchips bioreactor (WB) in Ryaa. The main system components are also indicated as sedimentation basin (SB), WB and clarification basin (CB) together with inlet (in) and outlet (out) (modified from [54])

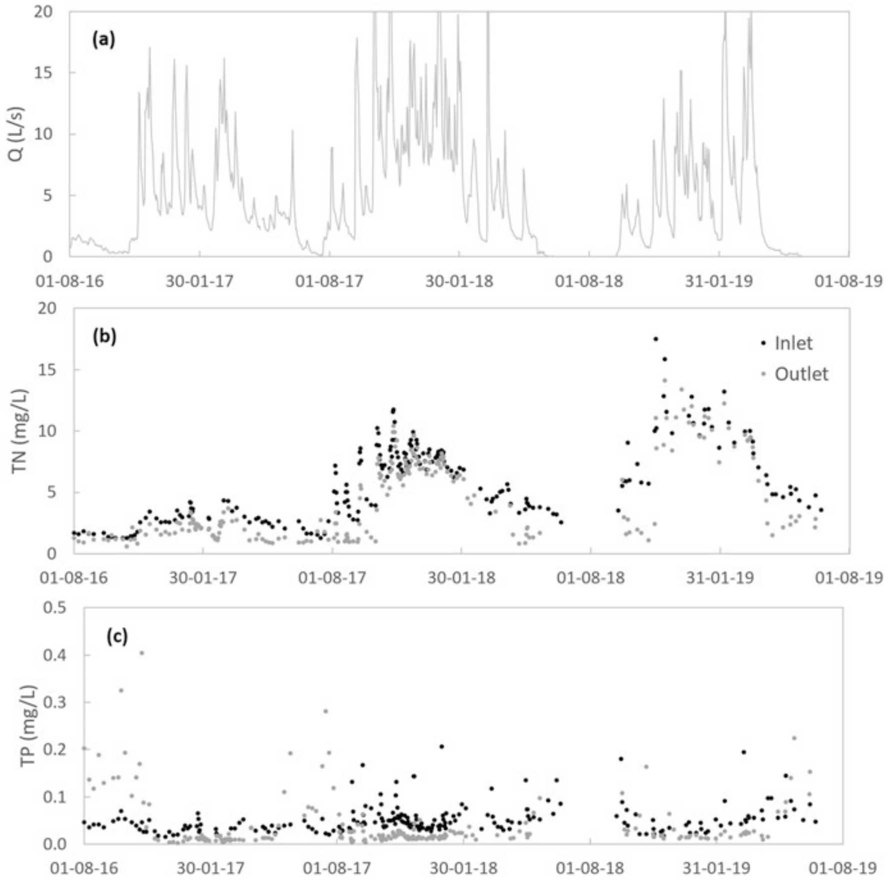


Fig. 5 Daily (**a**) drainage discharge (Q), (**b**) inlet and outlet concentration of total nitrogen (TN), and (**c**) total phosphorus (TP) for the SF CW + WB in Ryaa

and outlet TN concentration increased for increasing Q and their difference remained stable across the entire monitored period. The yearly TN removal efficiency of the system varied between 8 and 32% (Table 2). Discharge-weighted TP inlet concentrations varied between 0.0 and 0.4 mg/L, while outlet concentrations ranged from 0.0 to 0.2 mg/L (Fig. 5c). Differences between inlet and outlet TP concentrations did not follow a clear seasonal trend. Data scattering was observed during the first hydrological year with outlet TP concentrations bigger than inlet values. These variations must be due to the release of sediment-bound P, which is caused by biogeochemical factors affecting P cycling into the system [33]. The yearly TP removal efficiency varied markedly and ranged from 0 to 67% (Table 2).

Table 2 Yearly discharge (Q), total nitrogen (TN), anfd total phosphorus (TP) at the inlet, outlet, and removed (%) in Ryaa

Case study	Hydrological (year)	Q (m^3)	TNin (kg/ha)	TNout (kg/ha)	TNremoval (%)	TPin (kg/ha)	TPout (kg/ha)	TPremoval (%)
Ryaa GT[a]	2016/17	124,670	4	3	32	0.055	0.055	0
	2017/18	194,155	16	13	18	0.138	0.045	67
	2018/19	108,647	13	12	8	0.064	0.036	44

[a]Pugliese et al. [54]

3.3 Filter System: Rodstenseje

The filter system was located in Rodstenseje, within the Norsminde Fjord catchment – Denmark (55°57′22.0”N, 10°09′34.3″E). The system was constructed in 2011 to treat a fraction of the tile drainage water collected from a 100 ha agricultural fields with loamy, morainic soils [56]. Drainage water entered first a sedimentation pond and was subsequently abstracted by a submerged siphon pipe. The main components of the system filter were the following: (1) a distribution well, (2) a well for discharge measurements, (3) a sediment well, (4) a monitoring well, (5) a reactive P-filter, and (6) a monitoring well at the outlet of the system (Fig. 6). Cylindrical concrete wells housed the different components which were connected by 200 mm diameter PVC pipes. A hydraulic head of 0.45 ± 0.05 m existed between the distribution well and the outlet led water through the system over a distance of 7.2 m.

The focus of the filter system study was to evaluate the capability of the reactive filter to remove soluble P. The reactive P-filter was constituted of a purpose-build metallic cage defined by two concentric cylinders having an inner and outer diameter of 0.8 and 1.5 m, respectively, and a height of 1.8 m. This specific design was chosen to provide a high cross sectional area, thereby ensuring longer contact between flowing water and the sorption sites in the filter matrix. Commercially available crushed seashells (2–5 mm) were chosen as a filter material based on previous lab results evaluating its physicochemical properties [57]. Seashells were retained into the filter cage by a polypropylene net having a mesh opening of 1.5 mm.

The monitoring program ran from May 2015 to May 2017 under the SupremeTech project (https://supremetech.dk/). Values of Q entering the system were automatically measured at the second well through an electromagnetic flow meter and continuously logged every 15 min. Automatic water sample was collected at the distribution well (ISCOin) and in the monitoring well after the reactive P-filter (ISCOout). The majority of the water samples were analyzed individually and only 2% were analyzed as composite samples. Analysis for molybdate reactive P (MRP)

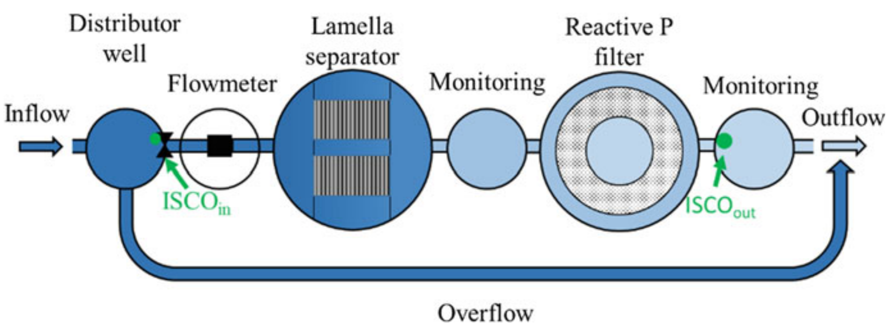


Fig. 6 Schematic of the filter system in Rodstenseje. The main system components are also indicated [56]

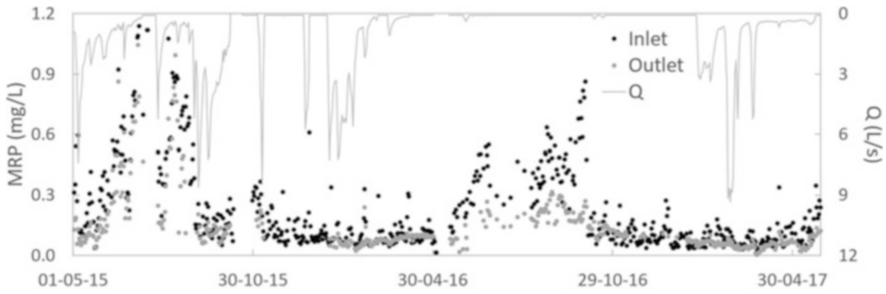


Fig. 7 Molydbate reactive phosphorus (MRP) for the filter system in Rodstenseje. Daily values of tile drainage discharge (Q) are given on the secondary axis (modified from [56])

was performed according to the method of Murphy and Riley [52] after filtration through a 0.45 μm cellulose-acetate membrane.

Higher Q characterized the first monitoring year with peaks of 8.9 L/s (May 2015–May 2016) (Fig. 7). Remarkable increase of Q during the second monitoring year was only registered between January and March 2017. Inlet values of MRP varied between 0.0 and 6.3 mg/L, while outlet values range from 0.0 to 1.3 mg/L. The highest values were generally measured during the spring–summer season with more pronounced differences between inlet and outlet during the second monitoring year. More scattering was recorded during the first spring–summer season.

4 Conclusions

This chapter presents the results from long-term monitoring programs of three edge-of-field technologies tackling nutrient losses from agricultural fields. The drainage water (Q) entering these systems has relatively low nutrient concentration and highly variable loads. Values of N and P removal performance varied between hydrological years and systems. Results showed that the system performance depends on the hydrological, hydrogeochemical, and biogeochemical factors.

The removal of N was generally lower than that of P for both Fillerup and Ryaa. Results from the monitoring campaign showed a recurrent trend between HRT, loading rate, seasonality, and removal rates. Higher removal efficiencies were in fact obtained for higher HRT and lower loading rates which generally characterize the spring–summer season. Removal of P was generally higher than removal of N. This is most likely due to the high fraction of PP from the total P, which is removed through sedimentation representing the primary and generally long-term retention mechanisms in these systems. Results from the statistical analysis demonstrated for Ryaa that the hydrological parameters (HRT and loading rates) have a large effect on P removal efficiency.

Results from the filter system in Rodstenseje showed that during a 2-year monitoring campaign a removal efficiency of dissolved reactive P equal to 62%

was reached. This result was obtained by using a numerical model for simulating the retention capacity of the filter material. In particular, the model showed high frequency of Q values being responsible for the highest retention capacity. Under optimal conditions Q peaks must be reduced.

5 Recommendations

Overall, the long-term monitoring carried out at the Department of Agroecology, Aarhus University (DK) showed a large nutrient removal variability across different edge-of-field technologies and hydrological years. The catchment characteristics and the system design regulate the hydrological, hydrogeochemical, and biogeochemical factors, which define the nutrient performance and its variability. Removal insufficiencies appeared primarily during autumn–winter seasons, which are generally characterized by the highest loading rate, shortest HRT and lowest temperature. Thus, there is a need to develop more effective technologies exhibiting a more stable removal throughout the entire hydrological year. A potential solution may be achieved by adding additional storage basins or reactive P-filters in parallel (Rodstenseje) activated during the autumn–winter seasons. However, a detailed cost-efficiency assessment must be carried out beforehand.

Numerical models represent valuable tools for cost-efficiency assessment of already operating and potential optimal edge-of-field technologies. The numerical simulation provides in fact insights of the systems and highlights their strengths and weaknesses taking into account different hydrological, hydrogeochemical, and biogeochemical factors. Thus, numerical models must be used where possible to find the optimal technology allowing to meet the nutrient removal targets.

Acknowledgements These research studies were part of the iDRAIN project funded by the Ministry of Food, Agriculture and Fisheries under the Green Development and Demonstration Program (grant number 3405-10-0142), Future Cropping project funded by Innovation Fund Denmark (grant number 5107-479 00002B), SupremeTech project funded by the Danish Strategic Research Council (grant number 09-067280). The authors are grateful for the research support provided by Charlotte Kjaergaard, Francesco Chidichimo, Henrik Skovgaard, Lipe R.D. Mendes, Mathias Kusk, Michele De Biase.

References

1. OSPAR Commission (2000) Quality status report 2000, region II – greater North Sea. OSPAR Commission, London
2. Snoeijs P, Andrén E (2017) Why is the Baltic Sea so special to live in? In: Snoeijs-Leijonmalm-P, Schubert H, Radziejewska T (eds) Biological oceanography of the Baltic Sea. Springer, Dordrecht, pp 23–84. https://doi.org/10.1007/978-94-007-0668-2_2
3. European Environmental Agency (2018) European waters – assessment of status and pressures 2018. EEA, Luxembourg

4. Strock JS, Kleinman PJA, King KW, Delgado JA (2010) Drainage water management for water quality protection. J Soil Water Conserv 65:131A–136A
5. Goudie AS (2000) The human impact on the natural environment.5th edn. MIT Press, Cambridge
6. Svanback A, Ulen B, Etana A (2014) Mitigation of phosphorus leaching losses via subsurface drains from a cracking marine clay soil. Agric Ecosyst Environ 184:124. https://doi.org/10.1016/j.agee.2013.11.017
7. Moller AB, Beucher B, Iversen BV, Greve MH (2018) Predicting artificially drained areas by means of a selective model ensemble. Geoderma 320:30–42
8. Hansen AL, Storgaard A, He X, Hojberg AL, Refsgaard JC, Iversen BV, Kjaergaard C (2019) Importance of geological information for assessing drain flow in a Danish till landscape. Hydrol Process 33(3):450–462
9. Rozemeijer JC, van der Velde Y, McLaren RG, van Geer FC, Broers HP, Bierkens MFP (2010) Integrated modeling of groundwater-surface water interactions in a tile-drained agricultural field: the importance of directly measured flow route contributions. Water Resour Res 46:11. https://doi.org/10.1029/2010WR009155
10. Rozemeijer JC, van der Velde Y, van Geer FC, Bierkens MFP, Broers HP (2010) Direct measurements of the tile drain and groundwater flow route contributions to surface water contamination: from field-scale concentration patterns in groundwater to catchment-scale surface water quality. Environ Pollut 158(12):3571–3579
11. Ernstsen V, Olsen P, Rosenbom AE (2015) Long-term monitoring of nitrate transport to drainage from three agricultural clayey till fields. Hydrol Earth Syst Sci 19:3475–3488
12. Heathwaite AL, Burke SP, Bolton L (2006) Field drains as a route of rapid nutrient export from agricultural land receiving biosolids. Sci Total Environ 365:1–3
13. King KW, Williams MR, Macrae ML, Fausey NR, Frankenberger J, Smith DR, Kleinman PJA, Brown LC (2015) Phosphorus transport in agricultural subsurface drainage: a review. J Environ Qual 44(2):467–485
14. Catt JA, Howse KR, Farina R, Brockie D, Todd A, Chambers BJ, Hodgkinson R, Harris GL, Quinton JN (1998) Phosphorus losses from arable land in England. Soil Use Manage 14:168–174
15. Rozemeijer JC, Visser A, Borren W, Winegram M, van der Velde Y, Klein J, Broers HP (2016) High-frequency monitoring of water fluxes and nutrient loads to assess the effects of controlled drainage on water storage and nutrient transport. Hydrol Earth Syst Sci 20(1):347–358
16. Ulen B, Persson K (1999) Field-scale phosphorus losses from a drained clay soil in Sweden. Hydrol Process 13:2801–2812
17. Ulen B, Stenberg M, Wesstrom I (2016) Use of a flashiness index to predict phosphorus losses from subsurface drains on a Swedish farm with clay soils. J Hydrol 533:581–590
18. Wesström I, Joel A, Messing I (2014) Controlled drainage and subirrigation – a water management option to reduce non-point source pollution from agricultural land. Agric Ecosyst Environ 198:74–82
19. Heckrath G, Brookes PC, Poulton PR, Goulding KWT (1995) Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. J Environ Qual 24:904–910
20. Heathwaite AL, Dils RM (2000) Characterising phosphorus loss in surface and subsurface hydrological pathways. Sci Total Environ 251:523–538
21. Grant R, Laubel A, Kronvang B, Andersen HE, Svendsen LM, Fuglsang A (1996) Loss of dissolved and particulate phosphorus from arable catchments by subsurface drainage. Water Res 30(11):2633–2642
22. Uusitalo R, Turtola E, Kauppila T, Lilja T (2001) Particulate phosphorus and sediment in surface runoff and drainflow from clayey soils. J Environ Qual 30(2):589–595
23. Schelde K, de Jonge LW, Kjaergaard C, Laegdsmand M, Rubæk GH (2006) Effects of manure application and plowing on transport of colloids and phosphorus to tile drains. Vadose Zone J 5 (1):445–458

24. Kadlec RH, Knight RL (1996) Treatment wetlands. Lewis Publishers, Boca Raton
25. Hoffmann H, Platzer C, von Munch E, Winker M (2011) Technology review of constructed wetlands—subsurface flow constructed wetlands for greywater and domestic wastewater treatment. Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH, Sustainable Sanitation—Ecosan Program, Eschborn
26. Vymazal J (2014) Constructed wetlands for treatment of industrial wastewaters: a review. Ecol Eng 73:724–751
27. Gorgoglione A, Torretta V (2018) Sustainable management and successful application of constructed wetlands: a critical review. Sustainability 10:11. https://doi.org/10.3390/su10113910
28. Wittgren HB, Maehlum T (1997) Wastewater treatment wetlands in cold climates. Water Sci Technol 35(5):45–53
29. O'Geen AT, Budd R, Gan J, Maynard JJ, Parikh SJ, Dahlgren RA (2010) Mitigating nonpoint source pollution in agriculture with constructed and restored wetlands. Adv Agron 108:1–76
30. Koskiaho J, Puustinen M (2005) Function and potential of constructed wetlands for the control of N and P transport from agriculture and peat production in boreal climate. J Environ Sci Health 40:1265–1279
31. Tanner CC, Sukias JPS, Yates CR (2010) New Zealand guidelines: constructed wetland treatment of tile drainage. NIWA information series no. 75, National Institute of Water and Atmospheric Research Ltd.
32. Vymazal J (2017) The use of constructed wetlands for nitrogen removal from agricultural drainage: a review. Scientia Agriculturae Biochemica 48(2):82–91. https://doi.org/10.1515/sab-2017-0009
33. Mendes LRD (2020) Edge-of-field technologies for phosphorus retention from agricultural drainage discharge. Appl Sci 10:634. https://doi.org/10.3390/app10020634
34. Schipper LA, Robertson WD, Gold AJ, Jaynes DB, Cameron SC (2010) Denitrifying bioreactors: an approach for reducing nitrate loads to receiving waters. Ecol Eng 36 (11):1532–1543
35. Christianson LE, Bhandari A, Hailers MJ (2012) A practice-oriented review of woodchip bioreactors for subsurface agricultural drainage. Appl Eng Agric 28(6):861–874
36. Bruun J, Hoffmann CC, Kjaergaard C (2016) Nitrogen removal in permeable woodchip filters affected by hydraulic loading rate and woodchip ratio. J Environ Qual 45(5):1688–1695
37. Pugliese L, Bruun J, Kjaergaard C, Hoffman CC, Langergraber G (2017) Non-equilibrium model for solute transport in differently designed biofilters targeting agricultural drainage water. Water Sci Technol 76(6):1324–1331
38. Chun JA, Cooke RA, Eheart JW, Cho J (2010) Estimation of flow and transport parameters for woodchip-based bioreactors: II. Field-scale bioreactor. Biosyst Eng 105(1):95–102
39. Robertson WD, Ford GI, Lombardo PS (2005) Wood-based filter for nitrate removal in septic systems. Trans ASAE 48(1):121–128
40. Schipper LA, Cameron SC, Warneke S (2010) Nitrate removal from three different effluents using large-scale denitrification beds. Ecol Eng 36:1552–1557
41. Gottschall N, Edwards M, Craiovan E, Frey SK, Sunohara M, Ball B, Zoski E, Topp E, Khan I, Clark ID, Lapen DR (2016) Amending woodchip bioreactors with water treatment plant residuals to treat nitrogen, phosphorus, and veterinary antibiotic compounds in tile drainage. Ecol Eng 95:852–864
42. Choudhury T, Robertson WD, Finnigan DS (2016) Suspended sediment and phosphorus removal in a woodchip filter system treating agricultural wash water. J Environ Qual 45 (3):796–802
43. Penn C, Chagas I, Klimeski A, Lyngsie G (2017) A review of phosphorus removal structures: how to assess and compare their performance. Water 9:8. https://doi.org/10.3390/w9080583
44. Stoner D, Penn C, McGrath J, Warren J (2012) Phosphorus removal with by-products in a flow-through setting. J Environ Qual 41:654–663

45. Penn C, McGrath J, Bowen J, Wilson S (2014) Phosphorus removal structures: a management option for legacy phosphorus. J Soil Water Conserv 69:51A–56A
46. Lyngsie G, Penn CJ, Hansen HCB, Borggaard OK (2014) Phosphate sorption by three potential filter materials as assessed by isothermal titration calorimetry. J Environ Manage 143:26–33
47. Allred BJ, Racharaks R (2014) Laboratory comparison of four iron-based filter materials for drainage water phosphate treatment. Water Environ Res 86:852–862
48. Allred BJ (2012) Laboratory evaluation of porous iron composite for agricultural drainage water filter treatment. Trans ASABE 55:1683–1697
49. Kirkkala T, Ventela A-M, Tarvainen M (2012) Fosfilt filters in an agricultural catchment: a long-term field-scale experiment. Agric Food Sci 21:237–246
50. Vandermoere S, Ralaizafisoloarivony NA, Van Ranst E, De Neve S (2018) Reducing phosphorus (P) losses from drained agricultural fields with iron coated sand (− glauconite) filters. Water Res 141:329–339
51. Pugliese L, Kusk M, Iversen BV, Kjaergaard C (2019) Internal hydraulics and wind effect in a surface flow constructed wetland receiving agricultural drainage water. Ecol Eng 144:5. https://doi.org/10.1016/j.ecoleng.2019.10566
52. Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal Chim Acta 27:31–36
53. Koreleff F (1983) Determination of total phosphor by alkaline persulphate oxidation. In: Methods of seawater analysis. Chemie, Weinheim, pp 136–139
54. Pugliese L, Skovgaard H, Mendes LRD, Iversen BV (2020) Treatment of agricultural drainage water by surface flow wetlands paired with woodchip bioreactors. Watermark 12:1891. https://doi.org/10.3390/w12071891
55. Kjærgaard C, Hoffmann CC, Iversen BV (2017) Filtre i landskabet øger retentionen. Vand og Jord 24:106–110. (in Danish)
56. Pugliese L, De Biase M, Chidichimo F, Heckrath G, Iversen BV, Kjaergaard C, Straface S (2020) Modelling phosphorus removal efficiency of a reactive filter treating agricultural tile drainage water. Ecol Eng 156:5. https://doi.org/10.1016/j.ecoleng.2020.105968
57. Canga E, Iversen BV, Kjaergaard C (2014) A simplified transfer function for estimating saturated hydraulic conductivity of porous drainage filters. Water Air Soil Pollut 225:1. https://doi.org/10.1007/s11270-013-1794-8

Cost-Effective Adsorbents for Reduction of Conventional and Emerging Pollutants in Modified Natural Wastewater Treatment

Omid Alizadeh and Donya Hamidi

Contents

Abstract The adsorption process has drawn significant academic interest as an efficient treatment method for controlling water pollution and it has exhibited considerable potential for removing different aquatic pollutants. This chapter reviews the literature on different types of adsorption processes, adsorption

O. Alizadeh (✉)
Department of Chemistry and Chemical Engineering, Rasht Branch, Islamic Azad University, Rasht, Iran
e-mail: Alizadeh@iaurasht.ac.ir

D. Hamidi
Department of Chemical Engineering, University of Guilan, Rasht, Iran

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 67–106, DOI 10.1007/698_2022_865,

mechanisms, various factors affecting adsorption, important operating parameters, desorption, and reactivation. The chapter provides a summary of adsorption models and scale-up considerations and represents an extensive list of cost-effective adsorbents along with their application in wastewater treatment. Finally, it ends with a list of recent researches of various modification methods applied to increasing the efficiency of adsorption processes and enhancing the capacity of adsorbents.

Keywords Adsorbents, Adsorption, Desorption, Reactivation

1 Introduction

1.1 Adsorption Process

Due to a different number of pollutants characterized by high toxicity and carcinogenicity, pollution of water resources has turned into a significant environmental issue. Industrial, municipal, and agricultural pollutants are among the main water pollutants. Different types of treatment methods employed for removing water pollutants have been assessed [1–4], among which adsorption is drawing significant attention due to its low cost and high effectiveness [5, 6]. The adsorption process, as observed, refers to the accumulation of compounds on the surface and/or a common phase between liquid–solid and/or gas/solid phases. In other words, transfer of one or some materials from the gas/liquid phase into the solid phase takes place in this process. Generally, the basic steps in the adsorption process include (1) transferring pollutants from solution bulk into the external surface of the absorbent, (2) transferring the pollutant from the external surface of absorbent into the internal porous surface, and (3) adsorption of pollutants in activated parts of absorbent pores [7].

By definition, the absorbed pollutant is known as adsorbate and the absorbing phase is known as adsorbent [8]. The adsorption process is usually called biosorption and the adsorptive is called biosorbent when using biological adsorbents [9]. All adsorption processes are dependent on liquid/solid balance and mass transfer velocity. These processes may be discontinuous, semi-continuous, or continuous [7].

1.2 Types of Adsorption Processes

According to types of intermolecular attractive forces, the adsorption process is divided into physical adsorption (Van Der Waals Adsorption) and chemisorption, to be elaborated in the following sections.

1.2.1 Physical Adsorption

Physical adsorption occurs in all solid/liquid or solid/gas systems. This adsorption is the result of intermolecular forces of attraction between molecules of solid adsorbent and adsorbate. Van der Waals forces of attraction in the physical adsorption process attract adsorbates on solid adsorbents. One can rarely observe the destruction of the electronic structure of an atom and/or a molecule in physical adsorption. Physical adsorption is observed only in a low-temperature environment with appropriate conditions. Commercial absorbents use physical adsorption for surface binding [7, 10].

This process is easily reversible and this feature is employed for recovery and reuse of absorbent, recovery of adsorbate, and/or fractionation of mixtures in the industrial adsorption operations.

1.2.2 Chemical Adsorption

Chemisorption known as activated adsorption is usually an irreversible process that results from the chemical interaction between solid adsorbent and adsorbate. In this process, some new electronic bounds are created through strong interaction between adsorbate and adsorbent (covalent, ionic) [7]. In the chemisorption process, adhesive force and liberated heat are higher than physical adsorption. It is possible for the adsorbed compounds through physical adsorption in low-temperature conditions to be adsorbed chemically at high temperatures, even with both of the adsorption processes simultaneously.

1.3 Adsorption Mechanisms

Due to the complexity of biological compounds, adsorption may be the result of more than one mechanism.

The effective parameters controlling and characterizing the biological adsorption mechanisms include (a) the specifications of biological absorbent such as its structure and nature, type of biding site (biological ligand) and their availability, (b) key process parameters such as pH, absorbent dosage and adsorbate concentration, and other competing metal ions, and (c) specifications of metal ions like chemical specifications, molecular weight, ionic radius, and oxidation state of considered species [10, 11]. Figure 1 shows different mechanisms involved in the removal of metals using biological adsorbent.

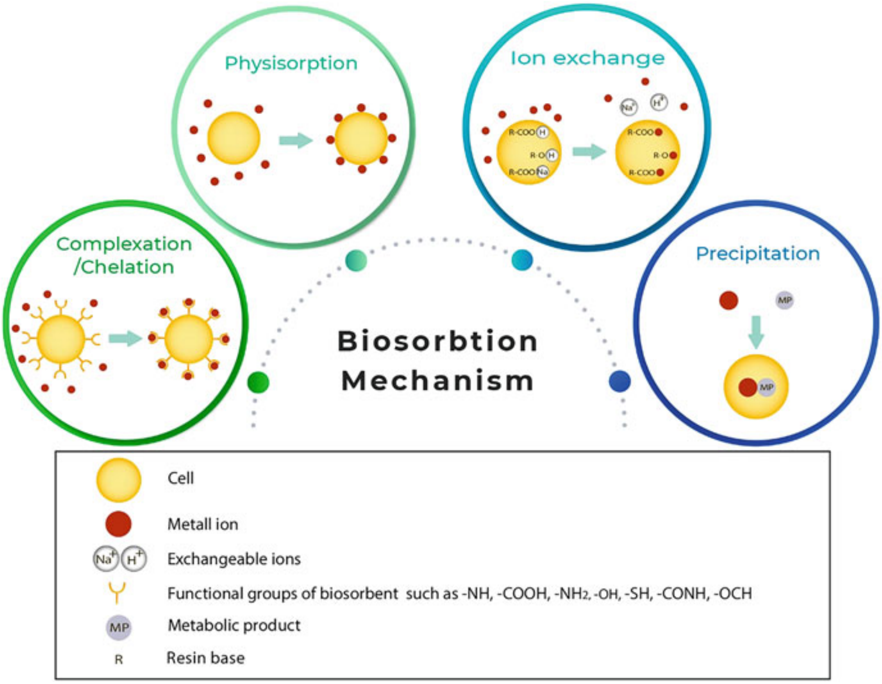


Fig. 1 Biosorption mechanisms of metals and metalloids

1.3.1 Physisorption

As already mentioned in Sect. 2.2.1, in this mechanism, the adsorption process occurs between adsorbate and cell surface through weak bonds such as van der Waals forces, hydrogen bonding, or hydrophobic interactions, and this mechanism is not dependent on cell metabolism. Activation energy in physical adsorption processes is lower than 1 Kcal/gmol [12]. The results of research conducted by Kahn et al. suggested that biosorption of Ni(II) and Cu(II) in various agricultural wastes depends on physical adsorption mechanism and is for affecting operational groups in biomass and metal features are affected significantly by solutions pH [13].

1.3.2 Chemisorption

Chelation

In this process, a chelating agent binds to metal ion at more than one place at a time, which forms a ring structure and a chelate complex [14]. Poly dissent ligands mainly form stable structures by participating in this reaction and forming multiple bonds. The stability of the complex increases upon increasing the bind sites of the ligands.

Complexation

Adsorption of metal pollutants from the solutions may occur through formation of a complex on the cell surface during interaction between metal ion and the groups activated on cell surface. These complexes may be in the form of mononuclear (monodentate) and/or polynuclear complexes (multidentate). Monodentate complexes form between metal ion and ligands. Metal atom is placed in the central state of this complex, while multinuclear complexes are formed through some metal ions. Complexes may be neutral with a negative or positive charge, while metal ions with ligands in these complexes may be electrostatic, covalent, or a combination of both [15, 16].

1.3.3 Ion Exchange

Ion exchange is a reversible process including double metal ions in solution with counter-ions on absorbent surface [17]. Functional groups of biomass like –OH, sulfate, phosphate, –COOH, and NH_2 may act as ion exchange sites [18].

1.3.4 Precipitation

This mechanism presents itself through interaction between metal ions in the solutions and extracellular polymers or anions produced by microbes. Heavy metal ions and functional groups on microbial cell surfaces form precipitates, which could remain intact or penetrate into the microbial cell. The precipitants may result in the formation of metal hydroxides, sulfides, carbonates, and phosphates. Besides, precipitants are usually insoluble solid particles (insoluble inorganic metal precipitates), while organic precipitates form by most of the extracellular polymeric substances excreted by the microbes. Furthermore, it is the most widely used mechanism for the removal of heavy metal pollutants from aqueous solutions.

1.3.5 Oxidation–Reduction

In oxidation–reduction mechanisms, metal ions are reduced through interaction with the functional groups like carboxyl, leading to the formation of crystals. The ion metal is reduced once it attaches to the biosorbent at distinct places. In this process, electron acceptors are the ions or molecules that act as oxidizing agents, and electron donors are the ions or molecules that donate electrons and act as reducing agents [19].

1.4 Operating Conditions and Factors Affecting Adsorption

The widest used chemical and physical factors affecting adsorption processes include pH, contact time, initial concentration of pollutant, adsorbent dosage, temperature, and particle size, which are introduced in the next sections.

pH of solution affects surface binding sites, absorbent charge, ionization rate, and adsorbate feature in the adsorption process. A review of previous studies shows that the proper pH of the adsorption process varies from acidic to alkaline [20–24].

The rate of adsorption and removal of pollutants is very fast at the beginning of the process due to the highly adsorptive characteristics of the absorbents. After a short while, the adsorption process begins its second step, transition phase, in which adsorption percentage gradually slows down because of decrease in the number of active sites and, also, reduction in the concentration of adsorbate pollutant in the solution. Finally, the process reaches equilibrium, after which no more adsorption will occur due to the shortage of free activated sites, no more adsorption will happen. Furthermore, contact time can significantly affect the economic efficiency of the process as well as the adsorption kinetics.

In general, the adsorption percentage is enhanced with increasing the adsorbent dosage, which promotes active exchangeable adsorption sites.

The effect of temperature depends on the thermodynamics of the process; it will have a growing effect on the endothermic process, but descending effect on the exothermic processes. Positive values of enthalpy change (DH^0) illustrate that the adsorption process remains endothermic. In addition, it is reported that the extent of DH^0 represents the type of adsorption such as physical adsorption ($DH^0 < 50$ kJ/mol) or chemical adsorption ($DH^0 > 50$ kJ/mol). Negative values of Gibbs free energy change (DG^0) indicate that the adsorption process is spontaneous. Likewise, the positive values of entropy change (DS^0) correspond to increasing entropy occurring due to the exchange of metal ions by more mobile ions in the adsorption process [25].

Absorbents with smaller particle size and a larger outer-surface area are of higher capacity in the adsorption process. On the other hand, excessive crushing of adsorbents faces some challenges. Large ions will not be able to diffuse in the whole structure of initial pores of absorbents. In the batch adsorption process that coincides with mixing during the process, excessive crushing of adsorbents makes the subsequent separation process more difficult. Meanwhile, in continuous processes (fixed bed) packed with a very small particle size of adsorbents, the bed capacity will be reduced, while the pressure drop accelerates.

1.5 Desorption and Reactivation of Adsorbents

Following a reduction in the capacity of adsorbents, they must be replaced with new adsorbents or regenerated. When expensive adsorbents like engineered adsorbents, which are modified using different methods [26], are used and/or adsorption processes are utilized for recovering valuable solutes, the possibility of recovery and its costs are among the most important factors in the economic efficiency of the whole adsorption process. Usually, cheap absorbents like wastes are not recovered after loading and are buried or burnt. For example, powder-activated carbon is not regenerated due to its small particle size and difficulty in separating its particles from the associated suspended solids.

In general, the release of adsorbate from the surface of sorbents is called desorption, which is explained by the ratio of adsorbent (solid phase) to desorbing eluent (liquid phase) (S/L ratio). Desorption not only decreases the costs of the adsorption process due to the reuse of the sorbents, but also helps one understand the reusability of the sorbents without any loss of effectiveness. This process goes in contrast to the adsorption process; thus, all effective parameters for the reduction of adsorption process could intensify the process of desorption. According to a phase in which the absorbed materials are desorbed, this process could be done by steam, solvent, pH variation, and extraction. Desorption is carried out by not only conventional solutions such as acids, bases, chelating agents, and salts but also supercritical fluids like CO_2. The desorbing eluents are chosen based on some main factors such as desorption efficiency, non-hazardous effect on the adsorbent, and economic and eco-friendly aspects. The regeneration involves rapid recycling or recovery of saturated adsorbents using technically and economically feasible techniques, which are classified into three main groups: biological, thermal, and chemical. Selecting an effective method depends on the type and nature of adsorbent and adsorbate along with the cost and processing conditions. In biological regeneration, the adsorption capacity can be completely recovered by biodegradation of adsorbed organic compounds on the adsorbents. The determinants of this process include the nature and type of microorganism and adsorbents, adsorbent dosage, microbial growth condition, and type of organic contaminants. In contrast, the biological process is suitable for biodegradable contaminants due to the toxic effects of some pollutants on microorganisms. In addition, in this process, fouling the pores of adsorbents may occur through microbial activity. Thermal regeneration is widely used on industrial scales. Heating time, temperature, and type of adsorbate and adsorbent are among the most effective factors in the thermal process. However, this process is subject to significant drawbacks such as not being cost effectiveness, slow regeneration rate, high-temperature requirement, release of harmful gases, weight and adsorption capacity losses, and incapable of being carried out in situ and of complete regeneration. Of note, chemical regeneration is recognized as a cost-effective method with a very short processing time. The process is affected by many factors such as solvent concentration, adsorbate solubility, adsorbent properties, and pH of the solution. The disadvantages of this method include its effect on the surface properties of adsorbents, production of oxidized sludge, need for further purification of the solvent, and incomplete recovery of adsorption capacity.

2 Adsorption Models and Scale-up Considerations

2.1 An Introduction to Fixed-Bed Versus Batch Adsorption Processes

Mixing adsorption is usually used on a laboratory scale and could provide some information about kinetic, thermodynamic features, and isotherms of the process. In contrast, the fixed-bed process provides information about saturation of adsorption beds over time for scale-up purposes. The system requires two columns: one column for the adsorption process and the other for regeneration. The process is batch and yet, following the saturation of adsorption bed, the fluid enters into the second bed, which has been regenerated. However, selection of the type of adsorption treatment in practical applications is based on the complexity of design, the difficulty of controlling the process, and the minimization of the adsorbent mass for achieving certain separation.

2.2 Batch Processes

2.2.1 Equilibrium Models

Equilibrium in the adsorption process is usually investigated using isotherms, which are plot of the equilibrium adsorption capacity (q_e) versus equilibrium concentration of adsorbate (C_e). There are several adsorption isotherm models such as Linear Henry, Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Brunauer–Emmett–Teller (BET), and Redlich–Peterson among which Langmuir (monolayer adsorption) and Freundlich (multilayer adsorption) are the most common ones.

Linear Henry Isotherm

Henry isotherm is useful in a relatively low adsorbent dosage, considering uniform adsorption on the adsorbent surface. In this respect, there is a linear relationship between concentration in active phase and equilibrium concentration (C_e) [27]:

$$q_e = K_H C_e \tag{1}$$

where the constant of this linear relationship (K_H) is equal to adsorption equilibrium constant and is referred to as Henry constant.

Langmuir Isotherm

In this isotherm introduced in 1918 as a theory [28], surface bounds are caused by physical forces. The forces imposed through the medium of the adsorbent on the adsorbed molecules are not over a molecular diameter; thus, adsorption will be monolayer [29]. The adsorbates are equal in terms of competition for attracting. The most important assumption on Langmuir isotherm is that an adsorbate molecule occupies just an activated site and the adsorbed molecules do not interact. Thus, upon the saturation of adsorbent, no more adsorption takes place. This isotherm is widely used for describing the equilibrium condition between liquid and solid phases [30].

Fractional adsorption on the adsorbent surface depends on adsorbate concentration. Further, adsorbent and adsorbate are in dynamic equilibrium. In this isotherm, the fractional adsorption, θ, is expressed as follows [31]:

$$\theta = \frac{\text{Number of adsorption sites occupied}}{\text{Number of adsorption sites available}} \tag{2}$$

It can also be defined as the ratio of equilibrium adsorption capacity (q_e) to maximum adsorption capacity (q_m):

$$\theta = \frac{q_e}{q_m} \tag{3}$$

The physical simplicity of this isotherm derives from four assumptions: (1) the adsorbent surface is considered uniform; (2) there is no chance to adsorb over monolayer coverage; (3) adsorption sites are equal energetically; (4) adsorbing a molecule in a site is independent of the occupation of neighboring areas [32]. This isotherm is expressed through the following equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

In Eq. (4), q_e is the equilibrium mount of adsorbed ion (mg/g) and C_e is the ion equilibrium concentration in the solution (mg/L). q_m is the maximum capacity of monolayer adsorption for adsorbent (mg/g) and K_L is the Langmuir adsorption constant (L/mg), used for estimating adsorption energy. Maximum adsorption occurs when all monolayer sites are occupied. The nature of adsorption process and its exothermic and endothermic reactions could be predicted through adsorption energy. The linearized form of Eq. (4) is as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{5}$$

Another significant parameter, which is employed to assess the desirability of the adsorption process, is the separation factor [33]. This parameter is illustrated through the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

For R_L greater than one adsorption would be undesirable; furthermore, in case $0 < R_L < 1$, then adsorption would be desirable. If $R_L = 1$, then adsorption would be linear and if $R_L = 0$, adsorption would be reversible.

Freundlich Isotherm

In contrast to Langmuir model, this model does not identify maximum adsorption capacity. Thus, it is used just in low or average concentrations. In this model, it is assumed that the stronger sites are occupied first and bounding strength is reduced by improving site occupation. Freundlich model is an empirical relationship in which it is assumed that adsorption energy is not dependent on whether the adjacent sites have been occupied or not [34]. This isotherm equation is written as follows:

$$q_e = K_F \, \mathrm{C}_e{}^{1/n_F} \tag{7}$$

where q_e is the mount of adsorbed ion in equilibrium (mg/g) and K_F is the Freundlich isotherm constant that indicates adsorption capacity (mg/g). n_F is another Freundlich isotherm constant which is called heterogeneity factor and shows the variety of adsorption sites and intensity of adsorption. C_e denotes the equilibrium ion concentration in the solution (mg/L) and $1/n_F$ is the adsorption intensity. The n_F is in the range of 1 to 10, in which a higher value for n_F indicates better adsorption [27, 29].

Temkin Isotherm

In this isotherm, the amount of adsorbed material is proportional to the logarithm of adsorbate partial pressure or concentration. In addition, it is assumed that the heat derived from the adsorption of all molecules in each layer is reduced linearly due to the interaction between adsorbent and adsorbate. Temkin isotherm is only valid for the intermediate range of ion concentrations [35, 36]. This isotherm is expressed through the following equations:

$$q_e = \beta . \, ln \, (K_T C_e) \tag{8}$$

$$\beta = \frac{RT}{b} \tag{9}$$

The linear form of this isotherm is expressed through Eq. (10):

$$q_e = \beta lnK_T + \beta lnC_e \tag{10}$$

where β is a constant related to adsorption heat (j/mol) and K_T is the equilibrium binding constant (L/g) related to maximum binding energy. R is the universal gas constant and T (K) is the solution absolute temperature. The values of β and K_T are obtained from the slope and intercept of plotting q_e versus ln (C_e).

BET Isotherm

BET isotherm is used for multilayer adsorption when the first adsorbed layer is converted to a surface for adsorbing more compounds. This isotherm was presented by Brunauer et al. [37] and is given as follows:

$$q_e = \frac{q_{\mathrm{BET}} k_1 C_e}{(1 - k_2 C_e)(1 - k_2 C_e + k_1 C_e)} \tag{11}$$

where q_{BET} is the monolayer adsorption capacity (mg/g). k_1 and k_2 are the BET constants (L/mg).

2.2.2 Kinetic Models

Kinetic profile may provide information about adsorption rate, time of reaching equilibrium, mass transfer mechanisms, and performance of adsorbents in the adsorption process, which are essential for designing industrial-scale adsorption systems. Different types of kinetic models are schematically shown in Fig. 2. Kinetic models may be divided into diffusional mass transfer models and adsorption reaction models, which are explained briefly below.

Diffusional Mass Transfer Models

Three stages of adsorption transfer kinetics include external diffusion, internal diffusion/intra-particle diffusion, and adsorption on active sites (Fig. 3). Thus, in the first phase, the driving force of the external diffusion causes adsorbate complexes to be transferred on the adsorbent surface and mass transfer is controlled through external mass transfer factor (k_f). In the second phase, adsorbing components diffuse in adsorbent pores. In fact, the intra-particle diffusion mechanism is dependent on the adsorbate movement within adsorbent particle and may be controlled

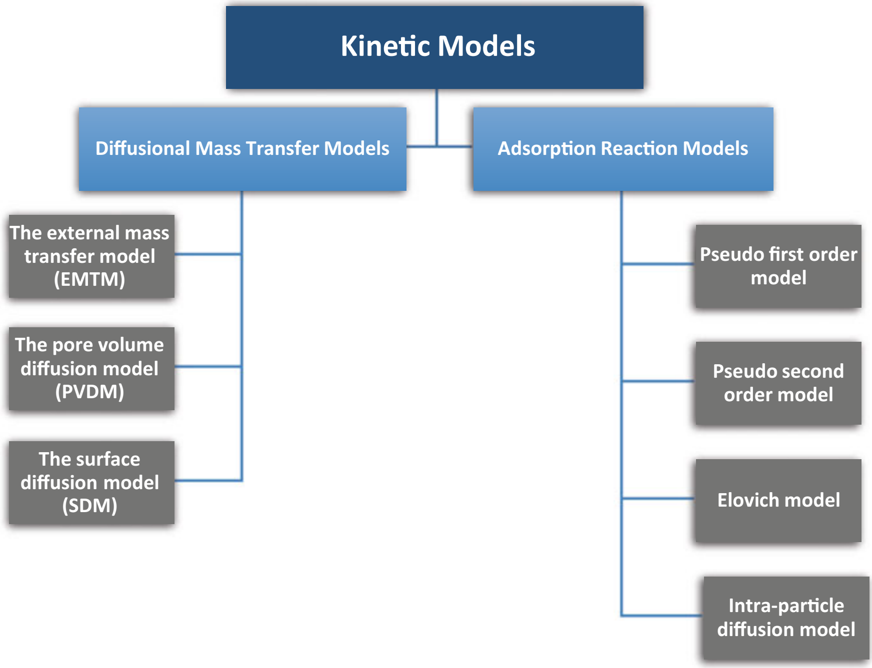


Fig. 2 Different types of kinetic models

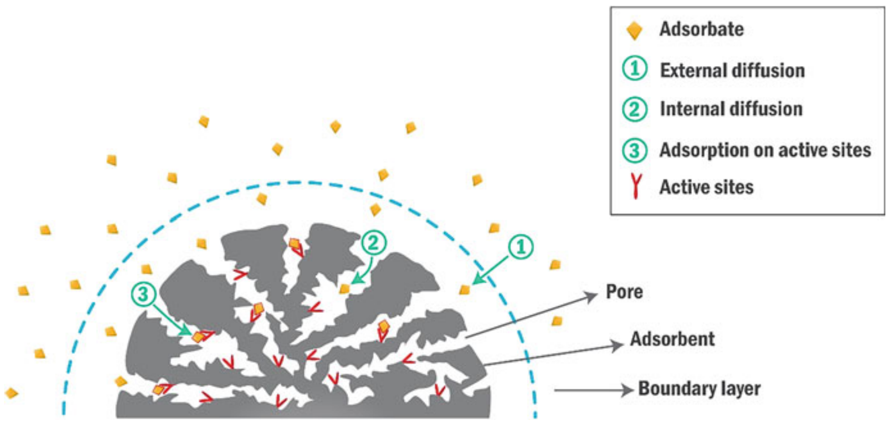


Fig. 3 Adsorption mass transfer kinetic phases

simultaneously or separately through two mechanisms of effective pore volume diffusion and surface diffusion. The third phase is the adsorptionof the adsorbates on the active sites.

According to Pore Volume and Surface Diffusion Model (PVSDM), it is assumed that mass transfer through convection in the particles is negligible. In this method, the temperature is assumed to be constant, the intra-particle diffusion is immediate, and the adsorption process occurs in a mixing adsorption system. This model is expressed as follows [38]:

$$V\frac{dC_t}{dt} = -mSk_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

$$t = 0, C_t = C_0 \tag{12}$$

$$\varepsilon_P\frac{\partial C_r}{\partial t} + \rho_P\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(D_P\frac{\partial C_r}{\partial r} + \rho_P D_s\frac{\partial q}{\partial r}\right)\right].$$

$$t = 0, 0 \le r \le R, C_r = 0 \tag{13}$$

$$\left.\frac{\partial C_r}{\partial r}\right|_{r=0} = 0 \tag{14}$$

$$D_P\left.\frac{\partial C_r}{\partial r}\right|_{r=R} + \rho_P D_s\left.\frac{\partial q}{\partial r}\right|_{r=R} = k_F\left(C_t - C_{s(t)}\big|_{r=R}\right) \tag{15}$$

In the above equation, V is the solution volume, m is the adsorbent amount, ε_p is the adsorbent volumetric fraction, ρ_P is the apparent adsorbent density, S is the external surface area in adsorbent mass, C_0 is the initial adsorbent dosage in the bulk solution, and C_r is the adsorbent dosage that varies according to the situation and time. Pore volume diffusion constant, D_P, and surface diffusion constant, D_S, are considered constant and the particles are assumed spherical. Three models including External Mass Transfer Model (EMTM), Pore Volume Diffusion Model (PVDM), and Surface Diffusion Model (SDM) could be derived from PVSDM model.

In EMTM, it is assumed that intra-particle diffusion is immediate and there is no concentration gradient within particles. In this model, external mass transfer is the only reason for transferring the adsorbate toward the adsorbent. Thus, intra-particle diffusional resistance may be ignored. PVDM is applied when intra-particle diffusion is controlled only by effective pore diffusion. SDM can be employed when intra-particle diffusion is controlled only through surface diffusion.

Adsorption Reaction Models

Pseudo-First-Order Model

This model was developed according to the capacity of adsorbents by Lagergren in 1898. It is usually used when adsorption rate is high and the system reaches equilibrium in a short span of time (20–30 min) [39]. This model is defined through Eq. (16).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{16}$$

where q_e (mg/g) is the capacity of adsorption in equilibrium, q_t (mg/g) is the capacity of adsorption at a certain time, t (min), and k_1 is the pseudo-first-order rate constant of the kinetic model.

Pseudo-Second-Order Model

This model is used in adsorption system of metal ions, dyes, and organic matters of aqueous solution [39] and is expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{17}$$

where q_e (mg/g) represents the capacity of adsorption in equilibrium, q_t (mg/g) is the capacity of adsorption at a certain time, t (min), and k_2 is the pseudo-second-order rate constant of the kinetic model.

Elovich Model

This model is used in gas chemisorption systems on the heterogeneous surface of adsorbents and was developed by Zeldowitsch in 1934. It is obtained through the following equation [40]:

$$\frac{dq}{dt} = ae^{-\beta q} \tag{18}$$

where q is the amount of adsorbed gas at time (t), a is the adsorption constant, and β is the initial adsorption rate.

2.2.3 Adsorption Thermodynamics

In order to predict the effect of temperature on the adsorption process and determine the whole mechanism and nature associated with it, it is crucial to find important thermodynamic parameters including standard Gibs free energy change, standard enthalpy change, and standard entropy change. These parameters include important information about the possibility, spontaneity, and exothermic or endothermic nature of the process.

Changes of Gibs free energy of adsorption (KJ/mol) are expressed through the following Equation [41]:

$$\Delta G^{\circ}_{\text{ads}} = -RTln(K_c) \tag{19}$$

In the above equation, R is the gas universal constant (J/mol/K), T is the absolute temperature (K), and K_C is the thermodynamic equilibrium constant, which can be obtained from Eq. (20).

$$K_c = \frac{v_s q_e}{v_e C_e} \tag{20}$$

In the above relation, υ_s is the activity coefficient of adsorbate through adsorbent and υ_e is the activity coefficient of adsorbate in the solution in equilibrium. When the concentration of adsorbate in the solution is reduced and tends to zero, the activity factor tends to one and, thus, Eq. (20) will be simplified into Eq. (21).

$$\lim_{q \to 0} = \frac{q_e}{C_e} = K_c \tag{21}$$

The value of K_c is obtained by plotting $\ln\left(\frac{q_e}{C_e}\right)$ versus q_e and extrapolating q_e toward zero as the intercept. By substituting the value of K_c in Eq. (21), standard Gibbs free energy change of adsorption is obtained. The relationship among changes in standard Gibs free energy, standard enthalpy change, and standard entropy change is expressed through Eq. (22) as follows [42]:

$$\Delta G^{\circ}_{\text{ads}} = \Delta H^{\circ}_{\text{ads}} - T\Delta S^{\circ}_{\text{ads}} \tag{22}$$

Upon substituting (19) into (22), we will have:

$$\ln(K_c) = \frac{\Delta S^{\circ}_{\text{ads}}}{R} - \frac{\Delta H^{\circ}_{\text{ads}}}{RT} \tag{23}$$

By plotting ln (K_c) versus $\left(\frac{1}{T}\right)$, $\Delta S^{\circ}{}_{\text{ads}}$ and $\Delta H^{\circ}{}_{\text{ads}}$ could be measured using slope-diagram, respectively.

It must be noted that negative ΔG° values indicate the spontaneity of the adsorption process. ΔG° values in the range of 0 to −20 kJ/mol indicate physical adsorption, while the values between −80 and −400 kJ/mol indicate chemical adsorption. Exothermic or endothermic process is evaluated with standard enthalpy change ($\Delta H^{\circ}{}_{\text{ads}}$). Negativity and positivity of the adsorption standard enthalpy change represent the exothermic and endothermic processes of the adsorption, respectively. Exothermic or endothermic process of adsorption is defined in two stages. In the first stage, the adsorbate must break the form of covered water, called dehydration. Since breaking the bound needs head and energy, this stage is endothermic. In the second stage, the adsorbate must diffuse in the holes and pores of the absorbent and contact the absorbent. This contact process is exothermic. Negativity of $\Delta H^{\circ}{}_{\text{ads}}$ points to the exothermic process and the possibility of physical adsorption.

Positive $\Delta H^{\circ}_{\text{ads}}$, in contrast, suggests the endothermic process and its irreversibility [42].

2.2.4 Scale-up Considerations for Batch Adsorption

Mixing adsorption systems are rarely used in industrial processes due to higher operational expenses than continuous fixed-bed processes. They face some challenges and problems such as corrosion and erosion of adsorbents and mixer impellers. Therefore, this process is usually used on a laboratory scale, merely for characterizing the adsorbent and adsorption process for use in industrial units as fixed-bed processes.

2.3 Continuous Processes (Fixed Bed)

2.3.1 Characteristics of Continuous Adsorption

Many different parameters including bed density (ρ_B), bed porosity (ε_B), adsorbent mass (m_A), adsorbent volume (V_A), and bed volume (V_B) are considered for determining the characteristics of adsorption bed and their dominant conditions, which will be explained in this section.

Bed Density (ρ_B)

This parameter is defined as the ratio of adsorbent mass to adsorber volume (sum of adsorbents volume and the spaces filled by liquid) [43].

$$\rho_B = \frac{m_A}{V_B} = \frac{m_A}{V_A + V_L} \tag{24}$$

Bed Porosity (ε_B)

This parameter is the ratio of the volume of spaces filled by liquid to adsorber volume [43].

$$\varepsilon_B = \frac{V_L}{V_B} = \frac{V_B - V_A}{V_B} = 1 - \frac{V_A}{V_B} \tag{25}$$

Bed Volume (V_B)

Bed volume (adsorber volume) is estimated by multiplying cross-sectional area by bed length [43].

$$V_B = A_B l \tag{26}$$

Flow Velocity (v_F)

The linear fluid velocity (v_F) is the ratio of volumetric flow rate (V) to the cross-sectional area of bed (A_B) [43].

$$v_F = \frac{V}{A_B} \tag{27}$$

Residence Time (t_r)

The residence time may be estimated as the ratio of adsorber length to flow velocity. It is defined as two forms of Empty Bed Contact Time (EBCT) for empty adsorber and effective residence time (t_r), where u_F expresses effective flow velocity [43]:

$$\mathrm{EBCT} = \frac{l}{v_F} = \frac{lA_B}{V} = \frac{V_B}{V} \tag{28}$$

$$t_r = \frac{l}{u_F} = \frac{lA_B\varepsilon_B}{V} = \frac{V_B\varepsilon_B}{V} = \mathrm{EBCT}\varepsilon_B \tag{29}$$

2.3.2 Breakthrough Curve Models

Using empirical models for breakthrough curves, it is possible to estimate the adsorber saturation time and breakthrough time and, also, the required length of the mass transfer zone. These models are crucial in designing and analyzing fixed-bed adsorption systems. Some of these models are discussed in this section.

Bohart–Adams Model

In this model, it is assumed that the equilibrium is not immediate and adsorption rate is proportional to adsorbate concentration in the liquid phase. Furthermore, this model is usually appropriate for the systems with irreversible isotherm. This model is defined as Eq. 30 [44]:

$$\frac{C_t}{C_0} = \exp\left(k_{\mathrm{AB}} C_0 t - k_{\mathrm{AB}} q_0 \frac{z}{v_z}\right) \tag{30}$$

where C_0 and C_t are input and output solute concentrations. k_{AB} is the Bohart–Adams kinetic constant, q_0 is the stoichiometric capacity of the bed, and Z is the bed length.

Thomas Model

This model considers adsorption bed as a plug flow. In this case, it is assumed that there is no axial diffusion. Thomas model may be estimated by solving differential mass balance for a system whose kinetics is defined by pseudo-second order model and its adsorption isotherm is considered as Langmuir [44]:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{\mathrm{Th}} q_0 m}{Q} - k_{\mathrm{Th}} C_0 t\right)} \tag{31}$$

where k_{Th} is the Thomas kinetic constant, m is the mass of adsorbent, Q is the operating flow rate, and q_0 is the adsorbate mass per adsorbent unit mass.

Wolborska Model

This model is used in low concentrations of pollutants (adsorbates) and has been obtained by solving the differential mass balance general equation in the low concentration of solutes in the liquid phase [45]:

$$\frac{C_t}{C_0} = e^{\frac{\beta C_0}{N_0} t - \frac{\beta z}{u}} \tag{32}$$

where u and β represent the transfer rate of adsorbate during adsorption and the kinetic coefficient of external diffusion, respectively.

Yoon–Nelson Model

In this model, it is assumed that reducing adsorbates concentration in the solution is proportional to the possibility of adsorption and its breakthrough on different adsorbents [44]:

$$\frac{C_t}{C_0} = 1 + \exp\left(\tau k_{\mathrm{YN}} - k_{\mathrm{YN}} t\right) \tag{33}$$

where k_{YN} is the Yoon–Nelson kinetic constant and τ is the prediction time for 50% completion of the adsorption process.

2.3.3 Scale-Up Considerations for Continuous Adsorption

Mass Transfer Zone (MTZ) Model

MTZ is a zone in the adsorbent bed where adsorption occurs and is known as the adsorption zone. This is a scale-up model based on mass transfer zone in the adsorption bed. This model is applicable to ion exchange processes and single-solute systems. In this model, MTZ length is distinct from the covered distance. Thus, it follows the constant condition pattern and is based on some hypotheses including isothermal adsorption, constant initial adsorbate concentration, negligible adsorbate accumulation in the void fraction of the bed, formation of a constant pattern of MTZ, and constant flow velocity. The following parameters are used for assessment of BTC (Breakthrough Curve) [46, 47]:

- length of MTZ; zone length, l_z;
- Velocity of MTZ movement along the adsorber; zone velocity, v_z; and
- The time required for passing through a distance as length as MTZ; zone time, t_z.

Equation (34) correlates these three parameters:

$$v_z = \frac{l_z}{t_z} \tag{34}$$

Zone time, t_z, is calculated through subtraction of the saturation time, t_s, and breakthrough time, t_b.

$$t_z = t_s - t_b \tag{35}$$

The mentioned time could be measured directly using the experimental BTC. Asymptotic BTC prevents calculation of exact breakthrough time and saturation time. Thus, the times at $\frac{C}{C_0} = 0.05$ and $\frac{C}{C_0} = 0.95$ are considered as breakthrough and saturation times, respectively. It is assumed that the ideal breakthrough time can be estimated by stoichiometric time. Therefore, zone velocity, v_z, could be measured using stoichiometric time, t_{st}, and the bed length, as well [43, 46].

$$v_z = \frac{l}{t_{\mathrm{st}}} \tag{36}$$

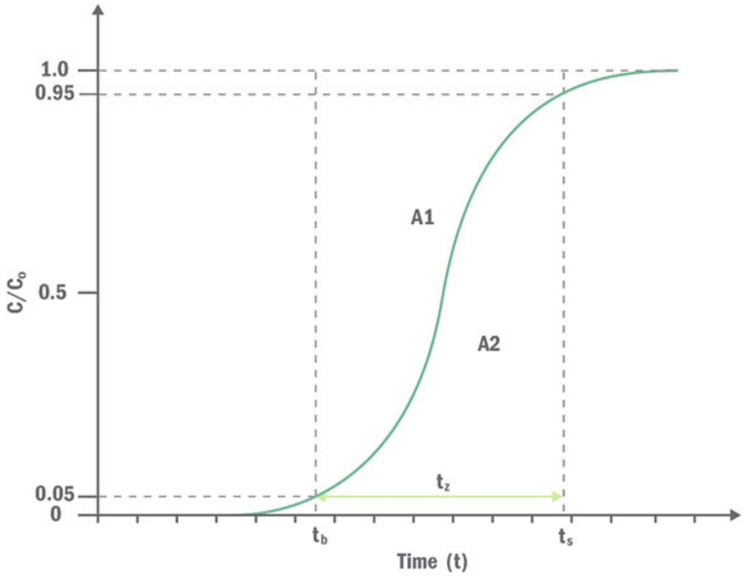


Fig. 4 Parameter of the MTZ model

The following equation can be obtained through equalization of (34), (35), and (36) used for determining MTZ length:

$$l_z = l\frac{t_s - t_b}{t_{\mathrm{st}}} = l\frac{t_z}{t_{\mathrm{st}}} \tag{37}$$

The stoichiometric time in a symmetric BTC is the time at $\frac{C}{C_0} = 0.5$. When the film and inter-particle diffusion contribute to the total mass transfer to the same extent, BTC will be symmetric. Otherwise, the barycenter of BTC is detected in higher concentrations (typical for rate-limiting intra-particle diffusion) and/or in lower concentrations (typical for rate-limiting film diffusion). In this case, BTC and graphical procedures must be used for estimating stoichiometric time. Figure 4 indicates A_1 and A_2 areas, which are used in Eq. (38) for calculating F_S as a symmetry factor.

$$F_S = \frac{A_1}{A_1 + A_2} \tag{38}$$

If t_{st} is assumed to be located in the barycenter of the curve, then the area ratio is as follows:

$$F_s = \frac{t_{\text{st}} - t_b}{t_s - t_b} = \frac{t_{\text{st}} - t_b}{t_z} \quad (39)$$

According to Eq. (39), F_S for a symmetric BTC is 0.5 and stoichiometric time is calculated as follows:

$$t_{\text{st}} = t_b + F_S t_z \quad (40)$$

Thus, the final equation for the zone length, l_z, is as follows:

$$l_z = l \frac{t_s - t_b}{t_b + F_S t_z} = l \frac{t_z}{t_b + F_S t_z} \quad (41)$$

$$1 - F_S = \frac{t_s - t_{\text{st}}}{t_z} \quad (42)$$

By using the two latter equations, another equation is obtained for l_z:

$$l_z = l \frac{t_s - t_b}{t_s - (1 - F_S) t_z} = l \frac{t_z}{t_s - (1 - F_S) t_z} \quad (43)$$

For characterization of the shape of the BTC, l_z and F_S parameters are used. The impact of the mass transfer is reflected indirectly through these values. In order to estimate the breakthrough time, saturation time, and breakthrough loadings for full-scale adsorption processes, parameters l_z and F_S can be obtained through lab-scale experiments. Equation (44) is employed for calculating the breakthrough time.

$$t_b = \frac{1}{v_z}(l - F_S l_z) = \frac{l}{v_z} - F_S t_z \quad (44)$$

In addition, the saturation time is obtained from Eq. (45):

$$t_s = \frac{1}{v_z}[l + (1 - F_S) l_z] = \frac{l}{v_z} + (1 - F_S) t_z \quad (45)$$

Equations (44) and (45) suggest the linear dependence of the breakthrough and saturation times on bed length.

Given that MTZ model is only valid under constant pattern condition, the adsorber length must be greater than zone length in this model ($l > l_z$) to have a constant pattern.

However, for a given adsorber length, the minimum breakthrough time required to obtain a constant pattern can be derived from Eq. (44) under the condition $l = l_z$.

It should be noted that development of the MTZ model in the multi-component adsorption process is only possible under restrictive conditions in which the adsorption zones of all components are wholly established and do not overlap. This condition strongly limits the practical applicability of this model [43].

Length of Unused Bed (LUB) Model

In this scale-up model, a parameter entitled the Length of the Unused Bed (LUB) is applied for characterizing the breakthrough behavior. For systems with best-fit isotherm model, the concentration profile develops a specific pattern in the mass transfer zone which does not change along the length of the bed. Accordingly, breakthrough curves in beds with different lengths give the same shape, though for longer beds, a greater fraction of the bed is utilized and the mass transfer zone is a smaller fraction of bed length. The breaking point is reached whenever the adsorbents between inlet of the bed and the beginning of the mass transfer zone are fully saturated. The adsorbent in the mass transfer zone goes from partly saturated to approximately no adsorbate. In other words, about half of the adsorbent in the mass transfer zone is completely saturated and half unused. The principle of scaling up is that the amount of unused adsorbent or length of unused bed does not change along the bed length. The total adsorbate up to the break point is defined by integration for calculating the length of unused bed from the breakthrough curve. As depicted in Fig. 5, if the adsorption process stops at the breakthrough point, LUB will be proportional to the distance between the location of the stoichiometric length (l_{st}) and the adsorber length (l) [43, 48, 49]. Thus, the length of the unused bed is obtained as follows:

$$\mathrm{LUB} = l - l_{\mathrm{st}} \tag{46}$$

Given that LUB corresponds to the adsorption rate, slower mass transfer leads to longer LUB. Since the travel velocity of stoichiometric and real lengths is the same, the travel velocity can be expressed in the following by using either real breakthrough time or stoichiometric time.

$$v_z = \frac{l_{\mathrm{st}}}{t_b} = \frac{l}{t_{\mathrm{st}}} \tag{47}$$

LUB could be estimated through a combination of Eqs. (46) and (47).

$$\mathrm{LUB} = v_z(t_{\mathrm{st}} - t_b) = l\frac{t_{\mathrm{st}} - t_b}{t_{\mathrm{st}}} \tag{48}$$

By using Eq. (48), LUB could be estimated experimentally based on the determined BTC. The required stoichiometric time, t_{st}, could be estimated in the same way as MTZ.

In order to perform the scale-up, first, breakthrough time must be determined. The mentioned time is used at different lengths of the bed and is estimated using Eq. (49).

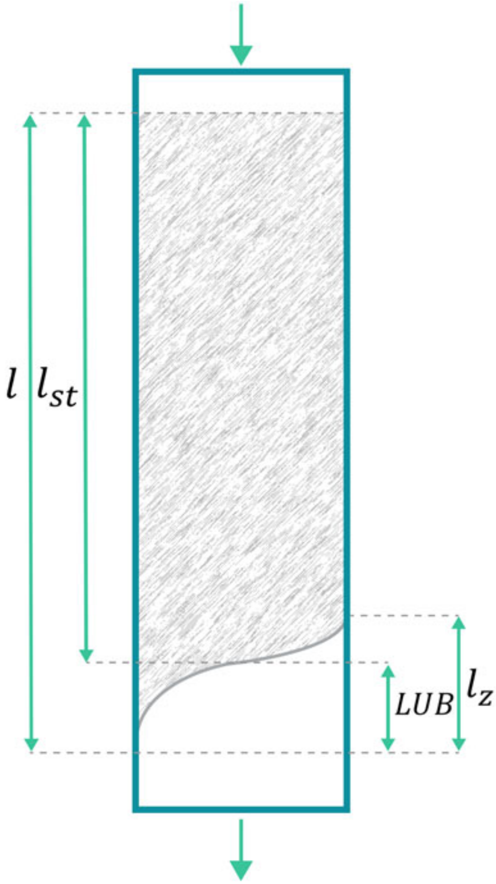


Fig. 5 Parameters of the LUB model

$$t_b = \frac{1}{v_z}(l - LUB) \tag{49}$$

Generally, the limitations of target LUB and MTZ models are similar. Effective parameters associated with LUB model include concentration, particle diameter, and flow velocity which must be similar on different scales. In addition, LUB dependencies must be determined experimentally. Equation (50) suggests the relationship between LUB and MTZ models.

$$\mathrm{LUB} = F_z\, l_z \tag{50}$$

3 Low-Cost Adsorbents

Due to the rapid industrial development and the growing pollution of aquatic environments around the world, accessing efficient, low-cost, and economically cost-effective strategies for reducing and controlling pollutants is of great concern. The adsorption process with Low-Cost Adsorbents (LCAs) is one of the existing methods applicable to treating and reducing the pollution load of contaminated water resources.

In order to reduce the costs of implementing the adsorption process, using low-cost wastes to regenerate and/or reuse them is considered. Usually, the adsorbents are used without applying pretreatment processes like chemical and/or physical processes. However, one of the main usual challenges of using low-cost adsorbents is their low adsorption capacity. For solving this problem, some efficient and non-expensive modification methods could be used. In addition to producing materials with a higher added value, the adsorption capacity of adsorbents and the adsorption process efficiency increase. As shown in Fig. 6, low-cost adsorbents may be classified into the adsorbents with natural resource, wastes and/or agricultural by-products, and wastes and/or by-products of industrial processes.

3.1 *Natural Materials*

The most applicable natural adsorbent materials include wood, coal, chitin/chitosan, clay, and natural zeolites, which are used for removing different contaminants from aqueous solutions. These adsorbents are effective in adsorption of metal contaminants. Also, in processing marine materials, a large number of by-products are produced which may be used as adsorbents. Table 1 lists some natural materials

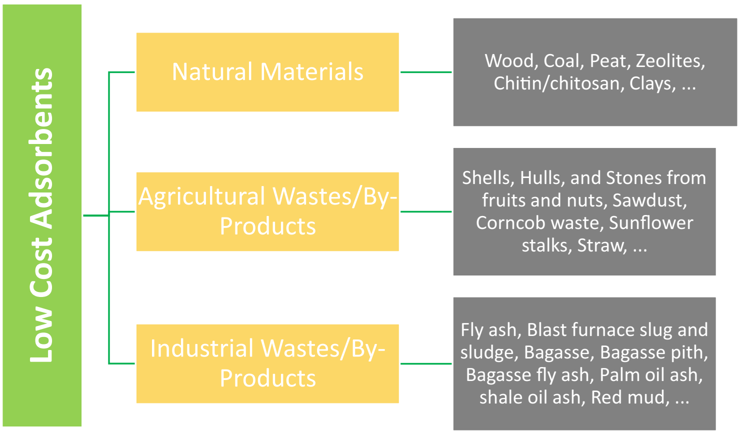


Fig. 6 Classification of low-cost adsorbents

Table 1 A list of low-cost adsorbents and their application in wastewater treatment

Types of low-cost adsorbents	Adsorbent	Adsorbent dosage	Pollutants type (adsorbate)	Concentration of pollutant	Surface area/particle size of adsorbent	Adsorption capacity	Contact time	Temp.	pH	Adsorption percentage
		g/L					(min)	°C		%
Natural materials	Plantain wood	0.8	Metronidazole antibiotic in hospital wastewater	50 mg/L	–	11.38 mg/g	60	25	6.5	91%
	An effective activated carbon (AC) from Maghara coal	1	Methylene blue (MB) dye in aqueous solutions	50 mg/L	0.478 mm	28.09 mg/g	60	25 ± 2	7	–
	Peat and coconut fiber	100 g/L of Peat and 100 g/L of coconut fiber	Cr^{6+} ion in aqueous solutions	10 mm	–	For peat = 8.02 mg/g, for fiber = 9.54 mg/g	1,200	Room temperature	1.5	95% for fiber and 92% for peat
	Bruneian peat	2	Congo-red (CR) dye in aqueous solution	10 mg/L	355–850 μm	10.1 mg/g	30	–	6.4	About 55%
	Chitosan powder	0.2	Cr^{6+} in aqueous solution	400 mg/L	72 ± 3 μm	97.4 mg/g	60	25	3.0	–
	Chitosan gel beads	1	Ag^{+} in aqueous solutions	352.95 mg/L	1.2–1.5 mm	89.20 mg/g	60	25	5	–
	Chitin	20	Gold in discarded computer microprocessor (DCM) leachate solutions	202 mg/L	105–125 μm	58 mg/g	240	25	1	80%
	Chitosan	1	Hg^{2+} removal in aqueous solutions	500 mg/L	<3 m^2/g, 75–125 μm	145 mg/g	200	25	5	58%
	Natural clay	63.33	Ni^{2+} in the wastewater-model samples	100 mg/L	<5 μm	1.48 mg/g	120	25	5.5	70–75%

(continued)

Table 1 (continued)

Types of low-cost adsorbents	Adsorbent	Adsorbent dosage g/L	Pollutants type (adsorbate)	Concentration of pollutant	Surface area/ particle size of adsorbent	Adsorption capacity	Contact time (min)	Temp. °C	pH	Adsorption percentage %
	Natural zeolite	50	Fluoride in wastewater	100 mg/L	–	1.766 mg/g	360	25	6.38	–
	Bacterial dead *Streptomyces rimosus* biomass	3	Pb^{2+} in aqueous solution	100 mg/L	50–160 μm	135 mg/g	180	Ambient temperature	2–12	–
Agricultural wastes/by-products	Granular activated carbon produced from palm kernel shell	1	Cu^{2+}, Ni^{2+}, and Pb^{2+} ions in a synthesized industrial wastewater	2.0 mg/L of Cu^{2+}, 1.5 mg/L of Pb^{2+}, and 0.8 mg/L of Ni^{2+}.	513.3 m^2/g, 1.68–2.38 mm	1.337 mg/g for Pb^{2+}, 1.581 mg/g for $Cu^{2+}$and 0.130 mg/g for Ni^{2+}.	30 min for Pb^{2+}, 75 min for Cu^{2+} and Ni^{2+}	27 (±2)	5	100%, 97%, and 55% removal for Pb^{2+}, Cu^{2+}, and Ni^{2+}, respectively
	Pecan shell based activated carbon (PSBAC)	3	Fe^{2+} in Fracking wastewater	55 mg/L	1,500 m^2/g	41.66 mg/g	90	30	3	69.9%
	Pistachio shell coated with ZnO nanoparticles (CPS)	80	Tetracycline (TEC) sequestration in wastewater	70 mg/L	87 μm	95.06 mg/ g	90	25	4	–
	Soybean hulls	1	Methylene blue	50 mg/L	350 μm	169.90 mg/g	180	25	The pH did not affect the cationic dye uptake, enabling a wide pH range	–
	Umbonium vestiarium snail shell (UVS)	3	Co^{2+} in aqueous solution	10 mg/L	17.02 m^2/g	93.46 mg/g	80	30	6	93.87%

	Waste peanut shells	4	Acid yellow 36 in wastewater	200 mg/L	965 m^2/g	66.7 mg/g	150	35	2	–
	Pistachio Hull powder	10	Ni^{2+} in aqueous solution	100 mg/L	150–400 μm (process is independent of particle size)	14.1 mg/g	60	25 ± 3	4–6	Higher than 75%
	Green longan hull	16.7	Cd^{2+} and Ni^{2+} in wastewater	50 mg/ L	Sieved to 100 mesh	4.19 mg (Cd^{2+})/g and 3.96 mg (Ni^{2+})/g	Approximately 15 and 20 min for Cd^{2+} and Ni^{2+}, respectively	Room temperature	5 and 4.7 for Cd^{2+} and Ni^{2+}, respectively	–
	Activated carbon prepared from date stones	2.5	Cu^{2+}, Ni^{2+}, and Zn^{2+} ions in multi-component aqueous mixture	100 mg/L	826 m^2/g, 100–160 μm.	18.68 mg (Cu^{2+})/g, 16.12 mg (Ni^{2+})/g, and 12.19 mg (Zn^{2+})/g	120	20	5.5	–
	Olive stones activated carbon (OSAC)	3	Zn^{2+}, Ni^{2+}, and Cd^{2+} in synthetic wastewater.	20 mg/L	886.72 m^2/g, 4.22 nm	11.14 mg (Zn^{2+})/g, 8.42 mg (Ni^{2+})/g, and 7.80 mg (Cd^{2+})/g	180	30	5	99.03% Zn^{2+}, 97.34% Ni^{2+}, and 94.88% Cd^{2+}
	Soybean hull	0.8	Safranin dye from aqueous solution	50 mg/L	<150 μm	47 mg/g	20	50	8	>80%
	Synthesis of sawdust-based poly (amidoxime) ligand	20	Heavy metals removal in wastewater	0.1 M metal ions solution	–	265.5 mg (Cu^{2+})/g, 270.1 mg (Fe^{3+})/g, 121.2 mg (Pb^{2+})/g, 161.7 mg (Zn^{2+})/g, and 165.4 mg (Co^{2+})/g	120	Room temperature	6	98.78%, 99.14%, 90.92%, 92.73% Cu^{2+}, Fe^{3+}, Pb^{2+}, and Zn^{2+}, respectively

(continued)

Table 1 (continued)

Types of low-cost adsorbents	Adsorbent	Adsorbent dosage g/L	Pollutants type (adsorbate)	Concentration of pollutant	Surface area/ particle size of adsorbent	Adsorption capacity	Contact time (min)	Temp. °C	pH	Adsorption percentage %
	Carbonized sawdust (CAS)	10	Phenol in wastewater.	20 mg/l	≤0.315 mm	1.39448 mg/g	180	22	5.79	–
	Corncob based activated carbon	15	Hexavalent chromium and COD in electroplating wastewater	72 mg/l and 122 mg/l for Cr^{6+} and COD removal respectively.	399.006 m^2 / g	About 13 mg (Cr^{6+})/g and 21.25 mg (COD)/g	360	25	3	95.27% and 82.28% for Cr^{6+} and COD removal, respectively
	Sunflower waste carbon	20	Cd^{2+} in water	100 mg/L	≤300 μm	–	180	25 ± 1	6	(Maximum adsorption 100 mg/L), 99.9%
Industrial wastes/by-products	Basic oxygen furnace slag	4	Phosphorus in synthetic wastewater	50 mg/L	0.038–0.045 mm	–	60	25	7	–
	Raw coal fly ash	40	Coking wastewater	COD = 80 mg/L	9.39 m^2/g	1.80 mg/g	240	20	7	89.9%
	Fly ash	5	Effluent of handmade paper industry (black dye)	50 mg/L	53–75 μ	76.33 mg/g	70	44.85	4	–
	Fly ash and iron ore tailing based porous geopolymer	3	Cu^{2+} in wastewater	100 mg/L	–	113.41 mg/g	70	40	5	98.3%
	Bagasse biochar	50	Pb^{2+} in battery manufacturing wastewater	2.393 ± 0.030 mg/L	12.378 m^2/g	12.741 mg/g	140	25 ± 3	5	75.376%
	Palm oil boiler ash composite	80	Ammonia nitrogen, nitrate,	COD (63.39 mg/L), ammonia nitrogen (6.01 mg/L),	2.00–3.15 mm	–	20 min for ammonia nitrogen, nitrate	–	6 for COD, nitrate and phosphorus	COD (65%), ammonia

			phosphorus, and COD in sewage wastewater	nitrate (0.63 mg/L), and phosphorus (0.43 mg/L).			phosphorus and 30 min for COD.		removal and 9 for ammonia and nitrogen removal.	nitrogen (63%), nitrate (100%), and phosphorus (97%)
	Activated palm oil fuel ash	5	Hg^{2+} ion in industrial wastewater	5 mg/L	–	–	300	Room temperature	2	91.18%
	Eggshell–treated palm oil fuel ash	1.18	Methylene blue	182 mg/L	3.7985 m^2/g, 42.4476 nm	714.29 mg/g	60	30	6	80.36%
	Palm oil fuel ash	80	Cr^{2+} in aqueous solution	100 mg/L	<250 μm	0.464 mg/g	6	–	2	92%
	Raw red mud (RM) and activated red mud (acid-activated (RM-A) and heat-treated (RM-H))	10	Methylene blue	30 mg/L	14.2 m^2/g	5.86, 6.84 and 5.86 mg/g for RM, RM-A, and RM-H, respectively.	120	23	6–10	–

along with their application for removing aqueous contaminants and their removal capacity.

3.2 Agricultural Wastes/By-Products

Considered to be environment-friendly and low-cost materials, agricultural wastes may be easily converted to valuable products. The main components of these wastes include lipids, lignin, starch, cellulose, and hydrocarbons, which are used for removing different contaminants from wastewater. Agricultural wastes may be used directly after pretreatment processes or after modification processes. Table 1 introduces some agricultural wastes and by-products along with their application for removing aqueous contaminants and their removal capacities

3.3 Industrial Wastes/By-Products

Industrial by-products and wastes are always considered to be useless wastes whose management and removal are of great challenges in related industries. Table 1 lists industrial wastes and by-products, which may be used as adsorbents.

4 Modification of Low-Cost Adsorbents

Modification methods could be effective in increasing the efficiency of the adsorption process through the alteration of the surface characteristics/groups by either removing or masking the groups or exposure to more metal binding sites. As demonstrated in Fig. 7, the modification methods can be classified into three groups: chemical, physical, and biological treatment methods [50]. The physical treatment methods include heating, boiling, freezing, thawing, drying, and lyophilization. These methods increase BET surface area and pore volume when running into some problems such as a reduction in the surface oxygen-containing functional groups. Moreover, biological treatment methods prolong adsorbent life through rapid oxidation of organics by bacteria before the material can occupy adsorption sites. In contrast, formation of thick biofilm in biological treatment may impede the diffusion of adsorbate species and reduce the adsorption efficiency by encapsulating the adsorbents. Among the existing pretreatment methods, chemical treatment is widely used due to its low-cost and ease of the procedure. In most cases, it is a one-step pretreatment process and is used with the objective of enhancement of active sites, improvement of surface heterogeneity, and transformation of surface morphology, thus increasing the adsorption capacity of adsorbents. Acids, bases, oxidizing agents, inorganic salts, and organic agents/detergents are among the most

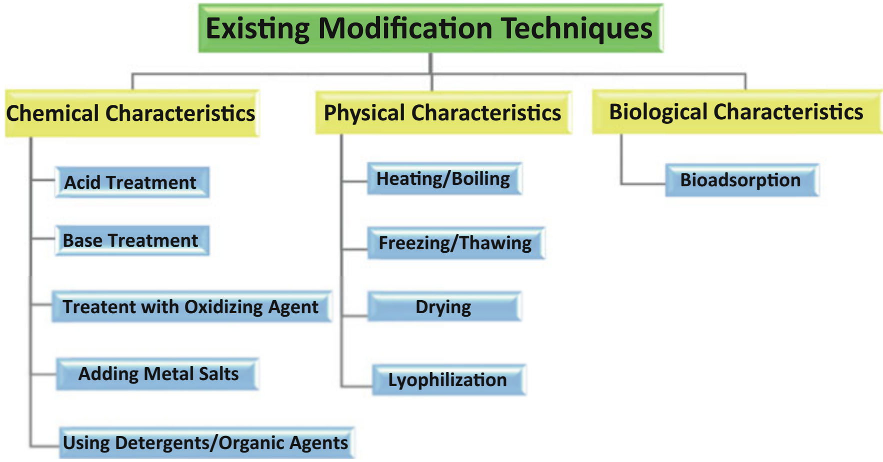


Fig. 7 Modification techniques for low-cost adsorbents

widely used reagents/solutions in one-step chemical pretreatment processes. A number of studies [51–56] focused on the mentioned pretreatment methods for increasing the removal efficiency of the adsorption process are given as examples in Table 2.

Modification using acids is usually applied for pretreatment of adsorbent with different acids such as HCl, HNO_3, H_2SO_4, and H_3PO_4, which are widely used in acid treatment method. The formation of free carboxyl groups, protonation, and removal of metal traces are the widely reported results and the main effects, which are responsible for the increase of the biosorption performance.

NaOH and $NaHCO_3$ are the widely used bases in modification. In this activation method, the composition of surface walls and formation of surface functional groups could lead to the enhancement of adsorption capacities [57, 58].

Potassium permanganate is the most widely used oxidizing agent in pretreatment. Oxidation of –OH links to –COOH and formation of surface functional groups are the main reasons for the rise in the adsorption capacity of the modified adsorbent [59].

Modification with metal salts like $MgCl_2$, NaCl, and $CaCl_2$ is another modification method that can be used. In this method, H^+ ions of active binding sites are exchanged with Na^+, Mg^{2+}, or Ca^{2+} ions. Thus, adsorption of heavy metals with the mentioned cations takes place easier and faster than the exchange of H^+ ions [60, 61].

Anionic surfactants, formaldehyde, and monosodium glutamate are the widely used compounds in pretreatment with detergents/organic agents. Formation of new functional groups due to putrefaction could improve the biosorption capability using commercial laundry detergent as a pretreatment agent [62].

Table 2 Modifying agents, pollutants type, adsorption capacity, and characterization techniques of different modified adsorbents

Adsorbent	Modifying agents	Pollutants type (adsorbate)	Adsorption capacity	Characterization methods
Corncob-derived char wastes	Calcination (at 600 °C for 2 h, ramp rate of 5 °C/min, under purified nitrogen atmosphere and 100 cm3/min), KOH (molar ratio of 4:1), HNO_3 (concentrated solution of nitric acid (65%) for 24 h)	Cu^{2+} and methyl orange	11.57, 10.86, and 9.14 mg/g on Base-CCW, Cal-Oxide CCW, and Cal-CCW, respectively	XRD, N_2 adsorption, CO_2 adsorption, FTIR, and He-TPD
Activated carbons from peach stone	$H_4P_2O_7$ (6 M, activation time (2 h), soaking time (12 h), 450 °C)	Acid red 18	1,274 mg/g	FTIR, SEM, EDX, and TG-DTA
Natural bentonite	Thermal activation (100 °C, 20 min), HCl (0.1 M at 100 °C. 1:10 mL/g (acid to clay ratio))	Congo-red	7.0 mg/g	FTIR and SEM
Alumina	H_2SO_4 (acid to alumina ratio 1:1 g/mL)	Fluoride	69.52 mg/g	SEM, EDX, FTIR, XRF, TGA, XRD, HI, and pH_{ZPC}.
Tea waste	H_3PO_4	p-Nitrophenol	142.85 mg/g	FTIR and pH_{ZPC}
Modified natural zeolite	Hexamethylenediamine (HMDA) (5% w/v, at 65 °C, 5 h)	Anionic dyes (reactive red 239 (RR-239) and reactive blue 250 (RB-250))	28.57 mg/g and 17.63 mg/g for RR-239 and RB-250, respectively	XRD, FTIR, and elemental analysis
Modified zeolite	Hexadecyltrimethylammonium (HDTMA) bromide (55 mmol/L was vigorously mixed with 10 g of ZFA, 50 °C, 4 h)	Ionizable phenolic compounds and non-ionizable organic compounds	37.74 mg/g, 52.36 mg/g, 90.91 mg/g, 303.03 mg/g, 12.15 mg/g, and 0.24 mg/g for phenol, p-chlorophenol, bisphenol A, aniline, nitrobenzene, and naphthalene, respectively	SEM, FTIR, XRD, Zeta potential

Modified zeolite	N,N-dimethyl dehydroabietylamine oxide (DAAO)	Anionic dye (Congo red)	69.94 mg/g	XRD, FTIR, SEM, N2 adsorption, elemental and thermogravimetric analyses
Surfactant modificated natural zeolites	Hexadecyltrimethylammonium bromide (HTAB) (20 mmol/L, at room temperature, shake for 24 h)	Acid red 18	20.42 mg/g	XRD and SEM
Modified kaolinite	Hexadecyltrimethylammonium chloride (HDTMA) (2% (w/w), 50 mL, 30 °C, 24 h)	Cr^{6+}	27.8 mg/g	FTIR, XRD, and SEM
Montmorillonite	Benzyloctadecyldimethylammonium chloride (BODMA-Cl)	Perchlorate	0.90 mmol/g	XRD, FTIR, TG-DTA, FESEM, zeta potential, and EDX
Composite of cetyltrimethylammonium bromide (CTAB) and carbonized coal (CC) (CTAB/CC)	H_2O_2 (2.5 g of CTAB, 50 mL of 30% H_2O_2, 50 °C, 15 min)	Cr^{6+}	82.58 mg/g	XRD, SEM, and FTIR
Activated carbon derived from waste bamboo culms	H_3PO_4 (253 K, 2 days, with the assistance of ultra-sonication (40 KHz, 300 W))	Azo disperse dye (disperse red 167 (DR167))	2.213 mg/g	SEM
Activated carbon from lignocellulosic wastes	$ZnCl_2$ (1:0.5 impregnation ratio, carbonized to 600 °C, 1 h), CASD_$ZnCl_2$ KOH (1:0.5 impregnation ratio, carbonized to 600 °C, 1 h), CASD_KOH	Cd^{2+} and Ni^{2+}	1.06 mmoles/g and 1.61 mmoles/g for Cd^{2+} and Ni^{2+}, respectively (for CASD_KOH). 0.23 Mol/g and 0.33 mmoles/g for Cd^{2+} and Ni^{2+}, respectively (for CASD_$ZnCl_2$)	FESEM and FTIR
Mesoporous activated coconut shell-derived	Hydrothermal treatment (2 h, 200 °C) NaOH (impregnation ratios 1:3, 4 h)	Methylene blue	200.01 mg/g	SEM and FTIR

(continued)

Table 2 (continued)

Adsorbent	Modifying agents	Pollutants type (adsorbate)	Adsorption capacity	Characterization methods
Protonated amine modified hydrochar	HCl (1 M, 473 K, 24 h)/NaOH (0.25 M, 1 h)/etherification reaction (with epichlorohydrin, 353 K, 4 h)/amination reaction (diethylenetriamine, 333 K, 4 h)/protonated reaction (HCl (1 M), 1 h, at room temperature)	Methyl orange	909.09 mg/g	FTIR, zeta potential, SEM, and N_2 adsorption
Engineered hydrochar from treated bamboo residues	Preparation of bamboo hydrochar (HCl, 200 °C, 24 h), Alkali treatment (NaOH (0.25 M), 1 h), Etherification using epichlorohydrin (immersed in epichlorohydrin and kept at 80 °C for 4 h), Amination (mixture of water and diethylenetriamine, 60 °C, 4 h) Dithiocarbamation using CS_2 in an alkaline medium (mixture of CS_2, NaOH, and aminated hydrochar, at room temperature, 24 h)	Pb^{2+}	151.51 mg/g	FTIR and XPS
Hydrochar of grape pomace	KOH (2 M, 1 h, at room temperature (25 ± 0.5 ° C))	Pb^{2+}	137 mg/g	XRD, SEM, pH_{ZPC}, and FTIR
Banana peel derived activated carbon	KOH (24 h, with 1:1 (wt%) ratio of char to KOH)	Cu^{2+}, Ni^{2+} and Pb^{2+}	Cu^{2+} (14.3 mg/g), Ni^{2+} (27.4 mg/g), Pb^{2+} (34.5 mg/g)	XRD, pore size distribution, SEM, and FTIR
Activated carbon from palm tree leaves	H_2SO_4 (25% (w/w), room temperature, 24 h)	Pb^{2+}	61.15 mg/g	FTIR, S_{BET}, and SEM
Spent tea leaves	Ca $(OH)_2$ (0.05 M, 8 h)	Cu^{2+}	7.81 mg/g	FTIR, S_{BET}, and SEM

Modified *Moringa oleifera* leaves powder	NaOH (0.1 N, 1 h, 23 °C) followed by citric acid (CA) (in ratio of 1.0 g leaves powder to 7.0 mL of CA, 50 °C)	Cd^{2+}, $Cu^{2+}$and Ni^{2+}	159.88 mg/g, 146.87 mg/g, and 138.04 mg/g for Cd^{2+}, Cu^{2+}, and Ni^{2+}, respectively	FTIR, pH_{ZPC}, SEM, and XRD
Oil palm leaves	Polyethylenimine (PEI) (10% (w/v) PEI/methanol solution, 298 ^{K}, 2 h − 1% (w/v) glutaraldehyde/ methanol solution., 298 ^{K}, 30 min.)	Pb^{2+}, Cr^{6+}	143 mg/g and 125 mg/g for $Pb^{2+}$and Cr^{6+}, respectively	HR-TEM, Raman, FTIR, and S_{BET}
Modified *desmostachya bipinnata* (Kush grass) leaves	NaOH (0.5 M, 1:20 solid–liquid ratio, 30 min)	Cd^{2+}	15.22 mg/g	FTIR and SEM
Modified *bambusa arundinacea* (bamboo) leaves	NaOH (0.5 M, 1:20 solid–liquid ratio, 30 min)	Cd^{2+}	19.70 mg/g	FTIR and SEM
Non-living leaves of *Posidonia oceanica*	HCl (0.1 N, 23 ± 2 °C, 24 h)	Cd^{2+}	1.11 mmol/g	Elemental analysis and FTIR
Non-living leaves of *Posidonia oceanica*	Formaldehyde (2 h, 50 °C)	Cd^{2+}	0.82 mmol/g	Elemental analysis and FTIR
Magnetically modified aloe vera leaves ash	Fe_3O_4 nanoparticles	Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}	333.3 mg/g, 345.0 mg/g, 71.4 mg/g, and 333.3 mg/g for Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cr^{3+}, respectively	SEM and TEM
Modified *Acacia nilotica* leaf	$ZnCl_2$ (room temperature, 24 h)	Cu^{2+}	38.31 mg/g	SEM and pH_{ZPC}
Rubber (*Hevea brasiliensis*) leaf powder	$KMnO_4$ (0.1 M, 2 h, 24.0 ± 0.5 °C)/ Na_2CO_3 (0.1 M, 2 h, 24.0 ± 0.5 °C)	Pb^{2+}	95.3 mg/g	FTIR, SEM, and EDX
Peanut shell biochar	$KMnO_4$ (0.5% solution, room temperature, 4 h) KOH (300 °C, 1 h)	Ni^{2+}	87.15 mg/g	FTIR, zeta potential, and XPS
Modified *Ficus carica* leaves	$MgCl_2$ (0.1 M, ambient temperature, 1 h)	Co^{2+}	82.64 mg/g	FTIR and XRF

(continued)

Table 2 (continued)

Adsorbent	Modifying agents	Pollutants type (adsorbate)	Adsorption capacity	Characterization methods
Activated carbon from *T. orientalis* (TO)	H_3PO_4 activation (40 wt. % solution, ratio of 1:2.5 (TO: H_3PO_4, w/w, at room temperature)/$KMnO_4$ treatment (10^{-3} M, 5:1 (w/v, g/L), 22 h, at room temperature)	Basic violet 14	263.16 mg/g	S_{BET}, XPS, and pH_{ZPC}
Activated carbon derived from astragalus residue	$KMnO_4$ (20 wt. %, at a ratio of 1:3 (residue: KOH, g/mL), 600 °C, 80 min.)	Cd^{2+}	217.00 mg/g	N_2 adsorption, FTIR, XRD, SEM, and Boehm titration
Poultry manure biochar	$MgCl_2$ (60 g $MgCl_2.6H_2O$ in 90 mL of deionized water, in a proportion solid: liquid of 1:10, 2 h)	Phosphorus	250.8 and 163.6 mg/g at 350 and 650 °C, respectively.	FTIR, XRD, SEM, and EDX
Sugarcane straw biochar	$MgCl_2$ (60 g $MgCl_2.6H_2O$ in 90 mL of deionized water, in a proportion solid: liquid of 1:10, 2 h)	Phosphorus	17.7 and 17.6 mg/g at 350 and 650 °C, respectively	FTIR, XRD, SEM. and EDX
Modified zeolite	NaCl (2 M, 35 ± 1 °C, 24 h)	Ammonium	17.3 mg/g	XRD, S_{BET}, EDX, and SEM

5 Conclusion

This chapter presents cost-effective adsorbents for the reduction of conventional and emerging pollutants in various wastewaters Various adsorption processes and mechanisms, effective parameters, optimum operating conditions, desorption and reactivation methods have been thoroughly discussed. Different types of adsorption models and scale-up considerations have been explained in detail. Natural materials, agricultural wastes/by-products, and industrial wastes/by-products are introduced as sources of Low-Cost Adsorbents (LCAs). Several modification techniques employed to increase the efficiency of the adsorption process are elaborately discussed. Though these sorbents are eco-friendly and inexpensive in wastewater pollutant sorption, further research is crucial to their management following their long-term usage.

6 Recommendation

Many studies have focused on the removal efficiency of wastewater pollutants by the adsorption technique. To reduce treatment costs, attempts are directed at finding cost-effective alternative adsorbents from waste materials of industrial, domestic, and agricultural activities. Nevertheless, it is required to explore and delve into the practicality of these adsorbents on a commercial scale. Future studies are recommended to consider enhancement of sorption capacity through modification, assessment of sorbent under multi-component pollutants, mechanistic modeling to correctly understand the sorption mechanisms, investigation of these materials with real industrial effluents, recovery of metal ions, regeneration studies, and continuous flow studies.

Acknowledgments The authors would like to acknowledge Islamic Azad University Rasht branch, Iran, for their valuable guidance, encouragement, and tremendous support.

References

1. Fard MB, Hamidi D, Alavi J, Jamshidian R, Pendashteh A, Mirbagheri SA (2021) Saline oily wastewater treatment using Lallemantia mucilage as a natural coagulant: kinetic study, process optimization, and modeling. Ind Crop Prod 163:113326
2. Fard MB, Mirbagheri SA, Pendashteh A, Alavi J (2019) Biological treatment of slaughterhouse wastewater: kinetic modeling and prediction of effluent. J Environ Health Sci Eng 17(2): 731–741
3. Gholami M, Shomali A, Abbasi Souraki B, Pendashteh A (2020) Advanced numerical kinetic model for predicting COD removal and optimisation of pulp and paper wastewater treatment by Fenton process. Int J Environ Anal Chem 2020:1–24

4. Pronk W, Ding A, Morgenroth E, Derlon N, Desmond P, Burkhardt M et al (2019) Gravity-driven membrane filtration for water and wastewater treatment: a review. Water Res 149:553–565
5. Crini G, Lichtfouse E, Wilson LD, Morin-Crini N (2018) Adsorption-oriented processes using conventional and non-conventional adsorbents for wastewater treatment. In: Green adsorbents for pollutant removal. Springer, pp 23–71
6. Burakov AE, Galunin EV, Burakova IV, Kucherova AE, Agarwal S, Tkachev AG et al (2018) Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: a review. Ecotoxicol Environ Saf 148:702–712
7. Tripathi A, Ranjan MR (2015) Heavy metal removal from wastewater using low cost adsorbents. J Bioremed Biodegr 6(6):315
8. Hu H, Xu K (2020) Physicochemical technologies for HRPs and risk control. High-risk pollutants in wastewater. Elsevier, pp 169–207
9. Fomina M, Gadd GM (2014) Biosorption: current perspectives on concept, definition and application. Bioresour Technol 160:3–14
10. De Gisi S, Lofrano G, Grassi M, Notarnicola M (2016) Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: a review. Sustain Mater Technol 9:10–40
11. Sulyman M, Namiesnik J, Gierak A (2017) Low-cost adsorbents derived from agricultural by-products/wastes for enhancing contaminant uptakes from wastewater: a review. Pol J Environ Stud 26(2):479–510
12. Volesky B (2003) Sorption and biosorption. BV Sorbex, St Lambert, p 326
13. Khan AM, Ahmad CS, Farooq U, Mahmood K, Sarfraz M, Balkhair KS et al (2015) Removal of metallic elements from industrial waste water through biomass and clay. Front Life Sci 8(3): 223–230
14. Witek-Krowiak A, Reddy DHK (2013) Removal of microelemental Cr (III) and cu (II) by using soybean meal waste–unusual isotherms and insights of binding mechanism. Bioresour Technol 127:350–357
15. Zhang M, Li A, Zhou Q, Shuang C, Zhou W, Wang M (2014) Effect of pore size distribution on tetracycline adsorption using magnetic hypercrosslinked resins. Microporous Mesoporous Mater 184:105–111
16. Tsezos M, Remoundaki E, Hatzikioseyian A (2006) Biosorption-principles and applications for metal immobilization from waste-water streams. In: Proceedings of EU-Asia workshop on clean production and nanotechnologies. Seoul, pp 23–33
17. Abdolali A, Guo W, Ngo H, Chen S, Nguyen N, Tung K (2014) Typical lignocellulosic wastes and by-products for biosorption process in water and wastewater treatment: a critical review. Bioresour Technol 160:57–66
18. Escudero LB, Maniero MÁ, Agostini E, Smichowski PN (2016) Biological substrates: green alternatives in trace elemental preconcentration and speciation analysis. TrAC Trends Anal Chem 80:531–546
19. Reddad Z, Gerente C, Andres Y, Cloirec PL (2003) Mechanisms of Cr (III) and Cr (VI) removal from aqueous solutions by sugar beet pulp. Environ Technol 24(2):257–264
20. Al-Othman ZA, Ali R, Naushad M (2012) Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: adsorption kinetics, equilibrium and thermodynamic studies. Chem Eng J 184:238–247
21. Kumar A, Jena HM (2016) Removal of methylene blue and phenol onto prepared activated carbon from fox nutshell by chemical activation in batch and fixed-bed column. J Clean Prod 137:1246–1259
22. Suksabye P, Thiravetyan P (2012) Cr (VI) adsorption from electroplating plating wastewater by chemically modified coir pith. J Environ Manag 102:1–8
23. Beker U, Ganbold B, Dertli H, Gülbayir DD (2010) Adsorption of phenol by activated carbon: influence of activation methods and solution pH. Energy Convers Manag 51(2):235–240

24. Hameed BH, Rahman AA (2008) Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material. J Hazard Mater 160(2–3):576–581. https://doi.org/10.1016/j.jhazmat.2008.03.028
25. Iftekhar S, Ramasamy DL, Srivastava V, Asif MB, Sillanpää M (2018) Understanding the factors affecting the adsorption of lanthanum using different adsorbents: a critical review. Chemosphere 204:413–430
26. Worch E (2021) Adsorption technology in water treatment. de Gruyter
27. Ayawei N, Ebelegi AN, Wankasi D (2017) Modelling and interpretation of adsorption isotherms. J Chem 2017:3039817
28. Langmuir I (1916) The constitution and fundamental properties of solids and liquids. Part I. solids. J Am Chem Soc 38(11):2221–2295
29. Chen X (2015) Modeling of experimental adsorption isotherm data. Information 6(1):14–22
30. Guo X, Wang J (2019) Comparison of linearization methods for modeling the Langmuir adsorption isotherm. J Mol Liq 296:111850
31. Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc 40(9):1361–1403
32. Heraldy E, Hidayat Y, Firdaus M (2016) The Langmuir isotherm adsorption equation: the monolayer approach. Mater Sci Eng Conf Ser 107:012067
33. Al-Ghouti MA, Da'ana DA (2020) Guidelines for the use and interpretation of adsorption isotherm models: a review. J Hazard Mater 393:122383
34. Zeldowitsch J (1934) Adsorption site energy distribution. Acta Phys Chim URSS 1(1):961–973
35. Vadi M, Mansoorabad AO, Mohammadi M, Rostami N (2013) Investigation of Langmuir, Freundlich and Temkin adsorption isotherm of tramadol by multi-wall carbon nanotube. Asian J Chem 25(10):5467
36. Araújo CS, Almeida IL, Rezende HC, Marcionilio SM, Léon JJ, de Matos TN (2018) Elucidation of mechanism involved in adsorption of pb (II) onto Lobeira fruit (Solanum lycocarpum) using Langmuir, Freundlich and Temkin isotherms. Microchem J 137:348–354
37. Brunauer S, Emmett P, Teller E (1938) BET equation. J Am Soc 60:809–815
38. Ocampo-Perez R, Leyva-Ramos R, Alonso-Davila P, Rivera-Utrilla J, Sanchez-Polo M (2010) Modeling adsorption rate of pyridine onto granular activated carbon. Chem Eng J 165(1): 133–141
39. Simonin J-P (2016) On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics. Chem Eng J 300:254–263
40. Largitte L, Pasquier R (2016) A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. Chem Eng Res Des 109:495–504
41. Chen H, Dai G, Zhao J, Zhong A, Wu J, Yan H (2010) Removal of copper (II) ions by a biosorbent—Cinnamomum camphora leaves powder. J Hazard Mater 177(1–3):228–236
42. Chen S, Qin C, Wang T, Chen F, Li X, Hou H et al (2019) Study on the adsorption of dyestuffs with different properties by sludge-rice husk biochar: adsorption capacity, isotherm, kinetic, thermodynamics and mechanism. J Mol Liq 285:62–74
43. Worch E (2012) Adsorption technology in water treatment: fundamentals, processes, and modeling. Walter de Gruyter
44. Biswas S, Mishra U (2015) Continuous fixed-bed column study and adsorption modeling: removal of lead ion from aqueous solution by charcoal originated from chemical carbonization of rubber wood sawdust. J Chem 2015:907379
45. Patel H (2019) Fixed-bed column adsorption study: a comprehensive review. Appl Water Sci 9(3):45
46. Hodaifa G, Alami SBD, Ochando-Pulido J, Víctor-Ortega M (2014) Iron removal from liquid effluents by olive stones on adsorption column: breakthrough curves. Ecol Eng 73:270–275
47. Verduzco-Navarro IP, Rios-Donato N, Jasso-Gastinel CF, Martínez-Gómez ÁJ, Mendizábal E (2020) Removal of Cu (II) by fixed-bed columns using Alg-Ch and Alg-ChS hydrogel beads: effect of operating conditions on the mass transfer zone. Polymers 12(10):2345

48. Dotto GL, Salau NPG, Piccin JS, Cadaval TRSA, de Pinto LAA (2017) Adsorption kinetics in liquid phase: modeling for discontinuous and continuous systems. In: Adsorption processes for water treatment and purification. Springer, pp 53–76
49. Liu J, Yan Y, Zhang H (2011) Adsorption dynamics of toluene in composite bed with microfibrous entrapped activated carbon. Chem Eng J 173(2):456–462
50. Gautam RK, Mudhoo A, Lofrano G, Chattopadhyaya MC (2014) Biomass-derived biosorbents for metal ions sequestration: adsorbent modification and activation methods and adsorbent regeneration. J Environ Chem Eng 2(1):239–259
51. Liu S, Ding Y, Li P, Diao K, Tan X, Lei F et al (2014) Adsorption of the anionic dye Congo red from aqueous solution onto natural zeolites modified with N, N-dimethyl dehydroabietylamine oxide. Chem Eng J 248:135–144
52. Feng N-c, Wei F, Zhu M-L, Guo X-Y (2018) Adsorption of Cd2+ in aqueous solutions using KMnO4-modified activated carbon derived from astragalus residue. Trans Nonferrous Metals Soc China 28(4):794–801
53. An Q, Jiang Y-Q, Nan H-Y, Yu Y, Jiang J-N (2019) Unraveling sorption of nickel from aqueous solution by KMnO4 and KOH-modified peanut shell biochar: implicit mechanism. Chemosphere 214:846–854
54. El-Sayed M, Nada AA (2017) Polyethylenimine− functionalized amorphous carbon fabricated from oil palm leaves as a novel adsorbent for Cr (VI) and Pb (II) from aqueous solution. J Water Process Eng 16:296–308
55. Li B, Wang Q, Guo J-Z, Huan W-W, Liu L (2018) Sorption of methyl orange from aqueous solution by protonated amine modified hydrochar. Bioresour Technol 268:454–459
56. Seliem MK, Mobarak M (2019) Cr (VI) uptake by a new adsorbent of CTAB–modified carbonized coal: experimental and advanced statistical physics studies. J Mol Liq 294:111676
57. Reddy DHK, Seshaiah K, Reddy A, Lee S (2012) Optimization of Cd (II), Cu (II) and Ni (II) biosorption by chemically modified Moringa oleifera leaves powder. Carbohydr Polym 88(3):1077–1086
58. Usha J (2015) Green sorption-an assessment of modified Michelia Champaca leaves in chromium removal from aqueous solutions. Int J ChemTech Res 8(2):501–507
59. Kamal MHMA, Azira WMKWK, Kasmawati M, Haslizaidi Z, Saime WNW (2010) Sequestration of toxic Pb (II) ions by chemically treated rubber (Hevea brasiliensis) leaf powder. J Environ Sci 22(2):248–256
60. Xu Z, Yuan Z, Zhang D, Chen W, Huang Y, Zhang T et al (2018) Highly mesoporous activated carbon synthesized by pyrolysis of waste polyester textiles and MgCl2: physiochemical characteristics and pore-forming mechanism. J Clean Prod 192:453–461
61. Novais SV, Zenero MDO, Tronto J, Conz RF, Cerri CEP (2018) Poultry manure and sugarcane straw biochars modified with MgCl2 for phosphorus adsorption. J Environ Manag 214:36–44
62. Mirzaei N, Hadi M, Gholami M, Fard RF, Aminabad MS (2016) Sorption of acid dye by surfactant modificated natural zeolites. J Taiwan Inst Chem Eng 59:186–194

Environmental-Friendly and Cost-Effective Agricultural Wastes for Heavy Metals and Toxicants Removal from Wastewater

Fathy Elbehiry, Tarek Alshaal, Nevien Elhawat, and Heba Elbasiouny

Contents

F. Elbehiry
Central Laboratory of Environmental Studies, Kafrelsheikh University, Kafr El-Sheikh, Egypt

T. Alshaal
Applied Plant Biology Department, University of Debrecen, Debrecen, Hungary

Department of Soil and Water, Faculty of Agriculture, Kafrelsheikh University, Kafr El-Sheikh, Egypt

N. Elhawat
Applied Plant Biology Department, University of Debrecen, Debrecen, Hungary

Department of Environmental and Biological Sciences, Faculty of Home Economic, Al-Azhar University, Tanta, Egypt

H. Elbasiouny (✉)
Department of Environmental and Biological Sciences, Faculty of Home Economic, Al-Azhar University, Tanta, Egypt
e-mail: Hebaelbasiouny@azhar.edu.eg

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 107–128, DOI 10.1007/698_2021_786,

Abstract According to released data from the United Nations (UN), about 60% of the world's populations could live in water-stressed situations by 2025. This could negatively affect many aspects of modern life and may also cause food and energy shortages leading to higher rates of illness. As world populations and their activities increase, wastewater generation increases as well. Releasing the toxic pollutants into water bodies has adverse consequences on human health, aquatic organisms, and ecosystems due to changing water properties making it unsuitable for consumption by humans, animals, and/or plants. In developing countries that suffer from acute shortage in water supply, remediation of the generated wastewater is a major issue since treated wastewater could be a valuable source of clean water. Treatment of wastewater can be physically, chemically, and biologically performed; however, the conventional methods have many disadvantages. Low-cost and environmental-friendly wastewater treatments can alleviate this issue and provide safe reusing of wastewater. Agricultural wastes can serve as natural adsorbents for pollutants from wastewater. A vast variety of ease regular adsorbents can be used for remediating sorts of toxins and pollutants from water and wastewater. Rice straw, cotton sticks, sugarcane bagasse, coconut husk, shells, etc., are examples of using agricultural wastes efficiently in wastewater treatment.

Keywords Aquaculture, Effluents, Horticulture, Industrialization, Wastewater treatment

1 Introduction

Water is a wellspring of imperativeness and life. It is an essential component of the daily activities of everyone. It also serves human needs such as drinking, cooking, bathing, washing, agriculture, industries, etc. Since ancient civilizations, water is utilized in waste disposal at all levels through the dilution technique. However, the dilution capacity of water bodies has now been exceeded by a tremendous load of pollutants as a result of the overgrowing population and increasing industrialization, so much so that some rivers adjacent to urban areas have been throttled to death whereas some others are on the edge of dying. Furthermore, over-extracting groundwater, basically for agriculture, has caused geological contamination of the charging area of groundwater in many parts of the world. Unfortunately, rivers and groundwater are the only water sources for drinking. Worldwide a large number of people are suffering from the absence of clean drinking water. Thus, the quality of drinking water has globally become a major concern. Recently, the water demand for human activities has expanded seven times because of the quadrupled global population. Many concerns such as unplanned use and extraction of water, expanding industrialization, rising food security issues, improper waste discharges, in addition to lack of appropriate and sufficient methods and mechanisms of treating wastewater have left the upcoming water security concerns rising [1, 2]. In this context, it is worth mention that water scarcity defines as a gap between available freshwater supply and demand in a specific domain, under prevalent institutional arrangements (such as arrangements include resource "pricing" and retail charging) and infrastructural conditions [3].

Drivers of the supposed water crisis are fully documented. The global water demands have been grown twice more than the population increase rate in the previous century. In the developing countries, the situation is more complicated because of irregular distribution and pressure on water resources due to major population changes and increasing demand. Indeed, there are many and interrelated reasons for water scarcity; in most circumstances, it ascribed to demands grow beyond available supplies. This has resulted in rising competition for water among peoples to capture scarce resources. These driving forces of water scarcity are represented in:

1. Population growth, especially in water-short regions (arid and semi-arid regions).
2. Major changes in migration and moving people from rural to the urban areas.
3. Increasing demands for food security and socio-economic well-being.
4. The increasing struggle between users and usages.
5. Increasing water pollution from many sources; municipal, agricultural, and industrial sources [3].

Therefore, the need to increase water resources and find alternative sources, in addition to economic and environmental concerns, is the key driving force for developing water reuse in many regions such as the Mediterranean region, where wastewater is used for irrigation for centuries. In addition to economic and environmental concerns is the key driving force for developing water reuse in many regions such as the Mediterranean region where it is used as an irrigation source for centuries. This has many advantages in addition to providing a low-cost water source such as:

1. The fertilizing properties of the wastewater that decline the demand for synthetic fertilizers and reduce nutrients level in receiving lands and waters;
2. Reuse of wastewater increases the availability of agricultural water; and.
3. Probable eliminating of the need for high-cost tertiary treatment [4].

In addition to irrigation, it may be used for many purposes like an injection to groundwater, construction, the formation of the recreation areas, desertification control, prevention of salt-water intrusion through groundwater recharge operations, etc. [4]. Thus, the treatment of wastewater is a renovation process before reusing or discharging it. The goal of the treatment is to decrease or eliminate the pollutants in wastewater, i.e. solids, organic matter, nutrients, the disease caused by organisms, and other wastewater pollutants [5].

To date, only about 10% of the generated wastewater is remediated and the remaining wastewater is released into water bodies or spread into groundwater. Therefore, remediation of wastewater is of importance before its discharge into water streams such as rivers and seas. Finding an effective method to remediate organic and inorganic pollutants in wastewater gains growing interest. Adsorption is an effective way to remove pollutants; however, the high cost of adsorbents is the main challenge for its wide usage. Nonetheless, this cost can be diminished if the adsorbent would be prepared from some low-cost materials such as agricultural waste [6].

2 Wastewater Sources and Estimations in Developing Countries

Water demand is rising at a higher rate than population growth, while the availability of water is declining as a result of increasing competing demand from many users, in addition to climate change. For example, it is estimated that the world will face about 40% of the water deficit by 2030 that seriously affects the livelihood of 33% of the world's population. As well, the global demand for food is likely to increase by 40% in 2030 whereas annual grain losses because of water scarcity are expected to be 30%. Subsequently, water security is counted to be one of the topmost five global risks concerning development impact [7]. According to the World Water Council, the number of individuals living in water scare will grow to approximately 3.9 billion by 2030, because of increasing urbanization, industries, and natural needs. Therefore, searching for the arrangements permitting effective water cleaning is important. In addition to increasing water demand, the enormous increase in population, industrialization, and unprompted urbanization has led to serious water and soil contamination. The primary reason for freshwater contamination can be attributed to the dumping of industrial wastewater, the release of untreated toxic industrial wastes, and runoff from agricultural fields. In developing countries, 70–80% of all problems and illnesses are heavily linked to water pollution [2]. Several poisonous substances such as toxic metals, pesticides, pharmaceuticals, surfactants, dyes, and others have polluted the water bodies and are ecologically dangerous for living organisms. The released toxic pollutants in wastewaters can cause adverse impacts on human health, aquatic organisms, and ecosystems [2, 8, 9]. Thus, accessibility and availability of safe drinking water is a crucial necessity and should be a basic public health priority. Although the availability of sanitation and clean water has been concerned in developed countries, it is not the same in the majority of developing countries. However, in developing countries, the scarcity of safe drinking water is considered one of the major worries [10].

According to Corcoran et al. [11] and Parween and Ramanathan [1], wastewater can be defined as one or more of the following:

1. Domestic effluent that consists of black-water (i.e., urine, excreta, and fecal sludge), and greywater (i.e., kitchen and bath wastewater).
2. Discharge from schools and hospitals and commercial institutions.
3. Industrial effluents, stormwater, and another urban runoff.
4. Agricultural, horticultural, and aquaculture effluents (suspended or dissolved matter).

Wastewater can, hence, be classified as domestic (i.e., fecal and non-fecal), industrial, commercial, or agricultural according to its sources and chemical composition that distinguish each type of them. Wastewater is approximately constituted of 99% water and 1% dissolved, suspended, and colloidal solids that make it a potential contender in participating in forthcoming world water security. Nevertheless, its threat to health and the environment makes it a key factor to be pertinent for managing [1].

3 The Contamination and the Need for Reusing Wastewater in Developing Countries

The management of wastewater in developing countries is increasingly becoming a priority issue. However, accelerated urbanization, inadequate control, and the implementation of sophisticated highly centralized treatment technologies restrict the expansion of such proper management of wastewater in these countries [12]. Intensified utilization of available water resources throughout the extension of water supply infrastructures, enhancing water productivity, and developing non-conventional sources are among several current strategies for increasing water supplies. However, efforts for improving wastewater management are mostly inadequate. Hence, about 75 to 90% of the supplied water is being discharged as untreated wastewater. Conversely, wastewater is considered an inexpensive and reliable alternative water supply in urban and countries for supporting their economy. Thus, reusing wastewater is of importance especially in semi-arid and arid regions and developing countries [7, 10].

Generally, the increasing process of modern civilization, industrialization, and excessive human utilization of available resources generate huge amounts of wastewater. Thus, continuous disposal of the untreated discharges into the ambient environments has led to significant environmental damages especially in developing countries and has emerged many global environmental issues such as water pollution. As well, these anthropogenic impacts have disrupted the ecosystem's balance of which human beings have relied upon during history. Hence, there is a speedy increase in organic pollutant discharge such as chlorinated products, antibiotics, and crude oil, which are toxic and persistent. Likewise, runoff of agrochemical residues such as pesticides and inorganic fertilizers decreases oxygen levels in the aquatic ecosystems hurting the aquatic organisms [13–15]. Also, the overutilization of water resources by humans, in their different activities, appears to be the most urgent environmental obstacle globally. Also, several sectors, namely agriculture, industry (e.g., chemical, mining, metal coatings, metallurgical, paints, batteries, textile dyes, tanneries, etc.), construction, and shipping generate huge amounts of wastewater. The different industries generally generate organics (e.g., benzene groups and dyes), organometallics, and inorganic materials (i.e., heavy metals) such as copper (Cu), zinc (Zn), mercury (Hg), cadmium (Cd), lead (Pb), tin (Sn), iron (Fe), manganese

(Mn), silver (Ag), chromium (Cr), cobalt (Co), nickel (Ni), arsenic (As), aluminum (Al), etc. Indeed, the existence of such heavy metals in wastewater makes it more toxic for receiving environments such as rivers, vales, mothers, etc. It causes imbalance to the vital circumstances of the aquatic flora and fauna; and thus, negatively impacts human health in one or another way. This requires the reduction and/or total removal of heavy metals before discharging into environments according to the required standard appropriate for the preservation of surface water quality [6, 16]. Accordingly, wastewater represents a major problem that threatens living species because of its high content of harmful compounds, which cannot be destroyed or degraded [6].

Certainly, the quality of water is an issue that sorely affects our food, health, and environment. Rising pollution levels and over-consumption of our resources need some serious solutions [17]. Indeed, exposure to high pollution levels causes adverse consequences on the living creatures, food chains, and the natural environment. For example, heavy metals pollution can cause several human health risks that impair the brain, lungs, and kidneys. Moreover, bone mineral loss, intestine irritation, carcinogenic infection, cardiovascular disease, and nervous system disturbance are other health problems caused by the consumption of heavy metals-polluted food and/or drink. Furthermore, pollution leads to several concerns about freshwater availability, photosynthesis and respiration processes, and thus food/feed safety and security. Additionally, when the soil receives a high level of these toxic elements, the inhibition of crop growth and germination, reduction of the microbial activity, as well as alteration of enzymatic functions occur. Also, pollutants may leak into groundwater encouraging the transfer of undesirable microorganisms and pathogens. As well, nutrients, solids, and organic pollutants that are discharged into water bodies cause depletion of dissolved oxygen, eutrophication, and clogging of fish gills. Consequently, proper and promising treatments should be developed for protecting the soil, water, and other environmental systems [18]. Industrial wastewaters like acid mine or electroplating wastewaters contain several toxic substances such as oil, fat, grease, alkaline cleaning agents, cyanides, degreasing solvents, nitrogen (N), phosphorus (P), and metals (such as Cu, Ni, Cr, Ag, and Zn), which are harmful and threat the environment when discharging without treatment [19, 20]. Al-Khafaji et al. [20] added that the industrial wastewater quality and subsequent discharges depend on the applied chemicals, the process itself, the season, and the fashion. Therefore, there is a need to monitor the water quality within and surrounding the wetland environments receiving polluted water, to assess the extent of pollutants. The accumulation of pollutants in the environment surely leads to food and water contamination. Consequently, the World Health Organization (WHO) strictly sets allowable limits of these toxicants in water [21].

Parween and Ramanathan [1] listed in some details of various pollutants as components of wastewater as follows:

(a) Organic pollutants (such as carbohydrates, proteins fats, nucleic acid, etc.)
(b) Inorganic nutrients (N, P, K).
(c) Toxic metals (Cd, Cr, Pb, Hg, Cu, Ni, Zn, As, Se, etc.)

(d) Pathogenic microorganisms (such as bacteria, viruses, protozoa, and helminths).
(e) Synthetic organic compounds (polyaromatic hydrocarbons, food additives, synthetic pesticides, polychlorinated biphenyls, synthetic detergents, pharmaceuticals, cosmetics, oils, paints, plastics, synthetic fibers, etc.)
(f) Radioactive and thermal pollutants (such as radioactive isotopes of Sr, U, I, Co, etc.)

Toxicants and pollutants in wastewater

1. Organic toxicants

   – *Chlorophenols* are a group of chemicals made by adding chlorine (Cl) to phenol (C_6H_6O) including mono-chlorophenols, dichlorophenols, trichlorophenols, tetra-chlorophenols, and pentachlorophenols. These substances are widely used as pesticides, herbicides, fungicides, antiseptics, and preservatives for vegetable fibers, wood, paint, glue, and leather. They are highly persistent in both terrestrial and aquatic environments and also are harmful to humans because of their carcinogenicity. As a result, the US Environmental Protection Agency (USEPA) listed them as priority pollutants [22]. Karn et al. [23] reported that pentachlorophenols are a major environmental concern as they are very toxic and dangerous. They are toxic to all forms of life as they act as an inhibitor of oxidative phosphorylation in plants.
   – *Halogenated hydrocarbons* include aliphatic, aromatic, alicyclic, polyaromatic, and heterocyclic hydrocarbons that have been commercially used for many decades. Each group of halogenated hydrocarbons may cause a widespread set of biological effects where their toxicity may vary among the group members. Transcriptional activation of CYP genes is one of the major toxicity mechanisms of polyaromatic halogenated hydrocarbons after their nuclear translocation by the cytosolic AH receptor [24]. Among them, halogenated aliphatics are organic chemicals where a halogen is replaced by one or more hydrogen atoms. Halogenated aliphatics are used as solvents, fumigants, insecticides, and chemical intermediates in the industry; and they are found in the chemical, pharmaceutical, textile, plastics, paint, varnish, rubber, dye-stuff, and dry-cleaning industries. Many of these compounds, particularly the chlorinated insecticides, as a result of their poor bioavailability, high toxicity, or xenobiotic structure, are persistent and recalcitrant in the environment, even though some of them can be broken down under certain conditions [22].
   – *Long-chain fatty acids (LCFAs)*: fatty acids are chains of carbons with attached, at one end, hydrogen (H) molecules, and an acid group at the other one. LCFAs are fats that have several carbons in their chain and can be saturated or unsaturated fatty acids. LCFAs are considered as important fractions of the organic matter (OM) in oil/fat wastewater [22].

2. *Petrochemicals*: Wastewater is generated in several ways from the petrochemical industry, containing cooling water, effluent from raw materials, factory rainwater, and domestic sewage. The global petroleum production has been reported to be 4.40 billion tons depending on related industrial statistics. Petrochemical wastewater largely contains many inorganic and organic toxic substances. Heavy metals, sulfides, fluorides, and others are examples of inorganic substances; while benzenes, aldehydes, and phenols are examples of organic. These petrochemical substances are a major concern in many studies where organic substances are considered as the main problem in petrochemical wastewater due to their high toxicity [25, 26].
3. *Ammonia, nitrogen, and phosphorus*

   The wastewater has high ammonia (NH_3) content; therefore, it would inhibit the process of natural nitrification resulting in water hypoxia and fish poisoning. Also, it reduces the capacity of water purification and ultimately led to great harm to the aquatic environment. NH_3 is a neutral molecule that can diffuse through the epithelial membranes of aquatic organisms more speedily than the charged NH_4^+ ion. Additionally, it was stated that NH_3 could block oxygen transfer in the fish gills; and the poisoned fish appears sluggish and arises to the water surface gasping for air [27].

   Nitrogen and phosphorus are two fundamental elements needed for life on Earth. In particular, phosphorus is a non-renewable resource and could be consumed in a few decades. On the other hand, economic development and rapid population growth have facilitated a huge demand for animal protein leading to an immense production of wastewater with high levels of ammonium and phosphate. Consequently, eutrophication, fish death, and oxygen depletion occur as a result of the discharge of these wastes into the natural water bodies. Hence, the remediation of wastewater is imperative for mitigating water pollution and improving resource sustainability [28].
4. *Sulfide*

   Sulfide in waste streams is generated by several industries such as petrochemical plants, viscose rayon factories, tanneries, and coal gasification for electricity production [22]. Sulfide in sewers is related to many problems, e.g. sewer assets corrosion, malodors, and health impacts. Sulfide is formed in submerged biofilms and this requires anaerobic conditions that are found in all of the networks [29].
5. *Heavy metals*

   Heavy metals (HMs) are elements that have atomic weights between 63.5 and 200.6 and a specific gravity higher than 5 [19]. The most frequent HMs found are Cu, Cd, Cr, Co, Fe, Pb, Hg, Mo, Ni, and Zn. However, many HMs are required for the functioning or activation of many coenzymes and enzymes in anaerobic digestion. Furthermore, some HMs, such as Cu, Zn, and Mo, are required at low levels in the cells. However, excessive amounts of HMs can lead to toxicity [22]. The HMs are found commonly in wastewater discharged from numerous industries, such as leather and battery manufacturing, mining, and smelting. Dissimilar to organic pollutants, HMs are not biodegradable. They have long been known as very dangerous environmental pollutants, as a result of their potential for bioaccumulation, high toxicity, and carcinogenicity, even at very low levels. Thus, HMs are considered a serious threat to the environment and human health. Additionally, HMs can coexist with other ions and simply form complexes with complexing agents such as ethylene diamine tetraacetic acid, which aggravates their toxicity and declines environmental risks [15]. The main source of HMs in wastewater is fertilizer industries, metal plating industry, tanneries, chloralkali, textiles, batteries, mining operations, paper industry, electroplating, petroleum refining, radiator manufacturing, metallurgy, manufacturing of dyes and pesticide, smelting, alloy industries, etc. These HMs are indirectly or directly discharged into the environment especially in developing countries [19, 30, 31]. Toxic HMs of particular concern in the treatment of industrial wastewater are Zn, Cu, Ni, Hg, Cd, Pb, and Cr because of their serious toxicological concerns at higher concentrations than the allowed [19, 32].

6. *Nanomaterials*

   In the past decades, nanomaterials have been intensively used and successfully applied in different fields such as medicine, catalysis, sensing, and biology. Particularly, its application in water and wastewater treatments has received wide attention. Because of their small sizes and their large specific surface areas, they have high adsorption capacities and reactivity in addition to their high mobility in the solution. Various kinds of nanomaterials have been reported to successfully remove HMs, organic and inorganic pollutants, and bacteria [33]. While the technological advantages of nanotechnology start to move speedily from laboratories to large-scale industrial applications, nanomaterials release into the environment is inevitable. The major environmental receptors of wastewater treatment will be soil, sediment, and biosolids [22].

4 Common Methods and Materials for Wastewater Treatment

In developing countries, environmental pollution due to the uncontrolled discharges of industrial and municipal wastewaters has forced a series of threats. The old-style of aerobic and anaerobic reactors, which are usually operated for wastewater treatment, is unaffordable there because of financial and technical skills and many other limitations. Consequently, large quantities of municipal wastewater discharged into the environment without any secondary treatments are very common [13]. There is a need to clean and recycle polluted wastewater to secure alternative water sources and to protect the food chains [34].

Many physical (e.g., sedimentation and mechanical filtration), chemical (e.g., ion exchange), and biological (e.g., biosorption and biofiltration) methods have been effectively used to remove the pollutants (e.g., organic acids, phosphates, dyes, nitrates, toxic heavy metals, etc.) from water and soil [5, 14, 18]. For instance, various conventional methods and technologies are applied to HMs remediation of polluted wastewater, and to maintain ecological sustainability and public safety. Ion exchange, adsorption, chemical precipitation/co-precipitation, chelation/complexation, photocatalytic biodegradation, flotation, membrane filtration, electrochemical treatment, and phytoremediation are examples of these methods. Nevertheless, these methods are low efficiency, applicable at a small scale, costly, and time-consuming. As well, these methods require a large use of reagents and cause secondary harmful wastes such as volatile organic compounds and persistent organic pollutants. In addition, there are other some drawbacks that have been stated to limit the wide use of physicochemical approaches such as high reagent utilization like in the coagulation/flocculation technique, incomplete removal of toxic materials, and exhausting adsorbent disposal as in ion-exchange high-energy consumption as in ultrafiltration, chemical regeneration phases, hazardous sludge formation, and frequent backwashing. Thus, these methods presented increasing prices, accumulation, and environmental risks. Subsequently, there is an urgent demand for environmentally friendly and cost-effective methods for the effective removal of pollutants and also for the sustainable development of human society [14, 15, 18, 28, 30, 32, 35–39].

4.1 Physical Methods of Removing Pollutants

Ling and Weimin [5] presented in detail these methods, and here we will summarize some of them:

- *Sedimentation* is the process that can settle out the suspended solids that have a greater density or specific gravity than water, and then be separated away from the main flow. There are four sedimentation types depending on the particle's concentration and their interaction with each other that are discrete, flocculent, or hindered, and compression settling. Settlement tanks can be used to separate most of the suspended solid wastes.
- *Mechanical Filtration* is also used for removing suspended solids. It includes several types such as sand filtration and screen filtration. This process requires a large quantity of wash-water with filters of 70 um or larger, although, this great removal of small suspended solids can be accomplished by either chemical or biological oxidation.
- *Aeration* is widely used in most of the rural areas to provide oxygen to the effluent to be treated, and also to reduce malodorous gases from sediment in the bottom. Exchanging the surface water that has plenty of oxygen with the bottom water in the pond allows decomposing some sediment rich in organic matter effectively.

4.2 Chemical Methods of Removing Pollutants

Ling and Weimin [5] presented also some of the chemical methods to remove pollutants from wastewater such as:

- *Liming*: Materials, e.g., agricultural limestone, quick lime, slaked lime, and liquid lime, have been used to liming the ponds which have an immediate influence on water quality. It raises pH, which kills most pests and disease agents, and causes water to be clearer of suspended solids, to decline soluble phosphorus, and lower free CO_2.
- *Chlorine dioxide (ClO_2)*: The stable form of ClO_2 is commonly considered the most effective disinfector in the treatment of wastewater. It can eliminate bacteria, viruses, pathogens, sporangium, fungus, and parasites without any side effects. Temporarily, as an oxidant, ClO_2 may destroy hydroxybenzene, sulfurated hydrogen, cyanide, and other organic matters. It can improve the water quality and raise the dissolved oxygen content for avoiding epidemic disease explosion and infection in the cultivation process. However, high levels of ClO_2 may be unsafe for aquatic life in receiving streams.
- *Ultraviolet Filter and Ozone (O_3) Water*: Treated wastewater is always passed through an ultraviolet filter or treated with O_3 to destroy any existed parasites, pathogens, and diseases. However, pH value, temperature, and ammonia concentration affect the sterilization speed. Chemical oxidation by O_3 can be used to reduce the organic load in conventional wastewater treatment. In a recirculating system for fish culture, O_3 is effective for degrading organic matter and for sterilization.
- *Flocculants*: Chemicals are always added during the wastewater treatment to help settle out or strip out P or N. Flocculants are materials that have at least one kind of monomer or polymerization (Al salt and multi-prices carboxylic acid mixture). They are particularly used for removing algae bloom in the aquatic system, which can purify the water body totally without any harm to aquatic organisms.

4.3 Biological Methods

Ling and Weimin [5] presented some of the biological methods to remove pollutants from wastewater such as:

- *Effective Microbes*, which generally include photosynthetic bacteria, nitration bacteria, lactic acid bacteria, sporangium bacillus, are used for decomposing and absorption of the sedimentary organic nitrogenous, nitrite nitrogen, and ammonia in the wastewater or for converting them into beneficial substances. The microorganisms have been suspended for several hours in the wastewater, and then they are settled out as sludge. Some of this sludge is drove back to the incoming wastewater as a "seed" microorganism, while the remainder is collected and sent to the process of sludge treatment. Through the sludge treatment, the sludge is stabilized, the odors are reduced, some of the water is removed, some of the organic matter is decomposed, disease-causing organisms are killed, and the sludge is disinfected. Many methods can be used to remove more water from sludge such as sand drying beds, and filters resulting in sludge with less water which is called a sludge cake. Then, aerobic and anaerobic digestions are applied to decompose organic matter for reducing volume. Caustic chemicals can be used to kill disease-causing organisms. Then, the liquid and cake sludge is often spread as fertilizer on fields.

– *Biological Filtration*: Fish produce nitrites and ammonia as metabolic toxic products that are toxic and required to be converted into non-toxic nitrates that cause no harm to the fish. For this purpose, biofilters (e.g., sand filters and rotating biological contactors) are used to convert nitrites and ammonia to nitrates via oxidation. They consist of a large surface area medium (such as rocks, sand, gravel, plastic, pebbles, and cinder) upon which microorganisms (such as nitrifying bacteria) will colonize after a few weeks. Because nutrients and organic matter are absorbed from the wastewater, the microorganisms' film grows and thickens. This biofiltration type is recommended; however, current technology depends on expensive bacterial systems. Furthermore, the drawbacks of biofilters are obvious such as unstable performance, excessive sludge production, and nitrate accumulation [5].

5 Low-Cost and Eco-Friendly Agricultural Wastes-Derived Absorbents

In developing countries, treatment and remediation of the generated wastewater are a major concern especially by those who consider vital points such as reusability, recyclability, cost, and sustainability. Since the population is growing rapidly, this would lead to severe water scarcity [40]. Also, the high-cost structure of many available techniques to control environmental pollution can burden society particularly low-income families. Therefore, wastewater treatment, nowadays, is a major issue because it requires a big cost in terms of types of equipment and chemicals used. For example, a fixed bed reactor is one of the best widely applied methods for the treatment of domestic greywater; however, the filters installed in this reactor are polymer-fiber based filters that are relatively expensive. Consequently, taking into consideration the need for domestic wastewater pre-treatment and the economic burden to install modern technology, it is necessary to develop more cost-effective wastewater treatment techniques [41]. As well, to minimize the problems related to using previous conventional methods, a lot of research has been carried out to find out low cost, easily available materials from agricultural wastes as sorbents [32].

Adsorption has become the most important waste treatment techniques. It has been widely applied for the disposal of wastewater as a result of its low cost, high efficiency, and simple design [38]. Feng et al. [28] also stated that adsorption is an effective technique because of its easy operation and high selectivity, particularly if the adsorbent is not expensive and commonly available. However, the application of conventional adsorbents such as diatomite and bauxite is impeded not only by their quite poor adsorption capacities but also by their potential ecological risks.

Bello et al. [37] and Akhayere et al. [42] stated that adsorption has grown as a front line of defense for pollutants removal; also, it has proven its potency over time. However, the efficacy of an adsorption process relies on the adsorbent [42]. Physical and chemical surface characterizations of adsorbents play an important role in adsorbing by predicting the adsorption capacity of these adsorbents. Out of these characteristics of adsorbent materials particle size, specific surface area, pore-volume, pore-size distribution, point of zero charges, and presence of surface functional groups that determine the adsorption efficiency and capability of adsorbents are very important. Moreover, the analysis of each characteristic may show the effect of this property that related to the adsorbate type such as metals, dyes, phenols, etc. [43].

Selective adsorption by activated carbons, mineral oxides, biological materials, or polymer resins has generated increasing interest. Therefore, investigating a more cost-effective adsorbent material is of huge interest in wastewater treatment [37]. Elbehiry et al. [44] stated also that many cost-effective and amendments can be used for the pollutants remediation such as Fe-oxides, biochar, and humic substances. Natural materials, which are widely available, or specific waste products resulted from agricultural operations, may be potentially inexpensive adsorbents [35].

As a global food production demand has resulted in increasing agricultural activities, more agricultural wastes are generated. Agricultural wastes, mainly from plant biomass such as husks, straw, peels, shells, etc., can either be disposed of after harvest or be utilized as valuable precursors for the production of other materials [42]. Currently, utilizing agricultural by-products, synthetic materials, and aquatic organisms for adsorbent fabrication to remove pollutants have been reported [37]. Afroze and Sen [43] emphasized that natural solid wastes from agricultural by-products can be applied as inexpensive sorbents for the removal of organics and inorganics contaminants from polluted water. Thus, the utilization of a large volume of agricultural wastes as effective adsorbents also provides a sustainable cost-effective solution for wastewater treatment.

Experimental adsorption characteristics of several biomass wastes such as wheat bran, sunflower stalk, rice husk, rice milling by-products (hulls and brans), spent grain, onion skin, almond husk, banana pith, modified barks, and soybean hulls have been examined for their capacity to remove pollutants from wastewater [32]. Renang et al. [41] stated that one of the ways to mitigate environmental pollution is using agricultural wastes as bio-packing media to treat the domestic wastewater before discharging it to water bodies. Agricultural wastes have no economic value and their accumulation can further cause environmental pollution. Thus, utilizing agricultural wastes as bio-packing media to treat domestic greywater is feasible not only because it reduces the cost of wastewater treatment, but it can also avoid a huge accumulation of agricultural wastes. It is also stated that the utilization of agricultural wastes as low-cost renewable materials for treating wastewater promotes minimizing wastes and cleaner operation. Some agricultural wastes such as rice husk and coconut coir are used as packing media and biofilm materials carriers for wastewater treatment via the biofiltration method. This method uses the supported living organisms grown on the packing media surface for degrading and hydrolyzing the pollutants since the water filtered over the packing media. Hence, biofiltration is becoming an attractive method for wastewater treatment because of its efficiency in removing biodegradable organic matter in addition to its low maintaining costs [41].

Recently, sustainable sorbents derived from renewable biomass such as cellulose- and/or lignocellulose-based materials, alginate, and chitosan have received growing attention. Lignocellulose is a cheap and promising biosorbent. Additionally, compared with other materials, it is naturally comprised of abundant free carboxyl and hydroxyl groups, providing reactive sites for additional surface modification. In addition to its green advantages and biocompatibility, it has a unique adsorption advantage because of its natural porous structure and large specific surface area. For example, wood as a porous and multi-hierarchical lignocellulosic material has unique properties such as an intrinsic mesoporous structure, exceptional optical and mechanical characteristics, and excellent capacity of water transportation; thus it is a major promising candidate for wastewater treatment. However, the most processing procedures of using wood as a sorbent is the use of strong acids; in addition, it has high cost and energy waste, impeding sustainable development. Thus, the current goal of the researchers is to use wood waste for treating the contaminated water and finally achieve the value-added utilization of natural resources by green and low-cost strategy [38].

5.1 Activated Carbon (AC) Derived from Agricultural Wastes

Currently, various agricultural wastes with high adsorptive capacity have been examined for their removal efficiency of heavy metal from simulated wastewaters. Activated carbon (AC) derived from agricultural wastes is an example of low-cost materials used for ions removal from wastewater [45]. AC is an amorphous C with a high porosity degree and very large surface area which allows heavy metals or toxic molecules to be adsorbed on its surface [6]. Adsorption by AC is also effective and widely employed in wastewater treatment. Unfortunately, commercial AC derived from wood, peat, and coal is expensive; this leads to searching for easily available and low-cost materials for AC production. Various types of carbons have been prepared from agricultural wastes such as cotton stalks, rice husks, coconut shells, sugar cane bagasse, paddy straw, and coir pith. Each sorbent has pros and cons. The nature of the initial biomass to a large extent determines the final properties of the sorbent carbon. The activation process of the initial material to an activated product goes on via two steps: carbonization and activation [46]. The carbonization of the carbonaceous raw material, usually N, is done at a temperature below 1,000 °C in an inert atmosphere [6]. In the carbonization step, the moisture and volatile matters such as H_2, CO, CH_4, and other hydrocarbons derived off to produce a high C content solid residue called char. This step also leads to an initial opening of the precursor C structure, and the resulting carbonized product that has only a small adsorption capacity. On the other hand, the activation process improves the adsorptive power of the previous product got from the carbonization step. Carbonization can be carried out in muffle furnace, tubular furnaces, reactors, and, more recently, in a glass reactor put in a modified microwave oven. Usually, there are chemical and physical methods for activation. In the chemical activation, the precursor material is saturated with a dehydrating and stabilizing chemical reactant to enhance the porous structure development upon heat treatment. The most widely applied activation agents are zinc chloride, potassium sulfide, aluminum chloride, phosphoric acid, caustic soda, and potash. In the physical activation, the carbonized product reacts with gases like carbon dioxide, oxygen, steam, or air [46–48]. Thus, these gases work as oxidizing agents in a temperature range between 600 and 900 °C resulting in the removal of the more disorganized C and the forming of a well-developed micropore structure. The chemical activation is characterized by the physical process by high yield, less activation time, lower temperature of activation, and generally higher porous structure [6, 46].

A high price and limited reusability, some are corrosive, and additional washing stages through the process are key problems hindering the extensive application of AC [36, 46]. Some reports have appeared on the preparation of activated carbons derived from rice husk, coconut shell carbon coconut tree sawdust carbon, and several types of activated carbon from agricultural by-products. As coir pith carbon was shown to remove heavy metals from synthetic solutions the aim of this study was to investigate the feasibility of using coir pith carbon for the removal of heavy metals from industrial effluents through varying parameters of pH and carbon concentration [35]. The AC commonly is used as an adsorbent in heavy metal treatment [36].

Noor et al. [45] stated that sugarcane bagasse is a plentiful agricultural residue resulted from the processing of sugarcane in countries such as South Africa, Brazil, and India. It has been converted into AC and used in several applications because of its high surface acidity, high surface area, and microporous structure. Sugarcane bagasse comprises three main components, i.e. cellulose, hemicellulose, and lignin. Each of these components has a different value. Because it is rich in cellulose, it can lead to producing higher microporous biochar. As well, sugarcane bagasse has carboxylic and hydroxyl groups showing high efficiency for the metal's removal over a wide pH range. Lignin is also an ideal precursor for AC since it has a high C content, and its molecular structure is similar to bituminous coal. Rice husk is a by-product generated through rice milling in rice-producing countries such as Egypt. Its accumulation results in problems related to solid waste management, which if not treated properly, increases the risk of fire, attracts disease-carrying animals, or even occupies large areas in landfills. In Egypt, rice husk is a promising biomass that resulted in large and almost stable yield, (500,000 tons yr^{-1} of which 10–20% is rice husk) and has low acquisition cost. Dry rice husk consists of 70–85% organic matter (i.e., lignin, cellulose, sugars, etc.) and the other part is silica, which is presented in the cellular membrane [30, 49]. The AC and porous C derived from rice husk were utilized to adsorb various dyes and organic pollutants such as humic acid, phenol, malachite green, neutral red, Rhodamine B, dibenzothiophenes, municipal solid waste landfill leachate, and in the biodiesel purification [49]. Hegazi [30] also reported that attention has been paid to the use of modified or unmodified rice husk as an adsorbent for the pollutant's removal. He mentioned that some batch studies used modified rice husk (by tartaric acid) as an adsorbent for the removal of Pb and Cu by studying the effects of different parameters such as pH, temperature, initial concentration of adsorbate, particle size, etc. These studies displayed the potential use of modified rice husk for the removal of Cu and Pb from polluted aqueous solutions. Benstoem et al. [50] reported that the AC can be applied to reduce organic micropollutants (e.g., pharmaceuticals and substances resulted from personal care products) in wastewater. They reported that although producing ACs conventionally is damaging the environment, using renewable raw materials can reduce this damage.

5.2 Biosorbents from Agricultural Wastes

Due to the disadvantages of AC, a wide variety of agricultural waste has been investigated to eliminate heavy metals [36]. Tatarchuk et al. [6] stated that biosorption works on the uptake of heavy metals, dyes, and radionuclides from aqueous environments using biological materials (e.g., agricultural waste, plant leaves, root tissues, bacteria, algae, and fungi), which can be applied as biosorbents to remediate pollutants in water purification. Thus, biosorption has developed as a promising method with some advantages such as low cost, easy operation, highly efficient even with low metal concentrations, no additional nutrient requirements, potential metal recovery, and without environmental harmful effects. Agricultural waste-based biosorbents may be different parts of the plant, i.e. stem, leaves, root, bark, flower, fruit biomass, skin, husk, shell, hull, bran, and stone. Agricultural waste-based biosorbents primarily are comprised of cellulose, hemicellulose, and lignin which contain a high content of hydroxyl groups. Accordingly, they have a good ability to attach to metals [36]. The functional groups in agricultural wastes are, for example, carboxyl, carbonyl, phenolic, structural polysaccharides, alcoholic, ester, acetamido, amino, amido, and sulphydryl, etc. These functional groups substitute H^+ for metal ions in the solution or donate an electron pair to form complexes with the ions in solutions. These groups have an affinity for removing ions by forming metal chelates or complexes. Thus, heavy metal ions removal from wastewater by agricultural wastes is based upon metals biosorption. The mechanisms of biosorption include complexation, chemisorption, adsorption on the surface, diffusion over pores as well as ion exchange, etc. [31, 36].

Soldatkina and Zavrichko [51] reported that the full introduction of adsorption technology into the deep cleaning practice of dye wastewater is reduced by the high cost of ACs and by some problems with their regeneration. Recently, the researcher's attention has been focused on biosorbents from agricultural wastes as low-cost adsorbents available abundantly in the agricultural countries. They mentioned also that agricultural waste is partially utilized as roughage and bedding for cattle, as an energy source for home heating and power generation, or as a soil amendment facilitating the humus formation. Unused agricultural wastes are burned in the fields causing regional and global environmental problems such as destroying and reducing microorganisms activity when burning in the top-soil increasing the emissions of carbon dioxide, generating a lot of dust and smoke, and other harmful gases leading to air pollution and appearing the risk of fires [43, 51, 52]. Agricultural wastes such as Jerusalem artichoke stalks and barley straw are distinguished by their unique chemical composition, contain natural polymers, and can be successfully utilized as a cheap adsorbent and as an alternative to ACs [51, 52].

Sugarcane bagasse, coconut husk, rice husk, sawdust, neem bark, oil palm shell, banana peel, orange peel, bamboo, peat, coconut, etc., have been investigated by many researchers to eliminate heavy metals from wastewater [6, 30]. Generally, if the adsorbent is abundant in nature, requires little processing, or is a by-product from another industry, it can be termed as a low-cost adsorbent. Of course, enhanced sorption capacity may recompense the cost of extra processing. Hence, there is an urgent need to explore all likely sources of agro-based inexpensive materials and their feasibility to remove pollutants in detail [30]. Recently, more attention has been paid also for removing P and N in wastewater by agricultural waste, as they are cost-effective, potential renewable, and eco-friendly; they also can be utilized as soil fertilizers. Nevertheless, most of the raw materials usually have insufficient adsorption capacity for N or P and lack practical applications in the real wastewater. Feng et al. [28] reported that in China, for example, a Chinese medicinal herbal residue, resulting after the decoction or extraction process and produced with millions of tons yearly, is rich in cellulose, hemicellulose, and lignin which contain many functional groups such as O–H and –COOH, and have a porous and large surface, high mechanical strength, and chemical stability. Then, they can become possible biosorbents. However, there is a lack of information regarding their application in N and P removal from wastewater [28]. Different sources, such as coconut leaf, babassu coconut, papaya seeds, tamarind seed, jambul seed, soapnut, etc., were also used to prepare low-cost AC for the removal of heavy metals and dyes from wastewater [6].

Recommendation: Because of there is an urgent need to reuse wastewater specially in developing countries, eco-friendly and cost-effective alternative methods should be adopted. In this context, the future research should focus on using agricultural wastes as an environmental-friendly and cost-effective in treating wastewater. As well, the future research should also focus on the using of agricultural wastes on treating emerging contaminants from wastewater.

6 Conclusion

Water is life. The global water demands grow more than twice the population increase rate in the previous century; this will lead to water crises in many countries especially developing countries. Increasing human activities generate many sources of wastewater. Discharging wastewater into water resources leads to many environmental problems including water contamination and human health problems if not treated. Wastewater contains many organic and inorganic pollutants such as chlorophenols, hydrocarbons, petrochemicals, heavy metals, etc. There are many traditional methods to treat wastewater, however, these methods are time and chemicals consuming, expensive, and have many disadvantages. Therefore, using cost-effective and eco-friendly materials, such as agricultural wastes, is a good alternative to conventional methods. Agricultural wastes can be effectively used in many forms such as activated carbon and biosorbents for wastewater remediation, especially in developing countries. These agricultural wastes are used for remediating organic and inorganic pollutants in wastewater making it a valuable source of clean water to solve even part of the water shortage problem.

References

1. Parween M, Ramanathan AL (2019) Wastewater management to environmental materials management. In: Hussain CM (ed) Handbook of environmental materials management. Springer. https://doi.org/10.1007/978-3-319-73645-7_72
2. Vardhan KH, Kumar PS, Panda RC (2019) A review on heavy metal pollution, toxicity and remedial measures: current trends and future perspectives. J Mol Liq 290:111197. https://doi.org/10.1016/j.molliq.2019.111197
3. Makoni FS, Thekisoe OMM, Mbati PA (2016) Urban wastewater for sustainable urban agriculture and water management in developing countries. In: Younos T, Parece TE (eds) Sustainable water management in urban environments. Hdb Env Chem, vol 47. Springer. https://doi.org/10.1007/978-3-319-29337-0_9
4. Zimmo OR, Imseih N (2010) Overview of wastewater management practices in the Mediterranean region. In: Barcelo D, Petrovic M (eds) Waste water treatment and reuse in the Mediterranean region. Hdb Env Chem, vol 14, pp 155–181. https://doi.org/10.1007/698_2010_63
5. Ling C, Weimin W (2010) Wastewater management in freshwater pond aquaculture in China. In: Fukushi K et al (eds) Sustainability in food and water: an Asian perspective. Alliance for global sustainability bookseries, vol 18. Springer. https://doi.org/10.1007/978-90-481-9914-3_19
6. Tatarchuk T, Bououdina M, Al-Najar B, Bitra RB (2019) Green and ecofriendly materials for the remediation of inorganic and organic pollutants in water. In: Naushad M (ed) A new generation material graphene: applications in water technology. Springer. https://doi.org/10.1007/978-3-319-75484-0_4
7. Amare E, Kebede F, Kloos H, Mulat W (2017) Wastewater confronting realities for sustainable livelihood in developing countries: case study Mekelle university, Ethiopia. Water Conserv Sci Eng 2:21–30. https://doi.org/10.1007/s41101-017-0021-7
8. WHO/UNICEF (2000) Global water supply and sanitation assessment report 2000. WHO, Geneva

9. Elbehiry F, Mahmoud MA, Negm N (2018) Land use in Egypt's coastal lakes: opportunities and challenges. In: Negm AM et al (eds) Egyptian coastal lakes and wetlands: part I – characteristics and hydrodynamics. The handbook of environmental chemistry. Springer. https://doi.org/10.1007/698_2018_250
10. Badejo AA, Omole DO, Ndambuki JM (2018) Municipal wastewater management using *Vetiveria zizanioides* planted in vertical flow constructed wetland. Appl Water Sci 8:110. https://doi.org/10.1007/s13201-018-0756-0
11. Corcoran E, Nellemann C, Baker E, Bos R, Osborn D, Savelli H (2010) Sick water? The central role of wastewater management in sustainable development. UNEP and UN-Habitat, Nairobi
12. Chirisa I, Bandauko E, Matamanda A, Mandisvika G (2017) Decentralized domestic wastewater systems in developing countries: the case study of Harare (Zimbabwe). Appl Water Sci 7:1069–1078. https://doi.org/10.1007/s13201-016-0377-4
13. Fito J, Alemu K (2019) Microalgae–bacteria consortium treatment technology for municipal wastewater management. Nanotechnol Environ Eng 4:4. https://doi.org/10.1007/s41204-018-0050-2
14. Hasija V, Raizada P, Sudhaik A, Sharma K, Kumar A, Singh P, Jonnalagadda SB, Thakur VK (2019) Recent advances in noble metal free doped graphitic carbon nitride based nanohybrids for photocatalysis of organic contaminants in water: a review. Appl Mater Today 15:494–524. https://doi.org/10.1016/j.apmt.2019.04.003
15. Wang L, Wang Y, Ma F, Tankpa V, Bai S, Guo X, Wang X (2019) Mechanisms and reutilization of modified biochar used for removal of heavy metals from wastewater: a review. Sci Total Environ 668:1298–1309. https://doi.org/10.1016/j.scitotenv.2019.03.011
16. Es-sahbany H, Berradi M, Nkhili S, Hsissou R, Allaoui M, Loutfi M, Bassir D, Belfaquir M, El Youbi MS (2019) Removal of heavy metals (nickel) contained in wastewater-models by the adsorption technique on natural clay. Mater Today Proc 13:866–875
17. Singh KP, Mohan D, Sinha S, Dalwani R (2004) Impact assessment of treated/untreated wastewater toxicants discharged by sewage treatment plants on health, agricultural, and environmental quality in the wastewater disposal area. Chemosphere 55:227–255. https://doi.org/10.1016/j.chemosphere.2003.10.050
18. Nasr M (2019) Environmental perspectives of plant-microbe nexus for soil and water remediation. In: Kumar V et al (eds) Microbiome in plant health and disease. Springer. https://doi.org/10.1007/978-981-13-8495-0_18
19. Bazrafshan E, Mohammadi L, Ansari-Moghaddam A, Mahvi AH (2015) Heavy metals removal from aqueous environments by electrocoagulation process– a systematic review. J Environ Health Sci Eng 13:74. https://doi.org/10.1186/s40201-015-0233-8
20. Al-Khafaji MS, Al-Ani FH, Ibrahim AF (2018) Removal of some heavy metals from industrial wastewater by Lemmna minor. KSCE J Civil Eng 22(4):1077–1082. https://doi.org/10.1007/s12205-017-1112-x
21. Saxena A, Bhardwaj M, Allen T, Kumar S, Sahney R (2017) Adsorption of heavy metals from wastewater using agricultural–industrial wastes as biosorbents. Water Sci 31:189–197. https://doi.org/10.1016/j.wsj.2017.09.002
22. Chen JL, Ortiz R, Steele TWJ, Stuckey DC (2014) Toxicants inhibiting anaerobic digestion: a review. Biotechnol Adv 32:1523–1534. https://doi.org/10.1016/j.biotechadv.2014.10.005
23. Karn SK, Kumari S, Chakrabarti SK (2015) Bio-removal of chlorophenols from industrial effluents in open bioreactor system. Chem Appl Biochem 2(1):108
24. Khan MAQ, Khan SF, Shattari F (2008) Halogenated hydrocarbons. In: Encyclopedia ecology. Elsevier, pp 1831–1843. https://doi.org/10.1016/B978-008045405-4.00399-2
25. Wei X, Zhang S, Han Y, Wolfe FA (2019) Treatment of petrochemical wastewater and produced water from oil and gas. Water Environ Res 91(10):1025–1033. https://doi.org/10.1002/wer.1172
26. Tian X, Song Y, Shen Z, Zhou Y, Wang K, Jin X, Han Z, Liu T (2020) A comprehensive review on toxic petrochemical wastewater pretreatment and advanced treatment. J Clean Prod 245:118692

27. Luo OX, Yan Q, Wang C, Luo C, Zhou N, Jian C (2015) Treatment of ammonia nitrogen wastewater in low concentration by two-stage. Int J Environ Res Public Health 12:11975–11987. https://doi.org/10.3390/ijerph120911975
28. Feng C, Zhang S, Wang Y, Wang G, Pan X, Zhong Q, Xu X, Luo L, Long L, Yao P (2020) Synchronous removal of ammonium and phosphate from swine wastewater by two agricultural waste based adsorbents: performance and mechanisms. Bioresour Technol 307:123231. https://doi.org/10.1016/j.biortech.2020.123231
29. Kiilerich B, van de Ven W, Nielsen AH, Vollertsen J (2017) Sulfide precipitation in wastewater at short timescales. Water 9:670. https://doi.org/10.3390/w9090670
30. Hegazi HA (2013) Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. HBRC J 9:276–282. https://doi.org/10.1016/j.hbrcj.2013.08.004
31. Renu MA, Singh K, Upadhyaya S, Dohare RK (2017) Removal of heavy metals from wastewater using modified agricultural adsorbents. Mater Today Proc 4:10534–10538
32. Chowdhury ZZ, Zain SM, Rashid AK (2011) Equilibrium isotherm modeling, kinetics and thermodynamics study for removal of lead from waste water. E-J Chem 8(1):333–339
33. Lu H, Wang J, Stoller M, Wang T, Bao Y, Hao X (2016) An overview of nanomaterials for water and wastewater treatment. Adv Mater Sci Eng 2016:4964828. https://doi.org/10.1155/2016/4964828
34. Godwin PM, Pan Y, Xiao H, Afzal MT (2019) Progress in the preparation and application of modified biochar for improving heavy metal ion removal from wastewater. J Bioresour Bioprod 4(1):31–42
35. Kadirvelu K, Thamaraiselvi K, Namasivayam C (2001) Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Bioresour Technol 76:63–65
36. Nguyen TAH, Ngo HH, Guo WS, Zhang J, Liang S, Yue QY, Li Q, Nguyen TV (2013) Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. Bioresour Technol 148:574–585
37. Bello OS, Atoyebi OM, Adegoke KA, Fehintola EO, Ojo AO (2015) Removal of toxicant chromium (VI) from aqueous solution using different adsorbents. J Chem Soc Pak 37 (1):190–206
38. Wen Y, Ji Y, Zhang S, Zhang J, Cai G (2019) A simple low-cost method to prepare lignocellulose-based composites for efficient removal of cd(II) from wastewater. Polymers 2019(11):711. https://doi.org/10.3390/polym11040711
39. Qin H, Hu T, Zhai Y, Lu N, Aliyeva J (2020) The improved methods of heavy metals removal by biosorbents: a review. Environ Pollut 258:113777. https://doi.org/10.1016/j.envpol.2019.113777
40. Jawed A, Saxena V, Pandey LM (2020) Engineered nanomaterials and their surface functionalization for the removal of heavy metals: a review. J Water Process Eng 33:101009. https://doi.org/10.1016/j.jwpe.2019.101009
41. Renang WA, Samat NASA, Baini R, Rahman R, Selaman OS (2018) The effectiveness of a fabricated bio-filtration system in treating the domestic greywater. Malays Appl Biol 47 (1):65–71
42. Akhayere E, Essien EA, Kavaz D (2019) Effective and reusable nano-silica synthesized from barley and wheat grass for the removal of nickel from agricultural wastewater. Environ Sci Pollut Res 26:25802–25813. https://doi.org/10.1007/s11356-019-05759-x
43. Afroze S, Sen T (2018) A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. Water Air Soil Pollut 229:225. https://doi.org/10.1007/s11270-018-3869-z
44. Elbehiry F, Elbasiouny H, Ali R, Brevik EC (2020) Enhanced immobilization and phytoremediation of heavy metals in landfill contaminated soils. Water Air Soil Pollut 231:204. https://doi.org/10.1007/s11270-020-04493-2

45. Noor NA, Othman R, Mubarak NM, Abdullah EC (2017) Agricultural biomass-derived magnetic adsorbents: preparation and application for heavy metals removal. J Taiwan Inst Chem Eng 78:168–177
46. Maiti S, Purakayastha S, Ghosh B (2008) Production of low-cost carbon adsorbents from agricultural wastes and their impact on dye adsorption. Chem Eng Commun 195:386–403. https://doi.org/10.1080/00986440701707917
47. Abatan OG, Oni BA, Agboola O, Efevbokhan V, Abiodun OO (2019) Production of activated carbon from African star apple seed husks, oil seed and whole seed for wastewater treatment. J Clean Prod 232:441–450. https://doi.org/10.1016/j.jclepro.2019.05.378
48. Mustafa R, Asmatulu E (2020) Preparation of activated carbon using fruit, paper and clothing wastes for wastewater treatment. J Water Process Eng 35:101239. https://doi.org/10.1016/j.jwpe.2020.101239
49. Yakout SM, Daifullah AAM, El-Reefy SA (2013) Adsorption of naphthalene, phenanthrene and pyrene from aqueous solution using low-cost activated carbon derived from agricultural wastes. Adsorpt Sci Technol 31:293–302
50. Benstoem F, Becker G, Firk J, Kaless M, Wuest D, Pinnekamp J, Kruse A (2018) Elimination of micropollutants by activated carbon produced from fibers taken from wastewater screenings using hydrothermal carbonization. J Environ Manag 211:278–286
51. Soldatkina LM, Zavrichko MA (2013) Application of agriculture waste as biosorbents for dye removal from aqueous solutions. Chem Phys Technol Surf 4(1):99–104
52. Elbasiouny H, Elbanna BA, Al-Najoli E, Alsherief A, Negm S, Abou El-Nour E, Nofal A, Sharabash S (2020) Agricultural waste management for climate change mitigation: some implications to Egypt. In: Negm AM, Shareef N (eds) Waste management in MENA regions. Springer water. Springer. https://doi.org/10.1007/978-3-030-18350-9_8

Green Synthesized Iron Nanoparticles for Environmental Management: Minimizing Material and Energy Inputs

Rachna Bhateria, Sharma Mona, and Yogita Sharma

Contents

Abstract Current development in nanotechnology has provided us with novel nanomaterials. This advancement in nanomaterial synthesis has resulted in their manipulation at the atomic level to achieve desired catalytic properties. The green routes used in synthesis of nanomaterials grab more attention as they are of low cost and environmental friendly, thereby reducing the risk of harmful effects of toxic

R. Bhateria and Y. Sharma (✉)
Department of Environmental Sciences, Maharshi Dayanand University, Rohtak, India

S. Mona
Department of Environmental Sciences and Engineering, Guru Jambheshwar University of Science and Technology, Hisar, India

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 129–150, DOI 10.1007/698_2021_789,

chemicals and derivative compounds. Iron nanoparticles have essential properties which are due to their multivalent oxidation states, abundant polymorphism and are also used as sensors, catalysts, medicinal uses, and remediation technology. Reducing the size increases the surface area of nanoparticles and hence the ratio of surface to bulk iron atoms. Consequently, both the rate of reaction and the fraction of iron atoms available for the reaction increase. As the iron nanoparticles are more reactive for water pollutants, they are used in water remediation technology. Iron nanoparticles are successfully used because of their exclusive properties, like very small size, high surface-area-to-volume ratio, surface modifiability, better magnetic properties, and great biocompatibility. This review describes the different applications of iron nanoparticles in environmental remediation. It also highlights the advanced routes for their synthesis by green resources. This review article concludes that green synthesized iron nanoparticles are highly efficient for the removal of different pollutants.

Keywords Dye removal, Green chemistry, Heavy metals, Iron nanoparticles, Pesticide

1 Introduction

Using different elements and methods for manipulating the matter for fabrication of compounds with specific attributes which can be used for different applications [1]. In 1959, Richard Feynman has given a famous statement, i.e. “There is a plenty of room at the bottom” which is the reason which enhanced the beginning of nanotechnology [2], a field that has since then greatly influenced science and engineering disciplines in which the exclusive properties of materials that are harnessed in applications impacting virtually every field of modern society, e.g. chemical synthesis, production of energy, lighting, biotechnology, electronics as well as health care. Out of the above-mentioned applications of nanotechnology, environmental remediation is at the leading edge. It is because the increasing population results in an increase of demand for clean water which is limited in supply, so more affordable technologies for water treatment are required for cleaner and faster water supply [3]. The present review compiles the recent green synthesis methods for fabrication of iron NPs and their prospective applications for environmental remediation.

2 Green Chemistry

Green chemistry is a philosophy that puts forward sustainable concepts. Following green chemistry routes decreases or perhaps eliminates the use as well as generating toxic products in the manufacture, design, and application of chemical products’ while forming novel chemical processes [4].

2.1 Principles of Green Chemistry

The promising field of green chemistry is the use of a group of principles (Fig. 1). The execution of green chemistry principles for developing new nanomaterials and their applications have significance in outlook of the fact that the technology is at the beginning of its expansion and is likely to be broadly distributed and applied throughout the world. Getting the structure–function relationships that relate particularly to nanomaterials and compilation of "key" data for life cycle assessment (LCA) of such processes could lead to new "design rules" for production of high-performance nanoscale substances that are benign and environmental friendly [5].

2.2 Merits of Green Chemistry

To deal with the demand of "going green" between the groups of scientists, researchers are following the natures' way of synthesizing nanomaterials [6]. Using the plant-based reducing agents and stabilizing/capping agents could be a better idea to reduce the bad effects along with amplification in the biological compatibility of inorganic nanoparticles for a range of applications. Though, it is not the entire story, prior to their applications in different fields these green products should be assessed for in vivo, in vitro, and ecological toxicity. However,

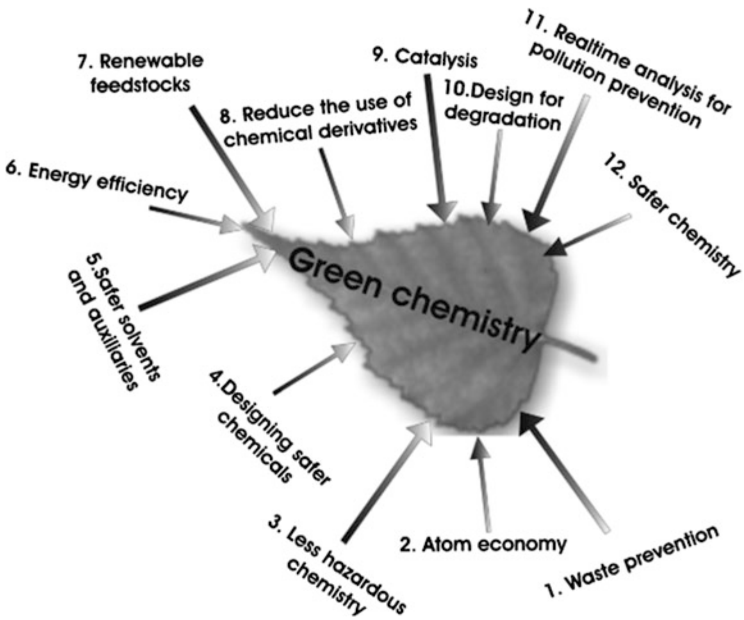


Fig. 1 The green chemistry principles [4]

enrichment, accessibility, efficiency in terms of time efficacy and circumvention of the use of noxious reagents are only a few of the preferred particular aspects of this approach [7, 8].

3 Green Synthesized Iron Nanoparticle

An engineered nanoparticle (NP) may be defined as any intentionally produced particles that have a characteristic dimension from 1 to 100 nm and have properties that are not shared by non-nanoscale particles with the same chemical composition [9]. Oxides of iron subsist in different forms in nature, like hematite (α-Fe_2O_3), magnetite (Fe_3O_4), and maghemite (γ-Fe_2O_3) are the most commonly known forms [10, 11]. Specifically, the rapid and much easier synthesis methods, manipulating the matter at the atomic scale level as well as controlling it, may offer supreme versatility [12, 13]. In addition, NPs synthesized using metal iron with chemical inertness, biocompatibility, and lower toxicity illustrate a great possibility in amalgamation with biotechnology [14–16]. The plant-based synthesis of iron nanoparticles (Fe NPs) is making place in the developing world [17]. Figure 2 is showing the flow chart of green synthesis of iron nanoparticles, the black color appeared after mixing up the plant extract as well as the iron salt solution in a particular ratio.

3.1 Properties of Iron Nanoparticles

As they have dimension in the nanoscale, high surface to volume association in addition to superparamagnetism, the fusion as well as utilization of Fe NPs with new properties and functions have been widely investigated in recent years [18–20]. NPs vary distinctly in their extremely high surface area from colloids or bulk substances.

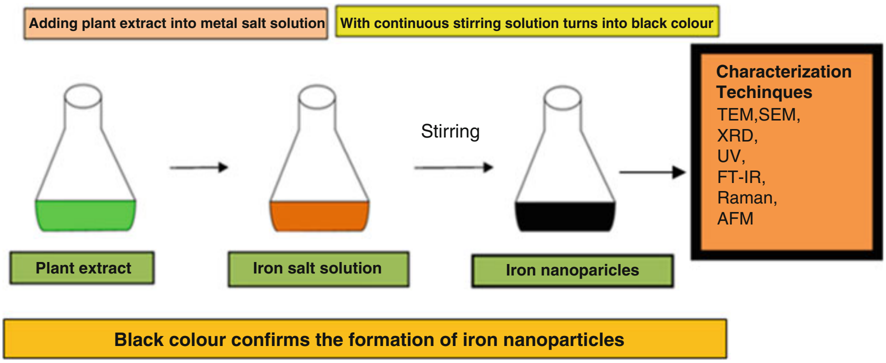


Fig. 2 A flow chart showing green synthesis of iron nanoparticles

However, surface area makes FeNPs particularly fascinating for any surface-limited heterogeneous chemistry, but the reactiveness of NPs does not completely depend only on the surface area. NPs hold a large amount of energy as surface-free energy and adding heat can involve increasing reactivity or altering magnetic characteristics of FeNPs. NPs' surface atoms differ greatly from the atoms in a bulk material and also differ from atoms present in a thin-film material. Most catalytic activities are known to be localized in defect crystal positions and NPs have an immense number of defect locations owing to their severe curvature. This is a simple reason that nanoscale catalysts have higher reactivity than their high surface areas alone are liable for. Surface area and confinement effects that can be viewed as defective both have an impression on the electronic structures of the NPs also. This leads to interesting band gaps property in semiconductors, but in the case of iron, the effects this has on another characteristic resulting from electronic interactions have been the most important: magnetism. The few magnetic rotations in iron nanoparticles contribute to a great difference in magnetic properties in bulk materials. As expected, smaller nanoparticles have characteristics that represent wide differences from bulk properties, but as we change in sizes of several times of NPs diameters these characteristics are steadily returned to the bulk properties. But, the size-dependent properties are not entirely surprising. For instance, the magnetic coercive nature of Fe NPs does not just approach the bulk behavior monotonously. The coercive effect of small particles, however, increases with increasing size and reaches the maximum of ten nanometers, then decreases and approaches bulk coercivity [21–23]. Using the ferromagnetic resources for fabrication of NPs, less than a particular size (generally 10–20 nm), could demonstrate an exclusive type of magnetism called superparamagnetism. The significant phenomenon is only found in iron NPs [24].

3.2 Crystal Structure and Atomic Arrangement

The critical dimensions of the crystal are strongly related to the exponential increase in atomic surface localization in the event of a decrease in volumes and formation of smaller numbers of NPs (typically diameter $<$ 20–30 nm). The small size of nanoparticles results in their different characteristics and crystalline properties then the bulk materials [25]. Crystalline particles have a long range of unit cells, which are replicated. In various studies amorphous particles are reported to be more reactive in cases than crystalline ones [26]. A crystalline transformation due to the reduction in surface-free energy excess for NPs less than 20 nm can improve the interfacial reactivity and alter its environmental reactivity.

3.3 Methods of Synthesis

Fabricating metal NPs or other nanomaterials through green synthesis way have many positive facets over the conventional as well as chemical ways, as it is much safer to handle and environmental friendly [27]. The chemical methods utilize many hazardous and aggressive reagents, while other produces pure and well-defined NPs [28]. The important points for using greener ways of nanoparticle synthesis include: the first may include the bio-components behaves reducing and capping agents, on this basis small size metal NPs can be synthesized in the course of large-scale manufacturing [29]. Second point consists of the role of the plants, their extract is used for reduction process as they hold the presence of different reducing and capping agents which reduce the metal ions in a less time and can be extensively used [30]. Therefore, there is an obvious necessity to form economic and also environmentally benign choices to these accessible methods. Selected solvent should be environmentally attuned, non-toxic reducing agent and eco-friendly capping agent for stabilization of NPs. These are the three bases for the process of "green" synthesis of NPs [31].

3.3.1 Plant Extracts

As studied by Kalaiarasi et al. [32], fabrication of metallic NPs by diverse parts of the plant like stem, leaf, roots, and seeds is the reproducible and simple way. Plants indeed construct stable metal NPs and it has been accepted that they are the most excellent apprentice for production at larger scale in comparison to others [33]. Choosing the plants or their derivatives in NPs fabrication lies in the plants' natural composition of diverse reducing agents. Metal NPs fabricated through plants as reducing agents show stability still after a month and without any change in its color and shape [34]. Studies on formation of photo catalytic hematite NPs (60 nm) using *Camellia sinensis* extract prepared from leaf were performed by Ahmmad et al. [35]. Similarly, Narayanan et al. [36] prepared IO NPs (~30 nm, super paramagnetic) in combination with grape seed extract (at room temperature). A single step production of mono dispersed IO NPs (4–8 nm) was reported by Awwad and Salem [37], used *carob*-leaf with crystalline structure. Super paramagnetic Fe_3O_4 (6–30 nm) were prepared by Phumying et al. [38] through aloe vera. In another study of iron NPs synthesis, the plantain peel extract was used by Venkateswarlu et al. [39] for fabrication of IO NPs (<50 nm). The NPs were polydispersed with high saturation magnetization (15.8 emu g^{-1}) and surface area of 11.31m^2 g^{-1}. In parallel lines, extracts obtained from the stem of the *Vitis vinifera* formed polycrystalline iron oxide NPs when added with a metal ion solution (av. particle size <50 nm) with high saturation magnetization and core-shell structure [40]. As analyzed by SEM irregular spherical shaped with rough surface IO NPs were synthesized by Balamurughan et al. [41] using an extract of *Ocimum sanctum* in aggregated form. Organic acids like citric and oxalic acid function as capping and reducing agents. Extract from *Passiflora tripartita* var. mollissima fruit has been analyzed by Kumar et al. [42] for the fabrication of magnetic and spherical IO NPs with size 22 nm, with better catalytic potential for production of 2-arylbenzimidazoles with excellent yields.

3.3.2 Tea Extracts

Spherical shaped Fe NPs of size 40–50 nm were synthesized using Oolong tea extract [43] and $FeSO_4$ (0.1 mol/L) was mixed to the extract (ratio of 1:2). Fe NPs formed were crystalline in nature as determined by X-ray diffraction (XRD). Following the last years, green tea extract-based Fe NPs were fabricated by Shahwan et al. [44]. The green tea extract is rich in oxyhydroxide and IO, which behaves as a Fenton-like catalyst for dye removal (methyl orange and methylene blue).

3.3.3 Biomolecules

Nadagouda and Varma [31] used ascorbic acid (vitamin C) for producing core-shell Fe nanoparticles through extract prepared by water extract of ascorbic acid. The vitamin is responsible for the reduction of transition metal salt into their respective nanostructures. In another similar study, stabilized zerovalent iron NPs of round shape were produced by Savasari et al. [45] using ascorbic acid (size range 20–75 nm). Highly stable NPs were formed by ascorbic acid. Sreeja et al. [46] functionalized and coated the IO NPs (super paramagnetic) with ascorbic acid to form a stable dispersion. The spherically shaped NPs were of size 5 nm. Likewise, Siskova et al. [47] worked on amino acids like L-glutamic acid, L-arginine, L-cysteine in addition to L-glutamine to create zerovalent NPs or metal iron. D-glucose and the oxidative product of glucose, i.e. gluconic acid were used for reduction and stabilization of prepared poly crystalline Fe_3O_4 NPs, respectively. Fe_3O_4 NPs were of roughly spherical shape (average size 12.5 nm) as revealed by transmission electron microscopy.

3.3.4 Microorganisms

Fabrication of nanomaterials using microorganisms (MOs) is less monodispersed and the slow rate of synthesis in comparison to plant-mediated synthesis [48]. The fabrication methods for production of NPs are based on microorganisms such as bacteria [49], algae and fungi [50]. Metallic NPs are fabricated in controlled surrounding by adding up metallic ions in the culture medium (MOs) [51]. Bacterial species which reduce metal iron are generally used for the iron NPs' fabrication. Under the aerobic environment *Actinobacter* sp. successfully produced spherical IO NPs. To form magnetic NPs, iron reductase has reduced the Fe^{3+} into Fe^{2+}. In the case of fungi, magnetic NPs of different sizes were synthesized extracellularly using fungal species like *Verticillium* sp. and *Fusarium oxysporum* with solution of ferrous and ferric salts (at room temperature). The anionic complexes of iron species were hydrolyzed by cationic proteins (by fungal secretion). As a result, crystalline magnetite NPs were formed which exhibits a ferromagnetic transition signature with less amount of spontaneous magnetization at low temperature [52]. Mahdavi et al. [53] biosynthesized IO NPs (Fe_3O_4) through the process of reduction of metal salt like ferric chloride by adding extract of macro algae and brown seaweed (*Sargassum muticum*). The presence of sulfate polysaccharides in the aqueous extract of brown seaweed was the main reason for the metal salt reduction contained. A species of soil micro algae called *Chlorococcum* sp. was employed for formation of iron NPs (20–50 nm) by Subramaniyam et al. [54]. The presence of biomolecules in algal cells like amines and carbonyl from glycoproteins and polysaccharides was the reason for this production of nano iron as revealed by Fourier transform Infrared spectroscopy.

3.4 Mechanism Behind the Green Synthesis of Iron Nanoparticles

Enrichment of plants with various capping and reducing compounds has much significance for their use in fabrication of different nanoparticles. It has been discovered that many potential antioxidant compounds are present in constituents of a variety of spices, herbs, and plants, for example, polyphenols, amino acids, reducing sugars, and nitrogenous bases [55]. The compounds play the role of a capping agent [56, 57] along with reducing agents [58] for NPs synthesis. There is abundance of plant species richness in nature which can be used to control the size and the morphology of the desired NPs by varying the source of the extract [59]. One more fabrication method of Fe NPs was from *Murraya koenigii* (curry leaves) [60], as the extract from leaves is having high concentration of water-soluble ingredients like flavonoids, alkaloids, polyphenols, and carbazole [61]. Utilizing leaf extract of *Dodonaea viscosa*, Daniel et al. [62] prepared the IO NPs (size range of ~27 nm). Different phytochemicals like tannin, saponins, and flavonoids were present which were responsible for the reduction of metal ions and the capping of NPs. In a different study the seeds' extract of the *Syzygium cumini* was prepared for documenting the study of ferromagnetic IO NPs (spherical ~20 nm) by Venkateswarlu et al. [63]. Seed extract contains an electrostatic stabilizing agent called sodium acetate. Extracts of *Rumex acetosa* and *Hordeum vulgare* were applied by Makarov et al. [64] for the fabrication of IO NPs, (30 nm, 10–40 nm sized, respectively). Some examples of potential phytoreducing agents are shown in Fig. 3.

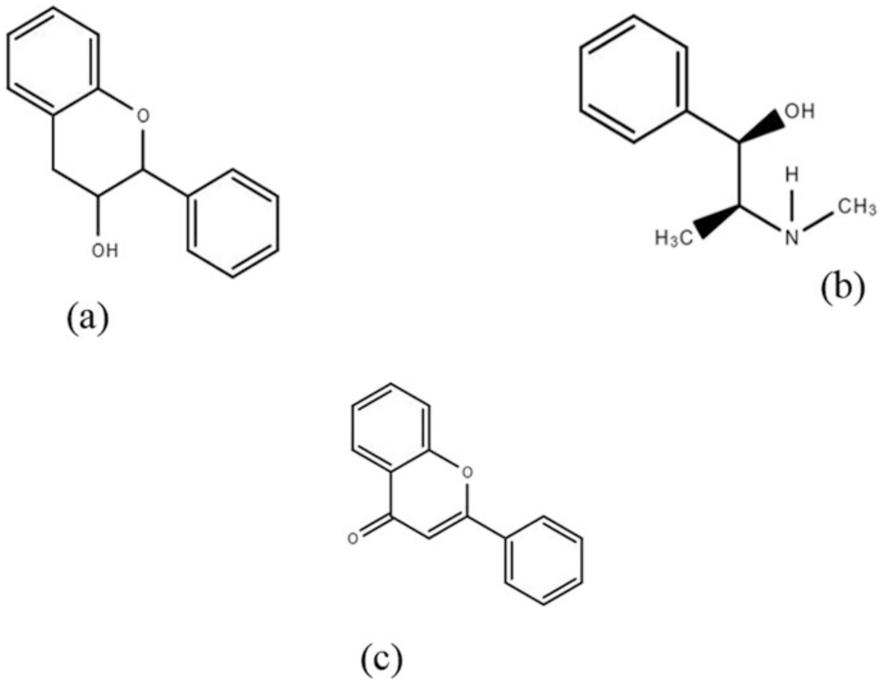


Fig. 3 Chemical structures of some potential reducing agents (**a**) tannins (**b**) alkaloids (**c**) flavonoids

4 Applications of Iron Nanoparticles

Nanotechnology holds out the assurance of enormous improvements in manufacturing technologies, telecommunications, electronics, health, and also environmental remediation [65–67], magnetic separation, heavy metals, nanoadsorbent, high adsorption, organic contaminant [68] (Fig. 4).

4.1 Wastewater Treatment

For all human activities clean water is necessary and precious. Increased population, heavy farming, rapid development, and steady industrial growth have significantly increased clean water demand. Industry operations need large amounts of water and produce huge quantities of wastewater. Strong color, odor, and high concentrations of dissolved organic colorants as well as inorganic contaminants (e.g. heavy metals, metal salts, etc.) typically characterize this water. Such control approaches for these wastewater treatments include methods for chemical separation including sludge activation system, photo catalysis, adsorption, ozonation, and filtration. But

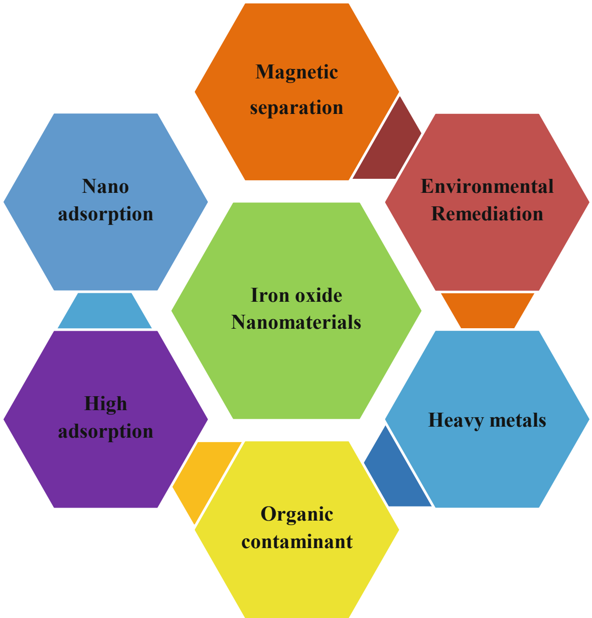


Fig. 4 The overview of iron-based nanoparticle application [68]

unfortunately, such generic methods are not successful in eliminating widespread for removing reactive dyes that preserve odor and color, heavy metals, and thus handle wastewater not so effectively. In addition, processes for chemical treatment lead to complicated compounds, making the reuse of salts or colors unavailable. Membrane and filtration systems are safer than chemical processes since harmful materials are removed, but membrane and filter fouling are the major drawbacks of these approaches. Microorganisms and other impurities accumulate in the substrate and clamp membranes over time, resulting in costly purification and removal. The chemical processes produce hazardous reactive compounds that are then incinerated or condensed and used in ground filling operations. The above approaches are not environmentally safe and damaging and trigger environmental disparities. So, new methods and techniques need to be investigated and implemented to fulfill the growing demand for water [69]. Nanotechnology is actively engaged in improving the performance of existing treatments and developing new processes. Nanomaterials have some exclusive properties such as surface adsorption, strong (photo) catalytic action, anti-microbial properties (for disinfection and biofouling regulation), particulate separation, super paramagnetic which make their use in different applications in wastewater treatment. The optical and electronic properties are also used to track water quality in new processes and sensors [70]. Magnetism is a unique physical component which aims to purify water by independently altering the physical characteristics of pollutants in water. Furthermore, in water treatment and environmental purification, adsorption techniques together with magnet isolation have been used widely [71, 72]. The industrial-scale of wastewater treatment offers iron oxide NMs due to their low cost, good adsorption, quick isolation, and increased stability [73–75]. In laboratory and field tests, the capacity of iron oxide NMs to extract pollutant has been demonstrated [76, 77]. Iron oxide NM can absorb strong visible light and is a successful photocatalyst. TiO_2 have band-gap of 3.2 eV, while Fe_2O_3 is with band-gap of 2.2 eV [78]. Numerous electron-hollow pairs can be obtained through the narrow band-length illumination of the photocatalytic performance of iron oxide NMs than TiO_2 [79]. Some Fe (III) oxide species are suggested for the degradation and reduction of organic pollutants and reduce their toxicity due to increased photocatalysis effects, e.g. γ-Fe_2O_3, α-Fe_2O_3, α-FeOOH, β-FeOOH also γ-FeOOH oxides [80].

4.1.1 Dye Removal

Caffeine and polyphenols enriched extract of oolong tea was used by [34] for the production of Fe-based NPs (40–50 nm) (iron hydroxides, maghemite (γ-Fe_2O_3), zerovalent iron, magnetite (Fe_3O_4), were analyzed for their potential for degradation of dye malachite green, and 61.9% where its removal efficiency using Fe NPs was observed to be at 10 min and reached equilibrium at 75.5% within 60 min with a rate of 0.045/min. Degradation of Malachite Green was achieved by breaking the □C□N─ and ─C□C─ bonds [81, 82]. With efficiency rate of 81% removal of dye, Beheshtkhoo et al. [83] formed IO NPs in size range of 6.5–14.9 nm, primed with the extract prepared by leaves of *Daphne mezereum*. For easy and fast single step fabrication the ethanol extract was prepared with the fruit of *Ficus carica* by Tharunya et al. [84] to synthesize IO NPs (superparamagnetic) for dyes removal using metal salt of ferrous sulfate. The fast removal of 2 azo dyes was accomplished under irradiation of UV light (Table 1).

4.1.2 Heavy Metal Removal

Synthesis method of polycrystalline, ferromagnetic IO NPs was reported by Venkateswarlu et al. [94] by adding the rind extract of *Punica granatum* with metal salt. High saturation magnetization was achieved by forming IO NPs with their surface covered by polyphenolics. The metal NPs were utilized for lead removal from wastewater. For arsenic removal crystal structured Fe_3O_4 (magnetite) of cuboid−/pyramid-shaped in size range of 5–25 nm primed by tea residue and $FeCl_3 \cdot 6H_2O$ were produced. NPs performed exceptionally well for As (III) with As (V) (arsenic ions) removal from water [95]. Additionally, IO NPs prepared from extracts of tea waste instead of tea residue were also analyzed for removal of two forms of arsenic, i.e. As (V) and As (III) at room temperature by Lunge et al. [96]. The adsorption achieved its maximum value at neutral pH. In another study, an orange peel treated with ethanol was utilized by López-Téllez et al. [97] for formation of IO NPs. Rod-shaped metal NPs formed were used to remediate the chromium ions from wastewater. The content of orange peel was enriched with cellulose which reduced the metal ions and capped the metal nanoparticles to provide them the stability [98]. In parallel line study of cadmium removal from

Table 1 Dye removal ability of green synthesized iron nanoparticles

Plants	Part used	Size and morphology	Dye removed	References
Camellia sinensis	Leaf	5–15 nm spherical crystalline	Bromothymol blue degradation (organic contamination)	[85]
Green tea	Leaf	40–60 nm amorphous	Degradation of aqueous cationic and anionic dyes	[86]
Eucalyptus tereticornis	Leaf	40–60 nm cubic	Adsorption of azo dyes	[87]
Grapes	Leaf	15–100 nm quasi-spherical shape amorphous	Azo dyes such as acid orange	[88]
Sorghum	Bran	40–50 nm spherical amorphous	Degradation of bromothymol blue	[89]
Oolong tea	Leaf	40–50 nm spherical	Degradation of malachite green	[90]
Green tea	Leaf	70–80 nm spherical amorphous	Degradation of malachite green	[91]
Green tea	Leaf	20–120 nm	Degradation of monochlorobenzene	[92]
Melaleuca nesophila and *Rosemarinus officinalis*	Leaf	50–80 nm spherical	Decolorization of azo dyes	[93]

Table 2 Heavy metal removal ability of iron nanoparticles

Plant	Part used	Size and morphology	Environmental application	References
Eucalyptus globules	Leaf	50–80 nm spherical	Adsorption of hexavalent chromium	[100]
Green tea	Leaf	5–10 nm spherical	Removal of hexavalent chromium	[101]
S. jambos, oolong tea, *A. moluccana* (L.)	Leaf	–	Removal of chromium	[45]
Green tea and eucalyptus	Leaf	20–80 nm quasi-spherical	Nitrates removal	[102]
Nano zerovalent iron nanoparticles	Ascorbic acid	20–75 nm spherical in chain	Cadmium (Cd) removal	[103]

wastewater, IO NPs were fabricated by preparing the solution of extract of *Excoecaria cochinchinensis* leaves with metal ion solution modified by low-temperature calcination [99] (Table 2).

4.2 Degradation of Pollutants

Undesirable substances present in air, water, and soil adversely affect the environment. NOx (nitrogen oxides), carbon monoxide, SOx (sulfur oxides), particulate matter, ground-level ozone, and lead are counted as the major pollutants of air. Different types of water pollutant may include pathogens, inorganic compounds, organic material and macroscopic pollutants. Pollutants causing soil contamination are herbicides, pesticides, petroleum hydrocarbons, ammonia, mercury, etc. Pesticides are the substances which are used to kill the pests. They can be classified according to the pests they kill, e.g. insecticides (killing insects), herbicides (plants), fungicides (killing fungi), and the rodenticides (killing rats and mice). A pesticide can be considered persistent and biodegradable. Chemically, they may be grouped into three categories: organophosphate, organochlorines, and the carbamates.

Since the 1940 insecticide like DDT [1, 1, 1-trichloro-2, 2-bis (p-chlorophenyl) ethane], an organo-chlorine is being used worldwide for controlling disease vectors like mosquitoes (malaria) and agricultural [104]. DDT is potentially toxic for animals as well as humans as it persists, bioaccumulates, and biomagnifies in the food chains [105]. During 1970s most of the Western nations banned its making and also usage. Also, various developing nations banned it as an insecticide [106]. As it persists in the environment, a half-life of 4 and 30 years is being estimated [107]. Due to its persisting nature detection of its residues is surely possible in the ecosystem even after three decades of its ban [108]. Many remediation techniques of DDT are there which include biodegradation treatments [109], using surfactants for soil washing [110] and advanced oxidation technologies like photochemical reactions [111] and also the reactions catalyzed by metals [112]. The above-mentioned techniques are much effective but expensive. Zerovalent iron NPs, a powerful, economical and eco-friendly is a better idea for degradation of DDT in soil and water [113–115]. Temsah and Joner [116] studied the nano-sized zerovalent iron for remediating polluted soil. A total of 50% degradation rate of DDT was achieved in spiked soil, while the degradation of DDT was less in aged DDT-polluted soil (24%). Considerable bad effects of DDT have been seen on soil organisms.

4.3 Detection of Pesticide Contamination

Developing new techniques or materials for pesticides removal from soil and water has much importance, it will be appreciable to know that these compounds have developed into much significant analytes for ultra-low concentration sensing. Using pesticides at larger scale or their extensive use has contaminated many water sources, so a fast, sensitive, and selective detection method should be formed for such toxic compounds [117, 118]. Many methods practiced like biosensors, mass spectrometry, and chromatography offer selectivity and high sensitivity. In the process of removal, more surface area is a prerequisite for the adsorption phenomenon, but in the detection of a contaminant, a change in the surface with adsorbate interaction and a consequent manifestation of reliable spectroscopic signatures are needed. Selection of molecular detection is a significant measurement for detecting a contaminant that can be ensured through the use of suitable NPs and the choice of a suitable ligand immobilization on the surface of NPs [119].

5 Critical Approach to Green Synthesized Iron Nanoparticle

Nanotechnology techniques have the potential to improve the treatment methods and efficiency with fewer changes to the existing infrastructure, which results in enabling the exploitation of non-conventional water sources like wastewater for different reuse scenarios. Nanotechnology provided techniques and methods are the need of time but it comes with both the pros and cons. Nanomaterials synthesized through green synthesis pathways may also affect the environment and human health. There is a need to evaluate the effects of nanomaterials on the ecosystem. Being aware of the pathways and toxicities of iron nanoparticles in terrestrial as well as aquatic systems is crucial. Particles in the nano range have been produced in bulk for many applications and will definitely enter the environment through above-mentioned pathways which results in exposure to humans through drinking water and having food grown in contaminated soil. But it is time to envisage the applications of these nanomaterials in degradation of various pollutants in water as well soil. The green synthesized nanoparticles are eco-friendly and non-toxic. Iron nanoparticles are efficient as a series of phytochemicals, enzymes, biomolecules have been explored for synthesizing them for the removal of contaminants like organic components (such dye), heavy metals and a detail study is needed about their toxicity. The combination of green chemistry and nanotechnology further assists or improves the reduction processes (the physical, chemical, and biological).

6 Conclusion

A green approach is an advantage over chemical or conventional processes. Utilization of less energy consumption techniques with reduced processing conditions is the better idea in this hogging world of technology. Also, it provides stability by products. The green chemistry methods may help in easy fabrication of the products using bio-renewable materials. Application of the principles based on green chemistry for developing novel nanomaterials and their applications in needed fields is all the more considerable at this beginning of nanotechnology advancement and could proceed to design novel rules that are benign in the perspective of shielding the human race in addition to the environment. This review has attempted to cover the broad and fast-changing subject of iron nanoparticles.

7 Future Prospects

The greener pathway is the safest, economical, eco-friendly route and usage of easy biodegradable materials makes the field more sustainable for future prospects. Conversely, a detailed study is needed to enhance the utility with the least adverse outcome. Although there is positive repercussion for iron nanoparticles in different fields of its application, the risk associated should be assessed to maintain the long-term environmental remediation sustainability. The focal point should be the various applications of iron nanoparticles possess in environmental remediation such as heavy metal and dye removal from contaminated areas. Potential of iron nanoparticles should be analyzed for the many possibilities of using them for sustainable production, consequently we can endow with a safe environment in near future. More research is required to steer ahead in diverse applications with minimal eco-toxicological impacts.

References

1. U.S. Environmental Protection Agency (2007) Chapter 2: environmental benefits of nano-technology. EPA 100/B-07/001. Office of the Science Advisor Science Policy Council, Washington, DC. https://www.epa.gov/sites/production/files/2015-01/documents/nanotechnology_whitepaper.pdf
2. Feynman RP (2012) There's plenty of room at the bottom: an invitation to enter a new field of physics. In: Handbook of nanoscience, engineering, and technology3rd edn. CRC Press, Boca Raton, pp 26–35
3. Yan W, Lien HL, Koel BE, Zhang WX (2013) Iron nanoparticles for environmental clean-up: recent developments and future outlook. Environ Sci Proc Imp 15(1):63–77
4. Anastas PT, Warner JC (1998) Green chemistry: theory and practice. Oxford University Press, New York, pp 29–56
5. Dahl JA, Maddux BL, Hutchison JE (2007) Toward greener nanosynthesis. Chem Rev 107 (6):2228–2269
6. Thakur S, Karak N (2015) Alternative methods and nature-based reagents for the reduction of graphene oxide: a review. Carbon 94:224–242
7. Husen A (2017) Gold nanoparticles from plant system: synthesis, characterization and their application. In: Nanoscience and plant–soil systems. Springer, Cham, pp 455–479
8. Siddiqi KS, Husen A (2017) Recent advances in plant-mediated engineered gold nanoparticles and their application in biological system. J Trace Elem Med Biol 40:10–23
9. Auffan M, Rose J, Bottero JY, Lowry GV, Jolivet JP, Wiesner MR (2009) Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective. Nat Nanotechnol 4(10):634
10. Cornell RM, Schwertmann U (2003) The iron oxides: structure, properties, reactions, occurrences and uses. Wiley, Weinheim
11. Chan HB, Ellis BL, Sharma HL, Frost W, Caps V, Shields RA, Tsang SC (2004) Carbon-encapsulated radioactive 99mTc nanoparticles. Adv Mater 16(2):144–149
12. Boyer C, Whittaker MR, Bulmus V, Liu J, Davis TP (2010) The design and utility of polymer-stabilized iron-oxide nanoparticles for nanomedicine applications. NPG Asia Mater 2(1):23

13. Dias AMGC, Hussain A, Marcos AS, Roque ACA (2011) A biotechnological perspective on the application of iron oxide magnetic colloids modified with polysaccharides. Biotechnol Adv 29(1):142–155
14. Huang SH, Liao MH, Chen DH (2003) Direct binding and characterization of lipase onto magnetic nanoparticles. Biotechnol Prog 19(3):1095–1100
15. Roco MC (2003) Nanotechnology: convergence with modern biology and medicine. Curr Opin Biotechnol 14(3):337–346
16. Gupta AK, Gupta M (2005) Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. Biomaterials 26(18):3995–4021
17. Bachheti RK, Konwarh R, Gupta V, Husen A, Joshi A (2019) Green synthesis of iron oxide nanoparticles: cutting edge technology and multifaceted applications. In: Nanomaterials and plant potential. Springer, Cham, pp 239–259. https://www.springer.com/gp/book/9783030055684
18. McHenry ME, Laughlin DE (2000) Nano-scale materials development for future magnetic applications. Acta Mater 48(1):223–238
19. Afkhami A, Saber-Tehrani M, Bagheri H (2010) Modified maghemite nanoparticles as an efficient adsorbent for removing some cationic dyes from aqueous solution. Desalination 263 (1-3):240–248
20. Pan B, Qiu H, Pan B, Nie G, Xiao L, Lv L, Zhang W, Zhang Q, Zheng S (2010) Highly efficient removal of heavy metals by polymer-supported nanosized hydrated Fe (III) oxides: behavior and XPS study. Water Res 44(3):815–824
21. Luborsky FE (1961) Development of elongated particle magnets. J Appl Phys 32(3):S171–S183
22. Cullity BD (1972) Introduction to magnetic materials. Addison-Wesley, Reading
23. Huber DL (2005) Synthesis, properties, and applications of iron nanoparticles. Small 1 (5):482–501
24. Fahmy HM, Mohamed FM, Marzouq MH, Mustafa ABED, Alsoudi AM, Ali OA, Mohamed MA, Mahmoud FA (2018) Review of green methods of iron nanoparticles synthesis and applications. BioNanoScience 8(2):491–503
25. Moreels I, Lambert K, De Muynck D, Vanhaecke F, Poelman D, Martins JC, Allan G, Hens Z (2007) Composition and size-dependent extinction coefficient of colloidal PbSe quantum dots. Chem Mater 19(25):6101–6106
26. Yokoyama A, Komiyama H, Inoue H, Masumoto T, Kimura HM (1981) The hydrogenation of carbon monoxide by amorphous ribbons. J Catal 68(2):355–361
27. Senapati S, Ahmad A, Khan MI, Sastry M, Kumar R (2005) Extracellular biosynthesis of bimetallic Au–Ag alloy nanoparticles. Small 1(5):517–520
28. Nadagouda MN, Varma RS (2006) Green and controlled synthesis of gold and platinum nanomaterials using vitamin B2: density-assisted self-assembly of nanospheres, wires and rods. Green Chem 8(6):516–518
29. Klaus T, Joerger R, Olsson E, Granqvist CG (1999) Silver-based crystalline nanoparticles, microbially fabricated. Proc Natl Acad Sci 96(24):13611–13614
30. Rai M, Yadav A, Gade A (2008) CRC 675 – current trends in phytosynthesis of metal nanoparticles. Crit Rev Biotechnol 28(4):277–284
31. Nadagouda MN, Varma RS (2007) A greener synthesis of core (Fe, Cu)-shell (Au, Pt, Pd, and Ag) nanocrystals using aqueous vitamin C. Cryst Growth Des 7(12):2582–2587
32. Kalaiarasi R, Jayallakshmi N, Venkatachalam P (2010) Phytosynthesis of nanoparticles and its applications. Plant Cell Biotechnol Mol Biol 11:1–16
33. Iravani S (2011) Green synthesis of metal nanoparticles using plants. Green Chem 13 (10):2638–2650
34. Huang L, Weng X, Chen Z, Megharaj M, Naidu R (2014) Synthesis of iron-based nanoparticles using oolong tea extract for the degradation of malachite green. Spectrochim Acta A Mol Biomol Spectrosc 117:801–804

35. Ahmmad B, Leonard K, Islam MS, Kurawaki J, Muruganandham M, Ohkubo T, Kuroda Y (2013) Green synthesis of mesoporous hematite (α-Fe2O3) nanoparticles and their photocatalytic activity. Adv Powder Technol 24(1):160–167
36. Narayanan S, Sathy BN, Mony U, Koyakutty M, Nair SV, Menon D (2011) Biocompatible magnetite/gold nanohybrid contrast agents via green chemistry for MRI and CT bioimaging. ACS Appl Mater Interfaces 4(1):251–260
37. Awwad AM, Salem NM (2012) A green and facile approach for synthesis of magnetite nanoparticles. J Nanosci Nanotechnol 2(6):208–213
38. Phumying S, Labuayai S, Thomas C, Amornkitbamrung V, Swatsitang E, Maensiri S (2013) Aloe vera plant-extracted solution hydrothermal synthesis and magnetic properties of magnetite (Fe_3O_4) nanoparticles. Appl Phys A Mater Sci Process 111(4):1187–1193
39. Venkateswarlu S, Rao YS, Balaji T, Prathima B, Jyothi NVV (2013) Biogenic synthesis of Fe3O4 magnetic nanoparticles using plantain peel extract. Mater Lett 100:241–244
40. Venkateswarlu S, Kumar BN, Prathima B, Anitha K, Jyothi NVV (2015) A novel green synthesis of Fe3O4-Ag core shell recyclable nanoparticles using *Vitis vinifera* stem extract and its enhanced antibacterial performance. Phys B Condens Matter 457:30–35
41. Balamurughan MG, Mohanraj S, Kodhaiyolii S, Pugalenthi V (2014) *Ocimum sanctum* leaf extract mediated green synthesis of iron oxide nanoparticles: spectroscopic and microscopic studies. J Chem Pharm Sci 4:201–204
42. Kumar B, Smita K, Cumbal L, Debut A (2014) Biogenic synthesis of iron oxide nanoparticles for 2-arylbenzimidazole fabrication. J Saudi Chem Soc 18(4):364–369
43. Njagi EC, Huang H, Stafford L, Genuino H, Galindo HM, Collins JB, Hoag GE, Suib SL (2010) Biosynthesis of iron and silver nanoparticles at room temperature using aqueous sorghum bran extracts. Langmuir 27(1):264–271
44. Shahwan T, Sirriah SA, Nairat M, Boyacı E, Eroğlu AE, Scott TB, Hallam KR (2011) Green synthesis of iron nanoparticles and their application as a Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes. Chem Eng J 172(1):258–266
45. Savasari M, Emadi M, Bahmanyar MA, Biparva P (2015) Optimization of Cd (II) removal from aqueous solution by ascorbic acid-stabilized zero valent iron nanoparticles using response surface methodology. J Ind Eng Chem 21:1403–1409
46. Sreeja V, Jayaprabha KN, Joy PA (2014) Water-dispersible ascorbic-acid-coated magnetite nanoparticles for contrast enhancement in mri. Appl Nanosci 5:435–441
47. Siskova KM, Straska J, Krizek M, Tucek J, Machala L, Zboril R (2013) Formation of zero-valent iron nanoparticles mediated by amino acids. Procedia Environ Sci 18:809–817
48. Dhillon GS, Brar SK, Kaur S, Verma M (2012) Green approach for nanoparticle biosynthesis by fungi: current trends and applications. Crit Rev Biotechnol 32:49–73
49. Rani PU, Rajasekharreddy P (2011) Green synthesis of silver-protein (core–shell) nanoparticles using *Piper betle* L. leaf extract and its ecotoxicological studies on *Daphnia magna*. Colloids Surf A Physicochem Eng Asp 389(1-3):188–194
50. Saif S, Tahir A, Chen Y (2016) Green synthesis of iron nanoparticles and their environmental applications and implications. Nano 6(11):209
51. Rotello VM (2004) Nanoparticles: building blocks for nanotechnology. Springer, Boston
52. Bharde A, Wani A, Shouche Y, Joy PA, Prasad BL, Sastry M (2005) Bacterial aerobic synthesis of nanocrystalline magnetite. J Am Chem Soc 127(26):9326–9327
53. Mahdavi M, Namvar F, Ahmad M, Mohamad R (2013) Green biosynthesis and characterization of magnetic iron oxide (Fe3O4) nanoparticles using seaweed (*Sargassum muticum*) aqueous extract. Molecules 18(5):5954–5964
54. Subramaniyam V, Subashchandrabose SR, Thavamani P, Megharaj M, Chen Z, Naidu R (2015) Chlorococcum sp. MM11 – a novel phyco-nanofactory for the synthesis of iron nanoparticles. J Appl Phycol 27:1861–1869
55. Valentin VM, Svetlana SM, Andrew JL, Olga VS, Anna OD (2014) Biosynthesis of stable iron oxide nanoparticles in aqueous extracts of Hordeum vulgare and *Rumex acetosa* plants. Langmuir 30:5982–5988

56. Raveendran P, Fu J, Wallen SL (2003) Completely "green" synthesis and stabilization of metal nanoparticles. J Am Chem Soc 125(46):3940–13941
57. Mervat FZ, EWael HE, Shabaka AA (2012) *Malva parviflora* extract assisted green synthesis of silver nanoparticles. Spectrochim Acta A 98:423–428
58. Malik P, Shankar R, Malik V, Sharma N, Mukherjee TK (2014) Green chemistry based benign routes for nanoparticle synthesis. J Nanopart 2014:302429
59. Tandon PK, Shukla RC, Singh SB (2013) Removal of arsenic (III) from water with clay-supported zerovalent iron nanoparticles synthesized with the help of tea liquor. Ind Eng Chem Res 52(30):10052–10058
60. Babu SA, Prabu HG (2011) Synthesis of AgNPs using the extract of *Calotropis procera* flower at room temperature. Mater 65(11):1675–1677
61. Wang J, Wan W (2008) Effect of $Fe2^{+}$ concentration on fermentative hydrogen production by mixed cultures. Int J Hydrog Energy 33(4):1215–1220
62. Daniel SK, Vinothini G, Subramanian N, Nehru K, Sivakumar M (2013) Biosynthesis of Cu, ZVI, and Ag nanoparticles using *Dodonaea viscosa* extract for antibacterial activity against human pathogens. J Nanopart Res 15:1319
63. Venkateswarlu S, Kumar BN, Prasad CH, Venkateswarlu P, Jyothi NVV (2014) Bio-inspired green synthesis of Fe3O4 spherical magnetic nanoparticles using *Syzygium cumini* seed extract. Phys B Condens Matter 449:67–71
64. Makarov VV, Makarova SS, Love AJ, Sinitsyna OV, Dudnik AO, Yaminsky IV, Taliansky ME, Kalinina NO (2014) Biosynthesis of stable iron oxide nanoparticles in aqueous extracts of Hordeum vulgare and *Rumex acetosa* plants. Langmuir 30(20):5982–5988
65. Gross M (1999) The nanoworld, miniature machinery in nature and technology. Plenum Trade, New York, London, p 254
66. Kim D, El-Shall H, Dennis D, Morey T (2005) Interaction of PLGA nanoparticles with human blood constituents. Colloid Surf B 40(2):83–91
67. Moore MN (2006) Do nanoparticles present ecotoxicological risks for the health of the aquatic environment? Environ Int 32(8):967–976
68. Nizamuddin S, Siddiqui MTH, Mubarak NM, Baloch HA, Abdullah EC, Mazari SA, Griffin GJ, Srinivasan MP, Tanksale A (2019) Iron oxide nanomaterials for the removal of heavy metals and dyes from wastewater. In: Nanoscale materials in water purification. Elsevier, pp 447–472
69. Dhakras PA (2011) Nanotechnology applications in water purification and waste water treatment: a review. In: International conference on nanoscience, engineering and technology (ICONSET 2011), pp 285–291
70. Qu X, Brame J, Li Q, Alvarez PJ (2012) Nanotechnology for a safe and sustainable water supply: enabling integrated water treatment and reuse. Acc Chem Res 46(3):834–843
71. Ambashta RD, Sillanpää M (2010) Water purification using magnetic assistance: a review. J Hazard Mater 180(1-3):38–49
72. Mahdavian AR, Mirrahimi MAS (2010) Efficient separation of heavy metal cations by anchoring polyacrylic acid on superparamagnetic magnetite nanoparticles through surface modification. Chem Eng J 159(1-3):264–271
73. Hu J, Chen G, Lo IM (2005) Removal and recovery of Cr (VI) from wastewater by maghemite nanoparticles. Water Res 39(18):4528–4536
74. Carabante I, Grahn M, Holmgren A, Kumpiene J, Hedlund J (2009) Adsorption of As (V) on iron oxide nanoparticle films studied by in situ ATR–FTIR spectroscopy. Colloids Surf A Physicochem Eng Asp 346(1–3):106–113
75. Fan FL, Qin Z, Bai J, Rong WD, Fan FY, Tian W, Wu XL, Wang Y, Zhao L (2012) Rapid removal of uranium from aqueous solutions using magnetic Fe3O4@ SiO2 composite particles. J Environ Radioact 106:40–46
76. White BR, Stackhouse BT, Holcombe JA (2009) Magnetic γ-Fe2O3 nanoparticles coated with poly-l-cysteine for chelation of As (III), Cu (II), Cd (II), Ni (II), Pb (II) and Zn (II). J Hazard Mater 161(2-3):848–853

77. Girginova PI, Daniel-da-Silva AL, Lopes CB, Figueira P, Otero M, Amaral VS, Pereira E, Trindade T (2010) Silica coated magnetite particles for magnetic removal of Hg2+ from water. J Colloid Interface Sci 345(2):234–240
78. Akhavan O, Azimirad R (2009) Photocatalytic property of Fe2O3 nanograin chains coated by TiO2 nanolayer in visible light irradiation. Appl Catal A Gen 369(1-2):77–82
79. Bandara J, Klehm U, Kiwi J (2007) Raschig rings-Fe2O3 composite photocatalyst activate in the degradation of 4-chlorophenol and Orange II under daylight irradiation. Appl Catal 76 (1-2):73–81
80. Feng W, Nansheng D, Helin H (2000) Degradation mechanism of azo dye CI reactive red 2 by iron powder reduction and photooxidation in aqueous solutions. Chemosphere 41 (8):1233–1238
81. Smuleac V, Varma R, Sikdar S, Bhattacharyya D (2011) Green synthesis of Fe and Fe/Pd bimetallic nanoparticles in membranes for reductive degradation of chlorinated organics. J Membr Sci 379(1-2):131–137
82. Wu Y, Zeng S, Wang F, Megharaj M, Naidu R, Chen Z (2015) Heterogeneous Fenton-like oxidation of malachite green by iron-based nanoparticles synthesized by tea extract as a catalyst. Sep Purif Technol 154:161–167
83. Beheshtkhoo N, Kouhbanani MAJ, Savardashtaki A, Amani AM, Taghizadeh S (2018) Green synthesis of iron oxide nanoparticles by aqueous leaf extract of *Daphne mezereum* as a novel dye removing material. Appl Phys A Mater 124(5):363
84. Tharunya P, Subha V, Kirubanandan S, Sandhaya S, Renganathan S (2017) Green synthesis of superparamagnetic iron oxide nanoparticle from *Ficus carica* fruit extract, characterization studies and its application on dye degradation studies. Asian J Pharm Clin Res 10:125–128
85. Hoag GE, Collins JB, Holcomb JL, Hoag JR, Nadagouda MN, Varma RS (2009) Degradation of bromothymol blue by 'greener' nano-scale zero-valent iron synthesized using tea polyphenols. J Mater Chem 19:8671–8677
86. Shahwan T, Abu Sirriah S, Nairat M, Boyacı E, Eroglu AE, Scott TB, Hallam KR (2011) Green synthesis of iron nanoparticles and their application as a Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes. Chem Eng J 172:258–266
87. Wang Z (2013) Iron complex nanoparticles synthesized by eucalyptus leaves. ACS Sustain Chem Eng 1:1551–1554
88. Luo F, Chen Z, Megharaj M, Naidu R (2014) Biomolecules in grape leaf extract involved in one-step synthesis of iron-based nanoparticles. RSC Adv 4:53467–53474
89. Njagi EC, Huang H, Stafford L, Genuino H, Galindo HM, Collins JB, Hoag GE, Suib SL (2011) Biosynthesis of iron and silver nanoparticles at room temperature using aqueous Sorghum bran extracts. Langmuir 27:264–271
90. Huang L, Weng X, Chen Z, Megharaj M, Naidu R (2013) Synthesis of iron-based nanoparticles using Oolong tea extract for the degradation of malachite green. Spectrochim Acta A 117:801–804
91. Huang L, Luo F, Chen Z, Megharaj M, Naidu R (2015) Green synthesized conditions impacting on the reactivity of Fe NPs for the degradation of malachite green. Spectrochim Acta A 137:154–159
92. Kuang Y, Wang Q, Chen Z, Megharaj M, Naidu R (2013) Heterogeneous Fenton-like oxidation of monochlorobenzene using green synthesis of iron nanoparticles. J Colloid Interface Sci 410:67–73
93. Wang Z, Fang C, Megharaj M (2014) Characterization of iron-polyphenol nanoparticles synthesized by three plant extracts and their Fenton oxidation of azo dye. ACS Sustain Chem Eng 2:1022–1025
94. Venkateswarlu S, Kumar BN, Prathima B, SubbaRao Y, Jyothi NVV (2019) A novel green synthesis of Fe3O4 magnetic nanorods using *Punica Granatum* rind extract and its application for removal of Pb (II) from aqueous environment. Arab J Chem 12(4):588–596

95. Nadagouda MN, Castle AB, Murdock RC, Hussain SM, Varma RS (2010) In vitro biocompatibility of nanoscale zerovalent iron particles (NZVI) synthesized using tea polyphenols. Green Chem 12(1):114–122
96. Lunge S, Singh S, Sinha A (2014) Magnetic iron oxide (Fe3O4) nanoparticles from tea waste for arsenic removal. J Magn Magn Mater 356:21–31
97. López-Téllez G, Balderas-Hernández P, Barrera-Díaz CE, Vilchis-Nestor AR, Roa-Morales G, Bilyeu B (2013) Green method to form iron oxide nanorods in orange peels for chromium (VI) reduction. J Nanosci 13(3):2354–2361
98. Madhavi V, Prasad TN, Reddy AV, Ravindra Reddy B, Madhavi G (2013) Application of phytogenic zerovalent iron nanoparticles in the adsorption of hexavalent chromium. Spectrochim Acta A 116:17–25
99. Mystrioti C, Xenidis A, Papassiopi N (2014) Reduction of hexavalent chromium with polyphenol-coated nano zero-valent iron: column studies. Desalin Water Treat 56:1162–1170
100. Xiao Z, Yuan M, Yang B, Liu Z, Huang J, Sun D (2016) Plant-mediated synthesis of highly active iron nanoparticles for Cr(VI) removal: investigation of the leading biomolecules. Chemosphere 150:357–364
101. Wang T, Lin J, Chen Z, Megharaj M, Naidu R (2014) Green synthesized iron nanoparticles by green tea and eucalyptus leaves extracts used for removal of nitrate in aqueous solution. J Clean Prod 83:413–419
102. Ehrampoush MH, Miria M, Salmani MH, Mahvi AH (2015) Cadmium removal from aqueous solution by green synthesis iron oxide nanoparticles with tangerine peel extract. J Environ Health Sci Eng 13(1):84
103. Lin J, Su B, Sun M, Chen B, Chen Z (2018) Biosynthesized iron oxide nanoparticles used for optimized removal of cadmium with response surface methodology. Sci Total Environ 627:314–321
104. World Health Organization (1979) DDT and its derivatives (No. 12). World Health Organization, Geneva
105. Behrooz RD, Sari AE, Bahramifar N, Ghasempouri SM (2009) Organochlorine pesticide and polychlorinated biphenyl residues in human milk from the Southern Coast of Caspian Sea, Iran. Chemosphere 74(7):931–937
106. Yang X, Wang S, Bian Y, Chen F, Yu G, Gu C, Jiang X (2008) Dicofol application resulted in high DDTs residue in cotton fields from northern Jiangsu province, China. J Hazard Mater 150 (1):92–98
107. Tomlin C (2006) The pesticide manual. The British Crop Protection Council Publication, Farnham
108. Guo Y, Yu HY, Zeng EY (2009) Occurrence, source diagnosis, and biological effect assessment of DDT and its metabolites in various environmental compartments of the Pearl River Delta, South China: a review. Environ Pollut 157(6):1753–1763
109. Li FB, Li XM, Zhou SG, Zhuang L, Cao F, Huang DY, Xu W, Liu TX, Feng CH (2010) Enhanced reductive dechlorination of DDT in an anaerobic system of dissimilatory iron-reducing bacteria and iron oxide. Environ Pollut 158:1733–1740
110. Smith E, Smith J, Naidu R, Juhasz AL (2004) Desorption of DDT from a contaminated soil using cosolvent and surfactant washing in batch experiments. Water Air Soil Pollut 151 (1-4):71–86
111. Lin C, Lin KS (2007) Photocatalytic oxidation of toxic organohalides with TiO2/UV: the effects of humic substances and organic mixtures. Chemosphere 66(10):1872–1877
112. Zinovyev SS, Shinkova NA, Perosa A, Tundo P (2005) Liquid phase hydrodechlorination of dieldrin and DDT over Pd/C and Raney-Ni. Appl Catal B Environ 55(1):39–48
113. Sayles GD, You G, Wang M, Kupferle MJ (1997) DDT, DDD, and DDE dechlorination by zero-valent iron. Environ Sci Technol 31(12):3448–3454
114. Eggen T, Majcherczyk A (2006) Effects of zero-valent iron (Fe-0) and temperature on the transformation of DDT and its metabolites in lake sediment. Chemosphere 62:1116–1125

115. Yang SC, Lei M, Chen TB, Li XY, Liang Q, Ma C (2010) Application of zerovalent iron (Fe0) to enhance degradation of HCHs and DDX in soil from a former organochlorine pesticides manufacturing plant. Chemosphere 79(7):727–732
116. El-Temsah YS, Joner EJ (2013) Effects of nano-sized zero-valent iron (nZVI) on DDT degradation in soil and its toxicity to collembola and ostracods. Chemosphere 92(1):131–137
117. Illman DL (2006) Water analysis in the developing world. J Am Chem Soc 78:5266–5272
118. Richardson SD, Ternes TA (2005) Water analysis: emerging contaminants and current issues. Anal Chem 77(12):3807–3838
119. Huang XJ, Choi YK (2007) Chemical sensors based on nanostructured materials. Sens Actuators B Chem 122(2):659–671

Part III
Natural Wastewater Treatment Technologies

Overview of Waste Stabilization Ponds in Developing Countries

Syeda Ulfath Tazeen Kadri, Adinath N. Tavanappanavar, R. Nagesh Babu, Muhammad Bilal, Bhaskar Singh, Sanjay Kumar Gupta, Ram Naresh Bharagava, Muthusamy Govarthanan, Mohammed Azharuddin Savanur, and Sikandar I. Mulla

S. U. T. Kadri
Department of Biochemistry, School of Applied Sciences, REVA University, Bangalore, India

Post Graduate Department of Biochemistry, Maharani's Science College for Women, Bangalore, India

A. N. Tavanappanavar and S. I. Mulla (✉)
Department of Biochemistry, School of Applied Sciences, REVA University, Bangalore, India

R. Nagesh Babu
Post Graduate Department of Biochemistry, Maharani's Science College for Women, Bangalore, India

M. Bilal
School of Life Science and Food Engineering, Huaiyin Institute of Technology, Huaian, China

B. Singh
Department of Environmental Sciences, Central University of Jharkhand, Ranchi, Jharkhand, India

S. K. Gupta
Environmental Engineering, Department of Civil Engineering, Indian Institute of Technology Delhi, New Delhi, India

R. N. Bharagava
Department of Microbiology (DM), School for Environmental Sciences (SES), Babasaheb Bhimrao Ambedkar University (A Central University), VidyaVihar, Lucknow, Uttar Pradesh, India

M. Govarthanan
Department of Environmental Engineering, Kyungpook National University, Daegu, Republic of Korea

M. A. Savanur
MIGAL – Galilee Research Institute, Kiryat Shmona, Israel

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 153–176, DOI 10.1007/698_2021_790,

Contents

Abstract Wastewater treatment facilities have high operational costs and are significant users of energy, due to which $<38\%$ percent of municipal as well as industrial wastewater generated by developing countries undergoes treatment of any kind. Waste stabilization ponds (WSPs) are man-made earthen basins used for the treatment of wastewater using individual and/or combination of physicochemical and biological agents with the aim of reducing various contents like nutrients, micro- and macro-pollutants and also removing pathogens from wastewater. Though used worldwide, WSPs are especially suitable for developing countries that have warm climates as they are cost-effective, highly efficient, entirely natural, and highly sustainable. Depending on the required final effluent quality, the ponds can be used individually or connected in a series of anaerobic, facultative, and maturation ponds. This, in turn, is based on what is to be done with the effluent. Whether it is to be used for restricted or unrestricted irrigation or aquaculture or discharged into surface water or groundwater. This chapter gives an overview of various types of WSPs, their design, function, and disinfection processes along with strategies and methods that can be adopted to improve their performance in developing countries.

Keywords Developing countries, Improvement strategies, Low-cost technique, Waste stabilization ponds, Wastewater treatment

1 Introduction

Water crisis possesses a global threat which is further compounded by the population growth and shifting global climate [1, 2]. As the overall demand for water grows, the quantity of wastewater produced also grows, since most human activities that use water produce wastewater. According to the United Nations World Water Development Report 2017, over 80% of the world's wastewater is released into the environment without treatment [3]. Developed nations treat about 70% of their municipal and industrial wastewater. The percentage falls in the range of 38–28% in middle-income developing countries, while in low-income developing countries, only 8% undergoes treatment of any kind. Consequently, water contaminated by pathogens, micro- and macro-pollutants is released into local water bodies, ultimately ending up in the oceans, negatively impacting public health as well as the ecosystem [4–6]. The mainstream technologies for wastewater treatment (WWT) are not an ideal option for solving the wastewater problems in developing regions, because of their high setting-up and maintenance cost [5]. Alternate to this, a low-cost, natural, and energy saving WWT technologies are best suited for these countries. Among the techniques, waste stabilization ponds (WSPs) treatment technique is more appropriate and suitable to use.

WSPs are ponds built to treat wastewater by entirely natural processes involving both algae and bacteria [7]. The wastewater is let into the pond and retained for several days during which the organic matter present in the water is acted upon by the microorganisms until it is rendered stable and safe for reuse or discharge into water bodies. Microorganisms utilize the organic matter (including toxic/hazardous chemicals) as a carbon and energy source for their growth and reproduction, wherein the organic matter is converted into carbon dioxide (CO_2) and water. This naturally occurring process is known as "stabilization" of organic matter and hence the name. Several organisms are found in such ponds, most important of which are bacteria and algae. Bacteria break down the complex organic matter into simple compounds and CO_2, which are taken up by the algae for their growth. Algae, in turn, through the process of photosynthesis, produce the oxygen necessary for the survival of aerobic bacteria [8]. UNEP in 1999 declared WSPs as the cheapest WWT technology which is highly efficient in the removal of organic matter and pathogens [9]. These treatment systems have been in use for a longer period. The first recorded construction dates back in 1901 [10]. According to Mara [7] and US EPA [11], WSPs presently constitute over 50% of WWT plants in the USA, 20% in Brazil, and 30% in Germany. Because of low-cost of construction, simple operation, high efficiency of pathogen removal and BOD reduction, WSPs are especially appropriate for developing countries as these countries cannot meet the expenses involved in capital and energy-intensive mainstream WWT techniques [12–16]. Moreover, most developing countries have warm or temperate climates along with ample land availability which is most favorable for the operation of WSPs [12]. The National River Conservation Directorate (NRCD), under the jurisdiction of Government of India, stated in 2003 that "only WSPs will be mainly supported to treat wastewater hereafter." The reason being, WSPs are not only low-cost, but also the most efficient option to reduce pathogens (>99%), nematodes, and helminth eggs, thus rendering the effluent suitable for safe re-use in agriculture or aquaculture or discharge into water bodies [17]. Therefore, WSPs are widely used for wastewater treatment in many developing countries such as Colombia, El Salvador, Ghana, Guatemala, Honduras, India, Israel, Jordan, Morocco, Nicaragua, Tunisia, Tanzania, Uganda, and many more [18–21]. However, these pond systems are ideal for rural communities with relatively small population having large, open, and unused lands, away from public spaces, but not so much for large urban communities with large population where the cost of land is high [15]. This chapter discusses the commonly used WSPs, their construction, operation, disinfection mechanisms, and application in developing countries.

2 Types of Waste Stabilization Ponds (WSPs)

WSPs are remarkably flexible in terms of their design, influent loading rates, applications, etc., and have thus gained popularity all over the world since their initial use. In the past few decades, many different types of WSPs have been designed having varied applications. However, there are three main types of WSPs, namely anaerobic, facultative, and maturation (aerobic) ponds, used individually or connected in series. They differ from each other in design, organic loading, and the biochemical processes they carry. All the other pond types are modifications of these three systems designed either for better performance or specialized applications. The wastewater first enters anaerobic or facultative pond as these are predominantly designed for BOD removal, and then their effluent is treated in maturation ponds which mainly deal with pathogen removal [13]. The main configurations of pond systems are – Facultative pond only; Anaerobic pond followed by facultative pond; Facultative pond followed by maturation ponds; Anaerobic pond followed by facultative pond followed by maturation ponds in series as shown in Fig. 1. The Dandora WSP in Nairobi, Kenya, Al Samra WSP in Amman, Jordan, and Ucubamba WSP in Ecuador are examples of multi-pond WSP systems serving about one million, 2.6 million, and 400,000 people, respectively [13, 22]. Table 1 provides a brief overview of the different WSP pond systems discussed in the chapter.

2.1 Anaerobic Ponds

The first type of pond performing primary treatment is the anaerobic pond. These are the deepest ponds in the series (depth reduces the possibility of the oxygen penetration) and, consequently, require relatively less land area. They operate under heavy organic loading and therefore contain little to none dissolved oxygen and algae [23]. Their principal function is pretreatment and BOD removal which is brought about by the sedimentation of suspended solids into the sludge and their subsequent anaerobic digestion. However, the effluent BOD is still high (Table 1) and requires post-treatment, which is generally carried out in facultative ponds. This being the case, anaerobic ponds can be replaced by facultative ponds. But, the removal of BOD in the anaerobic pond contributes significantly in reducing the total land requirement. In other words, the total land required for anaerobic + facultative

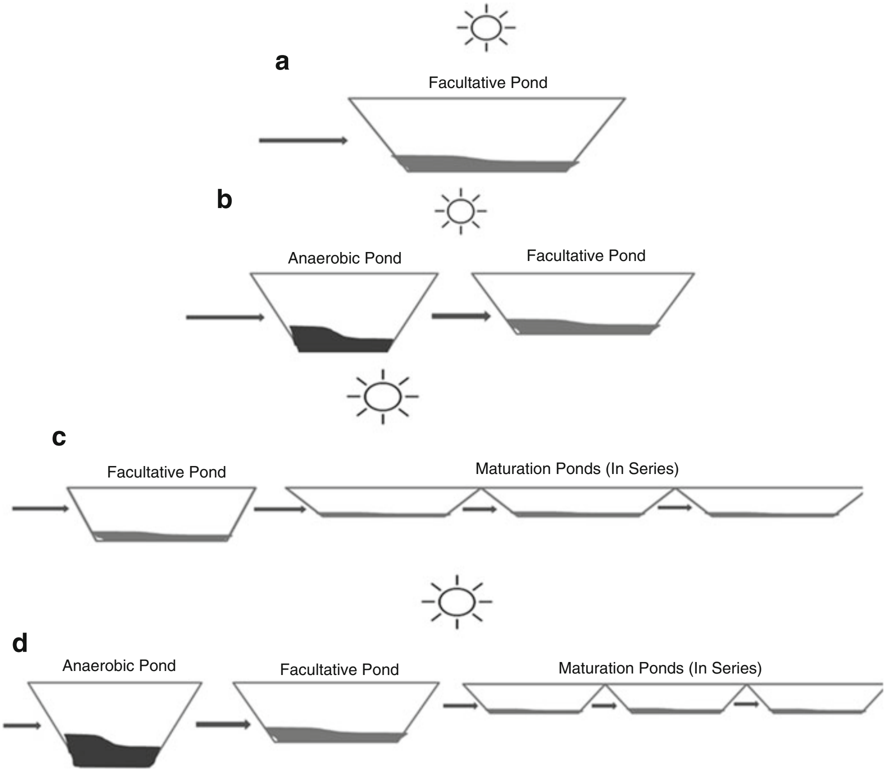


Fig. 1 Main configurations of waste stabilization pond system. (**a**) Facultative pond only, (**b**) Anaerobic pond followed by facultative pond, (**c**) Facultative pond followed by maturation ponds, and (**d**) Anaerobic pond followed by facultative pond followed by maturation ponds in series

ponds is equivalent to only 45–70% of the land required for a primary facultative pond receiving equivalent load of raw wastewater. Therefore, the use of anaerobic ponds as pre-treatment ponds is recommended in a WSP system [15].

2.2 Facultative Ponds

Facultative ponds (Fig. 2) are the most commonly used pond type all through the world. These ponds are less deep than anaerobic ponds, but require relatively more land area as their operation is sunlight dependent [15]. These ponds have both aerobic and anaerobic zones. The soluble organic matter is aerobically stabilized in the top aerobic zone due to the presence of dissolved oxygen produced by algae, while the suspended BOD settles into the sludge and is degraded anaerobically in the bottom anaerobic zone. These ponds are generally operated in series with anaerobic ponds and receive effluent from anaerobic ponds for treatment. But when operated

Table 1 Characteristics of main WSP systems

Pond type		Anaerobic ponds	Facultative ponds	Maturation ponds
Pond parameters	Depth (m)	3.0–5.0	1.5–2.0	0.8–1.2
	Length/breadth ratio	1 to 3	2 to 4	1–10 in case of single pond; 1–5 when connected in a series
	Retention time (days)	5–50	15–50 in warm climates and 90–180 days in colder climates	Determined on the basis of required effluent quality
Organic loading rate		>300 kg BOD5 h^{-1} d^{-1}	100–300 kg BOD5 h^{-1} d^{-1}	<100 kg BOD5 h^{-1} d^{-1}
BOD removal [%]		50–85	80–95	60–80
TSS removal [%]		20–60	70–80	NA
Major functions		Pretreatment and BOD reduction	BOD reduction, disinfection, and nutrient removal	Pathogen and nutrient removal
Applications		Treatment of domestic sewage and organic industrial wastewater. Pretreatment in municipal WWT systems	Treatment of raw municipal wastewater. Treatment of effluent from other ponds or processes	Post-treatment ponds receiving effluents from other ponds for disinfection
By-products formed		Methane, carbon dioxide, hydrogen sulfide	Suspended solids in the form of algal and bacterial cells, carbon dioxide	None

Source: [8, 15, 23]

individually, they can be used for the treatment of domestic sewage, wastewater from slaughterhouses, dairy milking sheds, piggeries, beverage industries, and other such industries [24]. Recently, Almasi et al. [16] studied the removal of phenol and carbon from wastewater generated by an oil refinery in facultative ponds and concluded that facultative ponds could be considered as a low-cost option for the treatment of oil industry wastewater in developing countries.

2.3 Maturation Ponds

These are shallow ponds with large surface area, placed last in the WSP system and are principally designed for the removal of pathogens. Since most of the BOD is removed in the previous ponds, maturation ponds serve largely to eliminate pathogenic organisms. They are also used with other WWT techniques as they are low-cost alternatives for efficient pathogen removal when designed and operated properly [12]. Goyal and Mohan [25] evaluated the performance of a 10-year-old

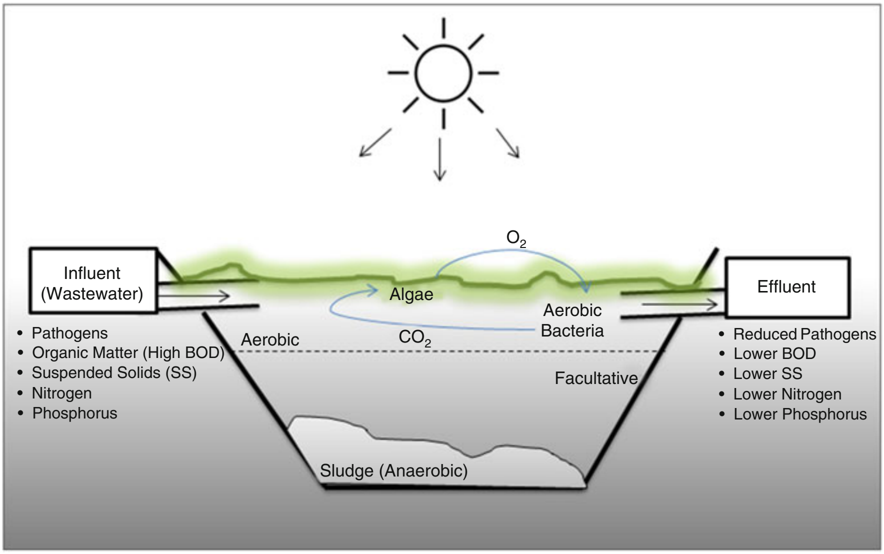


Fig. 2 Process Mechanism in a Facultative Pond

WSP system in Jodhpur, India, and reported that after treatment, pH, BOD, TSS, and total nutrients were found within the permissible limit, but the concentration of pathogenic organisms was higher than the permitted WHO limit [26]. This was attributed to the absence of maturation ponds in the WSP system, and they concluded that construction of maturation ponds would provide better removal of pathogens. Maturation ponds also enhance nutrient removal in WSPs [12, 24, 27]. The disinfection and nutrient removal mechanisms of maturation ponds are discussed in Sect. 4 of this chapter.

2.4 Other Pond Types

Over the decades, WSPs have been altered in various ways for enhanced performance and diverse applications giving rise to different types of pond systems. Some examples are facultative aerated lagoons, which are similar in construction and function to facultative ponds except for mechanized oxygen supply that enables faster decomposition. The mechanization reduces land requirements but increases energy requirements. Fermentation pits are ponds that have semi-enclosed anaerobic pit built within a facultative pond. This design is reported to have lower retention time, less odor, and reduce relatively more BOD than conventional anaerobic ponds [28]. Hi-rate algal ponds [29] have a paddlewheel that drives the water around the pond resulting in significantly higher oxygen production than typical facultative pond designs. A detailed outline of many more pond types like Advanced pond systems, the PETRO process, Integrated ponds and wetland systems, Aquaculture ponds, Storage ponds, Cold climate ponds, Agricultural wastewater ponds, and stormwater ponds are presented by Shilton [24].

3 Design, Operation, and Maintenance

3.1 Pond Location, Construction, and Design

Although WSPs are renowned for their simple design and low-cost of construction, they can be a failure when designed and constructed without adequate care and planning. Firstly, the selection of pond location must be carried out keeping in mind certain important aspects. The site selected must have free wind access enabling smooth mixing in the pond; it must be at least 400 m away from the nearest dwellings (given the odor problem) and at least 20 m away from the nearest drinking water source [30]. The site location, in relation to the site of wastewater generation (influent) as well as the location of the receiving body, must be evaluated as less distance corresponds to lower transportation costs. The topography and shape of the area should also be considered such that they favor excavation. Besides these, cost of the land, its availability, susceptibility to floods, and access conditions are some of the other aspects related to pond location.

Secondly, during pond construction, utmost importance must be given to the geotechnical aspects and physical factors, such as the length-to-width ratio of the pond followed by inlet and outlet arrangements, such that maximum efficiency can be achieved [24, 31]. Other important considerations for construction of WSPs are embankments, pond sealing, and baffling. Erosion due to winds and rains causes major problems in WSPs, which necessitates the construction of embankments (dikes, riprap, etc.) around the ponds. This is also necessary to protect the pond from infestation of rodents and other burrowing animals. In order to prevent seepage resulting in groundwater pollution, pond bottom must be sealed. Bentonite, asphalt, soil cement liners, and thin membrane liners are commonly used for pond sealing. Pattullo et al. [32] proposed pond-sealing by algae as an economical alternative to the above pond liners, which, although encouraging, is yet to be studied further. Baffles greatly improve the hydraulic and treatment efficiency of WSPs and are highly recommended [24, 33–38]. Although these provisions will increase the cost of construction, they will significantly decrease the operation and maintenance expenses.

Lastly, to get the desired effluent quality, it is imperative to have designed the WSP system properly. There are several guidelines for WSPs designs but most are outdated [12, 39–42]. Basically, there are four approaches to WSP design: loading rates or rules of thumb, regression equations, first-order models, and mechanistic models. A complete and detailed review and comparison of the above four approaches, and their chronological evolution over the past 60 years from simple rules of thumb to complex mathematical models is given by Ho et al.

[22]. Furthermore, they tested the applicability of all design models via a case study and concluded that rules of thumb is no longer an appropriate approach for pond designs and advise WSP designers to shift from the conventional approaches to more innovative mechanistic models.

3.2 Operation and Maintenance of WSPs

WSPs are a popular choice for WWT in developing countries because of their low-cost of construction, simple operation, and high efficiency. However, this holds true only if they are designed, maintained, and operated correctly. For instance, the actual efficiency of WSPs was found to be far less than the anticipated efficiency due to poor maintenance in India, Tanzania, Nigeria, and presumably elsewhere [43–45]. Even though the operation and maintenance of WSPs is fairly simple, its importance cannot be emphasized enough. Routine maintenance, such as removal of floating vegetation and scum from pond surface, removal of settled solids from the inlets and outlets, cleaning of screening and grit channels, cutting the grass on the embankments, and repairing damages, if any, to the embankments and fences, must be carried out regularly to avoid odor and mosquito problems. Depending on the organic load and size of the pond, desludging must be carried out once in 2–10 years. Less skilled and less number of operators is required for WSP operation in comparison to conventional WWT systems [13]. As per Pescod & Mara [46] two full-time operators will suffice for 8–20 ha pond system, serving a population of 50,000. Besides maintenance, routine monitoring of effluent quality and evaluation of pond performance are extremely important as this provides information on whether or not the effluent conforms to established quality standards. USEPA [47], Kerri [48] and Spellman [49] provide guidelines and detailed information on operation and maintenance of WSPs.

4 Effluent Disinfection and Nutrient Removal

4.1 Pathogen Removal

WSPs are remarkably efficient in removing various pathogenic microorganisms (bacterial, viral, protozoan, and helminthic pathogens) making them all the more suitable for use in the developing countries [50]. Pathogen inactivation in WSPs has been well investigated [41, 51–54] and reported to be more efficient than in conventional WWT processes. WSPs studies world-wide have shown removal up to 7 log units of bacteria, 5 log units of viruses, and over 99.99% removal of protozoan and helminth parasites [20, 55–58], whereas in case of activated sludge and primary treatment, reductions of 1–2 log units for bacteria, 57 and 70–99% for protozoan and helminth eggs have been observed [54, 59]. Moreover, the disinfection techniques employed in conventional WWTs (chlorination, UV irradiation, etc.) generally target pathogenic bacteria and viruses, while helminth eggs and protozoan cysts being resistant to the above methods are not targeted [60–62]. The evaluation results of pathogen removal efficiency in WSPs of some developing countries are summarized in Table 2.

Liu et al. [58] reviewed the various disinfection processes and mechanisms that occur in WSPs, and have also listed the factors that affect pathogen removal efficiency in these pond systems. Intense sunlight, high pH, adequate hydraulic retention time, increased levels of dissolved oxygen and temperatures are a few factors that favor disinfection in WSPs [52]. These factors alone or in combination aid in efficient reduction of pathogenic bacteria and viruses in maturation ponds, which are predominantly designed for the removal of pathogens. In anaerobic and facultative ponds, bacterial and viral reduction is also brought about by algal exudates (toxic to certain bacteria), biological disinfection, and sedimentation along with the action of the above-mentioned physical factors [52, 79, 80]. Biological disinfection refers to the ingestion of bacterial and viral pathogens by higher protozoans and flagellates. Protozoan cysts and helminth eggs are eliminated in WSP by sedimentation into the sludge which is primarily dependent on hydraulic retention time. Ayres et al. [81], based on studies of WSP in Brazil, India, and Kenya, concluded that there was no significant variation between egg and cysts removal between the three pond types.

Although pathogen removal in WSPs is usually very high, in some cases the disinfection is poor due to short-circuiting. This problem is often addressed by positioning baffles between the pond inlet and outlet design [82, 83]. Another factor to consider is cyanobacteria and their toxins, such as microcystins. These are not affected by the pond's natural disinfection mechanisms. Barrington et al. [84] suggested the use of hydrogen peroxide to remove cyanobacteria and microcystins from WSPs.

4.2 Nitrogen and Phosphorus Removal

Wastewater containing excess amounts of nutrients, mainly nitrogen and phosphorus, if discharged into water bodies can lead to eutrophication in the receiving waters. This, in turn, can lead to decreased levels of dissolved oxygen, death of fish and mollusks, increased turbidity, and depletion of desirable flora and fauna [8]. Nutrient removal in WSPs has been well investigated [52, 85–96]. Some common removal mechanisms of nitrogen and phosphorous in WSPs are listed in Table 3.

The effluent from WSPs in developing countries is mainly used for irrigation or discharged into water bodies. Effluent containing 20–85 mg/L total nitrogen is not only safe, but also beneficial for agricultural reuse as it adds nitrogen to the soil [17]. But when discharged into water bodies, maximum N-removal is desired. Nitrogen removal efficiency in WSPs is highly variable, ranging from 9% to 95%

Table 2 Efficiency of pathogen removal in WSPs of some developing countries

Country	Efficiency of pathogen removal	Retention time (in days)	Reference
Bolivia	>99.9% removal of culturable enteroviruses, norovirus, and rotavirus	25–26	[63]
Burkina Faso	>99.99% removal of the following protozoans – *Entamoeba coli, Entamoeba histolytica,* And *Giardia lamblia.* >99.99 removal of the following helminthes – *Ascaris lumbricoides, Ancylostoma* sp., *Trichuris trichiura*, and *Trichostrongylus* sp.	18	[64]
Chile	1.5–1.9 LU fecal coliforms	5–7	[65]
Colombia	3.1–3.5 LU fecal coliforms 3–4.4 LU *E. coli* 3–3.9 LU fecal *streptococci* and 93–99.99% removal of somatic phages	53	[66]
	4 LU fecal coliforms and 1.7 LU fecal *streptococci*	12	[67]
Egypt	6 LU total coliforms 4.6 LU fecal coliforms 3.8 LU fecal *streptococci* 4.9 LU fecal *streptococci* 3.9 LU *Salmonellae* and 2.1 LU *Listeria* as well as 79.98% removal of Coliphages and 99.66% removal of infectious rotaviruses	NA	[68]
Ghana	5.6 LU thermotolerant coliforms	10	[69]
	2.5 LU *E. coli* 1.6 LU thermotolerant coliforms 3.3 LU fecal *streptococci* and 99.92% removal of somatic coliphages	NA	[70]
Honduras	2.97 LU *E. coli* 2.93 LU fecal coliforms	7–35	[71]
India	2.30 LU total coliforms 2.30 LU fecal coliforms 2.40 LU fecal *streptococci*	11	[20]
Mexico	3.7 LU fecal coliforms	945	[72]
Morocco	100% removal of *Giardia* cysts and *Ascaris* eggs	16	[73]
	100% removal of protozoans like *Entamoeba coli, Entamoeba histolytica*, and *Giardia sp* as well as 100% removal of eggs of *Ascaris, Trichuris, Hymenolepis, Taenia*, and *Enterobius*	16	[74]
	100% removal of helminth eggs	57–59	[75]
Nicaragua	0.54–4 LU fecal coliforms	16	[76]
Palestine	3.3–3.6 LU fecal coliforms	28	[77]
Tunisia	1.4–2.2 LU *E. coli* 1.5–2.6 LU fecal *enterococci*	7–8	[78]

Logarithmic units (LU) indicate the pathogen removal efficiency. 1 LU corresponds to an efficiency of 90%, while 2 LU = 99%, 3 LU = 99.9%, 4 LU = 99.99%, 5 LU = 99.999%, and so on
LU Logarithmic unit, *NA* Data not available

Table 3 Common nutrient removal mechanisms in WSPs

Nutrient	The form in which the nutrient is found	Common removal mechanisms	Percentage removal
Nitrogen	Ammonia	Bacterial nitrification	0.15–0.34%
		Volatilization	1.2–3.1%
	Nitrites and nitrates	Bacterial denitrification	0.15–0.34%
	Particulate organic nitrogen	Sedimentation	23.5–45.6%
	All forms	Algal uptake	13.1–27.8%
Phosphorus	Soluble phosphorus	Microbial uptake (luxury uptake) and chemical precipitation	Highly variable depending on pond pH, temperature, type, concentration of phosphates and cations
	Particulate phosphorus	Sedimentation	

Source: [24, 94]

depending on the pond conditions. However, in general, it is reported to be <70% and thus not very efficient [39, 97–100]. Recent studies report algal uptake of nitrogen and subsequent sedimentation as the key nitrogen removal mechanism in WSPs [88, 101–103] contrary to the earlier belief that ammonia volatilization is the chief mechanism [100, 104–106]. Therefore, nitrogen removal can be enhanced in WSPs by the addition of maturation ponds, as these ponds facilitate increased assimilation into algal biomass [107]. Since algal uptake, as well as nitrification/ denitrification requires algal and nitrifier biomass, the problem of inadequate nitrogen removal in WSPs is attributed to the low nitrifier biomass present in the pond. To overcome this problem, several studies suggest the employment of biofilm attachment surfaces in the ponds [108–111]. For instance, using baffles as attachment surfaces enhanced nitrogen removal in WSPs [36, 37, 112].

Phosphorus removal efficiency of WSPs is lower than that of nitrogen removal and is rather poor, typically ranging between 15 and 50% [68, 98, 113–115]. Since the removal is inconsistent and inadequate, a number of strategies are suggested to improve the phosphorus removal efficiency in WSPs. Mara [27] recommended increasing the number of maturation ponds as the elevated pH in these ponds promotes phosphate precipitation with cations. Other studies show incorporation of limestone rock filters and blast furnace slag filters resulted in 77.8 and 75 to 99.8% removal of phosphorus, respectively [114, 116]. Besides the use of maturation ponds and filters, two other upgrade options, proven to be effective, are chemical dosing with coagulants (alum or ferric salts) and enhanced biological phosphorus removal using microbes that accumulate phosphorus as polyphosphates [117, 118]. However, while these strategies increase phosphorus removal, they also increase the cost and complexity of operation and, therefore, are not an ideal choice for developing nations. Few recent studies recommend the use of industrial by-products (fly ash, furnace slag, granular bentonite, and alum sludge) as a low-cost solution for improved phosphorus removal through adsorption in WSPs [119–122]. For example, Garfí and Puigagut [122] showed addition of 5% w/w adsorbent increased phosphorus removal efficiency up to 90% in microcosm WSP. However, there are no reports on the performance of these adsorbents in full-scale WSPs. Hence, there is a need to further develop and evaluate low-cost alternatives for effective phosphorus removal in WSPs.

4.3 Heavy Metal and Micropollutant Removal

Wastewater, especially industrial and urban run-off, contains elevated levels of heavy metals [9]. These high concentrations, when discharged into the environment, are not only toxic to microorganisms, higher organisms, and plants but also lead to bioaccumulation and biomagnification in marine organisms [123]. Removal of heavy metals in WSPs occurs through various mechanisms. Most predominant is sedimentation, where heavy metals associated with particulate matter settle into the sludge [124, 125]. Other mechanisms include adsorption and accumulation of heavy metals onto and into bacterial and algal cells [126, 127]. The efficiency of removal, however, varies depending on the type of heavy metal and the number of ponds. Increased number of ponds provide more efficient removal of heavy metals [107]. For example, two WSPs in Morocco were evaluated for their heavy metal removal efficiency [128, 129]. WSP comprising of only a single anaerobic pond showed 21, 11, and 28% removal of Cu, Pb, and Zn, respectively [128], whereas another WSP comprising of a system of one anaerobic pond followed by three facultative ponds and two maturation ponds in series showed 92, 71, and 91% removal of Cu, Pb, and Zn, respectively [129]. However, very few studies have been conducted on the effectiveness of WSPs in removing heavy metals [130], and as in cases mentioned above, the results are not uniform. Studies on heavy metal removal efficiency of WSPs in Birjand, Iran [131], and Egypt [130] showed that the effluent is suitable for agricultural reuse. In contrast, studies on WSPs in Nigeria [132] and Yazd, Iran [133] showed that the effluent heavy metal concentration exceeded the standards and is unfit for discharge or reuse in agriculture.

Several organic micropollutants, such as various medicines, antibiotics, steroid hormones, personal care products, and their derivatives have been reported in untreated as well as treated wastewater [5, 134–136]. Most studies on micropollutants in wastewater have focused on conventional WWT techniques such as activated sludge treatment, reverse osmosis, and advanced oxidation processes [137–140]. Very few studies have been conducted to evaluate micropollutant removal in WSPs and, only a fraction (40 out of hundreds) of the identified organic micropollutants has been studied [141]. Garcia-Rodríguez et al. [142] and Gruchlik et al. [141] have reviewed the effectiveness of WSPs in removing organic micropollutants and reported that, for the organic micropollutants that have been studied in WSPs; the removal efficiency is same or better than that of conventional

WWT techniques. However, the removal efficiency was highly variable and dependent on the type of micropollutant. The compounds that are recalcitrant and poorly removed in conventional WWTs (e.g., Carbamazepine, gemfibrozil) are also poorly removed in WSPs (<30%), whereas those compounds that are adequately eliminated in conventional WWTs (e.g., Ibuprofen, paracetamol) are also well removed (>95%) in WSPs. The chief mechanisms for the removal of micropollutants in WSPs are photodegradation, biodegradation, absorption, and adsorption into/onto organic matter. Biodegradation and absorption are mainly brought about by the action of algae found in WSPs [143]. A detailed overview of the removal of organic micropollutants (non-steroidal drugs, quinolone drugs, and steroidal hormones) by algae is presented by Mulla et al. [144].

5 Advantages and Disadvantages of WSPs

When compared to the conventional WWT systems WSPs have certain advantages and disadvantages. The major advantages are:

- Low-cost of construction, operation, and maintenance. This is a pre-requisite for selecting a WWT system in developing countries.
- Low energy consumption and chemical usage and fewer mechanical problems. WSPs being a biological WWT system require remarkably low energy and chemicals in contrast to the conventional biomechanical systems.
- Simplicity of operation – WSPs operators are often members of the local community and require very little or no special training. In other words, less skilled labor is required than other WWT technologies.
- Robustness – Owing to their long hydraulic retention times; WSPs are more resilient to both organic and hydraulic surge loadings than other WWT processes.
- Flexible – WSPs can be used for small communities of up to 2000 inhabitants as well as for large populations of up to one million [145].

The major disadvantages are:

- Large land requirements – WSPs require more land than other WWT processes. However, between WSPs and other electromechanical systems it comes down to a choice between spending on land, which can be considered an investment and spending on electricity.
- Possible groundwater contamination from leakage. This can be prevented by using pond liners as discussed in Sect. 3. Design, Operation, and Maintenance.
- Treatment is affected by climatic conditions. Since WSP operation is sunlight dependent, these systems are not ideal for places with frequent and heavy rainfall. However, currently with the aid of innovative computational models WSPs are designed to operate in cold climate countries and places with large temperature variations [146].

- Odor – anaerobic ponds can generate odorous compounds such as hydrogen sulfide and mercaptans giving rise to foul odor. A common practice to reduce odor is to recirculate water from a downstream facultative or aerated pond such that an aerobic layer is formed at the surface of the anaerobic pond, preventing odors from escaping out. Alternatively, a cover may also be used to contain odors.
- Mosquitoes generally present a problem in WSPs as these are open pond systems. *Gambusia*, commonly called mosquito fish, can be introduced to eliminate mosquito problems in the ponds [111, 147, 148]. Biochemical controls, such as the larvicides *Bacillus thuringiensis* israelensis (Bti), have also been effective when applied directly to the area containing mosquito larvae [11].

There are many more advantages of WSPs apart from those listed that find application in developing countries. The use of treated wastewater is not only limited to irrigation, but is also used very commonly for rearing of fish. The slightly elevated nutrient content in the treated water favors both agriculture (farmers save fertilizer cost) and aquaculture [13]. The economic benefits from by-products of WSPs are numerous. The algal biomass produced by WSPs can be used as high-protein feed for aquaculture and poultry; it can be used for energy generation (via methane or alcohol), for the production of oils, pigments, pharmaceutical products, and also as a selective adsorption material for heavy metals [149, 150]. WSPs have better ecological sustainability as these systems besides wastewater treatment bring about significant carbon sequestration, thereby contributing towards mitigating global warming [151]. WSPs can also be used for recreational and educational purposes such that developing countries can derive benefits from it in monetary terms. This concept, however, is still in its infancy. Ghermandi & Fichtman [152] have given a complete review and assessment of the recreational and educational benefits of WSPs including the monetary valuation.

6 Conclusions

Waste stabilization ponds exemplify low-cost natural systems which, when designed well and operated correctly, provide treatment equivalent to conventional WWT systems in terms of both BOD and pathogen removal. The low-cost and effectiveness of WSPs make it possible to bring sewage treatment within the scope of developing countries, reduce the pollution of rivers and streams, and provide treated water for irrigation. However, this holds true only if they are designed, maintained, and operated correctly. Flaws in design and improper operation and maintenance can endanger the functioning of WSPs. The drawbacks of these systems are high land requirements and problems associated with odor and mosquitoes when constructed near human settlements. Extensive research has been conducted on pond design and geometry and numerous hydrodynamic computational models have been proposed over the years to overcome the drawbacks and improve the performance of WSPs, but there exists a big gap between the testing of these models in modeled environments and their application in actual WSP setup. It is recommended to focus on the application of cost-effective and performance enhancing models in developing countries besides focusing only on the development of such models. However, more research is required to understand the mechanisms and enhance the efficiency of heavy metal and micropollutant removal in WSPs. Furthermore, there is a need to develop and evaluate low-cost alternatives for effective nutrient removal in WSPs. Also suggested are further studies exploring diverse facets of WSPs such as its high carbon sequestration potential, economic benefits from WSP by-products, and monetary gains from recreational and educational use of WSPs.

Acknowledgments NBR acknowledges support from DST-FIST and UGC-CPE platforms as well as DBT-Star College Scheme. SUTK is supported by University Grants Commission (UGC) Junior Research Fellowship (Sr. No: 212153046; Ref. No: 20/12/2015(ii)EU-V).

References

1. Haddeland I, Heinke J, Biemans H, Eisner S, Flörke M, Hanasaki N, Wisser D (2014) Global water resources affected by human interventions and climate change. Proc Natl Acad Sci 111 (9):3251–3256
2. Hoekstra AY (2014) Water scarcity challenges to business. Nat Clim Chang 4(5):318–320
3. (2017) Wastewater: the untapped resource. UN World Water Development Report. 180
4. Mulla SI, Ameen F, Tallur PN, Bharagava RN, Bangeppagari M, Eqani SAMAS, Bagewadi ZK, Mahadevan GD, Yu CP, Ninnekar HZ (2017) Aerobic degradation of fenvalerate by a gram-positive bacterium, Bacillus flexus strain XJU-4. 3 Biotech 7:320
5. Mulla SI, Hu A, Sun Q, Li J, Suanon F, Ashfaq M, Yu CP (2018) Biodegradation of sulfamethoxazole in bacteria from three different origins. J Environ Manag 206:93–102
6. Mulla SI, Asefi B, Bharagava RN, Saratale GD, Li J, Huang CL, Yu CP (2020) Processes for the removal of triclosan in the environment and engineered systems- a review. Environ Rev 28:55–66
7. Mara DD (2009) Waste stabilization ponds: past present and future. Desalin Water Treat 4:85–88
8. Spellman FR, Drinan JE (2014) Wastewater stabilization ponds. CRC Press, Boca Raton
9. UNEP (1999) Planning and management of lakes and reservoirs: an integrated approach to eutrophication. IETC Technical publication series no 11. http://www.unep.or.jp
10. Gloyna EF (1971) Waste stabilization ponds. World Health Organization monograph series no. 60. World Health Organization, Geneva
11. USEPA (2011) Principles of design and operations of wastewater treatment pond systems for plant operators, engineers, and managers. EPA 600-R-11-088. Office of Research and Development, Cincinnati
12. Mara DD, Pearson HW (1998) Waste stabilization ponds: design manual for Mediterranean Europe. World Health Organization Regional Office for Europe
13. Mara DD (2004) Domestic wastewater treatment in developing countries. Earthscan, London
14. Mara DD (2006) CIWEM good practice in water and environmental management. Charted Institution of Water and Environmental Management (CIWEM) Colder Park, Wakefield
15. Andreoli CV, von Sperling M, Fernandes F (2007) Sludge treatment and disposal, vol 6. Biological wastewater treatment series. IWA Publishing, London

16. Almasi A, Mahmoudi M, Mohammadi M, Dargahi A, Biglari H (2019) Optimizing biological treatment of petroleum industry wastewater in a facultative stabilization pond for simultaneous removal of carbon and phenol. Toxin Rev 40(2):189–197
17. WHO (2006) WHO guidelines for the safe use of wastewater excreta and greywater - volume IV: excreta and greywater use in agriculture. World Health Organization (WHO), Geneva
18. Khan MA, Ahmad SI (1992) Performance evaluation of waste stabilization ponds in subtropical region. Water Sci Technol 26:1717–1728
19. Oakley SM (2002) Monitoring of wastewater stabilization ponds in Honduras. In: Congreso Interamericano de Ingenieria Sanitaria y Ambiental, San Juan, Aug. 22–27, 2004
20. Tyagi VK, Sahoo BK, Khursheed A, Kazmi AA, Ahmad Z, Chopra AK (2011) Fate of coliforms and pathogenic parasite in four full-scale sewage treatment systems in India. J Environ Monit Assess 181:123–135
21. Kenneth J (2018) Sewage treatment by waste stabilization pond systems. J Environ Manag 3 (1):7–14
22. Ho LT, Van Echelpoel W, Goethals PLM (2017) Design of waste stabilization pond systems: a review. Water Res 123:236–248
23. Polprasert C, Kittipongvises S (2011) Constructed wetland and waste stabilization ponds. Treatise Water Sci 4:277–299
24. Shilton A, Mara DD (2005) CFD (computational fluid dynamics) modelling of baffles for optimizing tropical waste stabilization pond systems. Water Sci Technol 51(12):103–106
25. Goyal B, Mohan D (2013) Case study on evaluation of the performance of waste stabilization pond system of Jodhpur, Rajasthan, India. Water Pract Technol 8(1):95–104
26. WHO (1989) Health guidelines for the use of wastewater in agriculture and aquaculture. Report of a WHO Scientific Group, Geneva
27. Mara DD (1997) Design manual for waste stabilization ponds in India. Lagoon Technology International Ltd, Leeds
28. Oswald W, Green F, Lundquist T (1994) Performance of methane fermentation pits in advanced integrated wastewater pond systems. Water Sci Technol 30(12):287–295
29. Shelef G, Azov Y (1987) High-rate oxidation ponds: the Israeli experience. Water Sci Technol 19(12):249–255
30. Trivedy RK, Kaul S (2010) Low cost wastewater treatment technologies. https://priodeep.weebly.com/uploads/6/5/4/9/65495087/[r.k._trivedy__siddharth_kaul]_low_cost_wastewate_bookzz.org_.pdf
31. Crites RW, Middlebrooks EJ, Reed SC (2006) Natural wastewater treatment systems. Taylor and Francis, Boca Raton
32. Pattullo MB, Mayes MA, Mandal S, Mathews TJ, Dunlap J, Perfect E, Efroymson RA (2019) Soil sealing by algae: an alternative to plastic pond liners for outdoor algal cultivation. Algal Res 38:101414
33. Abbas H, Nasr R, Seif H (2006) Study of waste stabilization pond geometry for the wastewater treatment efficiency. Ecol Eng 28(1):25–34
34. Banda CG (2007) Computational fluid dynamics modeling of baffled waste stabilization ponds (PhD thesis), School of Civil Engineering, University of Leeds, Leeds, UK. http://sleigh-munoz.co.uk/wash/Mara/ThesisChimwemwe/Chim0.pdf
35. Bracho N, Lloyd B, Aldana G (2006) Optimisation of hydraulic performance to maximise faecal coliform removal in maturation ponds. Water Res 40(8):1677–1685
36. Kilani JS, Ognurombi JA (1984) Effects of baffles on the performance of model wastewater stabilization ponds. Water Res 18(8):941–944
37. Muttamara S, Puetpaiboon U (1997) Roles of baffles in waste stabilization ponds. Water Sci Technol 35(8):275–284
38. Winfrey BK, Strosnider WH, Nairn RW, Strevett KA (2010) Highly effective reduction of fecal indicator bacteria counts in an ecologically engineered municipal wastewater and acid mine drainage passive co-treatment system. Ecol Eng 36(12):1620–1626

39. Mara DD (1975) Design manual for sewage lagoons in the tropics. East African Literature Bureau
40. Arthur JP, Mundial B (1983) Notes on the design and operation of waste stabilization ponds in warm climates of developing countries. Technical paper no. 7. World Bank, Washington, DC
41. Mara DD (1997) Design manual for waste stabilization ponds in India. LTI, Leeds, 125 p
42. Kayombo S, Mbwette TSA, Katima JHY, Ladegaard N, Jorgensen SE (2005) Waste stabilization ponds and constructed wetlands design manual. United Nations Environment Programme (UNEP)-International Environmental Technology Centre (IETC) and Danish International Development Agency (Danida). http://www.unep.or.jp/Ietc/Publications/Water_Sanitation/ponds_and_wetlands/Design_Manual.pdf
43. Agunwamba JC (2001) Analysis of socioeconomic and environmental impacts of waste stabilization pond and unrestricted wastewater irrigation: Interface with maintenance. Environ Manag 27(3):463–476
44. Amerasinghe P, Asolekar S, Essl L, Grischek T, Gupta P, Heinze K, Starkl M (2013) Report on initial sustainability assessment (integrated sustainability assessment). https://doi.org/10.13140/RG.2.2.26380.92808
45. Kalderen E (2019) Investigation of possible strategies and solutions to improve the operation of DAWASAs stabilization ponds in Dar es Salaam Tanzania (dissertation). https://www.diva-portal.org/smash/get/diva2:1349134/FULLTEXT01.pdf
46. Pescod MB, Mara DD (1988) Design, operation and maintenance of wastewater stabilization ponds. In: Pescod MB, Arar A (eds) Treatment and use of sewage effluent for irrigation. Butterworths, pp 93–115
47. USEPA (1977) Operations manual for stabilization ponds EPA 430/9-77-012 NTIS No PB-279443. US Environmental Protection Agency, Washington, DC
48. Kerri KD (2002) Operation of wastewater treatment plants, vol 1. California State University, Sacramento
49. Spellman FR (2013) Handbook of water and wastewater treatment plant operations.3rd edn. CRC Press, Taylor and Francis, Boca Raton. http://ssu.ac.ir/cms/fileadmin/user_upload/Daneshkadaha/dbehdasht/markaz_tahghighat_olom_va_fanavarihaye_zist_mohiti/e_book/_lewis__handbook_of_water_and_wastewater_treatment_plant_operations__frank_r_spellman_.pdf
50. Mara DD (2001) Appropriate wastewater collection, treatment and reuse in developing countries. In: Proceedings of the Institutions of Civil Engineers, London, pp 299–303
51. Curtis TP, Mara DD, Silva SA (1992) Influence of pH oxygen and humic substances on ability of sunlight to damage fecal coliforms in waste stabilization pond water. Appl Environ Microbiol 58(4):1335–1343
52. Maynard HE, Ouki SK, Williams SC (1999) Tertiary lagoons: a review of removal mechanisms and performance. Water Res 33(1):1–13
53. Davies-Colley RJ, Donnison AM, Speed DJ (2000) Towards a mechanistic understanding of pond disinfection. Water Sci Technol 42:149–158
54. Bolton NF, Cromar NJ, Hallsworth P, Fallowfield HJ (2010) A review of the factors affecting sunlight inactivation of microorganisms in waste stabilization ponds: preliminary results for enterococci. Water Sci Technol 61:885–890
55. Zanotelli CT, Medri W, Belli Filho P, Perdomo CC, Mullinari MR, Costa RHR (2002) Performance of a baffled facultative pond treating piggery wastes. Water Sci Technol 45(1):49–53
56. Awuah E (2006) Pathogen removal mechanisms in waste stabilisation ponds. PhD thesis, Wageningen University/UNESCO-IHE Institute for Water Education, The Netherlands
57. Reinoso R, Blanco S, Torres-Villamizar L, Becares E (2011) Mechanisms for parasites removal in a waste stabilization pond. Microb Ecol 61(3):648–692
58. Liu L, Hall G, Champagne P (2018) Disinfection processes and mechanisms in wastewater stabilization ponds: a review. Environ Rev 26(4):417–429

59. Ansa EDO, Lubberding HJ, Ampofo JA, Amegbe GB, Gijzen HJ (2012) Attachment of fecal coliform and macro-invertebrate activity in the removal of fecal coliform in domestic wastewater treatment pond systems. Ecol Eng 42:35–41
60. Jiménez B (2007) Helminth ova removal from wastewater for agriculture and aquaculture reuse. Water Sci Technol 55(1–2):485–493
61. Jimenez-Cisneros BE (2007) Helminth ova control in wastewater and sludge for agricultural reuse. In: Water and health [Ed.W.O.K. Grabow], in encyclopedia of life support systems (EOLSS), developed under the auspices of the UNESCO. Eolss Publishers, Oxford. http://www.eolss.net. Accessed 9 Oct 2008
62. Drechsel P, Scott CA, Raschid-Sally L, Redwood M, Bahri A (2010) Wastewater irrigation and health-assessing and mitigating risk in low-income countries. Earthscan, London
63. Symonds EM, Verbyla ME, Lukasik JO, Kafle RC, Breitbart M, Mihelcic JR (2014) A case study of enteric virus removal and insights into the associated risk of water reuse for two wastewater treatment pond systems in Bolivia. Water Res 65:257–270
64. Konate Y, Maiga AH, Basset D, Picot B, Casellas C (2013) Occurrence removal and accumulation in sludge of protozoan cysts and helminth eggs in a full-scale anaerobic pond in Burkina Faso. Water Sci Technol 67:193–200
65. Herrera L, Castillo G (2000) Dynamics of a waste stabilization pond in Chile. Water Sci Technol 42:83–90
66. Campos C, Guerrero A, Cárdenas M (2002) Removal of bacterial and viral faecal indicator organisms in a waste stabilization pond system in Choconta Cundinamarca (Colombia). Water Sci Technol 45:61–66
67. Madera CA, Pena MR, Mara DD (2002) Microbiological quality of a waste stabilization pond effluent used for restricted irrigation in Valle Del Cauca Colombia. Water Sci Technol 45:139–143
68. Ghazy MM, Senousy WM, Aatty AM, Kamel M (2008) Performance evaluation of a waste stabilization pond in a rural area in Egypt. Am J Environ Sci 4(4):316–325. https://doi.org/10.3844/ajessp.2008.316.325
69. Keraita B, Drechsel P, Konradsen F (2008) Perceptions of farmers on health risks and risk reduction measures in wastewater-irrigated urban vegetable farming in Ghana. J Risk Res 11:1047–1061
70. Silverman AI, Peterson BM, Boehm AB, McNeill K, Nelson KL (2013) Sunlight inactivation of human viruses and bacteriophages in coastal waters containing natural photosensitizers. Environ Sci Technol 47:1870–1878
71. Oakley SM, Pocasangre A, Flores C, Monge J, Estrada M (2000) Waste stabilization pond use in Central America the experiences of El Salvador Guatemala Honduras and Nicaragua. Water Sci Technol 42(10–11):51–58
72. Escalante V, Moeller G, Rivas A (2000) Pond evaluation and upgrading in Mexico. Water Sci Technol 42:43–51
73. Amahmid O, Asmama S, Bouhoum K (2002) Urban wastewater treatment in stabilization ponds: occurrence and removal of pathogens. Urban Water 4(3):255–262
74. Bouhoum K, Amahmid O, Asmama S (2000) Occurrence and removal of protozoan cysts and helminth eggs in waste stabilisation ponds in Marrakech. Water Sci Technol 42:159–164
75. Kouraa A, Fethi F, Fahde A, Lahlou A, Ouazzani N (2002) Reuse of urban wastewater treated by a combined stabilisation pond system in Benslimane (Morocco). Urban Water 4:373–378
76. Buchauer K (2007) Comparison of model approaches for predicting coliform removal in waste stabilization ponds. Water Environ J 21(2):108–113
77. Zimmo O, Al-Sa'ed RM, Van der Steen P, Gijzen HJ (2002) Process performance assessment of algae-based and duckweed-based wastewater treatment systems. Water Sci Technol 45:91–101
78. Ouali A, Jupsin H, Vasel JL, Marouani L, Ghrabi A (2012) Removal improvement of bacteria (*Escherichia coli* and *Enterococci*) in maturation ponds using baffles. Water Sci Technol 65 (4):589–595

79. Oufdou K, Mezrioui N, Oudra B, Barakate M, Loudiki M (1998) Effect of extracellular and endocellular products from cyanobacterium Synechocystis sp on the growth of some sanitation system bacteria. Arch Hydrobiol (Suppl. 125):139–148
80. Manage PM, Kawabata Z, Nakano S, Nishibe Y (2002) Effect of heterotrophic nanoflagellates on the loss of virus-like particles in pond water. Ecol Res 17:473–479
81. Ayres RM, Alabaster GP, Mara DD, Lee DL (1992) A design equation for human intestinal nematode egg removal in waste stabilization ponds. Water Res 26:863–865
82. Pearson HW, Mara DD, Arridge HA (1995) The influence of pond geometry and configuration on facultative and maturation waste stabilization pond performance and efficiency. Water Sci Technol 31(12):129–139
83. Shilton A, Harrison J (2003) Integration of coliform decay within a CFD model of a waste stabilisation pond. Water Sci Technol 48(2):205–210
84. Barrington DJ, Reichwaldt ES, Ghadouani A (2013) The use of hydrogen peroxide to remove cyanobacteria and microcystins from waste stabilization ponds and hypereutrophic systems. Ecol Eng 50:86–94
85. Senzia MA, Mayo AW, Mbwette TSA, Katima JH, Jorgensen SE (2002) Modelling nitrogen transformation and removal in primary facultative ponds. Ecol Model 154(3):207–215
86. van der Linde ERC, Mara DD (2010) Nitrogen removal during summer and winter in a primary facultative waste stabilisation pond: preliminary findings from 15N-labelled ammonium tracking techniques. Water Sci Technol 61(4):979–984
87. Camargo Valero MA, Mara DD, Newton RJ (2010) Nitrogen removal in maturation waste stabilisation ponds via biological uptake and sedimentation of dead biomass. Water Sci Technol 61(4):1021–1034
88. Camargo Valero MA, Read LF, Mara DD, Newton RJ, Curtis TP, Davenport RJ (2010) Nitrification-denitrification in waste stabilisation ponds: a mechanism for permanent nitrogen removal in maturation ponds. Water Sci Technol 61(5):1137–1146
89. Powell N, Shilton A, Pratt S, Chisti Y (2011) Phosphate release from waste stabilisation sludge: significance and fate of polyphosphate. Water Sci Technol 63(8):1689–1694
90. Powell N, Shilton A, Pratt S, Chisti Y (2011) Luxury uptake of phosphorus by microalgae in full-scale waste stabilisation ponds. Water Sci Technol 63(4):704–709
91. Brown N, Shilton A (2014) Luxury uptake of phosphorus by microalgae in waste stabilisation ponds: current understanding and future direction. Rev Environ Sci Biotechnol 13(3):321–328
92. Mayo AW, Abbas M (2014) Removal mechanisms of nitrogen in waste stabilization ponds. Phys Chem Earth 72:77–82
93. Chalatsi M, Gratziou M (2015) Efficiency and design parameters of waste stabilization ponds in north-east Greece. Desalin Water Treat 56(5):1240–1247
94. Bastos RKX, Rios EN, Sanchez IA (2018) Further contributions to the understanding of nitrogen removal in waste stabilization ponds. Water Sci Technol 77(11):2635–2641
95. Crimp A, Brown N, Shilton A (2018) Microalgal luxury uptake of phosphorus in waste stabilization ponds - frequency of occurrence and high performing genera. Water Sci Technol 78(1):165–173
96. Sells MD, Brown N, Shilton (2018) Determining variables that influence the phosphorus content of waste stabilization pond algae. Water Res 132:301–308
97. Ferrara RA, Avci CB (1982) Nitrogen dynamics in waste stabilization ponds. J Water Pollut Contr Fed 54(4):361–369
98. Mara DD (1996) Waste stabilization ponds: effluent quality requirements and implications for process design. Water Sci Technol 33(7):23–31
99. Pearson HW, Mara DD, Cawley LR, Arridge HM, Silva SA (1996) Performance of an innovative tropical experimental waste stabilisation pond system operating at high organic loadings. Water Sci Technol 33(7):63–73
100. Joe Middlebrooks E, Reed SC, Pano A, Adams VD (1999) Nitrogen removal in wastewater stabilization lagoons. In: 6th national drinking water and wastewater treatment technology transfer workshop, Kansas City, Missouri

101. Zimmo O, Van der Steen P, Gijzen HJ (2003) Comparison of ammonia volatilisation rates in algae and duckweed-based waste stabilization ponds treating domestic wastewater. Water Res 37:4587–4594
102. Camargo Valero MA, Mara DD (2007) Nitrogen removal via ammonia volatilization in maturation ponds. Water Sci Technol 55(11):87–92
103. Assuncao FAL, von Sperling M (2012) Importance of the ammonia volatilization rates in shallow maturation ponds treating UASB reactor effluent. Water Sci Technol 66 (6):1239–1246
104. Pano A, Middlebrooks EJ (1982) Ammonia nitrogen removal in facultative wastewater stabilization ponds. J Water Pollut Control Fed 54(4):344–351
105. Somiya I, Fujii S (1984) Material balances of organics and nutrients in an oxidation pond. Water Res 18(3):325–333
106. Reed SC (1985) Nitrogen removal in wastewater stabilisation ponds. J Water Pollut Control Fed 57(1):39–45
107. Shilton A (2005) Pond treatment technology. IWA Publishing, London
108. Baskaran K, Scott PH, Conner MA (1992) Biofilms as an aid to nitrogen removal in sewage treatment lagoons. Water Sci Technol 26(7–8):1707–1716
109. Craggs RJ, Tanner CC, Sukias JPS, Davies-Colley RJ (2000) Nitrification potential of attached biofilms in dairy farm waste stabilization ponds. Water Sci Technol 42(10–11):195–202
110. McLean BM, Baskaran K, Connor MA (2000) Use of algal-bacterial biofilms to enhance nitrification rates in lagoons: experience under laboratory and pilot-scale conditions. Water Sci Technol 42(10–11):187–194
111. Pearson HW (2005) Microbiology of waste stabilization ponds. In: Pond treatment technology. IWA Publishing, London
112. Babu M (2011) Effect of algal biofilm and operational conditions on nitrogen removal in waste stabilization ponds: UNESCO-IHE PhD thesis, CRC Press
113. Garcia J, Mujeriego R, Bourrouet A, Penuelas G, Freixes A (2000) Wastewater treatment by pond systems: experiences in Catalonia Spain. Water Sci Technol 42(10–11):35–42
114. Camargo Valero MA, Johnson M, Mather T, Mara DD (2009) Enhanced phosphorus removal in a waste stabilization pond system with blast furnace slag filters. Desalin Water Treat 4:122–127
115. Mburu N, Tebitendwa SM, Bruggen JJA, Rousseau DLP, Lens PNL (2013) Performance comparison and economics analysis of waste stabilization ponds and horizontal subsurface flow constructed wetlands treating domestic wastewater: a case study of the Juja sewage treatment works. J Environ Manag 128:220–225
116. Strang T, Wareham DG (2006) Phosphorus removal in a waste-stabilization pond containing limestone rock filters. J Environ Eng Sci 5(6):447–457
117. Tchobanoglous G, Burton FL, Stensel HD (2003) Wastewater engineering: treatment and reuse. McGraw-Hill, New York
118. Blackall LL, Crocetti GR, Saunders AM, Bond PL (2002) A review and update of the microbiology of enhanced biological phosphorus removal in wastewater treatment plants. Antonie Van Leeuwenhoek 81:681–691
119. Zeng L, Li X, Liu J (2004) Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. Water Res 38(5):1318–1326
120. Xu D, Xu J, Wu J, Muhammad A (2006) Studies on the phosphorus sorption capacity of substrates used in constructed wetland systems. Chemosphere 63:344–352
121. Mortula M, Gibbons M, Gagnon GA (2007) Phosphorus adsorption by naturally-occurring materials and industrial by-products. J Environ Eng Sci 6(2):157–164
122. Garfí M, Puigagut J (2016) Reusing industrial by-products to enhance phosphorus removal in waste stabilization ponds: laboratory approach. Desalin Water Treat 57(4):1857–1864
123. Chowdhury S, Mazumder MJ, Al-Attas O, Husain T (2016) Heavy metals in drinking water: occurrences implications and future needs in developing countries. Sci Total Environ 569:476–488

124. Suffern JS, Fitzgerald CM, Szluha AT (1981) Trace metal concentrations in oxidation ponds. J Water Pollut Control Fed 53(11):1599–1608
125. Kaplan D, Abeliovich A, Ben-Yaakov S (1987) Fate of heavy metals in wastewater stabilization ponds. Water Res 21(10):1189–1194
126. Khummongkol D, Canterford GS, Fryer C (1982) Accumulation of heavy metals in unicellular algae. Biotechnol Bioeng 24:2643–2660
127. Gadd GM (1990) Heavy metal accumulation by bacteria and other microorganisms. Experientia 46:834–840
128. Nejmeddine A, Fars S, Echab A (2000) Removal of dissolved and particulate form of metals (Cu, Zn, Pb, Cd) by an anaerobic pond system in Marrakesh (Morocco). Environ Technol 21 (2):225–230
129. Toumi A, Nejmeddine A, El Hamouri B (2000) Heavy metal removal in waste stabilisation ponds and high rate pond. Water Sci Technol 42(10–11):17–21
130. Gad AAM, Abdalla AMA (2017) Fate of heavy metals and nutrients in waste stabilization ponds in arid zones. J Eng Sci 45(1):1–16
131. Mansouri B, Ebrahimpour M (2011) Heavy metals characteristics of wastewater stabilization ponds. Am-Eur J Agric Environ Sci 10:763–768
132. Ogunfowokan A, Adenuga A, Torto N, Okoh E (2008) Heavy metals pollution in a sewage treatment oxidation pond and the receiving stream of the Obafemi Awolowo university, Nigeria. Environ Monit Assess 143:25–41
133. Samaei MR, Ehrampoush MH, Maleknia H, Elhamiyan Z, Shahsavani E, Ebrahimi A (2016) Removal of chromium and cadmium from wastewater in waste stabilization ponds in Yazd-Iran. J Health Sci Surveill Syst 4(2):83–88
134. Schwarzenbach RP, Escher BI, Fenner K, Hofstetter T, Johnson CA, von Gunten U, Wehrli B (2006) The challenge of micropollutants in aquatic systems. Science 313:1072–1077
135. Barnes KK, Kolpin DW, Furlong ET, Zaugg SD, Meyer MT, Barber LB (2008) A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States - I groundwater. Sci Total Environ 402:192–200
136. Sui Q, Cao X, Lu S, Zhao W, Qiu Z, Yu G (2015) Occurrence sources and fate of pharmaceuticals and personal care products in the groundwater: a review. Emerg Contam 1:14–24
137. Chen Z, Ngo HH, Guo W (2012) A critical review on sustainability assessment of recycled water schemes. Sci Total Environ 426:13–31
138. Fernandez-Fontaina E, Omil F, Lema JM, Carballa M (2012) Influence of nitrifying conditions on biodegradation and sorption of emerging micropollutants. Water Res 46(16):5434–5444
139. Busetti F, Ruff M, Linge KL (2015) Target screening of chemicals of concern in recycled wastewater. Environ Sci Water Res Technol 1:659–667
140. Bonvin F, Jost L, Randin L, Bonvin E, Kohn T (2016) Super-fine powdered activated carbon (SPAC) for efficient removal of micropollutants from wastewater treatment plant effluent. Water Res 90:90–99
141. Gruchlik Y, Linge K, Joll C (2018) Removal of organic micropollutants in waste stabilisation ponds: a review. J Environ Manag 206:202–214
142. Garcia-Rodríguez A, Matamoros V, Fontas C, Salvado V (2014) The ability of biologically based wastewater treatment systems to remove emerging organic contaminants - a review. Environ Sci Pollut Res 21:11708–11728
143. Matamoros V, Gutierrez R, Ferrer I, Garcia J, Bayona JM (2015) Capability of microalgae-based wastewater treatment systems to remove emerging organic contaminants: a pilot-scale study. J Hazard Mater 288:34–42
144. Mulla SI, Bharagava RN, Belhaj D, Ameen F, Saratale GD, Gupta SK, Tyagi S, Patil SA, Hu A (2019) A review of micropollutant removal by microalgae. In: Gupta S, Bux F (eds) Application of microalgae in wastewater treatment. Springer, Cham. https://doi.org/10.1007/978-3-030-13913-1_3

145. Keffala C, Harerimana C, Vasel JL (2013) A review of the sustainable value and disposal techniques wastewater stabilisation ponds sludge characteristics and accumulation. Environ Monit Assess 185:45–58
146. Sunarsih S, Sasongko DP, Sutrisno S (2019) Process improvement on domestic wastewater treatment stabilization ponds by using mathematical optimization approach. Matematika 35 (2):171–176
147. Pipes WO (1961) Basic biology of stabilization ponds. Water and Sewage Works 108 (4):131–136
148. Ullrich AH (1967) Use of wastewater stabilization ponds in two different systems. J Water Pollut Control Fed 39(6):965–977
149. Rahman A, Ellis JT, Miller CD (2012) Bioremediation of domestic wastewater and production of bioproducts from microalgae using waste stabilization ponds. J Bioremed Biodegr 3:e113
150. Florentino AP, Costa MC, Nascimento JGS, Abdala-Neto EF, Mota CR, Dos Santos AB (2019) Identification of microalgae from waste stabilization ponds and evaluation of electroflotation by alternate current for simultaneous biomass separation and cell disruption. Engenharia Sanitaria Ambiental 24(1):177–186
151. Sarkar Paria D, Lahiri Ganguly S, Ghosh D, Jana BB (2019) Ecological processes-driven distribution of net-algal diversity and carbon sequestration potential across the sewage effluent gradient of stabilization pond system. Ecohydrol Hydrobiol 19(3):464–472
152. Ghermandi A, Fichtman E (2015) Cultural ecosystem services of multifunctional constructed treatment wetlands and waste stabilization ponds: time to enter the mainstream? Ecol Eng 84:615–623

Plasma Technology: A Novel Approach for Deactivating Pathogens in Natural Eco-Systems

Abimbola Motunrayo Folami, Samuel Ayodele Iwarere, and Feroz Mahomed Swalaha

Contents

Abstract Providing clean and potable drinking water for humans is an essential component of the continuous and sustainable existence of humanity. However, the inactivation of harmful pathogenic microorganisms during water treatment to make

---

A. M. Folami (✉) and F. M. Swalaha
Department of Biotechnology and Food Technology, Durban University of Technology, Durban, South Africa

S. A. Iwarere
Department of Chemical Engineering, University of Pretoria, Pretoria, South Africa

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 177–198, DOI 10.1007/698_2021_791,

the water safe and clean for human use is a requirement. Because of the shortcomings of current treatment technologies for the inactivation of pathogenic contaminants, new and emerging technologies are at the forefront as novel antimicrobial inactivation methods to meet the increasing demand for treatment of contaminated raw water. New and advanced technologies such as membrane filters, reverse osmosis, and ozonation have been explored for water treatment; however, most are cost-inefficient with robust treatment techniques. Therefore, this chapter aims at reviewing the application and mechanisms of using plasma technology as one of the cost-effective and sustainable technologies for the inactivation of waterborne pathogens and contaminated environmental samples. Besides, this review further focussed on some of the methods by which the different plasma discharges are generated and some of the optimum process parameters for the inactivation of microbial pathogens in water. In conclusion, some benefits and drawbacks of using plasma technology were identified, and further investigation of their application in the water sector was recommended.

Keywords Contaminant, Inactivation, Pathogenic, Plasma discharge, Wastewater

1 Introduction

Until now, the addition of chemicals to control the feed pH and inactivate or destroy microorganisms in water during treatment has been the norm and practice. Based on environmental and safety regulations, there is an increased pressure on natural resources, which has led to more new sustainable processes that reduce the chemical used during water treatment. Some of the emerging methods are for water to be exposed to plasma to adjust the pH and remove contaminants, thereby creating chemical-free treatment methods with a range of additional benefits. In recent times, the unique and distinct properties of plasma have made it an exciting area of study, not only for environmental applications but also for biomedical and agricultural practices. There has been extensive research on plasma applications ranging from its use in biomedical devices and materials, surface modification of textile, plasma-enhanced chemical vapour deposition, and water treatment to treat wounds and food sterilization [1–3].

In the last two decades, there is an increasing interest in the use of plasma discharge as an alternative option to conventional water treatment techniques [4]. For instance, the ability of plasma to dissociate molecular bonds, enhance oxidation, and stimulate chemical reactions through the production of free radicals made it a useful technology for the treatment of either water or wastewater [5, 6]. The term plasma is not a new word as it was first used in 1926 by Irving Langmuir [7, 8]; although, Sir William Crookes made a description of the phenomenon in 1879. Plasma is commonly referred to as “the fourth state of matter”, given its collective behaviour towards the presence of electric and magnetic fields. Hence, authors such as Korachi and Aslan [9] have commented on its capability to form filaments under magnetic fields. "*Plasmas are created by supplying energy to a volume containing a neutral gas, so that a certain fraction of free electrons and ions are generated from the neutral constituents. In technical plasma devices, the plasma is generally generated in electrical discharges and the input energy is supplied in the form of electrical energy*" [10]. Plasma is usually described as a fully or partially ionized gas consisting of light electrons and heavy ions. It is constituted by particles in permanent interaction; the particles include atoms, electrons, photons, negative and positive ions, free radicals, and excited or non-excited molecules [10, 11]. These make plasma to occur in a wide range of temperatures and pressures. Aurora borealis and fluorescent lamps are among the examples of plasma generated under a low-pressure. In contrast, the sun, as an example of high-temperature plasma alongside those generated in nuclear fusion reactors, is considered 99% plasma [12].

During water treatment using plasma technology, the high-energy electrons and the neutral radicals collide together to form an active substance that causes physical phenomena and chemical reactions [11, 13]. The chemistry of plasma driven in the gas phase during water treatment reduces large quantities of reactive oxygen species or gases within the system. When plasma interacts with the liquid water directly, it generates reactive species at the interface [14–16]. These reactive oxygen species produced during water–plasma interaction include the nitrate radical, ozone, OH radical, and hydrogen peroxide derived from water vapour, singlet oxygen, and superoxide (O_2^-). Hence, the plasma electrons and excited species provide the energy needed to break molecules' covalent bonds into reactive species [15]. The diffusion and Henry's law coefficients; $p = K_H. C$ govern the radical gases produced when plasma enters the liquid water; where p is the partial pressure above the liquid, K_H is the Henry's law constant, and c is the concentration in the liquid.

Applying the plasma technology for water treatment brings many value-added benefits than conventional reverse osmosis or other common advanced oxidation processes: (a) it does not require any consumables because plasmas can be generated in the liquid or regular air, (b) this makes the plasma technology an applicable point-of-use method for water treatment, especially for the underprivileged groups or regions, since there is no infrastructure or consumable costs, (c) the fast rate of degradation of the primary contaminants during water treatment has also been demonstrated to be superior to chemical methods due to the vast array of advanced oxidation processes, and (d) the application of plasma is inherently modular and can be used as a finishing stage in conventional water treatment systems, not unlike a conventional UV stage for disinfection [15]. Traditional sterilization methods through the use of chemical and heat treatments cannot be considered perfect disinfectant techniques because of their potential to cause secondary environmental pollution, i.e. disinfectant by-products. Therefore, a novel antimicrobial treatment technique, such as plasma treatment, is highly needed for water treatment because it is efficient, safer, and cost-effective [17]. Plasmas are classified into either "thermal (or hot) plasmas" (TP) or "non-thermal (or cold) plasmas" (NTP) (Fig. 1) based on the method of generation, heavy species of the plasma, temperature produced within the system, and relative energetic levels or regimes of electrons [18].

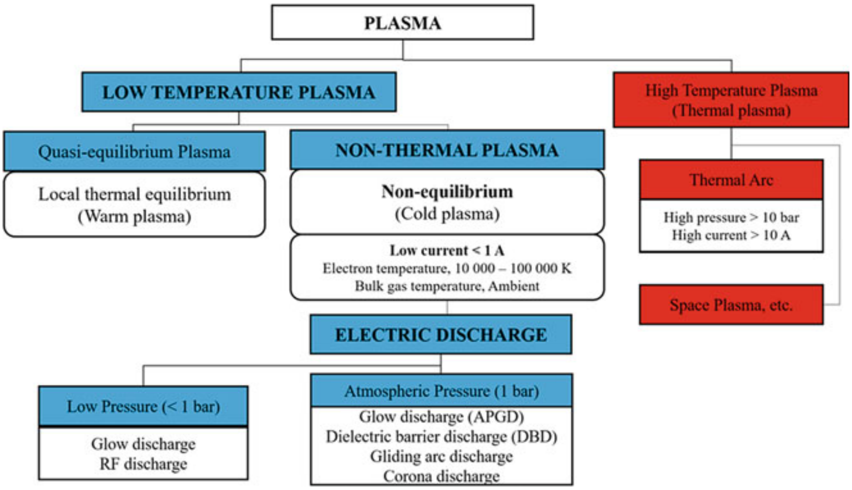


Fig. 1 Diagram to illustrate thermal and non-thermal (cold) plasmas generated using electric discharges at different pressures

2 Thermal Plasma

Thermal plasmas are obtained at high pressure ($\geq 10^5$ Pa) and need substantial power (up to 50 MW) to be observed [19]. This type of plasma is collision-determined. In the thermal plasma condition, there is a high collision frequency of the electrons and heavy ions at pressures above the atmospheric condition [11]. With a high rate of collisions or generation of plasma in a closed system, the heavy particles' temperature and the electrons become balance; hence, the plasma can be described by a single temperature. At this stage, when plasma is achieved, the plasma can be said to be a thermal plasma or exist in a state of local thermodynamic equilibrium. The gas temperature produced by thermal plasma can be as high as 5 to 20 $\times$ 10^3 K, with all the components having nearly the same temperature with a high electron density between 10^{21} and 10^{26} m^{-3} [10]. An example of thermal plasma is a welding torch, a lightning bolt, and the surface of the sun [20]. The high ion temperature makes a thermal plasma undesirable for water treatment applications, and the plasma is produced at high pressure using more power. For more application and review of this plasma for water treatment, see Shim [21].

3 Non-thermal Plasma

In contrast to the thermal plasma, a non-thermal or cold plasma can exist in a state of quasi-equilibrium or partial local thermodynamic equilibrium, as well as in non-equilibrium. As shown in Fig. 1, the electron temperature (10,000 K to more than 100,000 K) for non-thermal plasma is much higher than the temperature of the ions and neutrals, which are roughly the same and range from room temperature (300 K) to about 2,500 K [10]. This occurs when the heavy species' temperature is much lower than the electron temperature with a surrounding gas temperature at ambient temperature. Non-thermal plasmas are obtained at lower pressure gases using less power in comparison to the thermal plasma. Although the third plasmas categories have been proposed, it is not clearly defined; therefore, they are included in the non-thermal plasmas category. This is because this group of plasmas such as corona and the gliding arc discharges are formed near atmospheric pressure and ambient temperature; thus, they do not need extreme conditions [11]. In the last two decades, the low temperature of the non-thermal plasma, which sometimes makes it interact with the human skin without causing burns, has extended its application into a wide variety of fields in the sciences [4]. Hence, it is increasingly being explored as an alternative method in water purification and tertiary wastewater treatment [1, 22].

4 Generation Methods of Different Non-thermal Plasma

Generally, cold plasma discharges can be generated with stationary, pulsed (direct current, DC), and alternating (AC) electrical fields. As shown in Fig. 1, some common cold plasma discharges are DC glow discharge, radio frequency discharge, microwave plasma, dielectric barrier discharge (DBD), atmospheric pressure discharge plasma or atmospheric pressure plasma jet, corona discharges, and pulsed arc discharge.

4.1 Direct Current Glow Discharge

A Direct current (DC) glow plasma process is used as a source of light for material processing, ion deposition, and etching, as well as a physical method of surface modification [23]. This type of discharge is usually generated when gas passes between a high voltage powered electrode and a ground electrode. The configuration of the electrodes could be plane-to-plate, plane-to-plane, and plate-to-plate. The application of a DC electric field across the anode and cathode plate results in electrons being accelerated by the presence of an electric field. The resultant collision of the gas atoms and the electrons leads to excitation and ionization, creating new electrons and ions. However, continuous flow of current through the ionized gases generates a direct current (DC) glow discharge.

4.2 Radio Frequency Discharge

Radiofrequency (RF) discharge is usually generated using an alternating current (AC) power supply at 13.56 MHz or a typical radiofrequency generator. Capacitively coupled discharge (CCD) and inductively coupled discharge (ICD) are two types of discharges associated with the radio frequency range 20 kHz to 300 MHz, depending on the coupling mechanism employed. According to Ruma et al. [23], radio frequencies lead to the generation of plasma discharges with dissimilar behaviours of electrons and ions as a result of unlike masses, i.e., ions having a higher mass, lower mobility, lighter electrons, and strong influence due to AC electric field produced by the voltage from the radiofrequency generator. The radiofrequency plasma discharges are generated at low-pressure conditions and very useful in low-temperature plasma processes. Both the CCD and ICD have been found appropriate for a wide range of applications, especially in the semiconductor industries involving etching and deposition in semiconductor wafer processing, fabrication of optical fibres, the fields of microelectronics and aerospace [24].

4.3 Microwave Plasma

Microwave discharges are generated in the gas at high frequency (GHz range) and are widely reported for nanomaterials' synthesis, especially the growth of diamond films [25, 26]. Microwave discharge patterns are able to generate both thermal and non-thermal plasmas. According to Fridman [27], the frequency range of these sources is limited by system size, ionization frequency, and ion transfer. The most commonly used frequencies range from 300 MHz to 2,450 MHz. As mentioned by Bárdos and Baránková [28], high-frequency fields have a stabilizing effect on the plasma and generation of streamers in molecular gases. There are studies by several authors [11, 29, 30] on non-thermal plasma sterilization and decontamination using microwave sources, especially for water treatment [31–33].

4.4 Dielectric Barrier Discharge

Dielectric barrier discharge (DBD) is a specific type of AC discharge, which provides strong thermodynamic, non-equilibrium plasma at atmospheric pressure. This discharge can be generated through a high voltage powered electrode (cathode) positioned centrally inside a dielectric tube with a piece of metal forming the outer grounded electrode (anode). The discharge produced via different electrode configurations could result in either a volume dielectric barrier discharges (VDBDs) or a surface dielectric barrier discharges (SDBDs). The volume and surface dielectric barrier discharge can be used for similar applications. However, Ni and co-workers

[34] reported surface dielectric barrier discharge as a preferred choice for microbial decontamination applications due to its ease of implementation and its ability to generate high concentrations of reactive oxygen and nitrogen species (RONs). Based on literature sources [23, 34], this method has shown high removal efficiency of pollutants such as microbial decontamination from air and liquids. The dielectric barrier discharge has a wide range of technological applications, with one of the most industrially known being ozone generation. The DBD is being used in sterilization, pollution control, surface activation, chemical vapour deposition, water treatment, and bio-treatment of microorganisms, amongst many other applications [23, 35–38].

4.5 Atmospheric Pressure Plasma Jet

The atmospheric pressure plasma jet (APPJ) is a discharge characterized by the gas flow through a nozzle at a specific flow rate, and interestingly a non-thermal. Regardless of the atmospheric composition, the device for APPJ produces plasma in the open air (i.e. at atmospheric pressure). Thus, the exiting gas pressure and flow velocity influence its length, shape, and characteristics outside the quartz tube; therefore, ionization is limited by the volume where the gas flows. The APPJ is usually driven by a radio frequency power or alternating current power supply. Production of APPJ is much cheaper, convenient, and safer to use since the production only requires open air at atmospheric pressure and does not need a vacuum environment. Worldwide, this type of discharge has caught much attention for different applications in various fields such as surface modification of polymers, material processing, inactivation of microorganisms, thin film deposition, chemical vapour deposition, and biomedical application [39–42].

4.6 Corona Discharge

A corona discharge can be classified as a non-thermal plasma generated using different configurations. The use of sharp points and thin wires that can radiate outwards when an electric field is generated at a high voltage has been reported. The electron's strength in a corona discharge is not as strong as those in a direct current arc discharge or glow discharge. Depending on the electrodes' polarity, corona discharges can either be positive or negative [43]. A limiting factor, according to Fridman et al. [44], corona discharge can sometimes transit into a spark discharge if a breakdown in the electric field occurs as a result of a continuous increase in the voltage. Corona discharges have been used in different applications, i.e. the most common is for generating ozone like in the dielectric barrier discharge [45, 46]. There are works in the literature that have supported the capability of the negative coronas to generate up to ten times more ozone than that from a positive corona [47, 48]. The type of discharge produced in a reactor depends on the pin curvature, applied voltage, voltage polarity, and interelectrode distance [49, 50]. For the application of water treatment, both negative and positive DC, as well as monopolar pulsed voltage have been reported [51–53].

4.7 Pulsed Arc Discharge

The use of pulse generators or pulsed power supply to generate plasma has become very popular in the last decade. This has been attributed to the observed high removal efficiency towards contaminants or pollutants, small volume, low energy cost for many militaries, and industrial and environmental applications. Apart from organic degradation, *pulsed arc* electrohydraulic *discharge* has also gained more recent attention for the inactivation of biological contaminants, *including water treatment. R*esearchers like Ruma and co-workers [23] have reported that the reactor geometry, gap between the electrodes, the operating frequency, and applied voltage can define the characteristics of the type of discharge generated when a pulse generator is used. Besides, the different configurations of the electrodes could also impact on the kind of discharge generated. For example, a wire with a small diameter, or a needle with a sharp edge of different diameter connected to a high voltage, and a flat plate used as the ground electrode. In the last decade, there are literatures on the difference between the dielectric barrier discharge and the pulsed arc discharge, especially its capability to attain a higher electron temperature at a lower operating frequency and its use of electric arc for joule heating on the electrons instead of a built-up electric charge [45, 54, 55].

5 Electrohydraulic Plasma Generation

The use of plasma for the treatment of water or tertiary wastewater can be done either by generating the plasma discharges above the liquid medium (water) or inside the liquid. When the discharge is generated in a submerged state, it is often referred to as an electrohydraulic discharge. This type of discharges is categorized into high voltage submerged coronas, partial electrical discharges, and spark or high current submerged arcs discharges. The classification, in this case, is based on the flow of current from one electrode to the other (spark or arc discharges), or a partial electrical discharge when the discharge current flows from one electrode but does not reach the other electrode [56, 57]. However, the length of the needle electrode protruding from the surface of the insulating material determines the electric current and discharge pattern across the electrode gap in water [22]. Hence, proper insulation of the electrode edge or the interface between the metal and the insulator are fundamental requirements for the generation of high-intensity electric field in liquid water because electric charges concentrate on the edge of the electrode. Therefore, the shorter the length of the needle electrode protruding from the insulator surface, the better the generation of electric discharge in water than larger protrusion values. This is because water is known for its conductivity than air; hence, proper insulation of the electrode needle is very important. There are reports on the use of a point-to-plane electrode system for underwater pulsed discharge experiments. All concluded that a high-intensity electric field at the tip of the electrode is essential for the production of pulsed discharge in water [58–61]. A point electrode tip with appropriate insulation makes it possible to form a concentrated electric field. Thus, only corona and pulsed arc discharges have been mentioned to be viable in a solution to produce electrohydraulic state discharges [22] (Fig. 2).

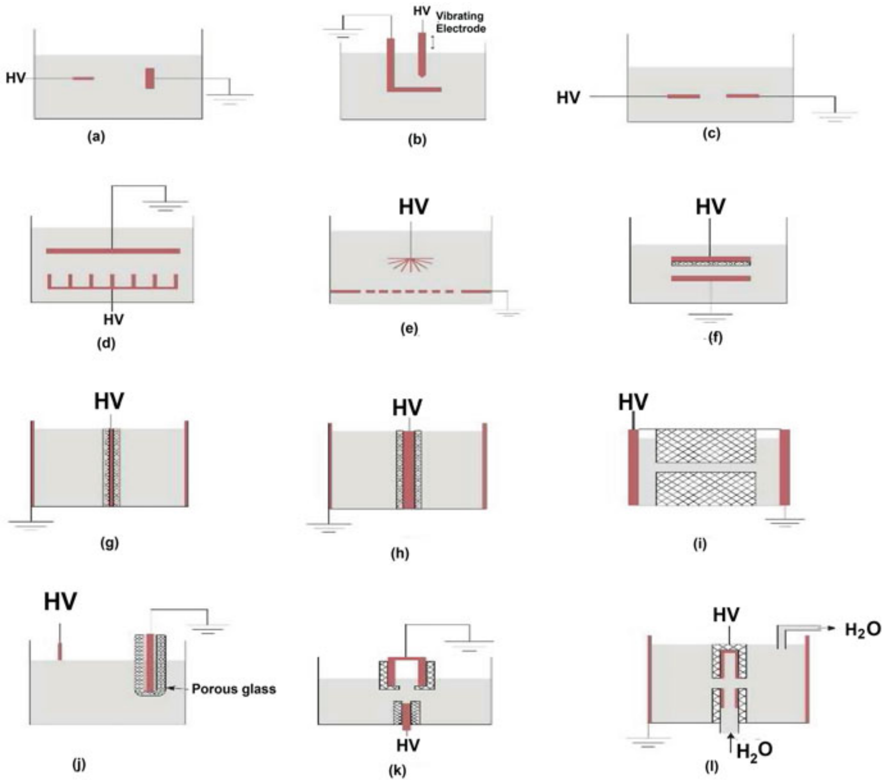


Fig. 2 Types of electrohydraulic discharge reactors: (**a**) pin-to-plate, (**b**) pulsed arc with vibrating electrode, (**c**) pin-to-pin, (**d**) multi-pin-to-plate, (**e**) brush-to-plate, (**f**) plate-to-plate with porous ceramic coating, (**g**) coaxial wire-to-cylinder with ceramic coating on wire, (**h**) coaxial rod-to-cylinder with ceramic coating on rod, (**i**) capillary discharge, (**j**) contact glow discharge electrolysis, (**k**) RF-discharge in cavitation bubble on electrode, (**l**) coaxial diaphragm discharge reactor from Šunka et al. [59] with perforations in tubular electrode covered by polyethylene layer

5.1 Pulsed Corona Electrohydraulic Discharge (PCED)

Pulsed corona, arc, and spark discharges can be generated when high voltage is applied to the gas phase above the liquid surface during water treatment [57]. With high power pulsed corona, energy is deposited in a gas or in a liquid at a high concentration based on the physical conditions [61]. It has been established in the review carried out by Locke et al. [57] that a high electric field in the order of 10^7–10^9 V/m is required to generate discharge of this nature if submerged in water. The use of water as the medium makes a PCED different from a pulsed corona discharge generated in air or oxygen gas. The use of water as the working medium in the PCED caused the formation of ozone, hydrogen peroxide, monatomic hydrogen, and other radicals instead of oxygen ions when air was used as a working fluid [16, 62, 63]. These reactive species have been shown to rapidly and efficiently degrade many organic compounds and biological contaminants like pathogens in water [63–69].

5.2 Pulsed Arc Electrohydraulic Discharge (PAED)

On the other hand, the pulsed arc electrohydraulic discharge (PAED) allows for the direct flow of current, transferred by electrons, from one electrode to the other. It allows for high current to pass through a plasma bubble containing ionized water vapour. Unlike pulsed corona or corona-like system that uses ~1 J/pulse energy, PAED uses different electrohydraulic discharge systems of ~1 kJ/pulse and above. This has been used as an alternative technology to remove chemical and microbial contaminants from water [70, 71]. The generation of this type of electrohydraulic discharge is technically challenging. This is because the current tends to form ions, which are partially discharged through the water. Some other differences between PAED and PCED systems are shown in Table 1. For more details and discussion on the features of PCED and PAED, see [10, 22, 57–61, 72, 73].

Table 1 Characteristics of different electrohydraulic discharges[a]

Value parameter	Pulsed arc	Pulsed corona
UV generation	Strong	Weak to moderate
Pressure wave generation	Strong	Weak to moderate
Current (peak)	10^3–10^4 A	10–10^2 A
Operating frequency	10^{-2}–10^{-3} Hz	10^2–10^3 Hz
Voltage (peak)	10^3–10^4 V	10^4–10^6 V
Voltage rise	10^{-5}–10^{-6} s	10^{-7}–10^{-9} s

[a]Data obtained from [70] as mentioned in [57]

6 Benefits and Current Challenges of Plasma in Environmental Applications

As an antimicrobial strategy, atmospheric cold plasma has many benefits, which include simple design, relatively low capital and operational cost, the capability to operate at ambient temperature, use of non-toxic gases, short treatment times, and the absence of harmful residues. Plasmas created in the ambient air are low cost, consumable free, and have numerous decontamination applications. For example, the plasma generated by an electrical discharge (e.g. fluorescent light tubes) has ~80% conversion rate from electricity to plasma [9]. The major advantages of the DBD include the ease of the discharge ignition, manifold adaptability due to the different electrode geometries, and treatment of objects inside sealed packaging material, whereby the DBD is especially interesting for industrial applications [74]. Most importantly, "*these plasmas produce large quantities of microbicidal active agents that have charged particles, electromagnetic fields, UV radiation, and chemically reactive species. The diversity and the small size of these active agents are believed to target multiple cellular components and metabolic processes in microorganisms and therefore make the emergence of resistance mechanisms less likely to occur*" [75].

Studies have shown that atmospheric pressure non-thermal plasma is efficient for a variety of potential bioapplications, including disinfection of contaminated surfaces in food-processing and clinical settings [11, 76], inactivation of viruses [77], and eradication of *Pseudomonas aeruginosa* biofilms using plasma jet, as shown in Fig. 3 [78–80]. A similar device was reported to completely eradicate biofilm containing ESKAPE pathogens (*Enterococcus faecium, Staphylococcus aureus, Klebsiella pneumoniae, Acinetobacter baumannii, P. aeruginosa, and Enterobacter spp*.) within 360 s [80–84]. The inactivation of methicillin-resistant *Staphylococcus aureus* (MRSA), *P. aeruginosa*, and *Candida albicans* by cold plasma by inducing cell surface damages has also been reported [85]. These pathogens inactivated by plasma are the leading group of causative organisms in most of the nosocomial infections and some of them are multidrug or antibiotic resistant pathogens. Hence, this is of great benefits to mitigate the negative socioeconomic, health, and environmental impacts that the pathogens might cause to humans.

Other interesting environmental applications of low-temperature plasmas include; gas water cleaning and effective technique for water and air treatment [61] and the decontamination of biological contaminants such as *Legionella pneumophila* in water [86–88]. The PAED has been applied as a direct plasma technique for various water treatment purposes, such as the decontamination of urban stormwater [72], lake water [70], river, and wastewater [62, 71]. A novel submerged arc reactor design for contaminations removal from liquid was recently patented [89]. Studies on the application of PCED have also been employed to remove pharmaceutical residues from hospital wastewater treatment [5, 90]. According to Shen and co-workers [91], the treatment of water using a direct current (DC) gas-liquid phase atmospheric-pressure argon (Ar) plasma for the

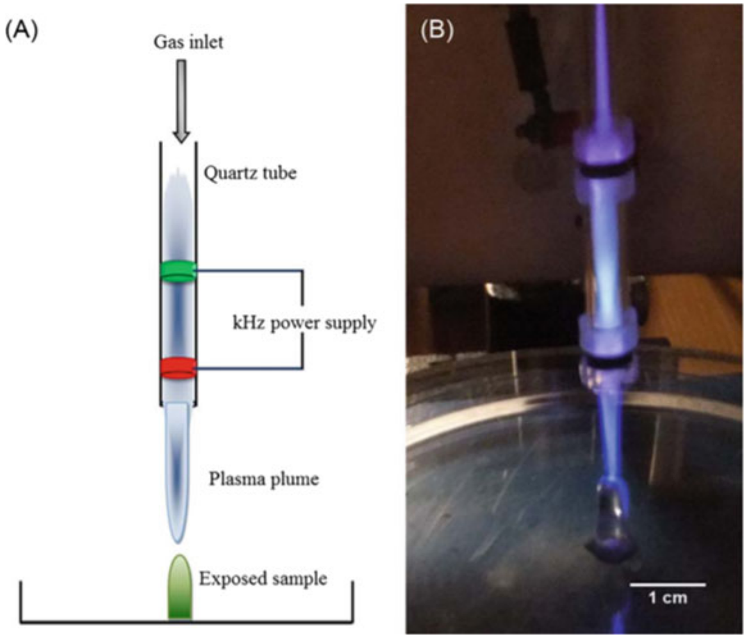


Fig. 3 Schematic diagram of (**a**) plasma jet used for the disinfection of biofilm and (**b**) photograph of the plasma jet interacting with a biofilm sample as cited by Alkawaeek et al. [78] under the Creative Commons Attribution (CC BY) license

inactivation of *Staphylococcus aureus* suspended in the liquid induces chemical effects such as the production of hydrogen peroxide and hydroxyl as well as the reduction of pH value is possible. The authors observed that plasma-treated water samples were not only pathogen-free, but also could retain the inactivation ability for a long time due to germicidal effects from residual H_2O_2 and acidic pH [91].

However, the main disadvantage of using non-thermal plasma, for example, in wastewater treatment, is its inability to remove physical contaminants. While the use of plasma in wastewater treatment could be more effective in the tertiary stage, its implementation at the secondary stage of wastewater treatment will require coupling with a secondary course filter to remove sediments. Nonetheless, this water treatment characteristic of not being able to remove physical contaminants present with various other chemical disinfection processes is a major disadvantage. Other key challenges in the commercialization of the plasma system for water treatment include; scale-up and inadequate understanding of the antimicrobial effect of different types of discharges in water treatment [15] as well as the unstable self-sustained diffuse plasmas at high pressure due to their susceptibility to filamentation and the transition to an arc [92, 93]. Indeed, plasma is still at a relatively early stage of technology development with different design issues that are yet to be perfected, making the complete understanding of the processes difficult; thus, limits the practical utility of non-thermal plasma.

7 Mechanism of Atmospheric Cold Plasma for Bactericidal Activities

In recent years, the use of atmospheric cold plasma (ACP) has gained increasing attention as an alternative method for the inactivation of waterborne pathogens [94, 95]. There is still inadequate information on the bactericidal mechanism of ACP. However, several factors and processes are considered by many researchers to be responsible for the microbiocidal action of pulsed discharges in water, depending on the plasma system used [62, 91, 96, 97]. Hence, the treatment mechanisms generated by plasma technologies that could be used as antimicrobial agents include; thermal reactions, pressure waves, electronic and ionic reactions, irradiation, electromagnetic pulses (EMP), and high electric fields [62, 95]. In general, both electron and ion densities are proportional to the electrohydraulic discharge technologies and have the potential to be more efficient than either indirect or remote plasma technologies. Figure 4 shows the treatment mechanisms initiated by PAED [98], having the potential to inactivate or kill harmful pathogens by combining several physical processes [56]. Physical processes such as (1) sonication by shock waves produced by the discharge in the water, (2) radiation, especially the use of UV radiation, (3) bombardment by energetic particles, (4) damage from chemical species (e.g. radicals) produced by the discharge introduced into the water such as ozone, hydrogen peroxide, etc., (5) vaporization of pathogens directly within the discharge, (6) heating of the fluid adjacent to the plasma bubble, and (7) interaction with nanoparticles produced by the discharge [96].

It is noteworthy that one of the targets of the atmospheric cold plasma as an advanced oxidation technology is to extend its application to various microbial pathogens, namely bacteria, protozoa, and viruses in water through the development and optimization of process parameters. This is because plasma discharge of high voltage intensity coupled with the release of a noble gas or gases could increase the microbial inactivation of waterborne pathogens, as shown in Shen and co-workers [91]. Many other studies have revealed that the generation of reactive oxygen species (ROS) such as atomic oxygen, ozone, hydrogen peroxide, and hydroxyl radicals aid in bacteria inactivation due to its high bactericidal potency [95, 99]. Korachi and Aslan [9] argued that these factors make atmospheric cold plasma processes a novel and exciting emerging antimicrobial method. On the mechanistic studies, researchers [100–102] pointed out that the formation of ROS is the product that resulted from the presence of oxygen in the air used as the carrier gas.

On the other hand, the nitrogen present in the air is responsible for forming reactive nitrogen species (RNS) [103–105], which has been linked to the formation of peroxynitrite, nitric oxide, and nitrite. These reactive species are responsible for the inactivation of microorganisms in water. This is also supported by Ziuzina [106], reporting that oxidizing agents such as hydroxyl radicals, ozone, and hydrogen peroxide ions are involved in indirect plasma treatment. However, Ehlbeck and co-workers [107] pointed out in their study that operating parameters such as gas

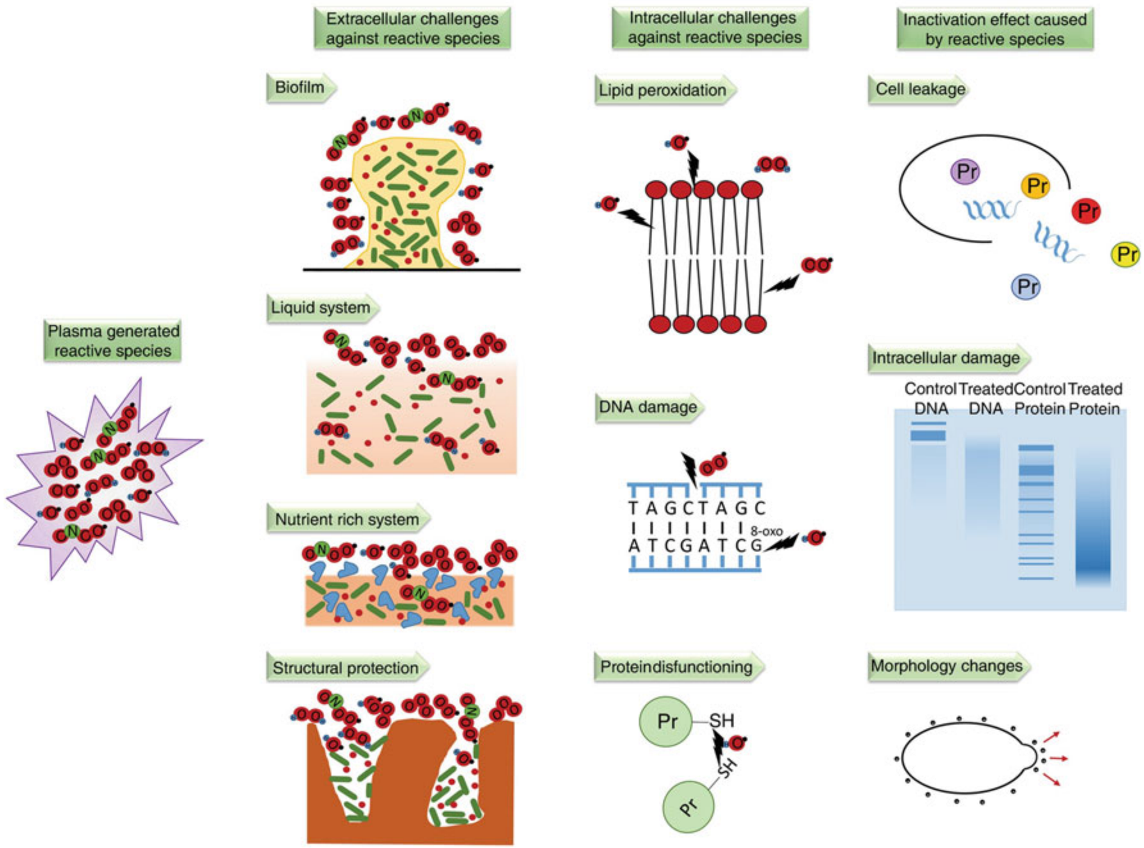


Fig. 4 Mechanisms of cold plasma generated reactive species concerning the complexity of microbiological challenges; figure taken from Bourke et al. [98]

pressure, composition, and plasma excitation properties play an essential role in the generation of these species. This argument is also supported by Misra et al. [108].

With reference to recent studies [98, 109, 110], treatment time and post-treatment storage time significantly influenced the plasma inactivation efficacy. Indeed, some researchers have investigated the efficiency of plasma inactivation in a post-treatment storage study [91]. These studies are based on the assumption that the diffusion and action of the residual reactive species can continue to affect inactivation in liquids, even after the plasma is off. Moreover, Ziuzina and co-workers [74] reported that "*only long-lived radicals affected the biological sample*". Another important aspect of using ACP that is of interest is the ability to act as a catalyst, i.e., to effectively improve a process, without affecting the material. This could be attributed to it being a weakly-ionized plasma. In the last decade, there have been significant technological and design improvements to make cost-effective plasma systems, with the ability to selectively generate a cold plasma at atmospheric pressure and ambient temperature showing great progress in plasma processing science. Thus, it opens up lots of possibilities of using non-thermal plasma for disinfection and sterilization of heat-sensitive materials and varied materials, including environmental samples, i.e. the opportunity that is not feasible with thermal plasma.

8 Conclusion

The inactivation of pathogens in the natural environment is a major concern worldwide because lots of pathogens are becoming resistant to the existing disinfectant, while some current chemical disinfectants are becoming a significant source of pollution by producing by-products during treatment. This chapter reviewed plasma technology as a novel and emerging approach for the decontamination of environmental samples. This review has shown that plasma technology in its non-thermal or cold atmospheric form holds excellent potential for the disinfection of water and food technology, even biomedical devices as a whole. Antimicrobial efficacy of the plasma generated could be influenced by the power source, the type of plasma gas, the flow rate of the gas, and the working pressure, amongst other factors such as the reactor geometry and electrode configurations. So, if the technology is employed in the tertiary stage of wastewater treatment, then the disadvantage of being unable to deal with physical substances will be eliminated. Nonetheless, there are research gaps that still need to be explored for this technology to be able to address some critical issues in the United Nations Sustainable Development Goals, such as access to clean water and sanitation. There are still research gaps for further investigation to better understand the difference in the treatment mechanisms between the direct plasma treatment and the indirect plasma treatment as well as the best reactor system or mechanism for decontamination of water.

9 Future Perspectives in the Study

Plasma technology, especially in the non-thermal form, offers a potential future for dealing with persistent organic pollutants and the inactivation of pathogens, which currently pose a significant health danger to the environment. Indeed, plasma reactors could be retrofitted to the tertiary stage in wastewater treatment plants. One of the current challenges for plasma technology in tertiary wastewater treatment to become competitive with some of the established tertiary treatment technologies has to do with scale-up from an industrial perspective. More research has to be done to understand further the mechanism involved in the inactivation of pathogenic organisms through non-thermal plasma. Energy cost studies will have to be compared with the existing and established treatment technologies. Further work on the removal of inorganic compounds from water should be explored.

References

1. Adhikari B, Adhikari M, Ghimire B, Park G, Choi EH (2019) Cold atmospheric plasma-activated water irrigation induces defense hormone and gene expression in tomato seedlings. Sci Rep 9:1–15
2. Jha N, Ryu JJ, Choi EH, Kaushik NK (2017) Generation and role of reactive oxygen and nitrogen species induced by plasma, lasers, chemical agents, and other systems in dentistry. Oxidative Med Cell Longev 2017:7542540
3. Petersen RC (2017) Free-radicals and advanced chemistries involved in cell membrane organization influence oxygen diffusion and pathology treatment. AIMS Biophys 4:240
4. Gharagozalian M, Dorranian D, Ghoranneviss M (2017) Water treatment by the AC gliding arc air plasma. J Theor Appl Phys 11:171–180
5. Ajo P, Preis S, Vornamo T, Mänttäri M, Kallioinen M, Louhi-Kultanen M (2018) Hospital wastewater treatment with pilot-scale pulsed corona discharge for removal of pharmaceutical residues. J Environ Chem Eng 6:1569–1577
6. Brandenburg R, Bogaerts A, Bongers W, Fridman A, Fridman G, Locke BR, Miller V, Reuter S, Schiorlin M, Verreycken T (2019) White paper on the future of plasma science in environment, for gas conversion and agriculture. Plasma Process Polym 16:1700238
7. Langmuir I (1928) Oscillations in ionized gases. Proc Natl Acad Sci U S A 14:627
8. Tonks L (1931) Plasma-electron resonance, plasma resonance and plasma shape. Phys Rev 38:1219
9. Korachi M, Aslan N (2013) Low temperature atmospheric plasma for microbial decontamination. In: Microbial pathogens and strategies for combating them: science, technology and education, vol 1. Formatex Research Center, pp 453–459
10. Zainal MNF, Redzuan N, Misnal M (2015) Brief review: cold plasma. J Teknol 74:57–61
11. Pahwa A, Kumar H (2018) Influence of cold plasma technology on food packaging materials: a review. Int J Chem Stud 6:594–603
12. Bonitz M, Horing N, Ludwig P (2010) Introduction to complex plasmas. Springer Science & Business Media
13. Cui Y, Cheng J, Chen Q, Yin Z (2018) The types of plasma reactors in wastewater treatment. IOP Conf Ser Earth Environ Sci 208:012002
14. Bruggeman P, Schram DC (2010) On OH production in water containing atmospheric pressure plasmas. Plasma Sources Sci Technol 19:45025

15. Foster JE (2017) Plasma-based water purification: challenges and prospects for the future. Phys Plasmas 24:055501
16. Malik MA, Ghaffar A, Malik SA (2001) Water purification by electrical discharges. Plasma Sources Sci Technol 10:82
17. Gupta TT, Ayan H (2019) Application of non-thermal plasma on biofilm: a review. Appl Sci 9:3548
18. Chang J (2009) Thermal plasma solid waste and water treatments: a critical review. Int J Plasma Environ Sci Technol 3:67–84
19. Pankaj SK, Wan Z, Keener KM (2018) Effects of cold plasma on food quality: a review. Foods 7:4
20. Corporation BM (2017) What is cold plasma? http://www.boviemedical.com/2016/01/04/what-is-cold-plasma/#. Accessed 29 Aug 2017
21. Shim SY (2001) Water treatment apparatus using plasma reactor and method thereof. Google Patents
22. Vanraes P, Nikiforov AY, Leys C (2016) Electrical discharge in water treatment technology for micropollutant decomposition. In: Plasma science and technology—progress in physical states and chemical reactions. IntechOpen, p 429
23. Ruma M, Habib A, Basha RH (2016) A survey of non-thermal plasma and their generation methods. Int J Renew Energy Environ Eng 4:2348–0157
24. Shearn M, Sun X, Henry M, Yariv A, Scherer A (2010) Advanced plasma processing: etching, deposition, and wafer bonding techniques for semiconductor applications. IntechOpen
25. Bower C, Zhou O, Zhu W, Werder D, Jin S (2000) Nucleation and growth of carbon nanotubes by microwave plasma chemical vapor deposition. Appl Phys Lett 77:2767–2769
26. Bates SC (2007) Net shape bulk diamond fabrication. Thoughtventions Unlimited LLC
27. Fridman G (2008) Direct plasma interaction with living tissue. p 69
28. Bárdos L, Baránková H (2010) Cold atmospheric plasma: sources, processes, and applications. Thin Solid Films 518:6705–6713
29. Ursache M, Moraru R, Hnatiuc E, Nastase V, Mares M (2014) Comparative assessment of the relation between energy consumption and bacterial burden reduction using plasma activated water. In: 2014 International conference on optimization of electrical and electronic equipment (OPTIM). IEEE, pp 1036–1041
30. Puligundla P, Mok C (2020) Microwave-and radio-frequency-powered cold plasma applications for food safety and preservation. In: Advances in cold plasma applications for food safety and preservation. Elsevier, pp 309–329
31. Ramón R, Del Valle M, Valero F (2005) Use of a focused microwave system for the determination of Kjeldahl nitrogen in industrial wastewaters. Anal Lett 38:2415–2430
32. Lo KV, Liao PH, Srinivasan A, Bailey S, Macsween J (2014) Briefing: H2O2 dosing strategy on microwave treatment of sewage sludge. J Environ Eng Sci 9:158–161
33. Wong WT (2006) Applications of microwave technology to wastewater treatment. University of British Columbia
34. Ni Y, Lynch M, Modic M, Whalley R, Walsh J (2016) A solar powered handheld plasma source for microbial decontamination applications. J Phys D Appl Phys 49:355203
35. Grinevich V, Kvitkova EY, Plastinina N, Rybkin V (2011) Application of dielectric barrier discharge for waste water purification. Plasma Chem Plasma Process 31:573–583
36. Hernández-Arias A, Rodríguez-Méndez B, López-Callejas R, Alcántara-Díaz D, Valencia-Alvarado R, Mercado-Cabrera A, Peña-Eguiluz R, Muñoz-Castro A, Barocio S, De La Piedad-Beneitez A (2012) Inactivation of Escherichia coli in water by pulsed dielectric barrier discharge in coaxial reactor. J Water Health 10:371–379
37. Hijosa-Valsero M, Molina R, Schikora H, Müller M, Bayona JM (2013) Removal of priority pollutants from water by means of dielectric barrier discharge atmospheric plasma. J Hazard Mater 262:664–673
38. Mok YS, Jo J-O, Whitehead JC (2008) Degradation of an azo dye Orange II using a gas phase dielectric barrier discharge reactor submerged in water. Chem Eng J 142:56–64

39. Bista P (2019) To study about atmospheric pressure plasma jet and it's electrical characterization
40. Ma S, Kim K, Huh J, Hong Y (2017) Characteristics of microdischarge plasma jet in water and its application to water purification by bacterial inactivation. Sep Purif Technol 188:147–154
41. Ma S, Kim K, Lee S, Moon S, Hong Y (2018) Effects of a porous dielectric in atmospheric-pressure plasma jets submerged in water. Phys Plasmas 25:083519
42. Mance D, Wiese R, Kewitz T, Kersten H (2018) Atmospheric pressure plasma jet for biomedical applications characterised by passive thermal probe. Eur Phys J D 72:98
43. Wang P, Fan F-G, Zirilli F, Chen J (2012) A hybrid model to predict electron and ion distributions in entire interelectrode space of a negative corona discharge. IEEE Trans Plasma Sci 40:421–428
44. Fridman A, Chirokov A, Gutsol A (2005) Non-thermal atmospheric pressure discharges. J Phys D Appl Phys 38:R1
45. Brandenburg R (2017) Dielectric barrier discharges: progress on plasma sources and on the understanding of regimes and single filaments. Plasma Sources Sci Technol 26:053001
46. Yehia DA (2019) Characteristics of the dielectric barrier corona discharges. AIP Adv 9:045214
47. Riba J-R, Morosini A, Capelli F (2018) Comparative study of AC and positive and negative DC visual corona for sphere-plane gaps in atmospheric air. Energies 11:2671
48. Yehia DA, Abdel-Salam M, Mizuno A (2000) On assessment of ozone generation in dc coronas. J Phys D Appl Phys 33:831
49. Bruggeman P, Graham L, Degroote J, Vierendeels J, Leys C (2007) Water surface deformation in strong electrical fields and its influence on electrical breakdown in a metal pin–water electrode system. J Phys D Appl Phys 40:4779
50. Bruggeman P, Guns P, Degroote J, Vierendeels J, Leys C (2008) Influence of the water surface on the glow-to-spark transition in a metal-pin-to-water electrode system. Plasma Sources Sci Technol 17:045014
51. Benetoli LODB, Cadorin BM, Postiglione CDS, Souza IGD, Debacher NA (2011) Effect of temperature on methylene blue decolorization in aqueous medium in electrical discharge plasma reactor. J Braz Chem Soc 22:1669–1678
52. Miyazaki Y, Satoh K, Itoh H (2011) Pulsed discharge purification of water containing nondegradable hazardous substances. Electr Eng Jpn 174:1–8
53. Magureanu M, Bradu C, Piroi D, Mandache NB, Parvulescu V (2013) Pulsed corona discharge for degradation of methylene blue in water. Plasma Chem Plasma Process 33:51–64
54. Rezaei F, Vanraes P, Nikiforov A, Morent R, De Geyter N (2019) Applications of plasma-liquid systems: a review. Materials 12:2751
55. Ni Y (2017) Non-thermal air plasma discharges for food and water security applications. University of Liverpool
56. Boxman R, Parkansky N, Mamane H, Meirovitz M, Orkabi Y, Halperin T, Cohen D, Orr N, Gidalevich E, Alterkop B (2008) Pulsed submerged arc plasma disinfection of water: bacteriological results and an exploration of possible mechanisms. In: Plasma assisted decontamination of biological and chemical agents. Springer, pp 41–50
57. Locke B, Sato M, Sunka P, Hoffmann M, Chang J-S (2006) Electrohydraulic discharge and non-thermal plasma for water treatment. Ind Eng Chem Res 45:882–905
58. Clements JS, Sato M, Davis RH (1987) Preliminary investigation of prebreakdown phenomena and chemical reactions using a pulsed high-voltage discharge in water. IEEE Trans Ind Appl IA-23:224–235
59. Šunka P (2001) Pulse electrical discharges in water and their applications. Phys Plasmas 8:2587–2594
60. Abou-Ghazala A, Katsuki S, Schoenbach KH, Dobbs F, Moreira K (2002) Bacterial decontamination of water by means of pulsed-corona discharges. IEEE Trans Plasma Sci 30:1449–1453

61. Kebriaei M, Ketabi A, Niasar AH (2015) Pulsed corona discharge, a new and effective technique for water and air treatment. Biol Forum 7:1686
62. Hartmann W, Roemheld M, Rohde K, Spiess F (2009) Large area pulsed Corona discharge in water for disinfection and pollution control. IEEE Trans Dielectr Electr Insul 16:1061–1065
63. Malik MA (2003) Synergistic effect of plasmacatalyst and ozone in a pulsed corona discharge reactor on the decomposition of organic pollutants in water. Plasma Sources Sci Technol 12: S26
64. Ajo P, Krzymyk E, Preis S, Kornev I, Kronberg L, Louhi-Kultanen M (2016) Pulsed corona discharge oxidation of aqueous carbamazepine micropollutant. Environ Technol 37:2072–2081
65. Gupta SB (2007) Investigation of a physical disinfection process based on pulsed underwater corona discharges. Forschungszentrum Karlsruhe
66. Lubicki P, Jayaram S (1997) High voltage pulse application for the destruction of the gram-negative bacterium Yersinia enterocolitica. Bioelectrochem Bioenerg 43:135–141
67. Lukes P, Brisset J-L, Locke BR (2012) Biological effects of electrical discharge plasma in water and in gas-liquid environments. Plasma Chem Catal Gases Liquids 1:309–352
68. Mouele ESM (2014), Water treatment using electrohydraulic discharge system,
69. Yantsis S, Chow-Fraser P, Li O, Guo Y, Chang J, Terui S, Watanabe K, Itoh M (2008) Zooplankton mortality in lake water treated by pulsed arc electrohydraulic discharge plasma. Int J Plasma Environ Sci Technol 2:128–133
70. Chang J, Urashima K (2008) Concurrent treatment of chemical and biological contaminants in water by a pulsed arc electrohydraulic discharge. In: Plasma assisted decontamination of biological and chemical agents. Springer, pp 87–97
71. Yamatake A, Angeloni DM, Dickson SE, Emelko MB, Yasuoka K, Chang J-S (2006) Characteristics of pulsed arc electrohydraulic discharge for eccentric electrode cylindrical reactor using phosphate-buffered saline water. Jpn J Appl Phys 45:8298
72. Li O (2010) Treatment of stormwater pond sediment by thermal plasma systems
73. Lin Q-X, Zhu L, He Z-H, Xia W, Xu X-Y (2015) The pulsed arc electrohydraulic discharge treatment study on waste water and its application. In: 2015 international conference on industrial technology and management science. Atlantis Press
74. Ziuzina D, Patil S, Cullen P, Keener K, Bourke P (2013) Atmospheric cold plasma inactivation of Escherichia coli in liquid media inside a sealed package. J Appl Microbiol 114:778–787
75. Alkawareek MY, Algwari QT, Laverty G, Gorman SP, Graham WG, O'connell D, Gilmore BF (2012) Eradication of Pseudomonas aeruginosa biofilms by atmospheric pressure non-thermal plasma. PLoS One 7:e44289–e44289
76. Yardimci O, Setlow P (2010) Plasma sterilization: opportunities and microbial assessment strategies in medical device manufacturing. IEEE Trans Plasma Sci 38:973–981
77. Yasuda H, Miura T, Kurita H, Takashima K, Mizuno A (2010) Biological evaluation of DNA damage in bacteriophages inactivated by atmospheric pressure cold plasma. Plasma Process Polym 7:301–308
78. Alkawareek MY, Algwari QT, Laverty G, Gorman SP, Graham WG, O'connell D, Gilmore BF (2012) Eradication of Pseudomonas aeruginosa biofilms by atmospheric pressure non-thermal plasma. PLoS One 7
79. Adamovich I, Baalrud SD, Bogaerts A, Bruggeman P, Cappelli M, Colombo V, Czarnetzki U, Ebert U, Eden JG, Favia P (2017) The 2017 plasma roadmap: low temperature plasma science and technology. J Phys D Appl Phys 50:323001
80. Flynn PB, Graham WG, Gilmore BF (2019) Acinetobacter baumannii biofilm biomass mediates tolerance to cold plasma. Lett Appl Microbiol 68:344–349
81. Flynn PB, Higginbotham S, Nid'a HA, Gorman SP, Graham WG, Gilmore BF (2015) Bactericidal efficacy of atmospheric pressure non-thermal plasma (APNTP) against the ESKAPE pathogens. Int J Antimicrob Agents 46:101–107

82. Belgacem ZB, Carré G, Boudifa M, Charpentier E, Cawe B, Gellé M (2016) Effectiveness of non-thermal O2–N2 plasma on P. aeruginosa multilayer biofilms cultured on hydroxyapatite. IRBM 37:68–74
83. Gilmore BF, Flynn PB, O'brien S, Hickok N, Freeman T, Bourke P (2018) Cold plasmas for biofilm control: opportunities and challenges. Trends Biotechnol 36:627–638
84. Mai-Prochnow A, Clauson M, Hong J, Murphy AB (2016) Gram positive and gram negative bacteria differ in their sensitivity to cold plasma. Sci Rep 6:38610
85. Kvam E, Davis B, Mondello F, Garner AL (2012) Nonthermal atmospheric plasma rapidly disinfects multidrug-resistant microbes by inducing cell surface damage. Antimicrob Agents Chemother 56:2028–2036
86. Abdel-Fattah TM, Cetinkaya E, Pell W, Hughes D, Malik M (2017) Biological decontamination of water using non-thermal plasma treatment. ECS Trans 75:1
87. Banaschik R, Burchhardt G, Zocher K, Hammerschmidt S, Kolb JF, Weltmann K-D (2016) Comparison of pulsed corona plasma and pulsed electric fields for the decontamination of water containing Legionella pneumophila as model organism. Bioelectrochemistry 112:83–90
88. Zhang R, Wang L, Wu Y, Guan Z, Jia Z (2006) Bacterial decontamination of water by bipolar pulsed discharge in a gas–liquid–solid three-phase discharge reactor. IEEE Trans Plasma Sci 34:1370–1374
89. Parkansky N, Boxman RL, Faktorovich SE, Alterkop BA, Berkh O, Vegerhof A (2019) Submerged arc removal of contaminants from liquids. Google Patents
90. Back JO, Obholzer T, Winkler K, Jabornig S, Rupprich M (2018) Combining ultrafiltration and non-thermal plasma for low energy degradation of pharmaceuticals from conventionally treated wastewater. J Environ Chem Eng 6:7377–7385
91. Shen J, Sun Q, Zhang Z, Cheng C, Lan Y, Zhang H, Xu Z, Zhao Y, Xia W, Chu PK (2015) Characteristics of dc gas-liquid phase atmospheric-pressure plasma and bacteria inactivation mechanism. Plasma Process Polym 12:252–259
92. Becker K, Kersten H, Hopwood J, Lopez J (2010) Microplasmas: scientific challenges & technological opportunities. Eur Phys J D 60:437–439
93. Becker KH (2018) 25 years of microplasma science and applications: a status report. Plasma Phys Technol 5:5–9
94. Memar MY, Ghotaslou R, Samiei M, Adibkia K (2018) Antimicrobial use of reactive oxygen therapy: current insights. Infect Drug Resist 11:567–576
95. Ziuzina D, Patil S, Cullen PJ, Keener K, Bourke P (2012) Atmospheric cold plasma inactivation of Escherichia coli in liquid media inside a sealed package. J Appl Microbiol 114
96. Gutsol A, Vaze N, Arjunan K, Gallagher M, Yang Y, Zhu J, Vasilets V, Fridman A (2008) Plasma for air and water sterilization. In: Plasma assisted decontamination of biological and chemical agents. Springer, pp 21–39
97. Shaw P, Kumar N, Kwak HS, Park JH, Uhm HS, Bogaerts A, Choi EH, Attri P (2018) Bacterial inactivation by plasma treated water enhanced by reactive nitrogen species. Sci Rep 8:11268
98. Bourke P, Ziuzina D, Han L, Cullen P, Gilmore B (2017) Microbiological interactions with cold plasma. J Appl Microbiol 123:308–324
99. López M, Calvo T, Prieto M, Múgica-Vidal R, Muro-Fraguas I, Alba-Elías F, Alvarez-Ordóñez A (2019) A review on non-thermal atmospheric plasma for food preservation: mode of action, determinants of effectiveness, and applications. Front Microbiol:622
100. Klockow PA, Keener KM (2009) Safety and quality assessment of packaged spinach treated with a novel ozone-generation system. LWT-Food Sci Technol 42:1047–1053
101. Oehmigen K, Hähnel M, Brandenburg R, Wilke C, Weltmann KD, Von Woedtke T (2010) The role of acidification for antimicrobial activity of atmospheric pressure plasma in liquids. Plasma Process Polym 7:250–257
102. Schwabedissen A, Łaciński P, Chen X, Engemann J (2007) PlasmaLabel–a new method to disinfect goods inside a closed package using dielectric barrier discharges. Contrib Plasma Physics 47:551–558

103. Girard F, Badets V, Blanc S, Gazeli K, Marlin L, Authier L, Svarnas P, Sojic N, Clément F, Arbault S (2016) Formation of reactive nitrogen species including peroxynitrite in physiological buffer exposed to cold atmospheric plasma. RSC Adv 6:78457–78467
104. Shaw P, Kumar N, Kwak HS, Park JH, Uhm HS, Bogaerts A, Choi EH, Attri P (2018) Bacterial inactivation by plasma treated water enhanced by reactive nitrogen species. Sci Rep 8:1–10
105. Tharmalingam S, Alhasawi A, Appanna VP, Lemire J, Appanna VD (2017) Reactive nitrogen species (RNS)-resistant microbes: adaptation and medical implications. Biol Chem 398:1193–1208
106. Ziuzina D (2015) Atmospheric cold plasma as a tool for microbiological control. Doctoral theses
107. Ehlbeck J, Schnabel U, Polak M, Winter J, Von Woedtke T, Brandenburg R, Von Dem Hagen T, Weltmann K (2010) Low temperature atmospheric pressure plasma sources for microbial decontamination. J Phys D Appl Phys 44:013002
108. Misra N, Tiwari B, Raghavarao K, Cullen P (2011) Nonthermal plasma inactivation of food-borne pathogens. Food Eng Rev 3:159–170
109. Han L, Sonal P, Daniela B, Milosavljević V, Cullen PJ, Bourke P (2016) Mechanisms of inactivation by high-voltage atmospheric cold plasma differ for Escherichia coli and Staphylococcus aureus. Appl Environ Microbiol 82:450–458
110. Patange A (2019) Atmospheric cold plasma interactions with microbiological risks in fresh food processing. Doctoral theses

Application of Anaerobic Hybrid Filters for Sewage Treatment

Santino Eugenio Di Berardino and Monica Alexandra Di Berardino

Contents

Abstract This chapter examines the feasibility of treating municipal wastewater by an anaerobic hybrid filter (AHF) under subtropical or Mediterranean temperature conditions, reporting the state of the art of main anaerobic reactors by focusing on their advantages and drawbacks.

S. E. Di Berardino
LNEG – National Laboratory for Energy and Geology, Lisbon, Portugal
e-mail: santino.diberardino@gmail.com

M. A. Di Berardino (✉)
IDMEC and Freelancer Engineer, Lisbon, Portugal

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 199–240, DOI 10.1007/698_2022_880,

It includes widespread laboratory work using AHF with one- and two-packing media operated at 35°C, 25°C, 20°C, and 15°C, and hydraulic retention times (HRT) ranging from 10 to 48 h. High removal efficiencies of chemical oxygen demand (COD) (78–90%) and total suspended solids (TSS) (77–85%) were achieved at HRT under 12 h and 15°C. The fixed media acted like a semi-permeable membrane, ensuring a stable specialized biologic sludge in the upper medium and bottom of the reactors.

It also presents a full-scale case study on sewage treatment of 7,500 inhabitants, using AHF combined with trickling filters (TF). The AHF started-up easily without special seeding, performed with stability, even in adverse flowrate and temperature conditions. Minimum COD removal efficiency (58%) was recorded at 15°C. Overall treatment performance was 82–88% of COD and 27–35% nitrogen removal. Pollutant concentrations meet lax environmental limits and could fulfill strict legislation.

Electricity consumption (30 kWh/day) corresponds to 12.5% of COD aerobic oxidation. Biogas produced by anaerobic degradation is methane rich (80–90%) with low hydrogen sulfide content. These results demonstrate that AHF systems have potential in the pre-treatment/treatment of municipal wastewater under subtropical–temperature conditions. This technology is robust, economic, efficient, and easy to operate.

Keywords Aggregated biomass, AHF reactor, Anaerobic hybrid filter, Biogas production, Low temperature, Methane, Municipal wastewater, Trickling filter, UASB reactor

Abbreviations

AD	Anaerobic digestion
AF	Anaerobic filter
AHF	Anaerobic hybrid filter
APHA	American Public Health Association
AS	Activated sludge
BOD	Biological oxygen demand
BOD_5	Biological oxygen demand (measured for 5-days)
BS	Bottom sludge (anaerobic reactor)
CH_4	Methane
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CODr	Chemical oxygen demand (removal)
CODs	Chemical oxygen demand (soluble)
CSTR	Continuous stirred-tank reactor
EGSB	Expanded granular sludge bed digestion
EUR	Euro
FA	Fatty acids

H_2	Hydrogen
H_2O	Water
H_2S	Hydrogen sulfide
HRT	Hydraulic retention time
HS^-	Bisulfide
IC	Internal circulation reactor
LCFA	Long-chain fatty acids
LNEG	National Laboratory of Energy and Geology (Portugal)
NH_4^+	Ammonium
NTP	Normal temperature and pressure
OL	Organic Load
pH	Potential of hydrogen
PMS	Packing media (anaerobic reactor)
PO_4^{3-}	Phosphate
PVC	Polyvinyl chloride
SRT	Solids retention time
SSAD	Solid-state anaerobic digester
TDS	Total dissolved solids
TF	Trickling filters
TOC	Total organic carbon
TOD	Total oxygen demand
TS	Total solids
TSS	Total suspended solids
UASB	Up-flow anaerobic sludge blanket
USB	Up-flow sludge blanket
VFA	Volatile fatty acids
VS	Volatile solids
VSS	Volatile suspended solids
WWTP	Wastewater treatment plant

1 Introduction

1.1 Anaerobic Sewage Treatment Evolution

The increasing worldwide population and the corresponding need for healthy conditions demands safe water supply and proper sewage treatment. In high population growing countries with poor economy, sewage represents the largest source of pollution.

Sewage contains appreciable quantities of organic compounds such as fats, carbohydroxides, and proteins, causing high concentrations of chemical oxygen demand (COD) and biological oxygen demand (BOD). It also contains suspended solids, nutrients, pathogens, detergents, and sanitizing agents. The biodegradability of the sewage is good, its temperature relatively high (depending on the climate), and pH is neutral. Such characteristics make these wastewaters suitable for biological anaerobic treatment processes.

According to McCarty [1], anaerobic digestion (AD) was discovered in the beginning of modern sanitation (late eighteenth century) and played initially an important role in protecting the environment. The innovation, published in 1881 in the French journal “Cosmos,” patented by the engineer Louis Mouras, was a tank retaining the sewage isolated from the air which settles the suspended particulates, forming a sludge bed. The sewage flows into the sludge bed, where anaerobic microorganisms perform hydrolysis and anaerobic degradation, making the effluent cleaner and odorless. This discovery triggered other similar systems as described by Jewell [2]. Septic tanks for domestic wastewater treatment become popular since 1886. Even today, this technology is widely applied in small communities, generally with <500 inhabitants. The efficiency of AD did not fulfill the environmental regulations, and the system had scarce dissemination.

The first world energy crisis in the 1970s increased the fossil fuel prices and awareness on renewable energy, encouraging low energy demanding systems. The anaerobic filter (AF) proposed by Young and McCarty [3] in 1969, and the UASB reactor suggested by Lettinga [4] in 1970, represented new friendly technologies for the treatment of sewage.

The treatment of domestic sewage has strong economic and social impacts. The current aerobic technologies (activated sludge or percolating beds) efficiently reduce organic and nutrient concentrations but entail high investment, operation, and maintenance costs, with production of big volumes of sludge for disposal. For this reason, it is widespread in countries with greatest economic power.

Since 1980, the new anaerobic technology started to replace the aerobic (despite technical hitches in some full-scale reactors) and rapidly proved its competitiveness for treatment of sewage in tropical country and hot industrial wastewaters. The UASB reactors became a cost-effective technology, providing a high degree of pollutant removal, low-level of capital investment, and few exploration and maintenance needs [5].

Hulshoff Pol et al. [6] summarize the state of the art and diffusion of anaerobic digestion, providing a wide perspective on a full-scale application in various countries around the world. In the developed countries, AD essentially degraded industrial hot effluents. In Latin American and other developing countries, AD’s major application is the domestic sector. The records excluded the agriculture/livestock facilities, centralized waste facilities, and any other waste treatment systems. It also disregarded the hundreds of thousands small-scale domestic sewage plants existing in China, India, and Colombia.

The UASB systems were the most used technology in 1998, especially for domestic sewage, representing about 65% of all existing applications.

The main limitation of anaerobic systems lies in the inability to achieve the limits imposed by environmental regulations on wastewater discharges. For this reason, the anaerobic processes need a final stage of depuration, which can be aerobic.

The anaerobic process can biodegrade toxic compounds contained in sewage, such as halogenated aliphatic compounds, which are converted to chlorides, carbon dioxide (CO_2), water (H_2O), and some methane (CH_4) [7]. A process defined "reductive dehalogenation," consisting of the removal of a halogen molecule and its replacement with a hydrogen atom [1], can gradually transform complex halogenated compounds. Anaerobic digestion may, therefore, play a significant role in the detoxification of effluents. The advantages of anaerobic processes, according to Lettinga [5], are the following:

- The treatment system may have a low-capital cost.
- Saves 80% energy costs compared to activated sludge (AS) process.
- Low-hydraulic loss; therefore, it may avoid pumping and electricity.
- Is applicable anywhere and to a wide scale range, up to 100,000 inhabitants.
- Accepts high organic loads even in low temperature conditions and with moderate load of suspended material, which results in small systems.
- Biological sludge production is about 12–15% of AS process.
- The sludge is already stabilized and well concentrated (>7–8% TS).
- Anaerobic microorganisms remain alive in the reactor for over a year, without seriously affecting their activity.
- The technology combines with any other treatment system or recovery scheme (ammonia, phosphate, and sulfur).
- Ability to remove halogenated compounds.

1.2 Anaerobic vs. Aerobic Processes

In aerobic biological treatment methods, the microorganisms grow in an oxygen-rich environment. The strong oxidant available for converting organic matter to CO_2, H_2O, and synthetizing cellular material (biological sludge), releases high amount of energy as heat. This energy promotes the microorganism's growth and favors the kinetics of the reactions, providing high removal rate over relatively short periods and high biomass production.

Systems of aerobic treatment include the activated sludge process, the rotating biological contactors, the trickling filters, etc. The system mostly used for sewage and industrial effluents is the activated sludge process, frequently operated at low organic load (extended aeration) in small-scale systems [8].

Aerobic treatment methods have the advantage to fulfill the very low COD concentrations fixed by environmental legislation, and a great potential to combine with various types of biological schemes (anoxic and anaerobic), achieving high removal of nutrients [9]. These technologies are compact and reliable, but involve high operational costs relative to aeration and biological sludge production, treatment, and disposal. Oxygen transfer kinetics limits the organic load of aerobic systems to about 2–3 $kg{\cdot}COD{\cdot}g^{-1}\ L^{-1}\ day^{-1}$, requiring dilution (recirculation) when operating with concentrated effluents [8].

Anaerobic digestion is a biological process performed by an active microbial consortium, in the absence of exogenous electron acceptors (oxygen), converting organic matter (carbohydrates, proteins, and lipids) into biogas (a mixture of methane (CH_4) and carbon dioxide (CO_2)) and biomass.

In methanogenic anaerobic degradation, the absence of a strong oxidant (oxygen) produces methane, a small organic compound with high calorific value. The release of this gaseous compound decreases the available energy in the culture medium of methanogens to about 0.21 kcal per kg of oxidized COD, making the reactions slower, compared to aerobic processes and other steps of the degradation process. Oxygen is toxic to methanogenic bacteria, requiring anaerobic reactors to be covered and tight, to prevent any entrapment of air. This also prevents the release of odors.

Several groups of microorganisms perform the methanogenic fermentative process. Methanogens, microorganisms that produce methane as a metabolic byproduct in hypoxic conditions, are prokaryotic and belong to the *Archaea* domain.

Each group in the consortium has minimum food requirements ($S_{\min}$), the lower threshold concentration, below which the reaction speed is insufficient to supply the organism with enough energy for net growth, and no steady-state activity exists [9] Using the Monod equation combined with the growth equation, McCarty [9] and Rittman and Baskin [10] calculated that for steady growth of methanogenic bacteria, the minimum substrate concentration ($S_{\min}$) is 48 mg/L and 78 mg/L acetate at 25°C and 35°C, respectively. The sum of minimum concentration of each trophic group of symbiotic microorganisms in a digester gives rise to a concentration of COD that generally exceeds the discharge limits set by law. Consequently, the AD process needs post-treatment systems. Another contributor to the high COD in the effluent is the dissolved methane.

High organic strength COD and warm temperature effluents are proper for anaerobic digestion (AD) [11], allowing high removal yield of organic matter and being a potential cost-efficient first treatment step, capable for acceptance in municipal sewer at a lower cost.

AD does not significantly remove nitrogen or phosphorus; essentially, it changes their oxidation level in reduced chemical condition (NH_4^+, HS^-, and PO_4^{3+}), suitable for fertilization of agricultural fields or for algae growth systems. Organic forms of nitrogen are transformed into ammonium nitrogen and other macronutrients.

Energy saving, small area footprint, the production of renewable energy from waste streams, and the fertilizing potential are major incentives for applying AD technology. Unpleasant odors are generally absent when the system is operated efficiently. Figure 1 compares the COD biodegradation in aerobic and anaerobic environment.

During aerobic wastewater treatment, around 40% of COD in the input is converted into biomass synthetized by the process (excess sludge), and about 50% is released as heat. On the contrary, anaerobic sludge yield is quite small and just 5–15% of inlet COD undergoes conversion to biomass. This corresponds to about 15–30% of excess aerobic biological sludge.

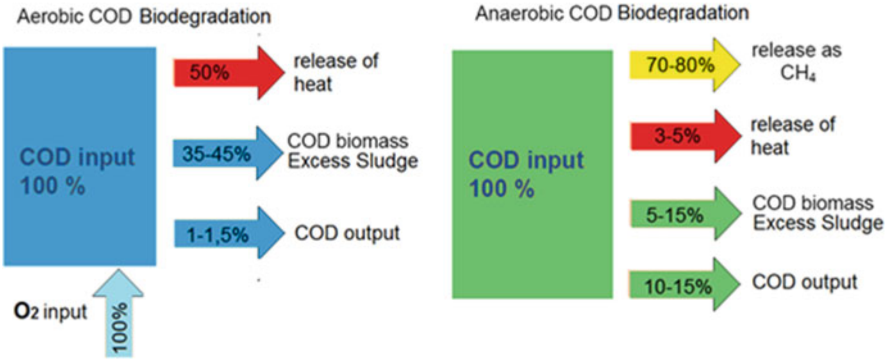


Fig. 1 COD degradation – aerobic vs. anaerobic treatment

Table 1 Comparison between anaerobic vs. aerobic treatment

Parameter	Anaerobic	Aerobic
Energy consumption	Low	High
Degradation rate (kg·COD·m^{-3} day^{-1})	0.5–20	0.1–1.8
Hydraulic retention time (HRT) (days)	0.3–20	0.1–5
Treatment COD removal	Moderate (60–90%)	High (95%)
Sludge production	Low	High
Process stability against charge loads and toxic	Moderate	Moderate
Degradation of recalcitrant compounds(phenolic, aromatics)	Average	Average
Startup time	2–4 months	2–4 weeks
Need of nutrients	Low	High
Odors	Potential problem	Low
Alkalinity	Average/high	Low
Biogas production	High	No

The COD removal obtained by the anaerobic process is generally high (70–95%) but lower than obtained in aerobic system (98–99%). The anaerobic technology can generate about 280 l of methane (at NTP) for each kg of COD degraded.

AD reactors work efficiently at organic loads averaging 6–8 kg·COD·m^{-3} day^{-1} and can accept values up to 12–16 kg·COD·m^{-3} day^{-1}, much higher compared to the classic activated sludge processes (1.5 kg·COD·m^{-3} day^{-1}).

Consequently, a number of studies in open literature suggest the sequence of anaerobic methods as pre-treatment upstream of the aerobic process [12]. Depending on the wastewater compounds and the level of purification required, anaerobic technology can reduce, on average, up to 75% the energy consumption of the aerobic treatment, thanks to the ability to scale down the aeration system.

Table 1 presents a comparison between anaerobic and aerobic treatment.

Anaerobic digestion produces gas consisting of a mixture of CH_4 and CO_2 with high calorific value. In the case of aerobic processes, the heat developed by the process has no practical use. Comparing the energy balance between the activated sludge system and anaerobic digestion, AD provides 0.35 L of methane (about 3,000 kcal) per kg of oxidized COD, while aeration of aerobic process consumes about 1,000 kcal per kg of oxidized COD. Energy difference is of 4,000 kcal per kg of COD removed.

1.3 Complementary Low-Cost Treatment Systems

Anaerobic wastewater treatment is ineffective in achieving acceptable levels for surface discharge, due to its content of organic matter, suspended solids, ammonia nitrogen, phosphates, and sulfur [11, 13, 14].

Chernicharo et al. [15] summarize the state of the art of post-treatment technology in Brazil. Most applications for removing organic matter and nutrients are aerobic/anoxic post-treatment, oxidation ponds, land application, physical operations, or a combination of those systems [16]. Removal of phosphate can be achieved by chemical methods [17].

Lagoons, in their various forms, and the "land treatments" are suitable options when proper land is available. In water-poor areas, the treated wastewater is useful for crop and/or landscape irrigation, reusing both water and nutrients, becoming one of the best ways to capture the full resource potential of wastewaters. Other viable alternatives for the treatment of anaerobic effluent are photosynthetic ponds, based on algae growth, for irrigation and/or fish farming [18]. Harvested algae is a primary matter suitable to produce chemicals and biochemical products, used in cosmetics, food industries, etc.

Constructed wetland systems can meet high quality effluent standards for discharge in watercourse. Therefore, there are many possible ways to increase and complete the degree of treatment after the anaerobic system, as shown in Fig. 2.

1.4 Anaerobic Technologies for Sewage Treatment in Temperate Climates

The most common configurations for treating sewage and food-processing wastewaters are UASB and anaerobic filters reactors. Figure 3 presents a cross-sectional schematic view of a UASB reactor, an anaerobic filter (AF), and an anaerobic hybrid filter (AHF).

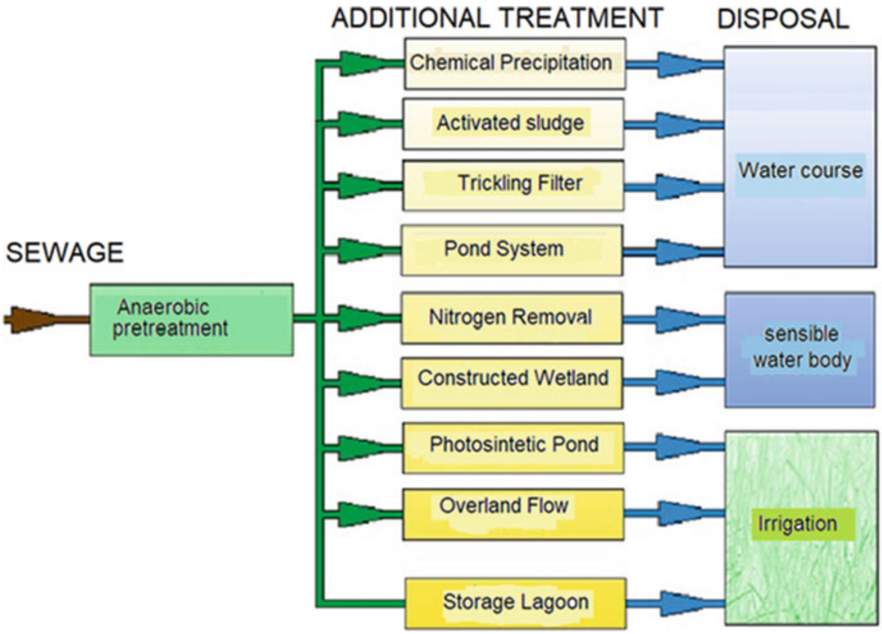


Fig. 2 Anaerobic sewage post-treatment alternatives

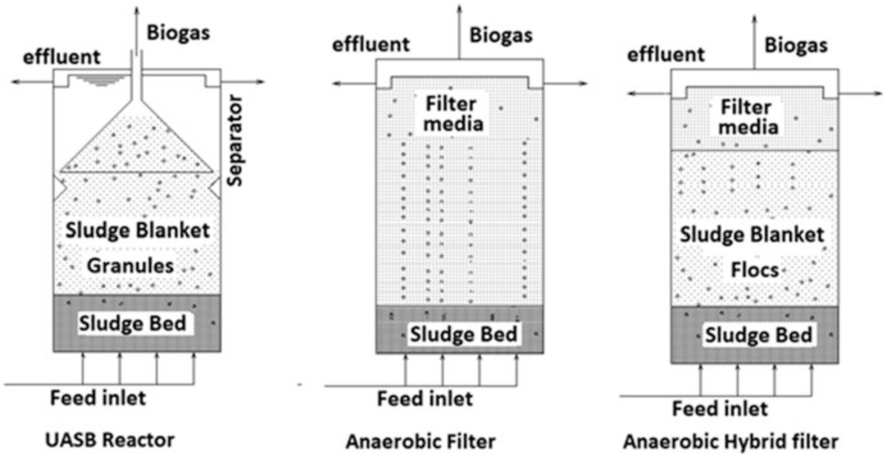


Fig. 3 Schematic cross-sectional view of UASB, AF, and AHF

1.4.1 UASB Reactor

Up-flow anaerobic sludge blanket (UASB) reactor, developed in the Netherlands by Lettinga [4] in 1970, has the capacity to treat various types of high to low-strength industrial wastewaters, from food industry, fermentation industry, dairy processing effluents [11, 12], and other industries [19–21]. Presently, it is the most used anaerobic technology for the treatment of industrial wastewaters [22, 23]. It has also successfully performed the treatment of domestic sewage at psychrophilic and mesophilic temperatures in Latin America [24].

The success of the UASB process lies in the capability to retain a high concentration of immobilized active biomass due to the phenomenon of granulation/flocculation of microorganisms [25, 26].

UASB reactor consists of a fermentation zone accumulating a blanket of suspended granular/flocculent sludge and an upper sedimentation compartment, which performs gas/liquid/solid separation. This configuration creates a quite active microbial consortium and stimulates the selection and growth of granular biological consortium. The granules, with about 3–4 mm in diameter, have a high settling rate [27]. They produce gas and float with effluent to the gas/liquid/solid separator which expels the gas, settling and returning the granules to the lower compartment, creating a sludge blanket.

The granulation mechanism is the key to the success of the UASB digester, which achieves a removal efficiency of 70–90%, even when receiving organic loads >15 kg·COD.

The major limitation of this technology is the time necessary for granule formation and development [28], when the key operating parameters are not adequately controlled. The system startup may need appropriate sludge for inoculation, feed and sludge loss control, proper ascending speed, mixing conditions, and avoidance of pH and toxic substances shock [25, 28].

The suspended solids in the effluent may inhibit granulation [29], (accumulating inside the reactor and deteriorating the granules by friction) impairing the reactor. The particulate matter present in domestic wastewater must be dissolved by hydrolysis, to be bioavailable to microorganisms. De Baere and Verstraete [30] calculated that, in UASB-type reactors, the VSS/COD ratio should not be >0.1. If it is greater, a primary decantation is necessary.

Lipids cause inhibition to several microbial strains (hydrogen-producing bacteria responsible for β-oxidation, acetoclastic bacteria converting acetate to methane, and hydrogenotrophic methanogens which produce methane from hydrogen). Due to its slow hydrolysis, they are released in the bulk of long-chain fatty acids (LCFA) [31–33]. This phase lasts several days, reducing the rate of methane production.

Another mechanism for the inhibition is the high hydrophobicity of unsaturated lipids which are absorbed into the biomass (limiting access and mass transfer with other substrates), interfering with bio assimilability by anaerobic digestion [34, 35]. The inhibited methanogens can recover their activity after conversion to methane of the LCFA, by pausing the feed for some time and applying batch feed regime. Studies on the intermittent operation of UASB reactors treating dairy wastewater showed good results at laboratory-scale [36]. The yield of methane produced from lipids is much higher than from carbohydrates or proteins.

1.4.2 Anaerobic Biofilm Reactors-Attached Growth

Biofilms are microbial communities attached to support materials that have the ability for effective removal of organics and methane production. Anaerobic biofilm reactors have high loading capacities, concentrated biomass, resistance to hydraulic or organic overloads, and no requirement of mechanical mixing [37].

Compared to the conventional digester systems, they are attractive since biofilm reactors could significantly reduce startup time and increase organic loading rates. Various types of biofilm reactors performed successfully for the treatment of high-strength effluents. The anaerobic filter and the anaerobic hybrid filter have been proposed for sewage treatment [2].

1.4.3 Anaerobic Filter Reactor

Young and McCarty [3] proposed, for the first time in 1968, the fixed-bed digester or anaerobic filter (AF) reactor for the treatment of industrial effluent. It promised a number of favorable potential advantages: good COD removal at relatively short HRT, no recirculation, low sludge production, high biological activity, and good performance, even at low temperatures.

The "classic anaerobic filter" is a reactor filled with a bed of random or structured packed medium and up-flow flux of the transient wastewater, which enters at the bottom. The packing medium promotes the adhesion in its surface of a bacterial consortium (biofilm) by extracellular polysaccharides and allows its retention in the interstitial space, providing close contact with the effluent. When the biofilm thickness is in excess, it is pushed by the gas, and either goes out with the effluent or settles in the bottom of the reactor. This system develops flocculent type biomass and does not create granular agglomerates.

The fixed-bed high-rate reactors have fast and easy startup and achieve efficient removal of organic matter without using specialized sludge, inspiring numerous applications in a full-scale industrial wastewater treatment, including dairies, from the late 1970s until 1992, [6, 38, 39] revealing an efficiency equal or greater than obtained at laboratory scale.

In the anaerobic filter, recirculation is optional, used with effluents with high organic load (> 10 g·COD·l^{-1}) [40], to improve homogenization and/or control the thickness and structure of the film.

The anaerobic filters require low HRT contact time for biodegradation, from a minimum of 3 h (obtaining 50–60% efficiency), up to more than 100 h (obtaining efficiency of 95%). Usually HRT varies from 0.5 to 3 days, according to the characteristics of the substrate. Due to the immobilization of biomass, organic load varies from 0.1 to 80 kg·COD·m^{-3} day^{-1}, according to the substrate. The operation is stable and restarting after a long stop is quick, which makes them adapted to seasonal effluents.

According to Young, the drawback of anaerobic filter is the hydrodynamics (due to the media) which hinders the horizontal mixing and accumulates suspended solids. Especially in the bottom of reactor, the input high organic load promotes high microbial growth, generating fouling dead zones and preferential paths. When the horizontal distribution of the feed is non-uniform, the reactor clogs when fully loaded. The mixing generated from gas flotation is low, giving rise to low mass transfer coefficient and biofilm activity. The insurgence of these problems in first-installed plants hindered its popularity and by the 1990s AF technology was almost abandoned in favor of UASB and AHF reactors, which dominated the anaerobic treatment market for the last 30 years.

1.4.4 Anaerobic Hybrid Filter (AHF)

By reducing the packing medium height until near the top of the AF reactor, the reactor configuration is called "hybrid," as it combines the advantages of AF and UASB [39], while minimizing their limitations.

In this reactor, the microbial sludge can grow, granulate, or flocculate (similarly to UASB), therein eliminating the major weakness of AF. In the top of the reactor, a layer of packing media replaces the gas/liquid/solid separator used in UASB reactors. It degasifies and retains the biological flocs inside the media.

Consequently, AHF is a simple and efficient configuration suitable for many wastewater treatments, according to the media used. Its main potential is that different microbial groups can develop under favorable conditions, enhancing the capability of hydrolysis, acidogenesis, and methanogenesis. This reactor allows long biomass retention time, as well as resistance to organic and hydraulic shocks.

The idea is attributed to Maxham and Wakamia [41] in 1980, which proposed an anaerobic hybrid filter (AHF) with a packing medium occupying a variable volume, from 10 to 50%, of the laboratory reactor.

The performance depends on contact time of the wastewater with the flocs grown in the sludge layer and in the attached biofilm media matrix. The biological bed in the bottom and the flocs moving inside the reactor perform the majority of the biological activity. The packing media in the top retains bacteria, suspended solids, and floatable pollutants (lipids), providing additional degradation [42].

The system has the capacity of self-developing active flocculent biomass, making the startup easy and averting inoculation with specialized granular sludge.

Support material may have a diverse arrangement, either ordered or random [39, 43]. The random medium may enhance the retention of organics and colloids, enabling additional hydrolysis and degradation. This configuration may washout the microbial biomass and any other suspended solid accumulated in the media, pulled by the biogas buoyancy forces, when high organic loads are applied. Therefore, this reactor is suitable when is applies to diluted streams with moderate gas production as it is the case of sewage. This technology reduces the cost for the support material, compared to the AF [44, 45].

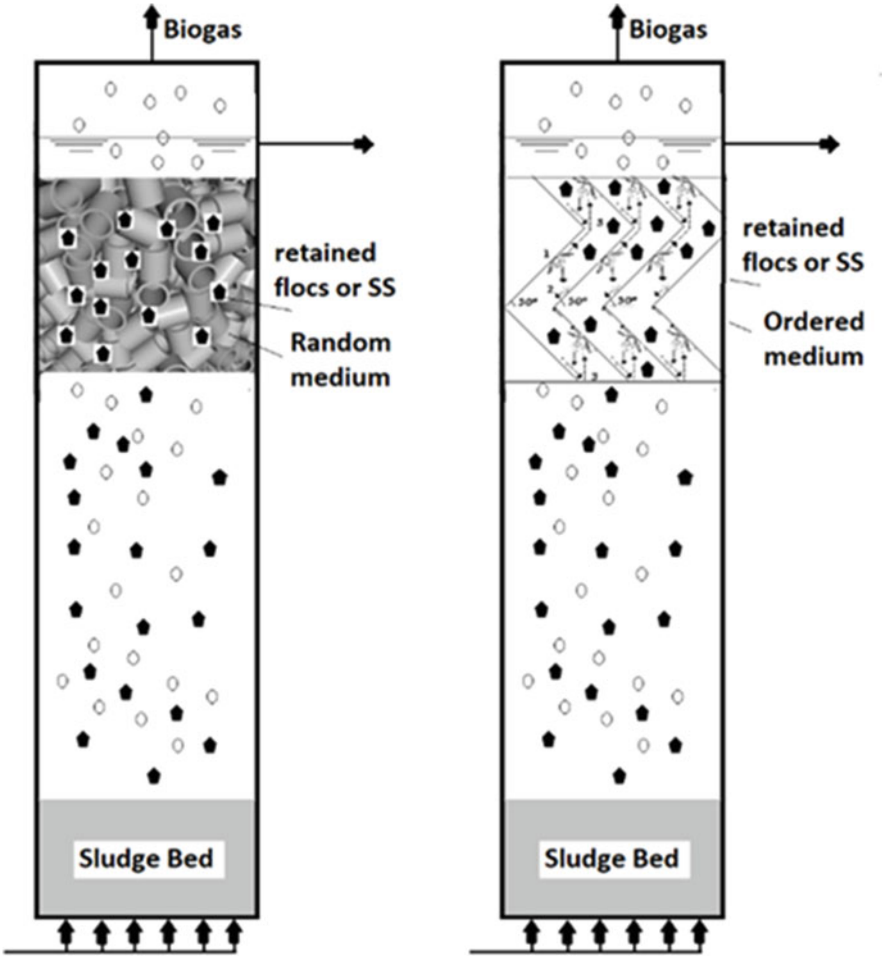


Fig. 4 Representation of random vs. structured packed bed medium

This problem is less relevant with oriented packing medium, which offers a better solid/gas separation, performing better than the randomly distributed medium [39] (Fig. 4).

1.5 Temperature Effect

Temperature strongly influences the hydrolysis-processing rate, being the rate-limiting step of the sewage degradation process. At low temperatures, the insufficient hydrolysis rate does not dissolve organic matter and causes the deterioration of the overall anaerobic reactor performance [46]. But when working with dilute solutions, anaerobic bacteria can adapt to low temperatures and can work efficiently at psychrophilic conditions [47, 48].

In the case of UASB reactors, several authors [49–52] observed moderate COD removal of about 65% at 20°C, and of 55–65% at 13–17°C. A big decrease (78%) in the effluent CODr occurred, along with a decline in the gas production rate [19], when the temperature dropped from 27 to 10°C. The lower gas production coincided with a 25% lower CODr at 10°C, indicating suspended solids accumulation in the reactor.

The high concentration of particulate matter present in sewage may recommend a good initial hydrolysis step, according to the temperature, to efficiently run an UASB reactor. Lew et al. [53] compared the performance of a classical UASB and hybrid UASB-filter reactor at low temperatures. The COD removal rates for the UASB reactor were better (70% and 48%, respectively) than the hybrid reactor (60% and 38%).

Elmitwalli et al. [46] compared the performances of a hybrid UASB-filter and a classical UASB reactor at 13°C. The hybrid UASB-filter reactor reached 64% COD removal, a 4% better removal than the classical UASB. The attached biomass on the filter provided a better colloidal fraction removal.

Anaerobic technology performance is limited in temperate and cold climates for sewage treatment unless anaerobic bacteria can adapt to low temperatures.

Lettinga et al. [54] proposed AD application to temperate or even frigid ($T < 10$°C) countries. Some known systems operate at full scale with varying retention times between 4 and 12 h, ensuring removals of 49–78% COD and 65–80% BOD_5 [55]. High-rate anaerobic treatment seems possible at psychrophilic conditions [47, 48]. Further studies need to examine the possibility of increasing the efficiency of the reactor in mild regions (average temperature of municipal wastewater ranging from 15 to 30°C).

2 Laboratory Experiences

2.1 Experimental Work

The basic idea of this research was to create a simple, robust, and reliable technology for sewage treatment in temperate climate countries, with favorable efficiency, operation stability, low cost, and easy operation and maintenance.

The characteristics of urban sewage creates serious difficulties for the operation of anaerobic treatment systems, due to variable flowrate and temperature, excessive dilution in rain period, presence of industrial streams, high suspended particulate matter, oil & grease. The methane production is small and insufficient to heat the reactor to more favorable mesophilic temperatures.

High-rate reactors based on highly selected biomass, such as UASB, are very fast to degrade hydrolyzed organic matter. They may need pre-treatment for suspended solids removal and careful startup operational procedures, seeming less well adjusted to a small-scale sewage treatment in temperate climate.

On the contrary, the AHF reactor is less sensitive to suspended solids concentration, appearing as a promissory technology for domestic wastewater treatment [56, 57].

This laboratory study evaluated the effect of media height and temperature on AHF reactor's performance, with the goal to understand the behavior of its effectiveness under varying conditions of OL, HRT, and temperature. Laboratory experiments with semi-continuous feeding and characterization studies of the interior of the reactor in terms of biomass concentration, biological activity, and physiology of the bacterial aggregates. Understanding the function of the biological bed at the top of the reactor and the underlying mechanisms was another of the main concerns of this study.

Laboratory tests took place over a period of about 4 years, covering various situations of organic loads, hydraulic regime, and operating temperature (15°C, 20°C, 25°C, and 35°C). In the final phase, the program carried out a simulation study of startup at 20°C temperature, without using any external inoculum.

2.2 *Effluent Characterization*

During the experimental period, 96 samples of domestic sewage fed the laboratory reactors. The physicochemical composition was quite variable, due to industrial wastewaters and to rainwater infiltrations in the municipal sewer grid. The average values and range of variation are presented in Table 2. The collected values indicate a "strong" effluent according to Metcalf and Eddy (1991) classification.

In general, the analyzed wastewater was quite concentrated with biodegradable organic material, which serves as food source for bacteria and other microorganisms, causing immediate and high BOD and COD. It also contains suspended solids, nitrogen, and oil and grease.

Table 2 Sewage composition

Characteristic	Average value	Range of value
Temperature (°C)	19	14–23
pH (units)	7.39	6.57–8.09
VSS (mg/L)	254	115–610
TSS (mg/L)	326	135–795
VS (mg/L)	426	132–769
TS (mg/L)	928	573–1,463
COD (mg/L)	788	187–2,740
COD_S (mg/L)	335	140–787
BOD (mg/L)	301	75–780
N (Kjeldhal) (mg/L)	67	24–104
P (Total) (mg/L)	48	20–76
Acetic acid (mg/L)	73	0–587
Propionic acid (mg/L)	15	4–32

The average suspended solid concentration is 300 mg/L and, although it is not globally very high, corresponds to a 0.25 VSS/COD ratio.

2.2.1 Materials and Methods

The chosen AHF reactors were provided with packing mediums placed on the top. Two laboratory AHF were used for the experiments, manufactured with transparent PVC pipes (110 mm outer diameter (OD) and 1,200 mm height). Their total volume of 10 L was partially filled with one and two packed medium layers. The packing medium was constituted by randomly placed small PVC pieces (50 mm OD and 50 mm length), forming a packed-bed height of 200 mm (Fig. 5). The basic idea was to use low-cost medium, obtainable from recycled pipes. The layers had a 100 mm spacing, to facilitate mass transfer, redistribute the flow, and economize media. They retain active biomass inside the interstices and perform solid/gas/liquid separation.

Four pipes placed laterally and equipped with a valve allowed to take samples at different points of the column. The first one was located near the bottom and the other were equally spaced at 200 mm interval.

Recirculation of heated water in an external jacket controlled the temperature of the reactor. A peristaltic pump fed the reactor, regulated according to the desired HRT.

The gas production was measured by a wet gas meter and its composition controlled by gas chromatography. The filters operated at a temperatures variable in the range from 15 to 35°C. All physical–chemical analysis followed the APHA Standard Methods (2005) [58].

2.2.2 Startup of Reactors and Reactor Operation

The anaerobic filter (AHF) with two layers of packed medium containing a dense flocculent *Methanothrix sp* biomass, previously used to treat dairy effluents,

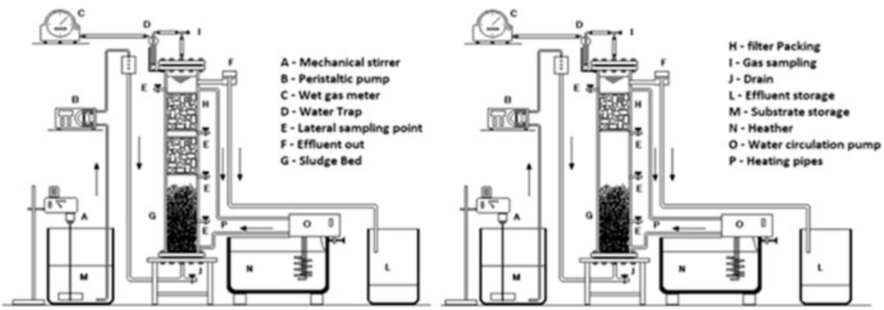


Fig. 5 Laboratory experimental setup

performed the initial laboratory experiments. The biological community revealed to be versatile and adapted to sewage composition without any problem. The acclimatization was immediate.

This reactor clogged after about 400 days of operation, making it impracticable to feed it regularly. The procedures used to unclog it, such as injection of pressurized sewage, backwashing, and draining the liquid through the side outlets, did not solve the problem. A compact non-removable sediment formed between the two packing modules. The reactor required disassembling and removal of the lower packing medium. Subsequently, it was cleaned and restarted with just one module of packing medium. The sludge removed from the bottom and between the two layers was used for inoculation. Although the sludge was kept on air for a few hours, the restart ran without observing any significant disturbance to the reactor performance. The biologic consortium removed all the oxygen absorbed and maintained the methanogens stable.

At the end of experimental period, a startup simulation with a new one-module reactor, without previous inoculation, at a temperature of 20°C, was tested. The objective was to assess if the reactor could startup spontaneously without seeding and to evaluate how long it would take.

2.3 Results

2.3.1 Startup Behavior

Figure 6 shows the evolution of biogas production during startup without seeding. At the beginning (fifth and sixth days), the system received overloading, due to failure of timer regulation, showing a peak of biogas production. Then the feed became regular and OL increased progressively, maintaining VFA buildup under

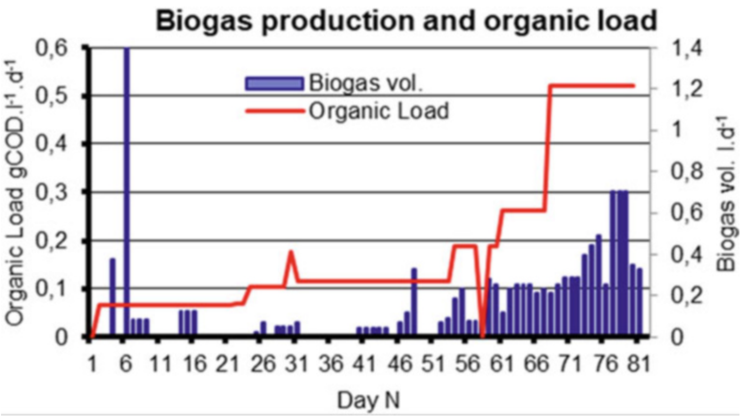


Fig. 6 Biogas volume production and organic load

control. After a lag phase of 50 days, the reactor increased biogas production, proportionally to the organic load, producing 0.6 L/day at OL of 1.24 g·COD·L^{-1}.

A specialized, stable, and efficient bacterial population was established. HRT lowered from 60 h to <12 h. The packing medium retained the natural bacteria in the sewage and allowed the development of a specific biological community. Biogas was quite rich in CH_4 (70–90%).

In the experiments, done at different temperatures with seeded reactors, the systems adapted quickly to the change of feedstock, performing regularly without appreciable transition when temperature decreased in steps (from 35 to 25°C; from 25 to 20°C; from 20 to 15°C).

2.3.2 COD and Suspended Solids Removal

Once acclimated, the reactors removed high concentrations of organic matter and suspended solids (TSS). Figure 7 shows the average efficiency of COD removal vs. OL during the studied period. The filter worked at HRT ranging from 60 h to about 10 h, with variable substrate concentrations and OL, ranging from 0.35 to 2.1 g·COD·L^{-1}·day^{-1}.

At 35°C and 25°C, the two-module reactor's efficiency was almost constant in all the range of organic load (>82%). At the lower temperature, a significant decrease of efficiency over the organic load occurred. At OL of 2 g·COD·L^{-1}·day^{-1} and 15°C, the filter's efficiency dropped to 73%, a significant reduction.

At 15°C, 20°C, and 25°C, COD removal efficiency of the one-module reactor depended on temperature and applied COD load.

The Fig. 8 shows the effect of temperature over the averaged efficiency of removal of COD, CODs, and TSS. Efficiency of the soluble COD refers to filtered samples of the effluent. The difference of this parameter to the COD shows the loss of efficiency due to suspended materials. The reactor with the higher temperatures

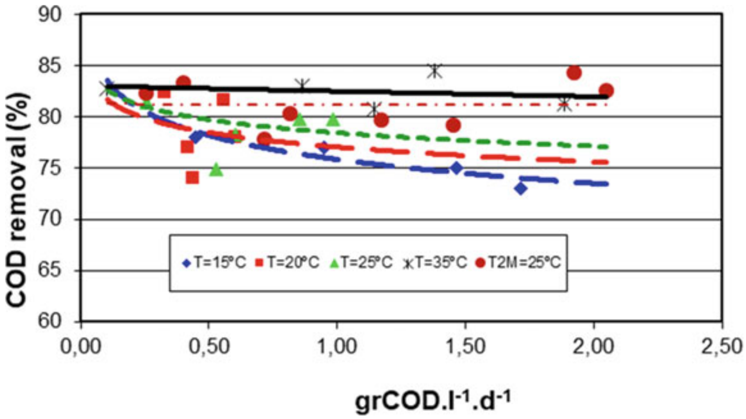


Fig. 7 COD removal efficiency vs. organic load

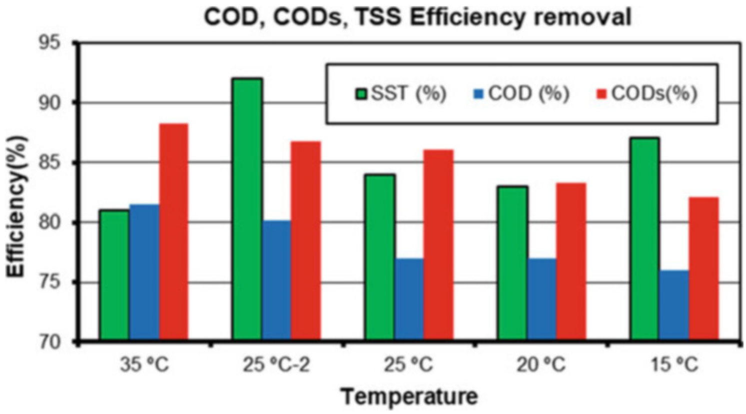


Fig. 8 Efficiency removal (COD, CODs, and TSS)

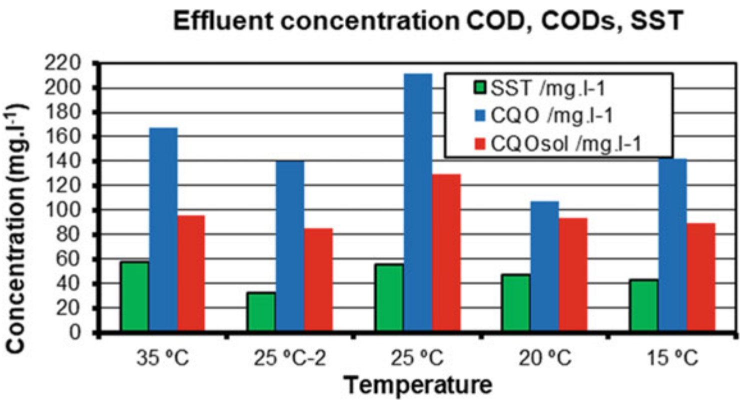


Fig. 9 Effluent concentration (COD, CODs, TSS)

(35°C) performed better, followed by the reactor with the two-packing media (25°C-2), which has 4% more efficiency than the filter with one-packing media at 25°C.

The averaged efficiency of organic removal in all the ranges was quite high, varying between 76 and 81.6%. The efficiency referred to the soluble COD varied between 82 and 88%. The removal of suspended material contributed to increase the system's efficiency more than 6%, making the effluent suitable to fulfill the discharge limits.

The total suspended solids (TSS) removal varied between 82 and 92% (Fig. 9). Once again, the best result occurred with the two-packing media reactor. The worst result occurred at higher temperatures (35°C), where the gas production is higher and capable to exacerbate flotation of suspended solids. In contrast, a good suspended solids removal occurred at lower temperature (15°C). In any case, the suspended solids removal in all reactors is very high (81–92%), proving the positive role of the filter. The TSS determination includes colloidal particles. The capability of the filter media to retain such particles seems quite good.

The behavior of the reactor with one-packing media layer shows a small difference (8%) in performance of TSS removal in relation to the system with two modules.

2.3.3 COD and Suspended Solids Concentrations

According to Fig. 9, the effluent has characteristics that comply with the values established for discharge into surface water, in terms of organic matter and suspended solids. The averaged effluent COD concentrations varied from 103 to 210 mg·COD·L^{-1}, depending on the temperature of the reactor. The suspended solids play a significant role in this context. The concentration of soluble COD (CODs) varied in a smaller range (between 83 and 127 mg·COD·L^{-1}). Those values were close to the minimum food concentration necessary to sustain the biological consortium [10].

Most of the soluble COD was below 125 mg/L, confirming that an additional treatment for suspended solids removal can be sufficient to guarantee the strict limits imposed by legislation. This result suggests the possibility of using coagulation/decantation or flotation in combination with the anaerobic filter to complete the treatment, without additional biological process.

The suspended solid losses found in the effluent varied between 35 and 59 mg/L, which confirms that the media has a good capacity to retain the colloids. The loss of suspended solids is higher at 35°C, in line with the gas production.

Comparing the performance of the reactors working at 25°C, the low efficiency of the two-layer reactor may be due to lower free space, which limited buoyancy forces mixing and energy from gas flotation. The double layer media reduced the loss of suspended material, as shown when comparing the TSS value in the reactor effluent at 25°C, but was responsible for the blockage of the reactor.

TSS concentration confirms the increased escape of solids related with temperature and gas production.

Figure 10 shows the influence of OL (between 0.35 and 2.1 g·COD·L^{-1}·day^{-1}) on COD concentration of the treated effluent in terms of COD. In all the studied temperature situations, the effluent output COD increased with the OL.

Hydraulic flows and biogas production were disturbing elements for the biological consortium in the filter, causing loss of cellular material and degrading the quality of the effluent. Based on the available elements, it is worth to highlight that the HRT, ranging from 48 h to about 10 h, did not noticeably influence the concentrations (no correlation was found) of the treated effluent in terms of COD, BOD_5; COD_S, and TSS.

Efficiency depended on the suspended solids washout, caused by the gas production, which is a more significant parameter than HRT.

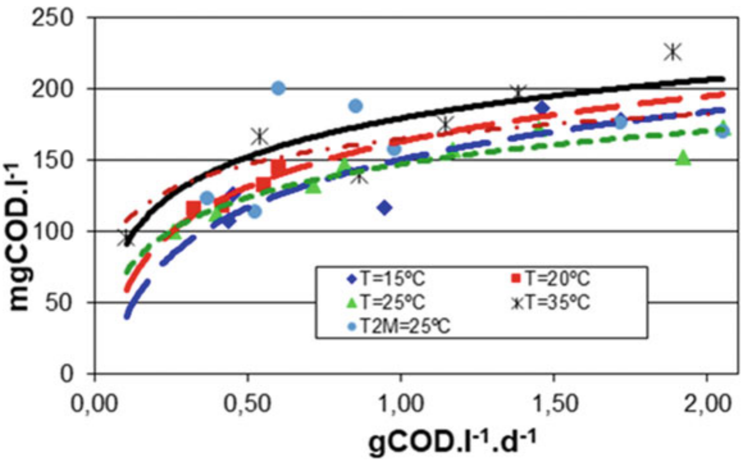


Fig. 10 Effects of organic load on COD

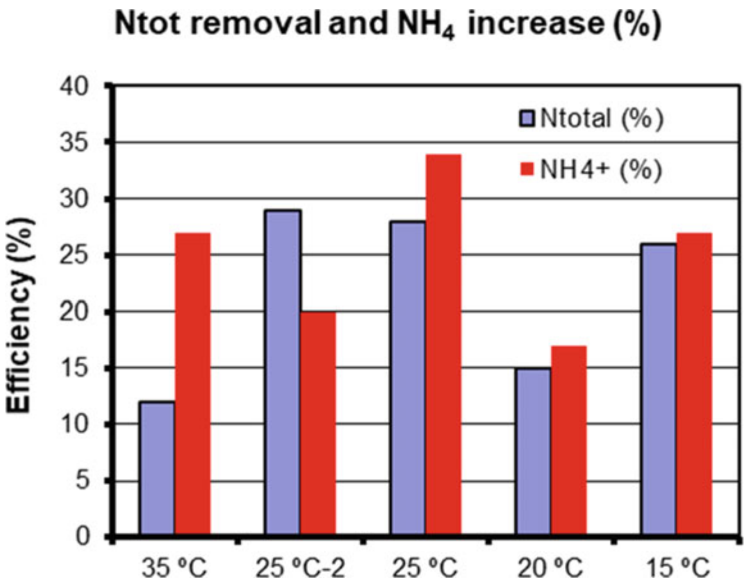


Fig. 11 Degradation of organic nitrogen and increase of ammonia

2.3.4 Removal of Nutrients

In terms of nutrients, the anaerobic process has a negligible total nitrogen removal. The degradation of proteins and amino acids causes a decrease in organic nitrogen (12–28%) and an increase in ammonia nitrogen (17–34%). In terms of phosphates, measured sporadically, no significant removal was recorded.

Figure 11 shows the averaged reduction of organic nitrogen and the corresponding increase of ammonia. The degradation of proteins proceeded reasonably.

2.3.5 System Stability

During the whole period of the experiment, the pH of the reactor effluent remained stable and was always higher than that of the influent. It always showed values slightly above neutrality, optimal for anaerobic digestion, with the average value equal to 7.68. The alkalinity of the sewage increased, due to ammonia release and CO_2 escape into the gas phase, indicating complete biodegradation of organic acids and balanced coexistence within acidogenic and methanogenic populations in the digester. No acidification of the medium and accumulation of volatile fatty acids (VFA) occurred. VFA values in the effluent were always extremely low or null. Most samples detected only acetic acid at low values (always <80 mg/L), which is favorable for the development of *Methanothrix archaea*.

2.3.6 Biogas Production and Characteristics

The production of biogas, which in certain situations reached 1.6 L/day, was quite variable according to the feed concentration and the organic load.

Temperature played an important role in the reactor's performance, affecting the hydrolysis of suspended compounds, biological degradation activity, and biogas production. At 35°C, the hydrolysis and AD degradation were maximum, providing higher biogas production. The organic suspended solids in the bottom and inside the media, which accumulated in the colder period, were degraded at 35°C, limiting accumulation of excess biological sludge and adding more biogas production, which increased the colloidal solids floated by the gas. These features negatively influenced the COD value, resulting in an average removal efficiency at 35°C lower than at other temperatures.

The methane production rate decreased with the temperature: from 0.18 $l \cdot g^{-1} \cdot$CODr, at 35°C, up to 0.03 $l \cdot g^{-1} \cdot$CODr at 15°C (Fig. 12). The stoichiometric theoretical value of the rate of production of CH_4 is 0.35 $l \cdot g^{-1} \cdot$CODr (at NTP, $T = 0°C$, $P = 1$ atm).

The low methane yield found in the experiments is due to the following:

- Loss of methane dissolved in the effluent, which depends on temperature and flowrate.

  The solubility of methane in water at low temperature increases from 0.0185 $mg \cdot CH_4 \cdot l^{-1}$ at 35°C to 0.0275 $mg \cdot CH_4 \cdot l^{-1}$ at 15°C. At HRT 12 h and 15°C, the loss of gases with the effluent corresponds to 0.55 $mg \cdot CH_4 \cdot l^{-1}$.

  Taking into account an effluent with COD 800 mg/L and 80% degradation rate, the methane available is 2.368 $l \cdot CH_4 \cdot g^{-1} \cdot$CODr. Practically 32% CH_4 is going out dissolved with the effluent at 15°C.
- COD consumption by the metabolism and growth of the population existing inside the reactor (8–15%).
- Accumulation of COD at low temperatures and successive hydrolysis contributes to the difference in CH_4 yield between 15°C and 35°C.

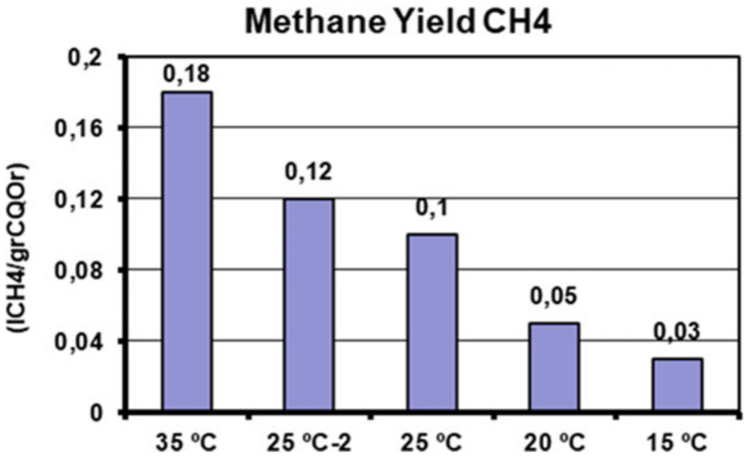


Fig. 12 Effect of temperature on methane yield

Table 3 Effect of organic load on methane yield

Organic load (g·COD·day^{-1})	Methane yield (L·CH4·g^{-1}·CODr)
0.16	0.07
0.4	0.08
0.61	0.11
0.7	0.14
1.2	0.21

Thus, this yield depends on the temperature, HRT, and the concentration of organic matter in the sewage. Methane yields increase linearly with the temperature (Fig. 12).

Table 3 shows the effect of organic load (OL) on methane yield.

Biogas had a remarkably high methane content (80–97%), due to displacement and absorption of CO_2 in the liquid phase for buffering the pH increase of the liquid. The loss of CO_2 dissolved in the effluent also contributes to reduce the CO_2 in the gas phase, since it is very soluble in water. The increase in pH during anaerobic digestion is due to the consumption of organic acids and to the release of ammonia nitrogen, from degraded amino acids. The organic load did not significantly influence the percentage of methane in the biogas, which is very high (always >80% in the different temperature ranges).

During the whole experiment, the concentration of H_2S in the biogas produced was below the detection limit of the chromatograph (>0.03%), indicating a low content of sulfates in the sewage. The presence of Hydrogen (H_2) in the biological gas was undetectable, confirming a continuous balance between the methanogenic and the acetogenic populations. The maintenance of a negative redox potential, inside the reactor (−290 mV) confirms the good performance of the biological communities.

2.3.7 Effect of the Packing Medium

The packed media ensures several important functions:

- Degassing of bacterial clusters by the contact of bacterial flocs with the medium.
- Flocculation of the settling floc when colliding with those that rise.
- Bacteria retention inside the medium, contributing to the treatment.
- Retention of colloids inside the medium, giving time to perform hydrolysis.
- Automatic purge from the reactor of excessive TSS dragged by the biogas.
- Self-control of clogging during 4 years of activity.
- No removal of excess sludge from the bottom during 4 years of activity.

The biological population in the media is rich in hydrolytic bacteria, enzymes, and hydrogenotrophic archaea, receiving low organic load metabolized in the bottom of the reactor.

For this reason, the packed medium works as a second active stage in the treatment of effluent with distinct microbial populations, and this mechanism may be the main advantage of this reactor, when applied in the treatment of relatively diluted effluents and with a significant content of suspended matter. The media retains suspended solids, provides opportunities for its hydrolysis, and prevents the accumulation of inert materials inside, washing them out when in excess. The AHF controls the concentration of suspended solids inside, as long as the medium is suitable for this purpose, and the gas flow is within certain limits.

However, in the case of effluents concentrated in organic matter, this mechanism may bring problems, since the high production of biogas can cause the complete washout of the reactor and consequent loss of active biological material.

In summary, there is a strong influence of packed media height, the number of modules, the reactor's geometric configuration, and gas production, on the behavior and performance of the reactor for a specific effluent.

Experiments have shown that AHF with one-packing module applied to sewage treatment with low packing medium height of 200 mm (20% of reactor volume) at 25°C, performed slightly lower (4%) than the system with two-packing modules. However, the one-packing module avoided reactor clogging. Increasing the packing medium height from 200 mm to 300 mm (30% of reactor volume) reduces the performance difference from the two-module reactor, without creating clogging problems. The use of two-packing modules, separated by 100 mm, proved to be an unfavorable option.

2.4 Reactor Characterization

Samples from the lateral outlet pipes for analytical determinations were taken regularly during the different steps of temperature. The parameters measured (COD, TSS, VSS, Nitrogen, VFA, and pH) indicated that the reactors were very stable. Most of the degradation work was carried out by the layer of sludge in the bottom of the reactor, having a height of about 200–300 mm, according to the reactor configuration. The highest percentage of acids disappeared before reaching the first side outlet (N1) of the reactor. The acetic acid, with the exception of a single sample, was always very low (< 100 mg/L). Only in one sample isobutyrate was detected with an extreme low content. The pH determinations along the column were alkaline, ranging from 7.1 to 7.8.

The profile of total COD shows that most of the reduction in organic matter (70–80%) occurs until the first lateral exit. The values determined in the remaining side outlets indicate the existence of small additional reduction of organic matter along the height of the filter COD. The community inside the filter media degrades the remaining (10–20%) COD. Consequently, the majority of acetoclastic activity occurs in the bottom. The CODs in the first lateral outlet was always below 300 mg/L.

The profiles of VSS show a thick layer of biomass at the bottom of the digester, which expands to the first outlet (N1) due to gas expansion. The concentrations of solids detected at N1 increase with OL and the period of operation of the filter. No high concentrations of suspended solids were detected in any other side outlets. This proves that bed expansion took place in the first part of the reactor. When clogging occurred at 25°C in outlet N3, a very high quantity of suspended solids was detected (67 $g{\cdot}TSS{\cdot}L^{-1}$).

The total organic nitrogen in the bottom varied between 1,100 and 1,500 $mg{\cdot}N{\cdot}L^{-1}$. This parameter is linked to proteins and provides information about biomass accumulation. It is presumed that the concentration of active microbial consortium may be around 7–10 g/L, in the sludge layer at the bottom of the reactor.

During the entire experimental period, the layer of biological sludge maintained a concentration variable between 20 and 80 $g{\cdot}TSS{\cdot}L^{-1}$, with a peak about 12% TS. The large variation is due to OL and the phase of expansion of the sludge bed. The active biomass varies between 12 and 30% of the total VSS at bottom.

Its degree of mineralization was low, since the organic matter content in relation to the total is large (60–70%). Over time the content of volatile solids in suspension has decreased in relation to TSS, which may be a sign of some accumulation of mineral materials (that has not evolved). During the 4 years of experiments, the concentration of TSS remained approximately constant, with the exception of the filter-clogging period. There is a very high increase in the COD of the sludge over time.

The percentage of VSS over TSS decreased with the time of operation, which suggests that there is a lower amount of bacterial biomass, but more specialized and/or an increase in the dissolution of organic suspended solids of the sewage, due to greater enzymatic activity. Estimating the value of bacterial biomass from organic nitrogen, it was confirmed that both, the total bacterial biomass and the relationship between cell biomass and suspended solids, increased in the final stage of the experiment, confirming the greater specialization of bacterial pools and increased enzymatic and hydrolysis activity of the suspended solids.

2.5 Methanogenic Activity

In order to understand the activity of the reactor samples of microbial sludge, from the bottom of the reactor (BS) and from inside the packing media (PMS) were collected. Acetotrophic Methanogenic activity tests were performed in all the samples, using the Mariotte methodology [59] with variable acetate concentrations and flasks with 130 mL capacity. Hydrogenotrophic methanogenic activity of PMS and BS was measured using the pressure transducer methods according to Colleran [58].

Tables 4 and 5 report the obtained values.

The bottom sludge (BS) shows good activity and varies with temperature. The flocs retained in the packed media performed greater activity (more 80%). According to VFA determinations, the acetate disappeared almost completely in the bottom of the reactor and no acetate from the feedstock is available in the packing media. The great acetotrophic activity can be attributed to the hydrolysis of suspended solids in the media and lipids, which slowly release LCFA in the bulk [58, 60], providing acetate to this microbial group.

The hydrogenotrophic methanogens activity obtained from the bottom sludge and from the packed media bed, revealed much higher values than the acetotrophic activity, in particular the PMS.

2.6 Bacterial Physiologies

Regular observations under the microscope of the various existing bacterial groups made it possible to verify the bacteria predominance of the genus *Methanothrix sp* in the reactor (Fig. 13), which, under conditions of low concentrations of acetic acid in the reactor, predominated over *Methanosarcina sp*, due to the greater affinity for the

Table 4 Hydrogenotrophic methanogenic activity

Methodology	Sludge	Temperature	Hydrogenotrophic methanogenic activity ($g \cdot COD \cdot CH_4 \cdot g^{-1} \cdot VSS \cdot day^{-1}$)
Pressure transducer	BS	35°C	0.578
Pressure transducer	PMS	35°C	0.618

Table 5 Acetotrophic methanogenic activity

Methodology	Sludge	Temperature	Acetotrophic methanogenic activity ($g \cdot COD \cdot CH_4 \cdot g^{-1} \cdot VSS \cdot day^{-1}$)
Mariotte flasks	PMS	35°C	0.201
Mariotte flasks	BS	35°C	0.160
Mariotte flasks	BS	25°C	0.129
Mariotte flasks	BS	15°C	0.072

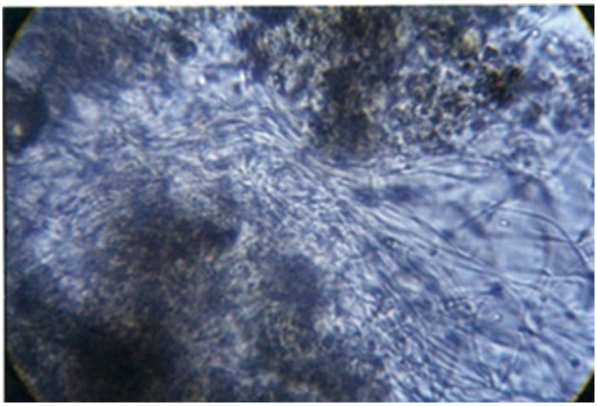


Fig. 13 Photograph of Methanothrix (optical ×1000)

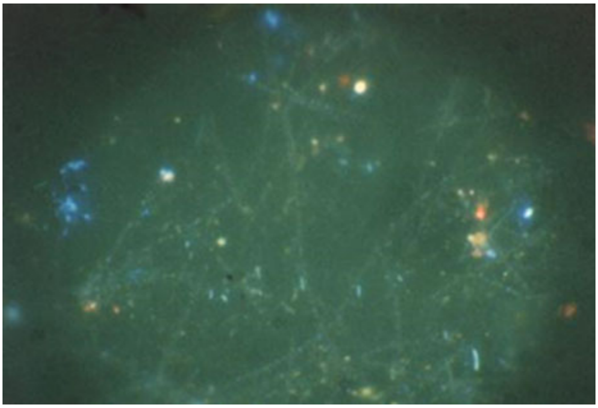


Fig. 14 Photograph of Archaea community (fluorescence 1,000×)

substrate. In fluorescence photography, other methanogenic bacteria such as "coccus" or "methanogenium" are also noted (Fig. 14).

2.7 Conclusion

The AHF with random medium layer is a suitable solution for the treatment of sewage, at temperatures ranging from 15 to 35°C, performing high degree of COD removal and obtaining values close to the lax limit for discharge in water body. It just needs a final polishing step for methane and suspended solids removal.

Two configurations of reactor have been tested. The reactor with two-module medium performed better (more 6% COD removal) than the one-module reactor, but clogged after 400 days of operation.

There is no significant influence of HRT on the concentrations of the treated effluent in terms of COD, BOD_5; COD_S, and TSS, within the studied range (from 48 to 12 h).

The height of the packing media (200 mm), corresponding to 20% of reactor volume, is not the best option, in terms of efficiency of removal. This media should be increased to 300 mm, in order to increase performance by 5–6%.

The media layer performs as a secondary biological stage. In the bottom grows active acetotrophic bacteria, removing 85% of the organic load in the first part of the reactor. In the top (inside the media), the filter bed retains colloidal solids, oil & grease and performs hydrolysis and hydrogenotrophic biodegradation.

The gas avoided clogging, removing the suspended solids accumulated and not degraded in the bed. The bed acts as a semipermeable membrane.

The filter can be suitable for all bacterial groups. The lipolysis activity (-β-oxidation) of the fatty long-chain organic acids is promoted by the hydrogen-producing bacteria, which are placed over the hydrogen-consuming bacteria in biofilm communities. A syntrophic association between those groups exists.

Additional advantages of hybrid reactor are that the biofilm exerts a favorable effect, avoiding the enzyme washout from the cellular wall, promoting fixed adherent bacteria that remain deposited over the TSS, which bond to cellulose favoring hydrolysis. For this reason, there is low accumulation degree.

The startup of the AHF for the treatment of sewage does not require addition of any inoculum. The media retention capability creates active flocculent biomass from the natural growing bacteria.

Due to all these specific characteristics, the AHF technology is suitable to treat small average size suspended solids and fats containing industrial effluents and sewage, where the capacity and care of operation are scarce.

The observed performance suggests that the AHF self-adjusts the concentration of suspended solids inside, as long as the medium is suitable for this purpose and the gas flow is within certain limits, a characteristic that is missing from the UASB.

The filter media can be optimized in terms of membrane performance, allowing adaptation and optimization of this technology to very specific effluent applications.

3 Case Study: WWTP Experimental AHF Treatment of Community Sewage

3.1 Plant Description

The opportunity to test a full-scale anaerobic treatment of sewage in subtropical climate emerged when a wastewater treatment plant (WWTP) of a community with a population of 7,500 inhabitants needed to recover its depuration system.

The original plant (constituted by an Imhoff tank, two trickling filters, and one settling tank) was severely damaged and out of operation, needing serious repairs.

This was an opportunity to make a full-scale experience using a combination of anaerobic hybrid filter followed by trickling filters.

The idea was to convert the original Imhoff tank, no longer in operation, into an AHF and build a second similar unit. The trickling filters, provided with stone bed, remained in operation. A second settling tank unit, built ex novo, was coupled to the existing unit to improve the performance. This way the capacity of the restored tanks plus the new units was adequate to hold on the actual sewage flowrate, achieve sludge stabilization, and fulfill parameters for discharge of the treated effluent on water bodies.

The new pre-treatment was inserted upstream the trickling filters. The following processes and operations constituted the WWTP:

1. Rainwater emergency discharge.
2. Coarse bar screening.
3. Sand and fat combined removal.
4. Anaerobic treatment with two AHF.
5. Trickling filter.
6. Clarifier/precipitation.
7. Effluent recirculation.
8. Secondary sludge pumping.
9. Sludge drying bed.
10. Maturation pond (second phase).

In the secondary settling tank, chemical products for phosphorus and suspended solids removal by chemical precipitation can be added when necessary. The final maturation lagoon serves to improve the treatment and reduce nutrients. The addition of this unit will be made in a second stage, after verifying the real performance of the new system. Figure 15 presents the flow diagram of this WWTP.

Due to its attractive characteristics, the anaerobic hybrid fixed-bed reactor (AHF) was selected for upgrading and performing the anaerobic treatment.

The new sewage pipeline (500 mm internal diameter) has a great capacity of transportation and the flowrate transported to the treatment plant is exceptionally variable in rainwater time. Table 6 summarizes the measured flowrate.

A very high hourly peak flowrate exists during the rain period and a big weir was placed at the inlet of the WWTP, to remove excessive flow rate, limiting the maximum flow to 155 m^3/h. The treatment sequence starts with a preliminary treatment, the screening of the coarser solids, dragged during the rains, which may harm the WWTP's structures.

The effluent from the screening goes to a "Parshall" type channel of critical regime, equipped with continuous measurement and recording instruments of the flowrate.

Then a combined grid chamber and oil & grease removal tank serves to prevent the entry of sand transported by rainy water that may clog the anaerobic filter. It also removes a great quantity of fats, discharged directly and periodically by homemade cheese producers. The fats can accumulate at the top of the AHF tank, affecting the performance of the biological community.

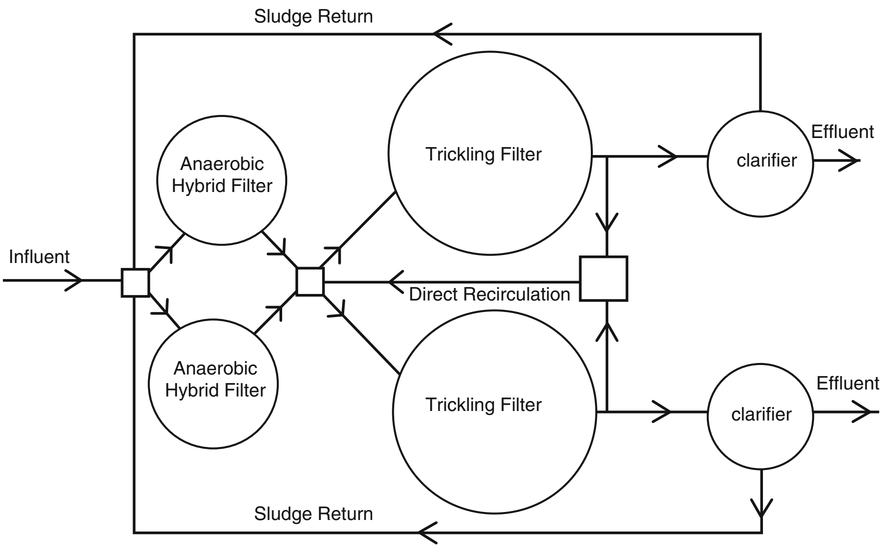


Fig. 15 Flow diagram of wastewater treatment plant

Table 6 Flowrates

Flowrate	Minimum	Average	Maximum
Average flowrate in raining time (m^3/day)	379	898	1,541
Average flowrate in dry time (m^3/day)	539	632	815
Peak flowrate (8 h) in rainy time (m^3/h)	---	50.95	154.4
Peak flowrate (8 h) in dry time (m^3/h)	---	29.6	127.8

Following the aforementioned preliminary operations, the sewage is directed to the anaerobic pre-treatment, which is carried out by two AHF working in parallel: the Imhoff tank, opportunely modified, and the anaerobic tank built ex novo with similar dimensions. The expected modifications for the existing Imhoff tank concern the change of the inlet, placed at the bottom of the digestion compartment of this tank, to create the up-flow movement and operate similarly to a AHF system.

The filling material was made of plastic material, placed randomly on the upper part of the tanks. On top of the cover of these tanks, plastic membranes collect the produced biogas, eventually usable in a small electrical energy motor generator for lighting the WWTP, according to the amount produced.

The effluent from the anaerobic pre-treatment goes to the secondary treatment. The two existing percolating beds, with 16 m diameter, work in parallel, providing aerobic degradation. The existing stone beds were the filling medium. The bed of stones is not as effective as the plastic material but reduces the capital cost investment. In this case, having an anaerobic pre-treatment that performs a good reduction of organic matter, the efficiency achievable by the stone bed was considered sufficient. The percolating filters were provided with a recirculation system to control the degree of purification.

The effluent from the trickling filters was directed to two sedimentation tanks: one obtained by cleaning and adapting the existing unit, and the second, working in parallel with the first one, built ex novo.

The system has a sludge return line, which pumps the secondary sludge into the anaerobic pre-treatment in order to be digested.

Finally, eight new conventional drying beds proceed to dry the excess digested sludge from the AHF.

3.2 *Objectives*

The main objective for the anaerobic pre-treatment was to reduce at least 60% of the organic load. This improves the effluent quality and reduce the recirculation rate of the tricking filters. It was presumed that the trickling filters, by receiving a lower organic load could also perform some nitrification/denitrification. Additional objectives for the project were the reduction of electricity consumption, minimization of capital investment, and reduction of operation and maintenance costs for wastewater and sludge treatment/disposal.

The final project goals were to setup a robust, easy to operate, low energy consumption plant that generated an effluent capable to fulfill at least the lax standard for discharge in water body. Table 7 lists the parameters for discharge, fixed by the legislation, for population between 10,000 and 100,000 inhabitants. In this case, being the population less than the minimum, the observation of the strict legislation may be not mandatory.

The reactors operate in the psychrophilic temperature range of 14–16°C in winter (December to March) and 22–24°C in summer (May to July).

This section reports the results of the full-scale operational experience of the hybrid anaerobic hybrid filter technology over a period of 2 years.

Table 7 Legal discharge parameters limit parameters for the WWTP

Parameter	Lax legislation	Strict legislation
COD	150	125
BOD_5	40	25
TSS	60	35
Nt	–	15
Pt	–	2

3.3 Full-Scale Performance of the AHF System

3.3.1 Technical Description

After the laboratory experience, two up-flow full-scale anaerobic hybrid fixed-film reactors (495 m^3 capacity and 10 m diameter) were built in a small municipality for demonstration purposes.

The anaerobic reactors have a cylindrical shape and conical bottom. In the center, a concentric central chamber receives and distributes the industrial effluent in the bottom of the reactor. Several pipes placed radially in the bottom provide a good distribution of the effluent, and promote upward spiral flow. In the tank, the packing medium is placed in the top and occupies a height of 1.4 m (¼ of the reactor's volume). It is constituted by randomly distributed plastic pieces similar to PP Aquatec trickling filter media FPM-500 (187 mm diameter and 51 mm long).

This media has quite a high specific surface area, high void fraction, large clear passage diameter, and good resistance to plugging or clogging. It has low-cost per surface area, offers good mechanical strength, is lightweight, and easy to keep.

The tanks were fabricated in reinforced concrete and formally designed for 24-h average HRT in dry season, 10-h HRT in wet season, and 6-h HRT in peak occurrence. The organic load varied between 0.8 and 5.3 $kg \cdot COD \cdot m^{-3}$ day^{-1}. The tanks have the following geometric characteristics: 10 m diameter, 4.65 m liquid height, and a 2 m conical bottom height.

The details of the tank shape are presented in Fig. 16.

The photographs in Figs. 17, 18, and 19 were taken from the final AHF reactor facilities.

3.3.2 Startup of the System

Startup conditions for the full-scale reactor are quite different than those observed in laboratory, regarding the operational parameters control. At full scale, uncontrollable variations of temperature and flowrate determined changes in the reactors' performance.

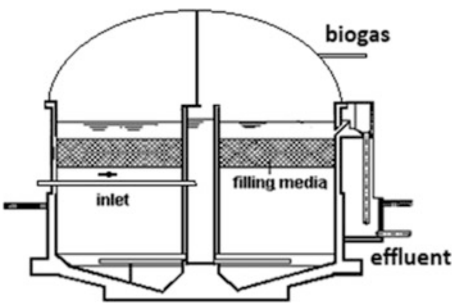


Fig. 16 Anaerobic hybrid filter (AHF) schematic

Fig. 17 Photograph of reactor view

Fig. 18 Photograph of tickling filter view

At the end of June, the system started-up without using inoculum to take advantage of the favorable temperature (24°C). Initially, the reactors were completely filled with sewage and received a progressively higher rate, starting from 100 m^3/day, until the entire flowrate. During the starting period, the reactors

Fig. 19 Photograph of filling medium

received a daily variable flowrate from 500 to 1800 m^3/day, due to rainwater infiltration.

The sewage conveyed periodically enormous quantity of oil and grease that clogged the skimmer, obliging to stop the feed and to manually remove oil and grease. This problem was frequent until the separator was modified to be able to laterally slice the grease. After such modification, it was possible to run the plant continuously.

During the startup period, the physical–chemical parameters were controlled twice: one at the first month after startup and another at the seventh month, end of the startup. In the first period (3 months) the recirculation system was not in operation.

Figures 20 and 21 show the concentrations of COD and TSS of the sewage, at the exit of the AHF and at the exit of the treatment plant (in the beginning and the end of the startup). The values are close to the limits defined by the lax legislation. Figures 22 and 23 show the efficiency of COD and TSS removal.

These values suggest the following:

- The startup was very fast. At the end of the first month the AHF was already in good operation. The major removal occurred in the AHF (CODr = 52%).
- The trickling filter, without recirculation, obtained low removal rate (CODr = 23.4%).
- The recirculation system (100% of flowrate) significantly improved the efficiency of the trickling filter (up to 38.9%).

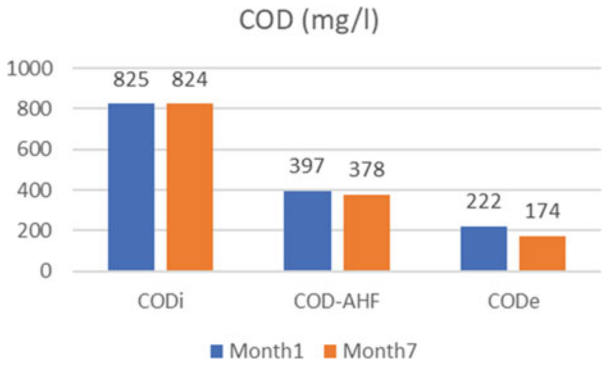


Fig. 20 Case study AHF results – COD concentration

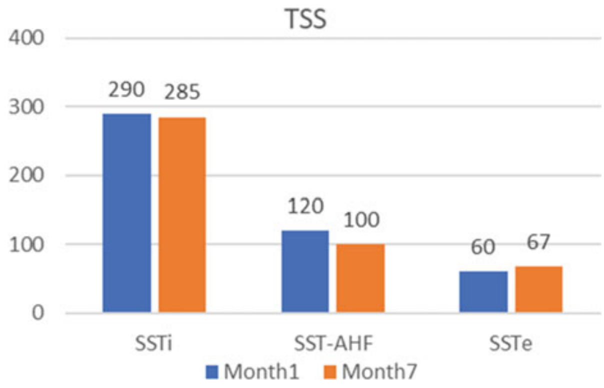


Fig. 21 Case study AHF results – TSS concentration

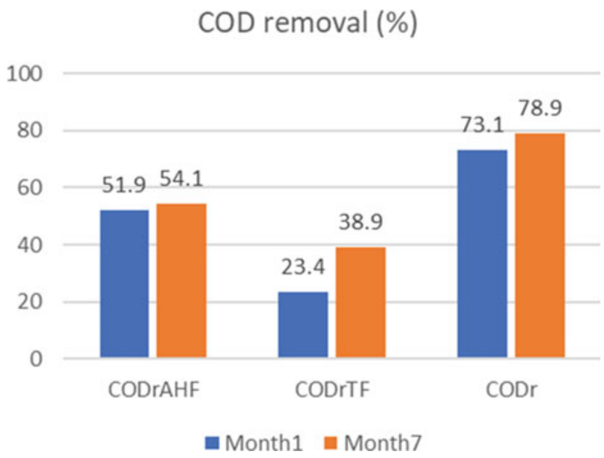
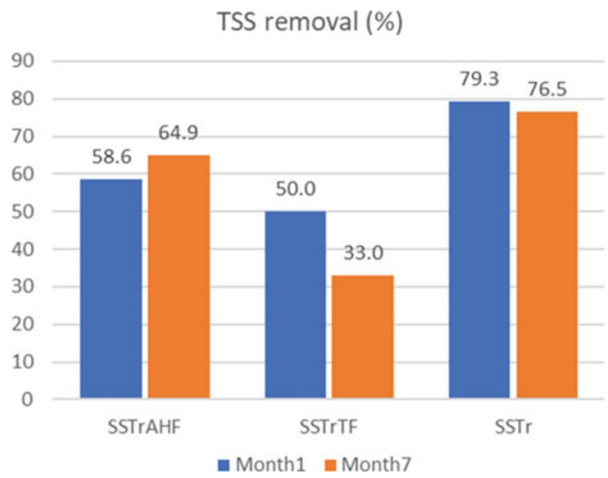


Fig. 22 Case study AHF results – COD removal

Fig. 23 Case study AHF results – TSS removal



- The biodegradability of the effluent after the anaerobic pre-treatment was poor for the trickling filter, creating biofilm in short time.
- The global COD rate reach 78.1%, an interesting value, but not very high.

The natural bacterial population of the sewage acclimated to the environment of the tank. The biologic flocs settled and thickened in the bottom and became anaerobic. After 1 month, a microbial population like *Methanothrix sp*. grew in the bottom of the digester. The non-obligate anaerobic bacteria initially present in the sewage created the necessary environmental conditions for the predominance of the anaerobes.

The trickling filter shows a low growth rate of the aerobic biofilm. The stones bed was not covered with the biofilm after 6 months, indicating poor availability of degradable organics.

3.4 WWTP Performance: Results and Discussion

The gas meters were not assembled on time and no data on gas production were recorded. After the startup period, the plant was monitored monthly, according to the environmental legislation. The data available cover a period of 2 years and report the concentration of the main parameters.

Figure 24 shows the value of COD in the inlet and outlet streams of the wastewater treatment plant. Due to the rainwater infiltration and cheese making wastewater, there is a large COD variability of at the inlet. At the outlet, the COD (excluding some days) shows value that are close or lower than the limits fixed by legislation.

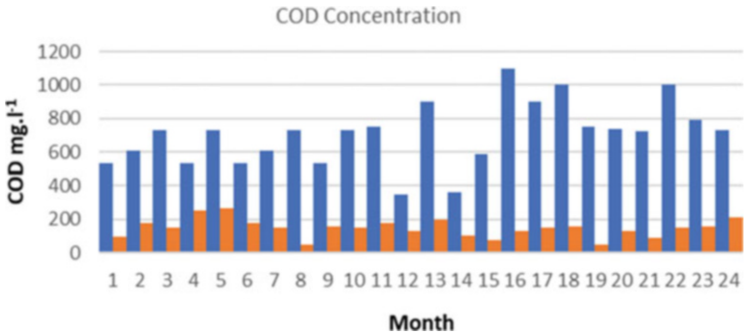


Fig. 24 WWTP COD concentration on inlet and outlet

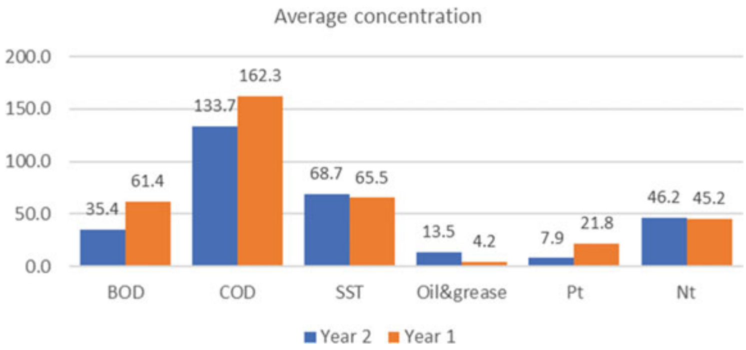


Fig. 25 WWTP average concentration of several parameters

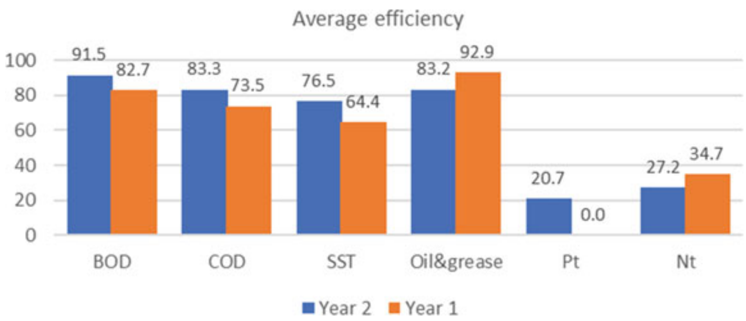


Fig. 26 WWTP average efficiency removal of several parameters

Figure 25 shows the average yearly concentrations of the relevant parameters. The BOD, COD, and TSS concentrations fulfill the lax legislation. The nutrient (Nt and Pt) and oil and grease are quite high and need further treatment.

Figure 26 shows the average efficiency of removal of several parameters. The COD removal rate in the second year was more than 83%, indicating improvements in the performance. The BOD and oil and grease are also high. The removal of phosphorus is low and insufficient to reach the environmental limits.

The removal of nitrogen reveals an interesting value, possibly due to nitrification/denitrification, as well as ammonia stripping in the trickling filters. Unfortunately, these removal rates are not sufficient to satisfy the strict standard.

pH control: During the startup and the monitoring period, the pH of effluent varied between 7.1 and 8.3, a favorable range of values.

Bacterial acclimatization: The performance of the system reveals very good bacterial acclimation and formation of flocculent type bacterial population, able to self-control the internal pH.

Volatile Fatty Acids (VFA): The organic acid in the effluent digester, after the commissioning period, decreased continuously reaching values lower than 50 mg/L, which are compatible with the development of *Methanothrix sp*., the desired bacterial population.

Biogas production: The full-scale reactors produced biogas containing 89% methane (similar to obtained in the laboratory tests) and 206 ppm of hydrogen sulfide (H_2S).

3.5 Economic Performance

The anaerobic reactor is simple, does not have complex mechanical equipment, and did not add significant additional operation and maintenance costs in the wastewater treatment system, performed by the existing staff.

The electricity consumption of the process concerns the recirculation pumping (1.0 kW) and the pumping of the secondary sludge to the AHF (1.2 kW). The electricity expenditure in these operations is 30 kWh/day, corresponding to 11,000 kWh/year.

The removal of organic matter using an activated sludge process would require at least 240 kWh/day for aeration and recirculation, corresponding to about 87,600 kWh/year.

The anaerobic process allowed electricity savings of about 76,600 kWh/year, corresponding to 114,900 EUR/year, by reducing the energy requirements in comparison with an AS system. Based on the above data, the expected payback of the plant is about 8 years.

3.6 Discussion and Conclusions

The anaerobic hybrid filter proved to be an effective and robust technology, capable to startup easily, and performing stably even in adverse flowrate conditions at variable temperatures. The experience confirmed the feasibility of reactor startup without using any inoculum, avoiding transportation of external sludge.

The AHF self-adapted to variable concentrations and flow regimes, ensuring high organic removal efficiency (estimated >58%). It enabled stable operational conditions in the subsequent trickling filter, which worked with very low organic loads.

Full-scale performance of the AHF was lower than the predicted by laboratory experiments due to the variable temperature and flowrate.

The tricking filter allowed increasing overall efficiency to more than 85%, fulfilling the parameters established in the lax legislation. The trickling filter removed about 35–40% of COD, a value lower than expected. The filter does not receive the easily biodegradable compounds, already degraded in the AHF, not facilitating the growth of active biofilms.

Otherwise, the trickling filter performed 27–35% of nitrogen removal, an encouraging result. The nitrification/denitrification process in the trickling filter can perform better by adjusting the recirculation rate. Another possible solution to increase the efficiency of the trickling filters is to put them working in series instead of parallel. This improves the performance and removes more nutrients. This layout changes require some adaptation work but is feasible (Fig. 27).

In conclusion, the obtained performance of the AHF and trickling filter allowed concentrations of the pollutants (TSS, BOD, COD) from the entire WWTP that meet the lax environmental limits, and with a small improvement, can reach the strict legislation. In terms of nutrients, chemical precipitation can remove and recover the phosphorus. In terms of nitrogen, the trickling filter can be optimized in order to improve nitrification/denitrification.

The electric energy spent is very low (about 30 kWh/day), corresponding to the amount necessary to oxidize aerobically the COD unremoved by the anaerobic step.

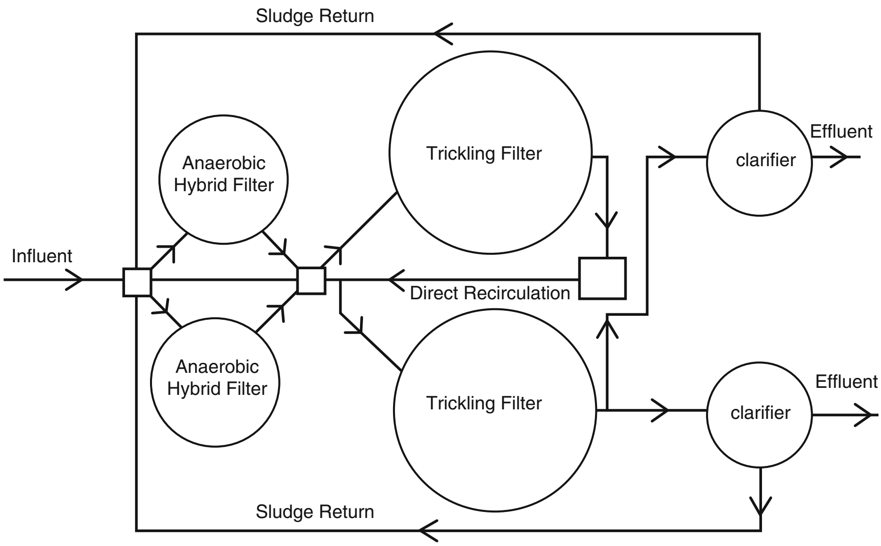


Fig. 27 Layout of the plan with trickling filters working in series

Acknowledgments The author thank Eng.[a] Monica Alexandra Valente Di Berardino for the precious contribution and support in writing and compilation of the present work.

References

1. McCarty PL (1985) Historical trends in the treatment of dilute wastewaters. In: Proceedings of the seminar/workshop on anaerobic treatment of sewage, Amherst, USA
2. Jewell WJ (1987) Anaerobic sewage treatment. Environ Sci Technol 21:14–21
3. Young JC, McCarty PL (1969) The anaerobic filter for waste treatment. J Water Pollut Control Fed 41:R160–R173
4. Lettinga G, van Velsen AFM, Hobma SW, de Zeeuw W, Klapwijk A (1980) Use of the upflow sludge blanket (USB) reactor concept for biological wastewater treatment, especially for anaerobic treatment. Biotechnol Bioeng 22(4):699–734
5. Lettinga G, ZEEUW DEE, others (1982) Anaerobic treatment of sewage and low strength waste waters
6. Hulshoff Pol LW, Euler H, Eitner A, Grohganz D (1997) GTZ sectoral project, promotion of anaerobic technology for the treatment of municipal and industrial sewage and wastes. In: Noike T et al (eds) Proc. of the 8th intl. conf. on anaerobic digestion, Sendai, Japan, vol 2. IAWQ, Sendai, pp 285–293
7. Bouwer EJ, Rittmann BE, McCarty PL (1981) Anaerobic degradation of halogenated 1- and 2-carbon organic compounds. Environ Sci Technol 15(5):596–599
8. Tchobanoglus G, Burton F, Stensel HD (2003) Wastewater engineering: treatment and reuse. Am Water Works Assoc J 95:201
9. Rittmann BE, McCarty PL (1980) Model of steady-state-biofilm kinetics. Biotechnol Bioeng 22:2343–2357
10. Rittmann BE, Baskin DE (1985) Theoretical and modelling aspects of anaerobic treatment of sewage. In: Proceedings of the seminar/workshop on anaerobic treatment of sewage
11. Demirel B, Yenigun O, Onay TT (2005) Anaerobic treatment of dairy wastewaters: a review. Process Biochem 40(7):2583–2595
12. Kushwaha JP, Srivastava VC, Mall ID (2011) An overview of various technologies for the treatment of dairy wastewaters. Crit Rev Food Sci Nutr 51(4):442–452
13. Collivignarelli C, Urbini G, Farneti A, Bassetti A, Barbaresi U (1990) Anaerobic-aerobic treatment of municipal wastewaters with full-scale upflow anaerobic sludge blanket and attached biofilm reactors. Water Sci Technol 22(1):475–482
14. De Sousa JT, Foresti E (1996) Domestic sewage treatment in an upflow anaerobic sludge blanket - sequencing batch reactor system. Water Sci Technol 33:73–84
15. Chernicharo CAL (2006) Post-treatment options for the anaerobic treatment of domestic wastewater. Rev Environ Sci Biotechnol 5(2):73–92
16. Strous M, Van Gerven E, Zheng P, Kuenen JG, Jetten MSM (1997) Ammonium removal from concentrated waste streams with the anaerobic ammonium oxidation (anammox) process in different reactor configurations. Water Res 31(8):1955–1962
17. Jetten MSM, Horn SJ, Van Loosdrecht MCM (1997) Towards a more sustainable municipal wastewater treatment system. Water Sci Technol 35:171–180
18. Liao PB, Mayo RD (1974) Intensified fish culture combining water reconditioning with pollution abatement. Aquaculture 3(2):61–85
19. Singh KS, Harada H, Viraraghavan T (1996) Low-strength wastewater treatment by a UASB reactor. Bioresour Technol 55:187–194
20. Agrawal LK, Ohashi Y, Mochida E, Okui H, Ueki Y, Harada H, Ohashi A (1997) Treatment of raw sewage in a temperate climate using a UASB reactor and the hanging sponge cubes process. Water Sci Technol 36:433–440

21. Seghezzo L, Zeeman G, Van Lier JB, Hamelers HVM, Lettinga G (1998) A review: the anaerobic treatment of sewage in UASB and EGSB reactors. Bioresour Technol 65(9):175–190
22. Lim SJ, Kim T-H (2014) Applicability and trends of anaerobic granular sludge treatment processes. Biomass Bioenergy 60:189–202
23. Latif MA, Ghufran R, Wahid ZA, Ahmad A (2011) Integrated application of upflow anaerobic sludge blanket reactor for the treatment of wastewaters. Water Res 45(10):4683–4699
24. Noyola A (1994) Diseño, inoculación y arranque de reactores UASB. In: Memorias del III Taller y seminario Latinoamericano de Tratamiento anaerobio de aguas residuales. Universidad de la República, Montevideo, Uruguay
25. Hulshoff Pol LW (1989) The phenomenon of anaerobic sludge. Wageningen Agricultural University, Wageneningen
26. Sam-Soon PALNS (1989) Pelletization in the upflow anaerobic sludge bed (UASB) reactor. University of Cape Town, p 271
27. Stronach SM, Rudd T, Lester JN (2011) Anaerobic digestion processes in industrial wastewater treatment, vol 2. Springer, pp 59–62
28. De Zeeuw WJ (1985) Acclimatization of anaerobic sludge for UASB reactor start-up. Wageningen University and Research
29. Kwong TS, Fang HHP (1996) Anaerobic degradation of cornstarch in wastewater in two upflow reactors. J Environ Eng 122:9–17
30. De Baere L, Verstraete W (1982) Can the recent innovations in anaerobic digestion of wastewater be implemented in anaerobic sludge stabilization. In: Recycling international–recovery of energy and material from residues and waste symposium
31. Angelidaki I, Ahring BK (1992) Effects of free long-chain fatty acids on thermophilic anaerobic digestion. Appl Microbiol Biotechnol 37(9):808–812
32. Hanaki K, Matsuo T, Nagase M (1981) Mechanism of inhibition caused by long-chain fatty acids in anaerobic digestion process. Biotechnol Bioeng 23(7):1591–1610
33. Cammarota MC, Teixeira GA, Freire DMG (2001) Enzymatic pre-hydrolysis and anaerobic degradation of wastewaters with high fat contents. Biotechnol Lett 23:1591–1595
34. Cirne DG, Paloumet X, Björnsson L, Alves MM, Mattiasson B (2007) Anaerobic digestion of lipid-rich waste-effects of lipid concentration. Renew Energy 32(5):965–975
35. Pereira MA, Sousa DZ, Mota M, Alves MM (2004) Mineralization of LCFA associated with anaerobic sludge: kinetics, enhancement of methanogenic activity, and effect of VFA. Biotechnol Bioeng 88:502–511
36. Vidal G, Carvalho A, Méndez R, Lema JM (2000) Influence of the content in fats and proteins on the anaerobic biodegradability of dairy wastewaters. Bioresour Technol 74(9):231–239
37. Dahab MF, Young JC (1982) Retention and distribution of biological solids in fixed-bed anaerobic filters
38. Bonastre N, Paris JM (1989) Survey of laboratory, pilot, and industrial anaerobic filter installations. Process Biochem 24:15–20
39. Young JC, Yang BS (1989) Design considerations for full-scale anaerobic filters. Res J Water Pollut Control Fed 61:1576–1587
40. Song KH, Young JC (1986) Media design factors for fixed-bed filters. J Water Pollut Control Fed 58:115–121
41. Maxham JV, Wakamiya W (1980) Innovative biological wastewater treatment technologies applied to the treatment of biomass gasification wastewater. In: Proceedings of the 35th industrial waste conference, May 13-15 1980, at Purdue University, Lafayette, Indiana, USA
42. Tilche A, Vieira SMM (1991) Discussion report on reactor design of anaerobic filters and sludge bed reactors. Water Sci Technol 24:193–206
43. Kennedy KJ, Gorur SS, Elliott CA, Andras E, Guiot SR (1989) Media effects on performance of anaerobic hybrid reactors. Water Res 23(11):1397–1405
44. Oleszkiewicz JA, Thadani VJ (1988) Effects of biofilter media on the performance of anaerobic hybrid reactors. Environ Technol 9:89–100

45. Frostell B (1981) Anaerobic treatment in a sludge bed system compared with a filter system. J Water Pollut Control Fed 53:216–222
46. Elmitwalli T, Zeeman G, Lettinga G (2001) Anaerobic treatment of domestic sewage at low temperature. Water Sci Technol 44(8):33–40
47. Van Lier JB, Rebac S, Lettinga G (1997) High-rate anaerobic wastewater treatment under psychrophilic and thermophilic conditions. Water Sci Technol 35:199–206
48. Dague RR, Banik GC, Ellis TG (1998) Anaerobic sequencing batch reactor treatment of dilute wastewater at psychrophilic temperatures. Water Environ Res 70(3):155–160
49. Elmitwalli TA, Zandvoort MH, Zeeman G, Burning H, Lettinga G (1999) Low temperature treatment of domestic sewage in upflow anaerobic sludge blanket and anaerobic hybrid reactors. Water Sci Technol 39:177–185
50. Lettinga G, Roersma R, Grin P (1983) Anaerobic treatment of raw domestic sewage at ambient temperatures using a granular bed UASB reactor. Biotechnol Bioeng 25(7):1701–1723
51. Vieira SMM, Souza ME (1987) Development of technology for the use of the UASB reactor in domestic sewage treatment. Water Sci Technol 18:109–121
52. Seghezzo L, Castaneda M, Trupiano A, Gonzáles S, Guerra R, Torrea A, Cuevas C, Zeeman G, Lettinga G (2000) Anaerobic treatment of pre-settled sewage in UASB reactors in subtropical regions (Salta, Argentina). In: Preprints, VI Latin-American workshop and seminar on anaerobic digestion
53. Lew B, Tarre S, Belavski M, Green M (2004) UASB reactor for domestic wastewater treatment at low temperatures: a comparison between a classical UASB and hybrid UASB-filter reactor. Water Sci Technol 49(6):295–301
54. Lettinga G (1996) Sustainable integrated biological wastewater treatment. Water Sci Technol 33:85–98
55. Yu H, Tay JH, Wilson F (1997) A sustainable municipal wastewater treatment process for tropical and subtropical regions in developing countries. Water Sci Technol 35:191–198
56. Di Berardino S, Bersi R, Converti A, Rovatti M (1997) Starting-up an anaerobic hybrid filter for the fermentation of wastewater from food industry. Bioprocess Eng 16:65–70
57. Henze M, Harremoes P (1983) Anaerobic treatment of wastewater in fixed film reactors - a literature review. Water Sci Technol 15(8):1–101
58. Colleran E, Concannon F, Golden T, Geoghegan F, Crumlish B, Killilea E, Henry M, Coates J (1992) Use of methanogenic activity tests to characterize anaerobic sludges, screen for anaerobic biodegradability and determine toxicity thresholds against individual anaerobic trophic. Water Sci Technol 25(4):31–40
59. Soto M, Méndez R, Lema JM (1993) Methanogenic and non-methanogenic activity tests. Theoretical basis and experimental set up. Water Res 27(8):1361–1376
60. Kim SH, Han SK, Shin HS (2003) Two-phase anaerobic treatment system for fat-containing wastewater. J Chem Technol Biotechnol 79(12):63–71

Impact of Combined Sewer Overflows Events on Recipient Water Quality

M. Sokáč and Y. Velísková

Contents

Abstract This chapter analyses the impacts of discontinuous pollution sources on the water quality of receiving water bodies and offers the possibility to solve such type of water management problem by numerical modelling way. Typical examples of such pollution sources are the combined sewer overflows (CSOs), but generally also different types of storm water management in urban areas. There were designed and performed numerical simulations for four feasible alternatives of storm sewer management (different mixing ratio, different size of storm tanks) in the town Banská Bystrica at the Hron River (Slovak republic). The model MIKE11 was used for numerical simulations of water quality. Results of each modelled

M. Sokáč (✉) and Y. Velísková
Institute of Hydrology, Slovak Academy of Sciences, Bratislava, Slovak Republic
e-mail: sokac@uh.savba.sk

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 241–272, DOI 10.1007/698_2021_782,

alternatives were analysed. Simulation was performed in two alternatives – for Q_a and Q_{355}, whereas Q_a is the yearly average discharge and Q_{355} is a discharge, which exceeded 355 days in a year. Results of the study show practical implications and impacts on the receiving water body quality depending on the type of the storm water management.

Keywords Denitrification, Deoxygenation, Deterministic, Nitrification, Quality simulation, Stochastic

1 Introduction

Water is considered one of the most precious natural resources. Its availability and quality determine the conditions of the existence of life on the Earth. It is a component of each living organism and one of the major factors influencing the biological diversity on the entire planet. The relationship between human and this natural resource, the ways of using it, methods of water resources management and the extent of understanding the negative impacts on the environment characterize the complete approach of mankind in regard to the environment [1].

For this reason, the European Commission (EC), European Parliament (EP) and the Council of Ministers agreed in 1995 on the necessity of a fundamental reform of the European water policy [2]. At the beginning of this process, in 1996, a water policy report of the commission was issued. EC since the beginning has been careful to ensure that this policy has evolved and formed in an open process involving all stakeholders. Consequently, during the years 1997 and 1998, a Water Framework Directive proposal was created, which went through an approval process in the years 1999–2000. It has been adopted as an official document entitled Directive 2000/60/EC of the European Parliament and the Council of 23 October 2000 establishing a framework for Community action in the field of water policy [3], later amended by the EWQSD [4].

In contrast with the previous legislation protecting individual categories of water, this Directive regulates all the categories of water in Europe. The accepted Directive formulates the goal to accomplish and maintain a good status of water bodies during a defined period of time. The criteria defining the good status of groundwater include requirements related to quantity and quality, whereas the status of the surface water will be assessed mainly by the ecological quality. A systematic monitoring of the quantity and quality of water is required as a tool for planning and monitoring the success of the taken measures [5].

The Directive advocates a combined approach to reduce water pollution by introducing emission standards, simultaneously sets the immission goals and in individual cases, it is required to adhere to more rigorous concept. The pollutant concentrations are defined by subsidiary directives. It is assumed that the hazardous substances will be eliminated from water using special mechanisms. As before, water will be protected particularly for drinking purposes.

The protection of water bodies against their pollution by wastewater has an extraordinary significance in Slovak Republic (SR). Currently, in this context, some aspects of the historical evolution of wastewater disposal and liquidation are causing serious environmental problems. For the design of sewerage networks, large river basins and generous prognosis for development and population growth were generally used. Combined sewer overflow structures (CSOs) and storm water tanks served as simple measures to reduce the runoff especially in cases of overloaded parts of the sewer network. CSOs located on combined sewer systems were usually designed to fulfil the mixing ratio criterion, without considering the pollution concentration. In other words, the traditional approach dwells on the principle to protect the human from nature. Increased sensitivity to the protection of nature and dissemination of ecological approaches contributed to different views at the natural streams and to the introduction of new concepts of draining the cities. Today, new and opposite opinions and requirements on environmental protection of the nature from humans prevail.

For this reason, this study is dedicated to the protection of natural streams from the pollution entering the streams via combined sewer systems. The study investigates the impact of the sewer systems and their structures on the natural streams by using simulation model of runoff from qualitative and quantitative points of view.

2 Mathematical and Numerical Models

Practically every quantitative and qualitative analysis of a problem can be called a model. In general, it is the same in the case of hydrologic and hydrodynamic models simulating, for instance, rainfall-runoff process or changes of water quality in a catchment.

Generally, models used in hydrology or hydrodynamics are divided into:

- Physical,
- Mathematical.

Both types of models make efforts to simulate the reality by achieving higher or lower levels of complexity. Physical models emulate the reality while maintaining the physical principles of modelling similarities such as scale and hydraulic similarity. Instead of that, mathematical models describe the reality – the modelled phenomenon – through the system of mathematical equations striving to give a true picture of the phenomenon core by identifying the causes and consequences. These models are more economic than the physical models and lend themselves to a widespread utilization in scientific and technical fields. This study is oriented toward the work with mathematical (numerical and simulation) models.

Mathematical model is a system of equations approximating the reality by including description of relationships among the individual components of the modelled phenomenon.

Numerical model is a numerical representation of the mathematical model, i.e., mathematical model solution by the application of numerical methods. Physical characteristics have the numerical values. Numerical model comprises also algorithms necessary for numerical solution of mathematical relationships defined in mathematical model.

Simulation model is an application of numerical model in the computer (software tool). The requirement of simulation model accuracy is always satisfactory only to a certain extent, i.e., only with a certain error, because the simulation of the phenomenon is usually realized by a pre-selected approximation of the reality with respect to the numerical model and the physical nature of the modelled problem.

From the current point of view, hydrologic and hydrodynamic models should represent a complex of quantitative and qualitative processes, such as intensity and the amount of precipitation, rainfall-runoff process in an urban area, flow rates and water quality as well as complete hydrological and quantitative forecasts, which all are represented by certain mathematical relations applied in the computer [6].

According to the base of mathematical apparatus, models can be split into:

- linear–nonlinear,
- stochastic–deterministic,
- static–dynamic.

Linear models use linear differential equations. Similarly, nonlinear models use equations describing reality through nonlinear differential equations.

Stochastic models are based on statistical analysis of a long-term time series of monitored parameters. They focus on the consequence instead of on the cause of the phenomenon. Their application is therefore suitable for modelling and generating long-term prediction, especially in case of phenomenon which is not quite known or is very complicated. Their drawback is certain limitation of their validity, occasionally complete uselessness, in case of any change in the catchment or modelled system.

Deterministic model defines and determines the impacts of exact causes (changes expected in the future; for example, changes of parameters in the catchment). The majority of existing rainfall–runoff models are deterministic models. Their advantage is the ability to simulate impacts of the changes in the catchment (for example, land use and land development).

At present time, increasing rate attention is paid to the combined stochastic–deterministic models.

Static models presume steady state of a phenomenon, i.e., input data and parameters do not change with time (usually do not contain members like $\partial/\partial t$, i.e., time derivatives of parameters). Whereas dynamic models assume unsteady condition, i.e., the model inputs and outputs vary over time.

Modelled area of hydrologic and hydrodynamic model is a time–space part of environment area where the simulation of quantity and quality of water is performed. There are several types of simulations from time point of view:

- simulation of runoff and quality during short-term events (isolated events such as strong storms and acute toxic spill emergencies while transporting chemicals),
- simulation of runoff and quality during a long-term period (long-term continuous simulation; for example, long-term runoff, transport and storage of strongly contaminated pollutants such as heavy metals and eutrophication),
- simulation of isolated events, extracted from the long-term period (isolated events selected from the long-term time series observations using certain characteristics, such as floods, ecological emergencies and low flow conditions).

At the concept level it is necessary to specify the problem as well as to define the goals, time range of the model and on that basis choose the model, necessary input data and the means.

From the spatial point of view, the selection of modelling area is a similar task, since the range of the area of interest should be clear at the conceptual stage. It needs to be emphasized that the following has to be taken into account while selecting the modelled area:

- select an area where the initial boundary conditions can be clearly defined (inflow, outflow, lateral influent streams, amount and quality).
- select an area covered by sufficient geometric data (cross-section profiles, stream alignment and pathway).
- take into account the flow direction and condition, pollution transport to the outside, but also into the modelled area.
- select an area where modelled processes will show fully in the spatial and time scale of the model (e.g., oxygen insufficiency or eutrophication).
- consider whether we have sufficient information about the flow condition in the stream parts (roughness coefficients), respectively, about kinetics of physical, chemical and biological processes in the stream (coefficients of dispersion, reaeration and deoxygenation).

To satisfy the complexity of modelling as well as practical purposes, the model area is often chosen as an integral part of the catchment.

2.1 Modelling of Quantity and Water Quality of Surface Streams

Over the last decades, models of water quantity and quality in watercourses have become an important tool in water management [7]. These models can be used to solve a lot of water related problems, such as prediction of discharges in streams, regulation of water resources as well as water quality predictions in open channels and reservoirs. The advantage of the mathematical simulation modelling dwells in relatively economic and non-demanding technology in contrast with physical models. The fact that this kind of simulation models find their place also in cases where detailed or long-term observations do not exist is a great advantage as well.

Currently, complex models are being more frequently used for emphasizing a necessity of an integrated approach in solving tasks associated with water management in sub-catchments and basins as a whole.

A wide array of models is offered, but each one is fitting different modelling and application conditions. So, it is necessary to be careful while selecting the best suited model as each product has own limitations of application. Simultaneously, another problem emerges – calibration and data acquisition. Once the model has been selected appropriately and calibration has been completed, such a tool becomes irreplaceable for regulating or assessing various specific situations in the catchments and open channels, rivers and streams.

Hydrodynamic modelling of flow discharges in rivers or a river network is an essential condition for water quality modelling in them. It is based on the same principles as the flow modelling in the sewer network. However, there are differences between the flow modelling in the sewer network and in the river, network resulting from the different nature of the basin and the hydraulic system of the riverbeds or sewers. The catchments differ usually in size and hydrologic characteristics, time of response and dynamics of runoff. River or open channel flow and flow through sewer network have different hydraulic characteristics. Rivers are usually described with naturally irregular (non-prismatic) shape of cross-section profiles, free surface flow conditions (under atmospheric pressure), with the structures placed in the streams regulating flow and consequently, impacting the hydraulic performance of the stream and runoff from catchment.

The goal of water quality modelling is to produce a distribution of water quality parameters over time and space. They lend themselves to a wide application of water quality studies and assessments of changes in the stream. Various approaches can be used for modelling the quality of water in a stream. In case of modelling long-term predictions, it is advisable to use a stochastic model based on statistical analyses of long-term observation of time series of monitored water quality indicators. This type of model is suitable for long-term evaluation of trends in water quality changes, as well as determination of the probability of occurrence of certain concentrations or concentration dependence on various parameters (e.g., precipitation, temperature and flow rate) [8]. Deterministic models instead are being used in cases of modelling the changes in the catchment (the changes should be well defined) or in cases of analysing existing conditions. Hydrodynamic approach is useful for prediction of impact of watercourse flow condition changes. In this case it is necessary to take into account just hydrodynamic parameters of the watercourse and impact of different singularities influencing its flow conditions (e.g., weirs, inflows and their type of inlet, various barriers, etc.).

Nowadays, several complex models of hydrological, hydrodynamic and chemical processes in surface waters or throughout the basin are available. These complex models very often contain a hydrological rainfall–runoff sub-model followed by a water quality model.

They treat a wide array of phenomena influencing the water quality and include parameters controlling kinetics of the processes. Popular models of this type are simulation models QUAL2, MIKE 11 and MIKE 21. These models have the capacity to model all crucial phenomena occurring in the streams as:

- degradation of organic matter,
- photosynthesis,
- respiration,
- nitrification,
- denitrification,
- oxygen atmosphere exchange,
- sedimentation and resuspension of sediments,
- presence of underwater vegetation,
- circulation of nutrients,
- sorption and desorption of metals.

These models can be used for modelling water quality alterations as a result of pollutant inflow from point sources and non-point sources as well.

2.2 Methods Used for Evaluating the Effect of Wastewater on the Receiving Water

The Slovak Republic Legislation currently uses to check and permit the CSO discharges the emission principle (method), which is based on the so-called mixing ratio. Alternatively, for large sewer networks, the limited number of CSO events is allowed [9]. Some methods being in practice abroad are based on a given amount of CSO volume, eventually a given mass of pollutants as a function of the drainage area (for example, the amount of CSO total volume in m^3 from 1 ha of drainage area per year, kg of BOD_5 for 1 ha per year). One of them is, for example, ATV A 128 [10].

Advantage of the emission method for appraisal and permission of CSO discharge is its simplicity and clarity. Conversely, this approach disregards the recipient and water quality (neither in the recipient nor in the discharged water).

The second method is the immission method. This method is known from the foreign literature and also legislation and takes into account CSO discharge and its impacts on the recipient. Complex British manual UPM [11], German regulations BWK ([12, 13] or Austrian regulation Regelblatt 19 ÖWAV [14] illustrates examples of the aforementioned method. The principle of these regulations is complex monitoring of water quality and documentation of the impacts of wastewater discharge, as well as extensive modelling studies for justified cases.

Fundamental approach while assessing the impact of wastewater requires to maintain the desiderative water quality in the recipient as a function of its usage (drinking water, irrigation water, fish protection and recreation purposes) [15]. It is required that the qualitative indicators of surface water are preserved. This is expressed through the water status (ecological, chemical). Assessment of chemical water status is based on monitoring of chemical indicators of surface waters, such as oxygen concentration and concentration of ammoniacal pollution (NH_3-N). These parameters may have a significant impact on the general ecological status of the surface water as they can remarkably impact the biological indicators of the water quality (for example, occurrence of fish and invertebrate). For that reason, the so-called IDF (intensity–duration–frequency) curves are often used as ancillary criteria expressing the surface water pollutant load at the considered concentration and exposure time for the selected frequency. These IDF curves are then compared to LC_n curves, where n is the degree of organism mortality at a given lethal concentration (LC). Typical example is comparison of ammoniacal concentration (NH_3-N) dependence on pH and water temperature in the recipient for the values of LC_{50} (50% mortality of fish at a given concentration and exposition of pollution).

This approach of assessing the impact of CSO discharge on the recipient assumes the implementation of the most advanced techniques. It includes an estimate of impact on the recipient using rainfall–runoff models and models of water quality in open channels, eventually modelling of processes at a wastewater treatment plant (WWTP).

This kind of complex approach is often unrealistic, considering the amount of input data (the data either do not exist or they are unavailable), models prices, insufficient experience with handling the software and modelling processes and problems related to the calibration and verification of the model (verification even of the most trivial model requires a vast amount of field work).

Nevertheless, it is obvious that the demonstration of meeting or not meeting the required criteria or limits is possible only via direct and continuous field measurement or mathematical modelling. Despite of all difficulties and problems mentioned above, the immission method of assessment of CSO discharges is applicable. Question is how to apply it under conditions where mathematical models already exist, but the necessary data (database) is missing.

3 Case Study Banská Bystrica: Hron River

3.1 Overall Goals of the Study

A case study for the Banská Bystrica town (BB) was prepared to solve the problems concerning the protection of recipients from an instant release of large quantities of CSO discharges. The main objective of this study was analysis of the impact of CSO discharges on the recipient – the Hron River – under different scenarios of storm events using the guidelines of current engineering practice and the legislation of the Slovak Republic.

The first part of the study was to set up the simulation model of storm water runoff from the urbanized area through the sewer system of the Banská Bystrica town. This model is set up to handle four alternatives of central detention of storm water–mixing ratio 1:4 and 1:8 and two alternatives of storm water tanks connected with the CSOs. The runoff was simulated using the rainfall–runoff model MOUSE [16].

The second part of this study was the creation of the model to simulate the flow rates and water quality in the Hron River. The model MIKE 11 [17] was used for this task. Geographically, the Hron River from river kilometre 261.300 (Valkovňa) down to the mouth (river kilometre 0.000) was modelled, e.g., almost the entire length of the Hron River with the exception of a short segment at the source.

It is important to mention that for both models, the data necessary for modelling were insufficient. Therefore, we adopted the missing data from the literature, manuals and recommendations of the software author, respectively (DHI), especially when modelling the water quality in the recipient – the Hron River. For the model we did not have enough information, for example, about the values of the coefficients of river bed roughness, but mainly data on the kinetics of physical, chemical and biological processes in the river (coefficients of dispersion, reaeration and deoxygenation). However, the most serious problem is the lack of monitoring data – water quality indicators in the tributaries of the Hron River (only few of tributaries are regularly monitored; e.g., the Čierny Hron, the Bystrica, the Slatina and the Sikenica stream). However, this is a much more complex problem and it ultimately concerns all Slovak streams.

The third part of the study was a simulation of surge inflow of the pollutant into the recipient from the sewer network through the CSOs. It was beneficially that both models come from the same software developer as they are compatible and collaborate well. Therefore, it was possible to seamlessly use the outputs from one model as inputs to the other model, i.e., the result files from the rainfall–runoff model of modelled urbanized area and calculated flow rates in the sewer network were used as an input into the water quality model of the Hron River.

For the assessment of point source pollution in the Hron River, two scenarios were considered. Simulations of long-term discharges (Q_a – average annual flow rate in the Hron River as well as in all of the tributaries) and the discharges approaching the low flow conditions – 355-day flow rate Q_{355}. First scenario (Q_a) uses average values of pollution indexes. The second alternative (Q_{355}) uses values c_{90} – 90% quantiles of the worst-case scenario concentrations of individual indexes of water quality. The input data was extracted from the Annual Report on Water Quality [18].

3.2 *Runoff Modelling from the Urban Catchment of the Banská Bystrica Town*

In this part of the study, the results of previous studies performed on the sewer network of the Banská Bystrica town were used. They covered the investigation of the volumes and discharges of extraneous water in the sewer network, analyses of proposed sewer network project as well as assessment of the General Proposal of draining the Banská Bystrica town.

The Banská Bystrica town operates a combined sewer system conveying both storm and sanitary wastewater into one central WWTP located downstream of the town and near the Hron River. In the town itself, a combined sewer system is built; however, some parts of the town are drained by a storm water system discharging the storm water directly into the recipient (the Hron River or local recipients). The new town development areas, eventually the municipalities located nearby are drained by a sanitary sewer system.

The total length of the simulated sewer network (main sewer line, collectors and the street sewers) is 146.893 km long. The length of the main collector is approximately 10.16 km with the diameter of 1,000–1,800 mm.

As an input for the model of sewer network digitalized maps were used. Digital map was used as for localization of nodes and segments of the sewer network, as well as for interactive editing of sewer catchment data (covering partial areas of the sewer lines) and automatic calculation of the area, runoff coefficients and other hydrologic parameters. The surface of parts of urbanized areas are described as impervious (roofs and roads) and pervious (for example, green areas). The impervious surfaces were defined as closed polygons and they were automatically stored in the database, as well as the other boundary of sewer network parts – elementary catchment areas.

The program is checking the data accuracy using the user visual check of the geographical data and numerical check of the data – minimum and maximum data limits as well as the logical data check. Automatic check of topology data is also carried out.

Complete database of the sewer network input was then transferred by a built-in routine into the simulation model MOUSE [16].

The main data of the simulated sewer network of the Banská Bystrica town are shown in Table 1.

Table 1 The main data of the simulated sewer network of the Banská Bystrica town

Data item	Units	Value
Total drainage area of the urban catchment	Hectares	1,209.367
Total reduced drainage area of the catchment	Hectares	302.68
Average runoff coefficient	–	0.25
Number of elementary catchments	–	963
Minimum ground elevation (WWTP)	Meters above sea level	319.5
Maximum ground elevation	Meters above sea level	495.0
Number of inhabitants	–	84,919
Number of nodes (manholes)	–	1,288
Number of CSOs	–	29
Minimum pipe bottom elevation (WWTP)	Meters above sea level	318.0
Maximum pipe bottom elevation	Meters above sea level	492.90
Number of outfalls from sewer network	–	25
Number of sections (pipes) of sewer network	–	1,291
Length of sewers	Kilometres	146.893
Volume of sewers	m^3	50,789

The difference in ground elevations between the centre town and outskirt town parts is more than 160 m.

The modelling was performed using block rainfalls with constant intensity of various frequencies and durations from 15 to 180 min.

3.3 Water Quality Modelling in the Receiving Hron River

The goal of this impact study was the assessment of short-term changes in water quality of the Hron River as a result of a point source pollution from the CSO spills. For that reason, the study focused on the simulation of the water quality in the Hron River. Since the detailed information on water quality (daily observations) was missing, two model scenarios were used, as it was mentioned above, namely:

1. Q_{355} flow rate; 90% statistically determined quantiles of the worst-case scenario of concentrations of individual water quality parameters (c_{90}) were attributed to this flow rate (these values approximately correspond to a summer season, including temperature).
2. Q_a (average annual flow rate); statistically determined yearly averages of individual water quality parameters were attributed to this flow rate (temperatures for this case approximately correspond to the spring and fall seasons).

Average annual concentrations of point source pollutants were considered for all tributaries (Fig. 1).

Geographically, we focused on the reach of the Hron River beginning at the river km 261.000 (profile Valkovňa) down to the river mouth (river km 0.000). This modelled area can be defined by initial and boundary conditions (inflow, outflow, lateral tributaries and water quality data). Geometric data such as cross-sections

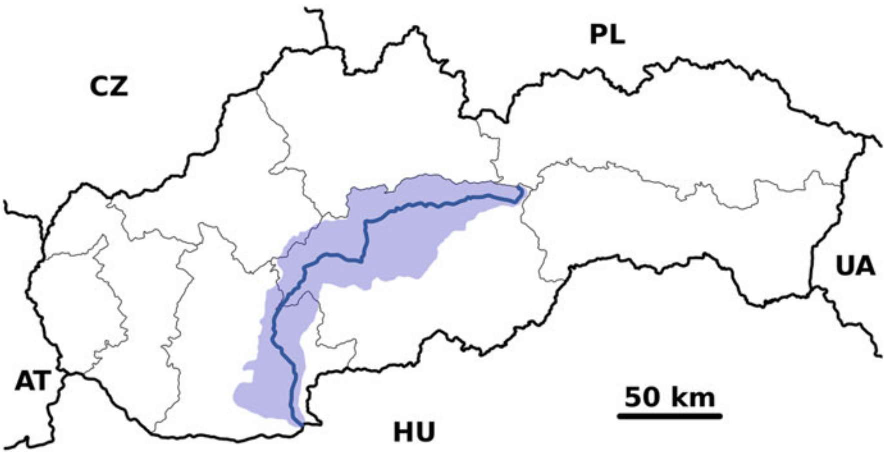


Fig. 1 Modelled area of the Hron river

profiles and longitudinal profiles of this area were also available. The modelled part of the Hron river covers almost the whole river, so the modelled processes are clearly visible over the time and space scale of the model (for example, oxygen regime of the river).

Besides the geometric characteristics of the river (topology), the initial and boundary conditions had to be defined as they determine the model results and its behaviour. Correctly defined initial and boundary conditions (geometry and topology) and correctly calibrated model are able to simulate the modelled system behaviour under various conditions (by changing the initial and boundary conditions); for example, under increased flow rates or pollution loads. Therefore, the initial and boundary conditions are often taken into account in the literature as a kind of "input data".

Initial conditions are defined as conditions at the beginning of the calculation of the modelling system; e.g., at the time $t = 0$. Model allows using the zero value of the flow rate using as initial condition, but this value created some problems during simulations. Therefore, the constant flow rate was entered into the model as an initial condition, which was approximately equal to the inflow into the modelled area. The initial instability and fluctuation of the computed values were removed by this way.

Mathematically, the calculation is impossible without defining the boundary conditions at the modelled area boundary. For the beginnings of the main river, as well as for all the tributary sections, the boundary condition represents the entrance to the modelled area. Therefore, at the beginning of the modelled area, the river km 261.300, the hydraulic boundary condition was Q_{355} and Q_a, the values we entered for both alternatives mentioned before. The second boundary condition at this point, the water level, was computed by the model automatically using the Manning's equation for steady uniform flow [19].

Since the goal of this study was the modelling of water quality as well, it was necessary to provide the initial concentrations of pollutants entering the modelled area. A definition was needed for each state variable that is considered in the quality model for simulation. We used the c_{90} values. Data were entered on the basis of the water quality monitoring at the cross-section profile Valkovňa (river km 261.300).

Other necessary input data for the model includes all lateral inflows (tributaries) into the modelled area – flow rates, as well the water quality parameters. The model encompasses data from approximately 130 tributaries of the Hron River with the flow rate bigger than 0.1 $m^3.s^{-1}$ (100 $l.s^{-1}$). The flow rates were determined from the hydrological monitoring data, the missing data were estimated utilizing the hydrologic catchment balance.

The determination of the qualitative parameters of the Hron River tributaries was a much more difficult task. The qualitative parameters monitored at given locations published in the Annual Report on water quality [18] were used, the remaining data were determined from the water quality balance of the Hron River. The pollution data from municipal and industrial WWTPs, as well as all other pollution point sources (domestic, industrial, agricultural sectors) were also required.

At this point it is appropriate to mention that our model did not take into account the infiltration (nor exfiltration) of groundwater into or from the Hron River, which may affect the water quality and quantity in the river immensely.

The downstream border of the modelled area ($x = L$, river km 0.000) requires the definition of the boundary conditions as well. Our model defines the lower boundary condition by a constant water level. At this location, the water quality parameters were needed, too. These concentrations are unknown and from the user point of view, actually represent the result of the simulation. Therefore, this boundary condition is defined as an "open boundary condition", based on the mass balance and assumption of steady concentration in the downstream boundary of the modelled area.

Hydrodynamic module is a fundamental computational block necessary to run other computational modules. The module simulates unsteady flow in the rivers and their mouths using the method of finite elements following an implicit computational scheme. The simulation was not using any simplified simulation assumptions and the complete dynamic equation was used, e.g., unsteady non-uniform flow was simulated.

The river bed horizontal alignment was defined in the graphical editor of the model MIKE 11 [17]. Digitalized maps at a scale 1:50,000 [20] served as a background map layer. All singularities of the stream bed, such as tributaries, lateral and other inflow and outflow points, eventually other structures built in the river, were also identified. The tributaries, entered only schematically, were modelled on the length of approximately 500 m. All lateral inflows were connected to the main branch of the Hron River. By this way, the model topology was established.

Stationing of the river bed was adopted from the water resources map 1:50,000 [21]. The model allows the user to directly specify the river at individual points. The stationing of the intermediate locations was computed through automatic interpolation between the stationed points.

Cross-section profiles at given computational points were coded using a set of coordinates (width, depth and the water surface elevation). Information from the study by Mišík [22], in which cross-section profiles as well as longitudinal alignment of the Hron River are generalized, was used. Intermediate points were interpolated by the model in between two neighbouring cross-section profiles. These data are used to compute the bottom slope of individual modelled sections.

The input into the model covered also other hydrodynamic parameters, such as hydraulic resistance of the river bed, e.g., coefficients of roughness. The values by Mišík [22] were used again. The remaining input data were either not specified (effect of wind, hydraulic resistance of the floodplain bottom, etc.) or set at the values recommended by the software manual (weight and relaxation coefficients, convergence factors and number of iterations) or by literature [23].

The model was calibrated based on quantitative and qualitative monitoring values of the Hron River. For the model calibration, we changed the flow rates, coefficients and parameters of the model to achieve the best match between model results and monitored values. As mentioned above, the calibration was performed for two alternatives: low flow conditions Q_{355} with the corresponding values of pollution concentration (c_{355}, eventually c_{90}) and for the annual average flow rate Q_a with the concentrations being consistent with the average pollution concentrations (c_a).

3.4 CSO Spills Modelling

For simulation of the runoff (CSO spills) the model MOUSE [16] was used. The original intention of the whole modelling study was to use a real 28-year series of rainfall data from the station Sliač, but the necessary time for modelling exceeded our possibilities. Instead, we reached out to a substitute solution – we used statistical block rains (constant intensity) with the probability of 0.033, 0.1, 0.2, 0.5, 1.0, 5.0 and duration of 15, 30, 60 and 180 min.

For the runoff simulation from the catchment of the Banská Bystrica town through the sewer network, we used the following sewer network set-up scenarios:

1. Dilution (mixing) ratio 1:4 (minimum according to the Slovak Republic legislation).
2. Dilution (mixing) ratio 1:8 (maximum according to the Slovak Republic legislation).
3. Rain tank to store CSO discharges at frequency $p = 0.5$.
4. Rain tank to store CSO discharges of the frequency $p = 5$.

Selection of individual scenarios followed the current legislation of the Slovak Republic, namely the Government Regulation No. 296/2005 Col. [9], completed by the government regulation No. 167/2015 Col. [24]. These regulations are addressing the whole problematic of wastewater discharge in a complex way; therefore, the requirements for discharges of wastewater from CSOs into surface waters are also included in the Regulation.

The fundamental criterion for wastewater discharge from CSOs is defined as a ratio between the wastewater average daily flow discharge and the storm water runoff. As a basic, mixing ratio was selected 1:4. The State authority has the power to set the mixing ratio up to 1:8, especially in the regions with highly protected surface waters. For large sewer networks with numerous CSO structures, it is required to limit the number of CSO events; they should not exceed 15 events, while the travel time (concentration time) is equal or larger than 15 min and 20 events if the travel time is shorter [9]. The goal is to transport part of the wastewater according to the mixing ratio to the WWTP and treat it at the primary stage of the WWTP (pre-treatment) prior to entering the receiving water ([25, 26]. In cases when the capacity of the mechanical treatment at the WWTP is lower than the discharge flowing into the WWTP during the storm event, it is necessary to construct a storm water tank (connected with the CSO prior to the WWTP) to control the flow rate entering the WWTP.

In the first and second alternative we did not simulate the accumulation of wastewater in the storm water tank. The CSO structures at the ratio 1:4 (1:8, respectively) were considered only. The model is schematically shown in Fig. 2.

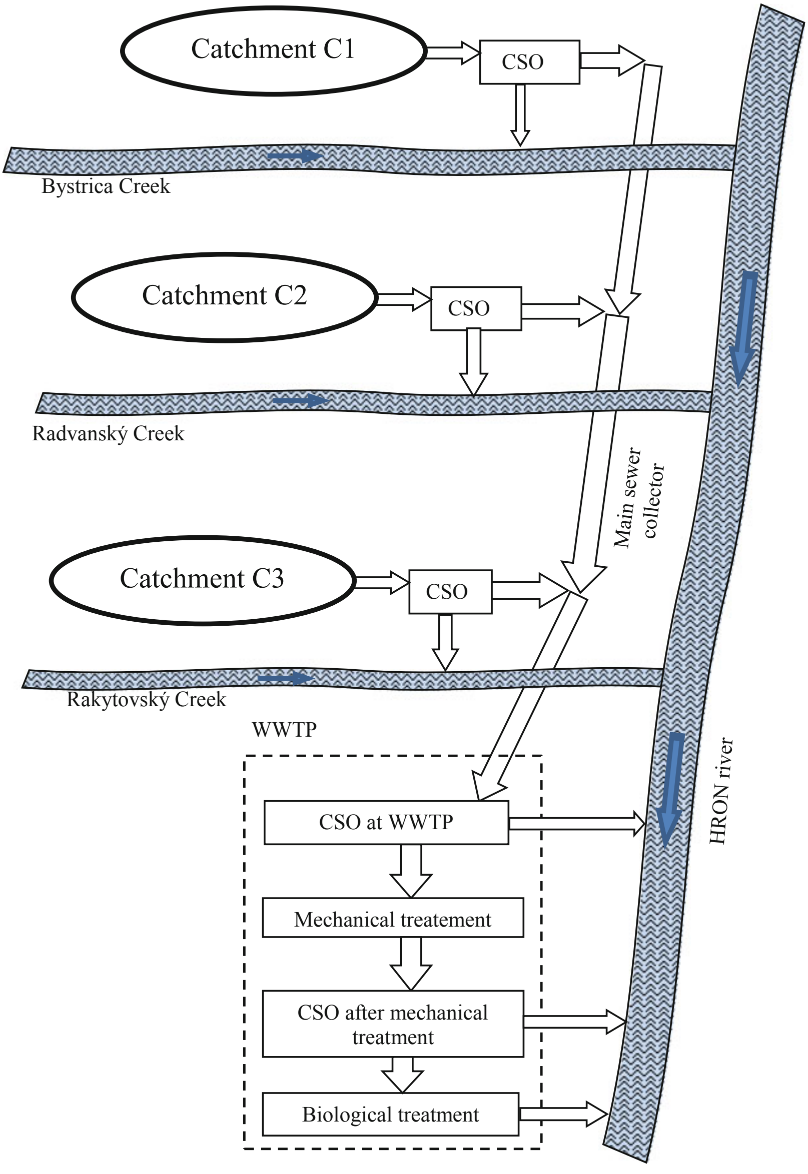


Fig. 2 Hydraulic scheme of the WWTP, the Banská Bystrica town (alternative 1 and 2)

Alternative 3 and 4 simulate storm water tanks located on the sewer network, with pumping of water from the storm tanks back into the sewer system. Because of large number of CSOs we have made some simplification. The CSOs on the territory of the town were clustered into three areas. Fictitious storm water tank was introduced into each of these areas. Their spillways directed the flow into one of the Hron River

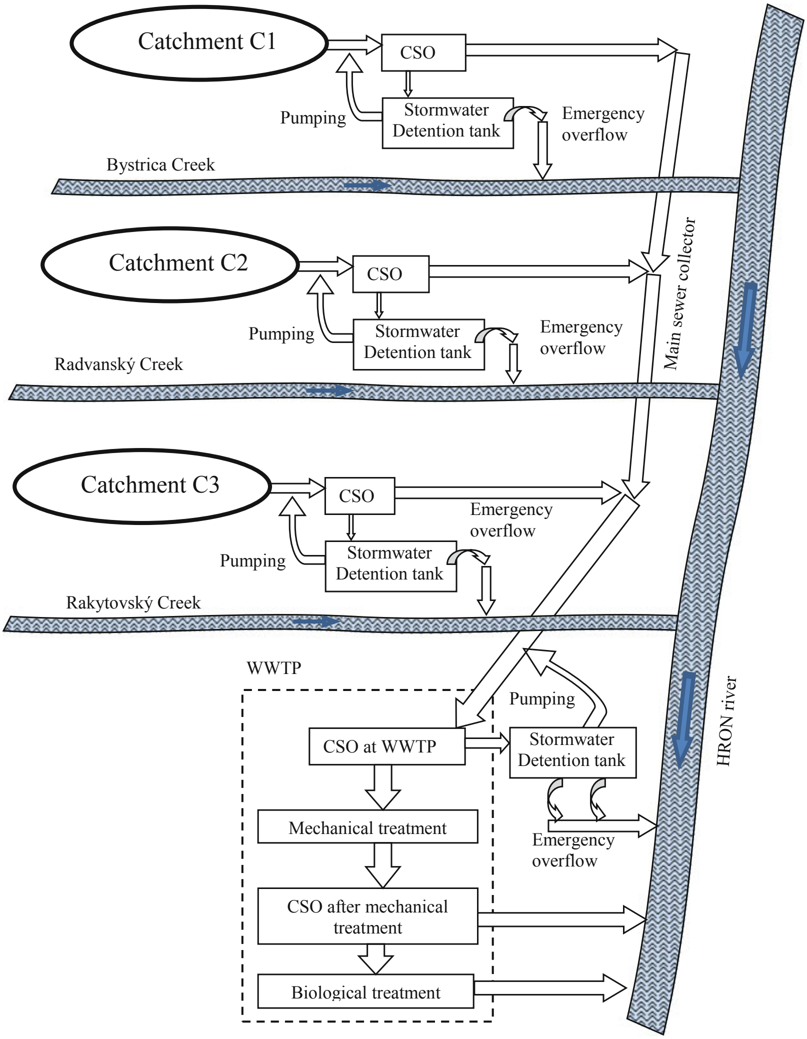


Fig. 3 Hydraulic scheme of the WWTP, the Banská Bystrica town (alternative 3 and 4)

tributaries (the Bystrica stream, Radvanský Creek and Rakytovský Creek). These local streams are quite deteriorated by the CSO spills and should be restored by the spill's reduction [27].

The storm water tank was also placed at the WWTP inflow, Fig. 3.

The size of the storm water tanks was designed to handle the maximal volume of the block storm event of the probability $p = 0.5$ (alternative 3), respectively, $p = 5.0$ (alternative 4); in other words, to catch almost the entire volume of the block storm water event. The volumes of these tanks are summarized in Table 2. At the first sight,

Table 2 Volumes of the storm water tanks, alternative 3 and 4

Drainage catchment	CSO location	Recipient	Volume of storm water tank for $p = 0.5$	Pumped discharge	Volume of storm water tank for $p = 5.0$	Pumped discharge
C1	CSO located on the sewer system	Bystrica creek	10,270 m^3	0.4 m^3 s^{-1}	4,250 m^3	0.1 m^3 s^{-1}
C2	CSO located on the sewer system	Radvanský creek	10,800 m^3	0.4 m3.s-1	4,870 m^3	0.2 m3.s^{-1}
C3	CSO located on the sewer system	Rakytovský creek	41,150 m^3	1.4 m^3 s^{-1}	18,000 m^3	0.6 m3.s^{-1}
C4	CSO located at the WWTP inflow	Hron River	14,200 m^3	0.5 m^3 s^{-1}	4,740 m^3	0.2 m^3 s^{-1}

Table 3 Average concentrations of pollution parameters in CSO water [28]

Parameter	Average concentration (mg.l^{-1})	Parameter	Average concentration (mg.l^{-1})
NL_s	430	NEL	3.97
COD	445	Zn	0.57
BOD_5	175	Cd	<0.02
N_{total}	16.8	Pb	<0.20
NH_4-N	6.21	Cu	<0.50
NO_3-N	1.28	Cr	<0.20
NO_2-N	0.10	Ni	<0.10
P_{total}	2.63	As (μg.1^{-1})	3.0
PO_4	0.63	Coli Bacteria (CFU.$m1^{-1}$)	1.3 × 105

the volumes seem to be large, but it is necessary to realize that each of these fictitious subareas covers several CSO structures, e.g., the total fictitious volume is distributed over the entire number of the CSOs. The outflow from the storm water tanks is designed to empty the tanks within maximum 8 h after they are filled.

For the quality of CSO, water results from an extensive research performed in Slovak Republic during the years 1996–1999 [28] were used.

Table 3 illustrates the CSO spill wastewater quality parameters. The concentration of relevant parameters of wastewater quality during CSO spill event was set constant. Specific parameters of the pollution, used as an input for water quality modelling in the Hron River, are shown in Table 4.

Table 4 Concentrations of pollution parameters used in the water quality model

Parameter	DO	TEMP	BOD	NH_4-N	P_{part}	P_{diss}	NO_3-N
Outflow from CSO (mg l^{-1})	8	20°C	175	6	1.3	1.3	1.28
CSO located after primary treatment (mg l^{-1})	5	20°C	120	4	1.3	1.3	1.28
Outflow from WWTP (mg l^{-1})	2	18°C	15	2	1	1	5

Note: *DO* dissolved oxygen, *TEMP* water temperature, *BOD* biological oxygen demand, NH_4-N ammonium nitrogen, P_{part} particulate phosphorus, P_{diss} dissolved phosphorus, NO_3-N nitrate nitrogen

4 Results

4.1 Results of Water Quality Simulation in the Hron River

4.1.1 Results of Hydrodynamic Modelling

The results of hydrodynamic modelling of the Hron River were represented by hydraulic values of the water depths, flow rates and velocities over time and river length. The model results can be arranged into tables or graphs showing the value of the variables along the river at a given time (longitudinal reach of the river) or as time dependant variables at given points of the modelled area (hydrographs).

Figure 4 illustrates a sample of graphical output of hydrodynamic model. The left side axis shows the ground elevations in metres above the sea. The graph also shows a simplified longitudinal slope of the river; the main points along the river and urban settlements are also indicated. Longitudinal axis shows the river station in metres, equal to the river km. The right-side axis shows the flow rates.

4.1.2 Results of Water Quality Modelling

The results of water quality simulation are represented by a concentration distribution over time and river lengths. These variables can be arranged again into tables or graphs as the water quality parameters distribution over the length of river at given times (longitudinal profile) or into a time distribution curve of the water quality parameter at given points of the area (pollutograph).

The samples of graphical outputs of water quality modelling are shown in the following part of the text. The left side axis shows again the ground elevations while the longitudinal axis displays the river station in metres. The right-side axis shows the values of concentrations in mg.l^{-1} and temperature in °C. The simulated parameters of water quality were biological oxygen demand over 5 days (BOD_5), dissolved oxygen (DO), temperature, ammonium nitrogen (NH_4-N), nitrate nitrogen (NO_3-N) and phosphorus (P) in two forms: dissolved phosphorus (P_{diss}) and particulate phosphorus (P_{part}) (see Figs. 5, 6, 7, 8 and 9).

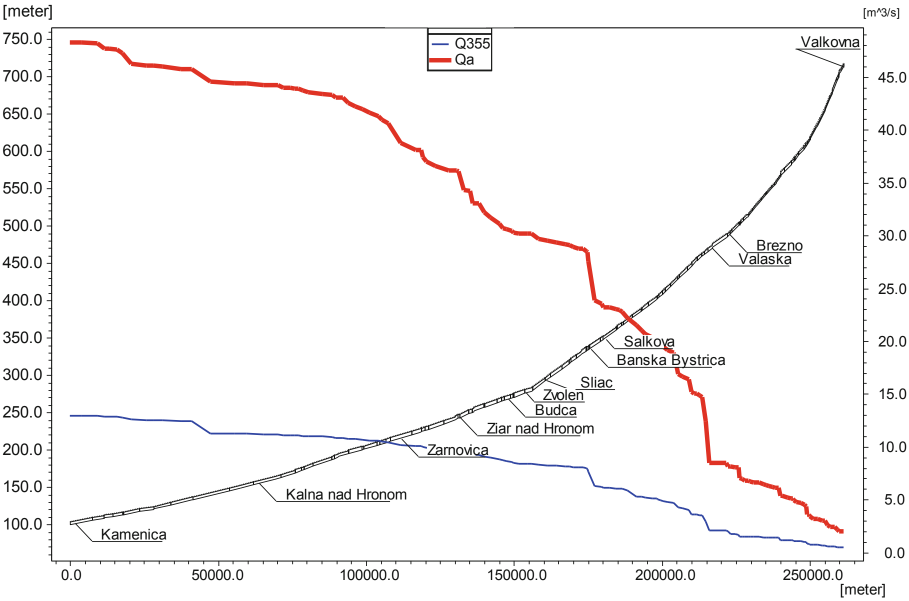


Fig. 4 Flow rates in the modelled reach of the Hron River at the average annual flow rate (Q_a, red line) and at the 355-day flow rate (Q_{355}, blue line)

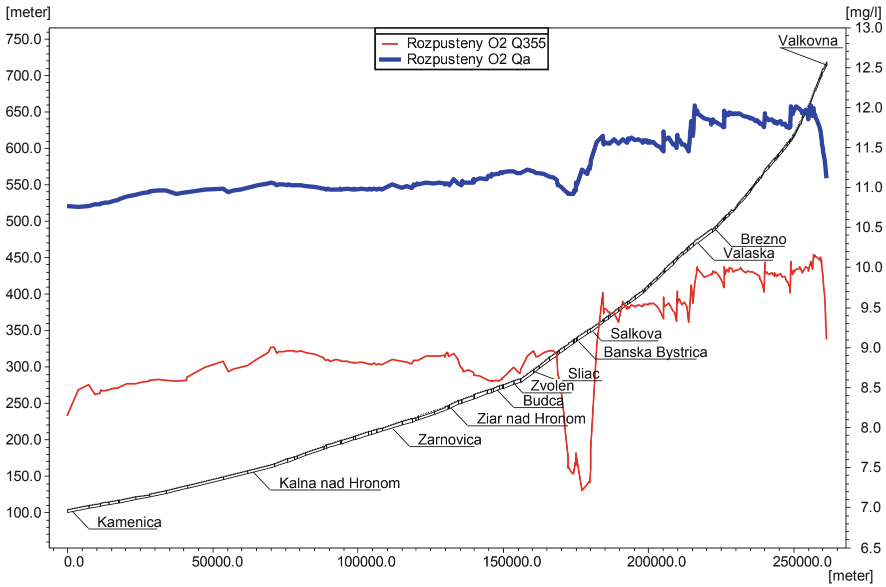


Fig. 5 Graph of simulated concentration of the dissolved oxygen along the modelled reach of the Hron River at the average annual flow rate Q_a (blue line) and 355-day flow rate (red line) Q_{355}

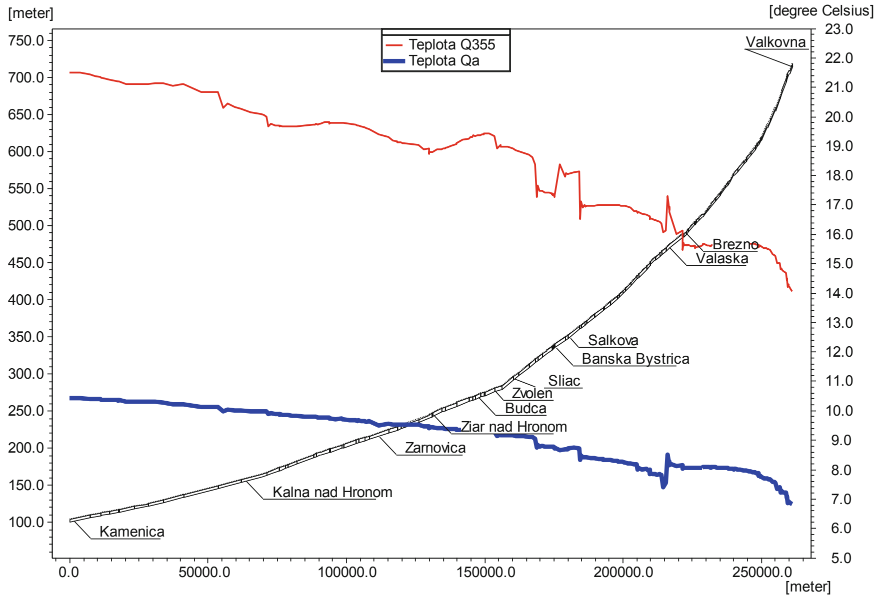


Fig. 6 Graph of simulated temperature in the modelled reach of the Hron River at the average annual flow rate Q_a (blue line) and 355-day flow rate Q_{355} (red line)

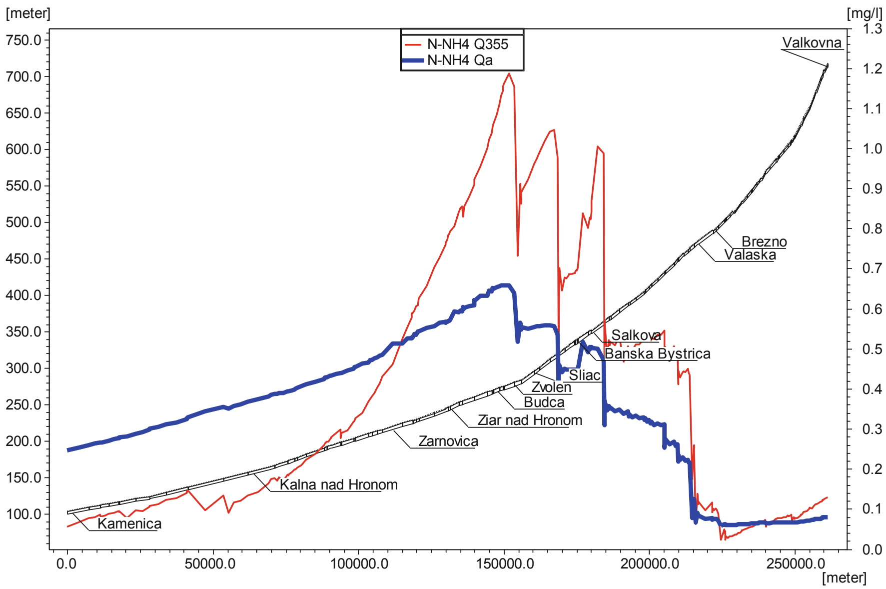


Fig. 7 Graph of simulated concentration of the ammonia nitrogen NH_4-N in the modelled reach of the Hron River at the average annual flow rate Q_a (blue line) and 355-day flow rate (red line) Q_{355}

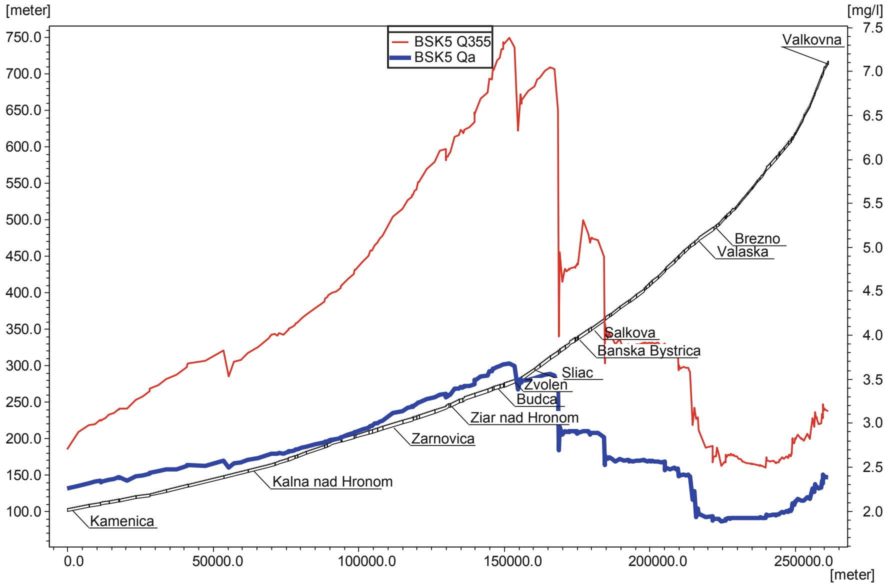


Fig. 8 Graph of simulated concentrations of the BOD_5 in the modelled reach of the Hron River at the average annual flow rate Q_a (blue line) and 355-day flow rate Q_{355} (red line)

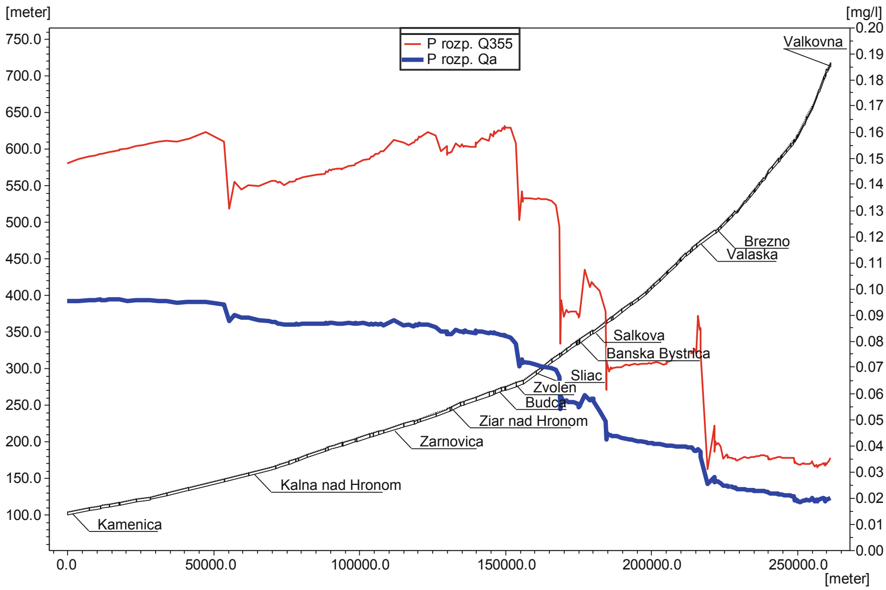


Fig. 9 Graph of simulated concentrations of the dissolved phosphorus in the modelled reach of the Hron River at the average annual flow rate Q_a (blue line) and 355-day flow rate Q_{355} (red line)

4.2 Results of Modelling of the Impact of CSO Discharge on the Recipient

The results of simulations of water quality in the Hron River at the short-term event including CSO discharge for individual cases (duration, storm periodicity of occurrence, qualitative and qualitative conditions in the recipient) are illustrated in graphs in the form of the intensity–duration–frequency (IDF) curves of concentration of dissolved oxygen, BOD_5 and NH_4-N in a Hron river profile close downstream to the city of Banská Bystrica (see Figs. 10, 11, and 12). As shown on the figures, the specific CSO event causes only slight oxygen concentration depletion, which does not endanger the river biocenosis. This is only the immediate oxygen depletion, the delayed oxygen effect takes place further downstream and its impact is reduced by dilution, dispersive processes and reaeration. The ammonium nitrogen (NH_4-N) concentration increases approximately eight times, the BOD_5 concentration approximately four times. This represents an extreme case, caused by short rainfall duration (15 min) and consecutive rainfall intensity (191 l.sec^{-1}.ha^{-1}), as well by the storm periodicity of occurrence ($p = 0.1$, i.e., once in 10 years). For longer storms duration

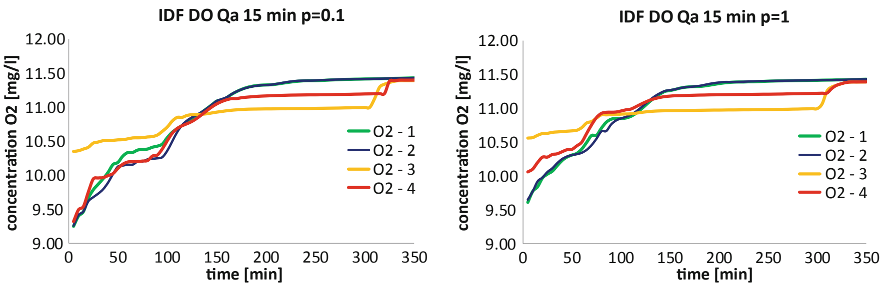


Fig. 10 IDF lines of the dissolved oxygen concentration (DO) in the receiving water during a 15-min rain event with a periodicity of occurrence p = 0.1 and 1.0 (the numbers in the legend represent the storm water management alternative)

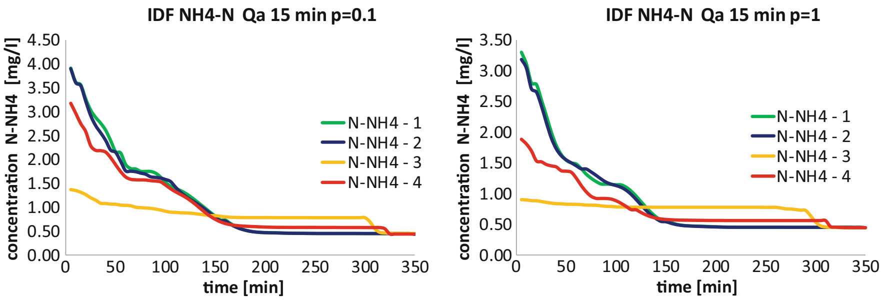


Fig. 11 IDF lines for the ammonium nitrogen (NH_4-N) concentration in the receiving water during a 15-min rain event with a periodicity of occurrence p = 0.1 and 1.0 (the numbers in the legend represent the storm water management alternative)

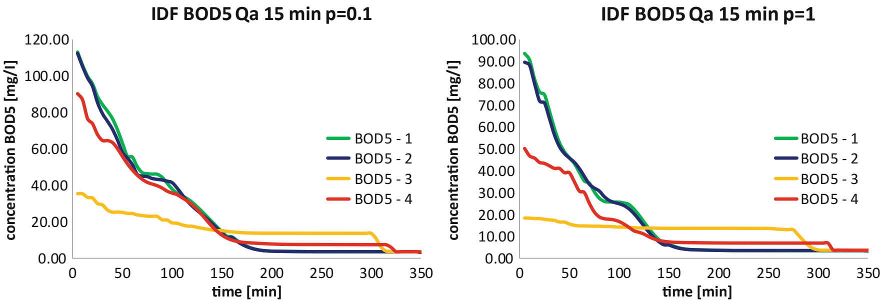


Fig. 12 IDF lines for the biochemical oxygen demand (BOD_5) concentration in the receiving water during a 15-min rain event with a periodicity of occurrence $p = 0.1$ and 1.0 (the numbers in the legend represent the storm water management alternative)

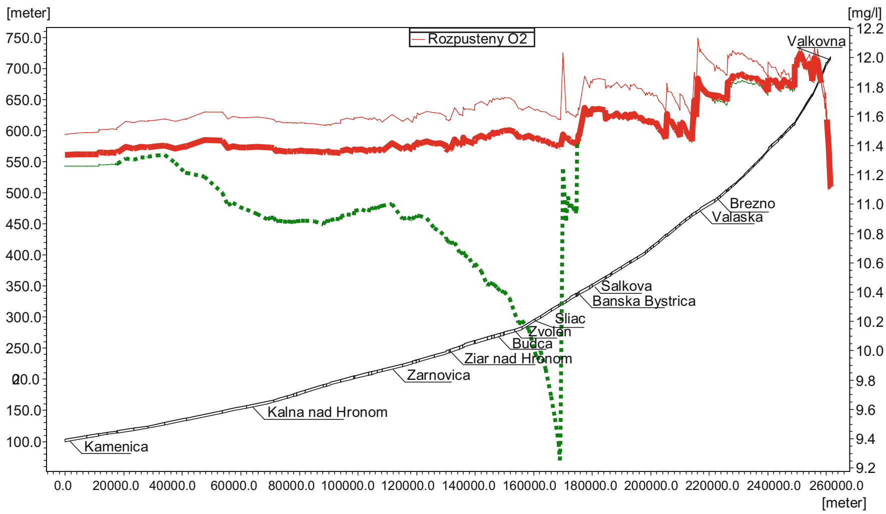


Fig. 13 Concentration of dissolved oxygen (DO) in the receiving water (longitudinal profile of the Hron River) during a 15-min rain with a periodicity of occurrence p = 0.1 and 1.0, alternative no. 1 (full red line – state without the storm event, dotted green line – minimum concentration caused by storm event)

and higher periodicity of occurrence are the impacts (pollutant concentrations) smaller.

To complete the results overview, the longitudinal profiles including the water quality parameters, dissolved oxygen (DO) and the biochemical oxygen demand BOD_5 in the Hron River are shown in Figs. 13 and 14.

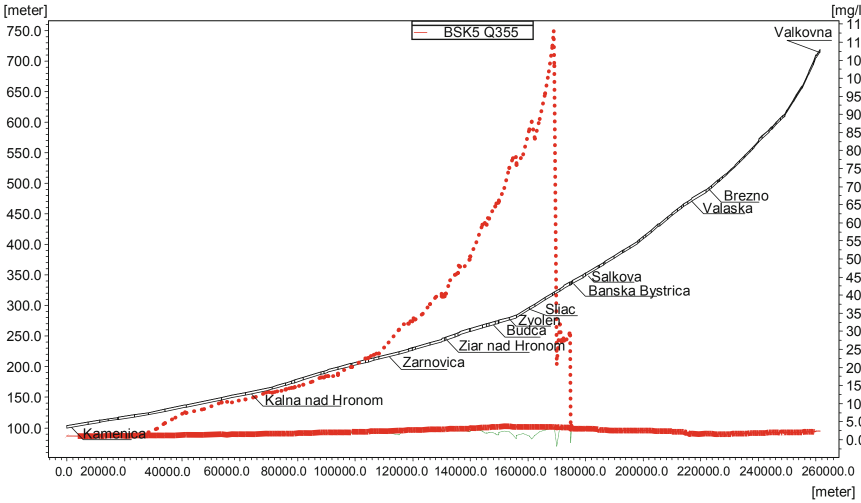


Fig. 14 Concentration of BOD_5 in the receiving water (longitudinal profile of the Hron River) during a 15-min rain with an occurrence periodicity $p = 0.1$ and 1.0, alternative no. 1 (full red line – state without the storm event, dotted red line –maximum concentrations caused by storm event)

5 Discussion

Comparison of simulation results with the values monitored by Slovak Hydrometeorological Institute (SHMU) in the years 1999–2009 [18] at the control points showed some discrepancies between these two sets of data. This inconsistency can be explained by the simplifications we used in the simulation, respectively, lack of input data, which had to be replaced by approximate values. The impact of neglecting the non-point source pollution is also an important factor, as certain reaches of the Hron River may be significantly affected by the non-point source pollution. Conversely, this approach enables us to quantify the effect of the non-point source pollution of the total pollution of the Hron River.

Another factor affecting the results is certainly the absence of full model calibration, especially regarding the dispersion coefficients ([29, 30] and coefficients determining the kinetics of biochemical processes in the river. As we found out during the simulation works, the other parameters also have a high significance [31]; e.g., sedimentation velocity of suspended solids, eventually the critical velocity (velocity lower than critical initiates sedimentation, higher velocity causes resuspension of bottom noncohesive sediments).

The largest source of errors is however the fact that out of 130 tributaries entered into the model as an inflow into the modelled area, only 4 were regularly monitored for the water quality parameters (the Čierny Hron stream, the Bystrica stream, the Slatina and the Sikenica stream).

If we expressed this ratio according to the flow rates, only about 30% of the inflow volume from tributaries in the system were monitored. For all other small streams, we only provided qualitative data so that the concentration in these streams was approximately 1/3 lower than the concentration in the Hron River at the point of their entry to the Hron River. We assumed that the residual approximately 1/3 of the pollution would reach the stream by point sources of pollution. Generally, our modelling confirmed that this assumption is acceptable. Some locations, primarily the upstream branches of the Hron River, show large deviations from this assumption. Small tributaries of the Hron River may be relatively clean streams draining the mountainous areas, at the same time they may carry large amount of pollution specially if they flow through the municipalities without existence of sewer systems. Other sources of pollution can be, e.g., direct sewage discharges, groundwater contaminated through leaking septic and industrial and mining activities [32].

An interesting question is the probability of the occurrence of CSO discharges in relation to the recipient. It is obvious the impacts of CSO discharges on the recipient significantly depend on the flow rate and water quality in the recipient during the CSO process and also on various factors affecting, for example, the kinetics of self-cleaning ability of the recipient.

Therefore, an analysis of the probability of occurrence of CSO discharge from the sewer network in relationship to the flow rates in the river has to be performed; in other words, the following question has to be answered: are there CSO discharges into the river under low flow conditions? If so, what is the probability of such event? In the model approach of assessing the impact of CSO, we encounter the problem of the probability of multiple occurrences at the same time. We have to take into account four factors:

1. the CSO discharge (flow rate),
2. the quality of CSO discharge,
3. the discharge (flow rate) in the recipient,
4. the water quality in the recipient.

Obviously, the results of this probability analysis are not valid generally, but only in the particular (analysed) catchment.

Basic analysis of the rainfall–runoff relationship in the catchment under this study is shown in Fig. 15. As relevant rainfall, we regarded the rain with duration of 20 min and with the intensity larger than 0.1 mm.min^{-1}. We performed a variety of analyses using different rainfall intensities and durations; however, the results were almost identical. For that reason, in this study we focused on this specific case.

We assume that rainfall with the intensity larger than 0.1 mm.min^{-1} causes a CSO event (outflow from the CSO structure) in the Banská Bystrica sewer network. As it is obvious from Fig. 15, majority of such events initiating the CSO discharge occur between the months of June to September, statistically (except June) a season of under average flows.

Another task was to investigate the relationship between storm occurrence (storm causing CSO event) and the flow rate in the recipient. The correlation coefficient for our case is very low: it means that the relationship between these phenomena is not significant, e.g., the CSO flow rate (at the 20-min rainfall intensity) is not statistically correlated with the flow rate in the receiving water (Fig. 16).

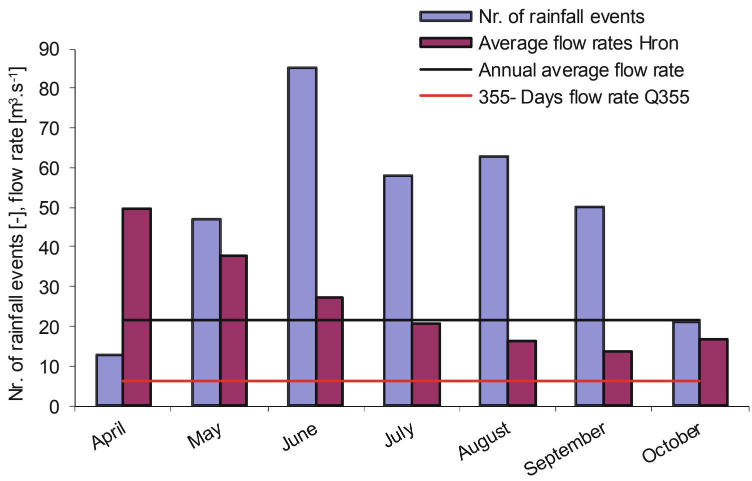


Fig. 15 Relationship between the number of rainfall events and the flow rates in the Hron river at the Banská Bystrica town cross-section profile (dataset of 28 years)

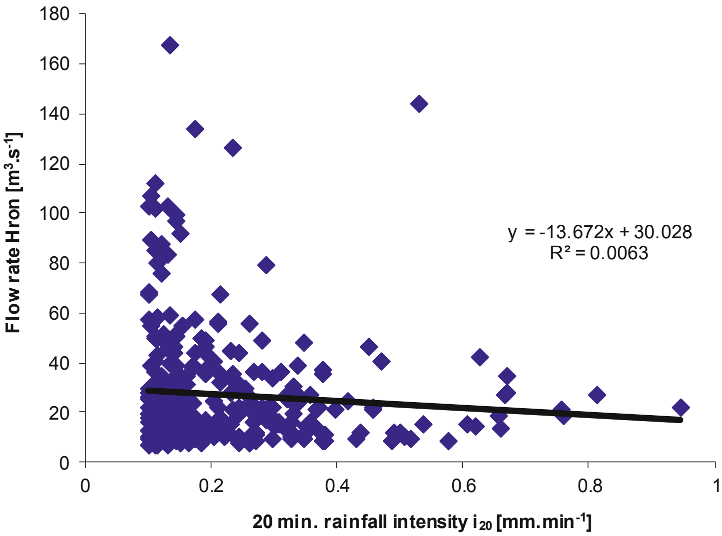


Fig. 16 Relationship between the rainfall intensity and the flow rate in the Hron river at the Banská Bystrica town cross-section profile (dataset of 28 years)

Another investigated relationship was the flow rate in the recipient versus number of storm events initiating CSO (we assume again storm events with the intensity larger than 0.1 mm.min^{-1}). The number of storms occurring at certain flow rate in the recipient, defined as N-th day flow rate, is illustrated in Fig. 17.

As shown in the graph, it is evident that the most frequent case is CSO discharge into the recipient nearing the average annual flow (approximately 180-day flow),

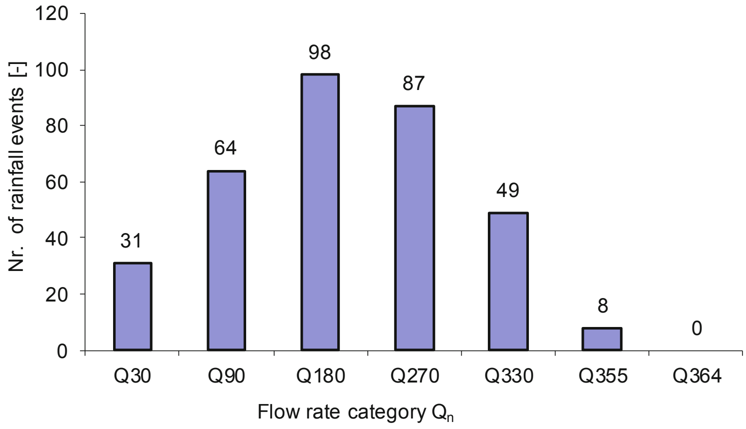


Fig. 17 Relationship between the number of rainfall events and the flow rate category in the recipient (dataset of 28 years)

eventually the flow rate somewhat lower (Q_{270}). In case we wish to use, for example, 90% quantile of probability of higher than CSO discharge up to certain flow, according to the data used to generate this graph such flow rate is equal to $Q = 9.28\ m^3\ s^{-1}$. That corresponds to the range from 270-day to 330-day flow rate ($Q_{270} = 10.63\ m^3\ s^{-1}$, $Q_{330} = 7.8\ m^3\ s^{-1}$).

The next question pertains to the concentrations of pollutants in the recipient as a function of flow rates, e.g., whether the combination of the concentrations and the low flow conditions represent the worst-case scenario of water quality. It is clear that there is no universal answer to this question, the results are valid also for the analysed area only. General experience usually shows either none or very low correlation between the flow rate and particular concentration values of water quality parameters. Also, the behaviour of the particular water quality parameters cannot be generalized – it varies at different sites and is also depending on the portion of the point and non-point sources [33]. It has to be noted that there is a lack of input data for a detailed analysis of this problem in the study area.

6 Conclusions

This chapter deals with the possibilities and limits of numerical simulation model applications for the storm water management in urban catchments. The modelled approach analyses the impacts of the combined sewer overflows (CSOs) on the receiving water body (recipient – the Hron River). The chapter gives basic knowledge state regarding this topic and aspect of water body management and also results of one practical application of that as a case study.

The first step of the case study was modelling the storm water runoff from the Banská Bystrica town by its sewer network and simulation of CSO overflows to the Hron River (with the model MOUSE). The second step was the simulation of the water quality in the Hron River with the model MIKE 11. For the simulation of the water quality, the following processes were simulated: reaeration, degradation of organic substances – oxygen depletion, nitrification and denitrification.

The last step and the goal of this study was to evaluate the outflow of discharged water from the CSO structures in the Banská Bystrica town and its impacts on the receiving water – the Hron River, using both previous models, described in first and second steps. The block rainfalls with the various periodicity and duration were used. We simulated 4 alternatives of the storm water management (according to the SK legislation):

1. Dilution ratio (mixing) with the ratio of 1:4 (minimum required according to the SK legislation).
2. Dilution ratio (mixing) with the ratio of 1:8 (maximum required according to the SK legislation).
3. Storm tank with the volume for accumulation of discharged storm volume with the periodicity $p = 0.5$.
4. Storm tank with the volume for accumulation of discharged storm volume with the periodicity $p = 5$.

We also took into account the quality of wastewater discharged from CSO structures. When the CSO was placed in the WWTP we took into account that some of the pollution will be removed due to the mechanical pre-treatment.

Simulations in two river discharge alternatives were carried out in order to evaluate the impacts of the point sources of pollution on the modelled reach of the Hron river: the yearly average flow rate (Q_a – for the Hron river and also for all tributaries) and for flow rates, which are close to the minimal flows – for the 355-days flow rate – Q_{355}. In the first of the alternatives (Q_a) we used average pollution concentrations to simulate the water quality; in the second alternative (Q_{355}) we used for the simulation the value c_{90} (90% distribution percentile of the most unfavourable value of concentration).

Simulation results of the water quality are presented by the IDF (intensity–duration–frequency) lines of concentration of the dissolved oxygen concentration, BOD_5 and NH_4-N concentration for all simulated alternatives of storm water management.

The simulation results show that the discharging of sewage water through CSO structures represents a relatively short-term, but significant stress on the recipient. It is necessary to mention that the catchment of the Banská Bystrica town is relatively specific one – it has a relatively big slopes and a large amount of CSO structures, which means that the large volumes of the sewage water get very fast to the recipient through the CSO structures (very small retention capacity of the system, a total absence of accumulation structures in the system). This causes up to 30-fold increase in the concentrations of pollutants in the recipient in critical cases (see subchapter "Results").

Comparing results from individual alternatives of storm water management, the following facts can be stated:

1. In case of short-term intensive rain events the size of the mixing ratio has practically no effect on the quality of water in the recipient,
2. In spite of many doubts and problems, the most effective method of regulation is the construction of storm tanks, even with relatively small specific volume.

Ad 1. The investigated scenarios represent the minimum and maximum requirements of the actual Slovak Legislation. The short storm events with low frequency occurrence do not significantly differ in the impact on the water quality in the recipient. The difference increases in the case of the long-term storm event, respectively, at the higher frequency of the block rainfall used for simulation. At the same time the higher mixing ratio lowers the frequency of CSO events and discharges into the recipient. That may play a significant role in some cases [34].

Ad 2. This conclusion is not surprising, the obtained results were expected. Despite, we show them as they visibly demonstrate the impact of storm water tanks on the water quality of the recipient. The concentrations of pollutants in the recipient reach three to four times lower values (scenario 3) compared to the scenarios without the storm water tanks.

Modelling of the water quality in the recipient, we have come to the conclusion that the pollution concentration in the Hron River does not decrease only by the self-cleaning ability of the river, but also in a high degree of probability by the hydrology aspects and the river hydraulics, where the dilution, mixing and dispersion processes are very important. For example, after a CSO event, due to the lateral inflows of the Hron River, flow rate in the river doubles within a few hours (from the cross-section profile Sliač to the cross-section profile Žarnovica); due to this fact the pollution concentration decreases by half. This fact has a significant effect on the modelling of the concentration of dissolved oxygen, when water with a relatively high oxygen concentration flows in the Hron River from the tributaries (mountain areas, big slope of inflows), which improves the oxygen balance of the Hron River after the CSO event. This situation is relatively specific, even though it is possible to expect it on a large number of rivers and streams in Slovakia.

7 Future Aspects

Despite many problems concerning relevant model inputs and other problems with simulation models application in real condition, the results of this case study show that complex modelling approach can be very useful for solution of water quality problems in streams (recipients) and can be also very helpful in evaluation of various strategies and management practices of the water quality improvement. The future research in this field should be focused on the impacts of the climate change on the operation of existing CSO structures, their hydraulic regime, as well as on the green/

grey urban infrastructure measures and quantification of their impact on the CSO spills reduction.

Acknowledgement The chapter was created with support of the project No. VEGA 2/0085/20. This publication is also the result of the project H2020 "SYnergy of integrated Sensors and Technologies for urban sEcured environMents", Acronym: SYSTEM, no: 787128 and APVV – 18 – 0205.

References

1. Bárek V, Halaj P, Fuska J, Halajová D, Báreková A (2011) Changes in water management strategy as a way for increasing of agro-ecosystems resilience towards drought. Ecol Saf 59:199–202
2. Giakoumis T, Voulvoulis N (2018) The transition of EU water policy towards the water framework Directive's Integrated River basin management paradigm. Environ Manag 2018:1–13
3. WFD (2000) Directive 2000/60/Ec of the European Parliament and of the council of 23 October 2000 establishing a framework for community action in the field of water policy (EU water framework). Off J Eur Commun 327(1):1–72
4. EWQSD (2008) Directive 2008/105/EC of the European Parliament and of the council of 16 December 2008 on environmental quality standards in the field of water policy. Off J Eur Union Legislation 348:84–97
5. Pekárová P, Pramuk B, Halmová D, Miklánek P, Prohaska S, Pekár J (2016) Identification of long-term high-flow regime changes in selected stations along the Danube River. J Hydrol Hydromech 64(4):393–403
6. Maršálek J (1992) Urban drainage systems: design and operation. In: INTERURBA Workshop, Wageningen
7. Jurík Ľ, Kaletová T, Halaj P (2016) Water management for sustainable growth strategies. Visegrad J Bioecon Sustain Develop 5(1):31–35
8. Zeleňáková M, Čarnogurská M (2013) A dimensional analysis-based model for the prediction of nitrogen concentrations in Laborec River, Slovakia. Water Environ J 27:284
9. 269/2010 Col (2010) Decree of the Government of the Slovak Republic No. 269/2010 Col. laying down requirements for achieving good water status. Parliament of Slovak Republic, Bratislava
10. BWK (2018) Arbeitsblatt ATV-A 128 – Richtlinien für die Bemessung und Gestaltung von Regenentlastungsanlagen in Mischwasserkanälen (Standard ATV-A 128 – standards for the dimensioning and design of stormwater structures in combined sewers). 1992, rev. 04/2018. DWA Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e.V., Hennef
11. UPM (1998) Urban pollution manual. Foundation for Water Research (FWR), Marlow
12. BWK (2001) Merkblatt BWK-M3: Ableitung von immissionsorientierten Anforderungen an Misch- und Niederschlagswassereinleitungen unter Berücksichtigung örtlicher Verhältnisse. Bund der Ingenieure für Wasserwirtschaft, Abfallwirtschaft und Kulturbau (BWK) e.V, Sindelfingen
13. BWK (2008) Merkblatt BWK-M7: Detaillierte Nachweisführung immissionsorientierter Anforderungen an Misch- und Niederschlagswasser einleitungen gemäß BWK-Merkblatt 3. Bund der Ingenieure für Wasserwirtschaft, Abfallwirtschaft und Kulturbau (BWK) e.V., Sindelfingen
14. ÖWAV (2007) Regelblatt 19: Richtlinien für die Bemessung von Mischwasserentlastungen. Österreichische Wasser- und Abfallwirtschaftsverband (ÖWAV), Wien

15. Bárek V, Halaj P, Igaz D (2009) The influence of climate change on water demands for irrigation of special plants and vegetables in Slovakia. In: Střelcová K, et al Bioclimatology and natural hazards. Springer, Cham 271–282
16. DHI (2000) MOUSE user manual, version 2000b. Danish Hydraulic Institute, Hørsholm
17. DHI (2011) MIKE 11 User manual, Version 2000b. Danish Hydraulic Institute, Hørsholm
18. SHMU (1999–2009) Surface water quality in Slovakia. www.shmu.sk
19. Schügerl R (2019) Field study for determine Manning's roughness coefficient with different flow conditions. Acta Hydrologica Slovaca 20:2
20. MTI (1998) Topographics maps 1:50 000. Military Topographic Institute (MTI), Harmanec
21. WRI (2003) Water management map of Slovak republic 1:50000. Water Research Institute (WRI), Bratislava
22. Mišík M (1998) Examination of the geomorphologic and hydrodynamic parameters of river Hron. (in Slovak). Water Research Institute, Bratislava
23. Ani EC, Wallis S, Kraslawski A, Agachi PS (2009) Development, calibration and evaluation of two mathematical models for pollutant transport in a small river. Environ Model Software 24:1139–1152
24. 167/2015 Col (2015) Regulation of the Government of the Slovak Republic no. 167/2015 Col. on environmental quality standards in the field of water policy. In Slovak. Parliament of the Slovak Republic, Bratislava
25. EN 752 (2017) Drain and sewer systems outside buildings – Sewer system management. Comite Europeen de Normalisation
26. Kabelková I, Stránský D, Bareš V (2015) Basic principles of the Czech technical standard on sustainable stormwater management. In: Hlavínek P, Zeleňáková M (eds) Examples from Czech Republic, Slovakia and Poland. Springer, Cham, pp 179–195
27. Halajová D, Halaj P, Macura V, Škriniar A (2019) Urban river design: a river restoration case study. IOP Conf Ser Mater Sci Eng 471:092090
28. Sztruhár D, Sokáč M, Holienčin A, Markovič A (2002) Comprehensive assessment of combined sewer overflows in Slovakia. Urban Water 4:237
29. Halmová D, Miklánek P, Pekár J, Pramuk B, Pekárová P (2014) Longitudinal dispersion coefficient in natural streams. Austrian J Agric Res 65(3–4):23–29
30. Julínek T, Říha R (2017) Longitudinal dispersion in an open channel determined from a tracer study. Environ Earth Sci 76:592
31. Manina M, Halaj P (2019) Sensitivity analysis of input data in surface water quality models. Acta horticulturae et regiotecturae 22(2):84–87
32. Ilavský J, Barloková D (2018) Influence of mining activities on quality of groundwater. In: Negm A, Zeleňáková M (eds) Water resources in Slovakia: part I. The handbook of environmental chemistry. Springer, Cham, pp 303–331
33. Hanslík E, Marešová D, Juranová E, Vlnas R (2016) Dependence of selected water quality parameters on flow rates at river sites in the Czech Republic. J Sustain Develop Energy Water Environ Syst 4:127
34. Stránský D, Kabelková I (2015) Review of the implementation process of sustainable stormwater management in the Czech Republic. In: Hlavínek P, Zeleňáková M (eds) Storm water management. Examples from Czech Republic, Slovakia and Poland. Springer, Cham, pp 13–25

Part IV
Wastewater Management and Sustainability

Water–Energy Nexus in Wastewater Management for Irrigation

Lamha Kumar, Neha Kapoor, and Archana Tiwari

Contents

Abstract Owing to the importance of water and increasing water crises, wastewater analysis has become extremely important. For water to be usable, there are certain physical, chemical and biological criteria which need to be fulfilled, such as the concentration of elements for drinking as well as for agricultural purposes. Quality of water is affected by natural and human interferences and the major factor is pollution created by human. The wastewater from the population if handled and treated with care should be able to promote the sustainable use of water and make the water available for our upcoming generations. Countries are stressing on water management and have certain specifications for the water being potable. The

L. Kumar
Department of Botany, Hindu College, University of Delhi, New Delhi, India

N. Kapoor
Department of Chemistry, Hindu College, University of Delhi, New Delhi, India

A. Tiwari (✉)
Diatom Research Laboratory, Amity Institute of Biotechnology, Amity University, Noida, India

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 275–298, DOI 10.1007/698_2022_861,

water–energy nexus describes the relationship between water and energy wherein wastewater can act as a reservoir of renewable energy leading a way towards sustainability. This chapter elaborates the energy–water nexus, strategies towards wastewater remediation and the technological interventions in wastewater application for irrigation.

Keywords Pollution, Remediation, Sustainability, Wastewater management, Water–Energy Nexus

1 Introduction

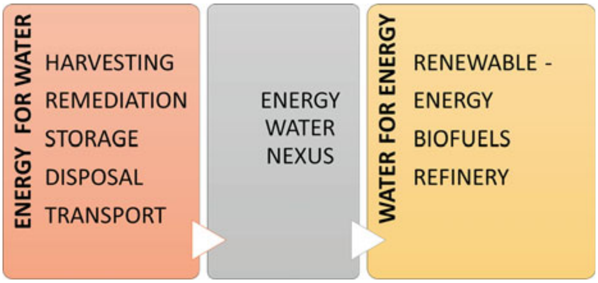
Water, energy and food are inextricably linked and considered the basic resources for the development of social economy and maintenance of life. Freshwater resources are largely used by agriculture which serves as the backbone of food security. Energy security is influenced by this use of freshwater resources [1]. Globally, 90% of freshwater and 30% of energy is consumed for food production [2]. Challenges are being imposed due to the increasing population. There would be a 50% increase by the year 2050 in the urban population of most developing countries, according to estimates made by UNICEF [3]. It is estimated that there will be a 50% increase in the demand for food, 40% increase in demand for energy and 30% increase in demand for water by 2030, leading to water shortage [4]. The primary demands for energy of the world will increase by 40% by the year 2035 as compared to 2010 [5].

A great amount of pressure will be added to the limited resources such as water, energy, food, etc., due to rapid growth in the population, urbanization and economic development. The growing demand is increasing the water crisis and will continue to make it worse due to the increase in pollution and climate change resulting in differentiating weather conditions that increase the occurrence of floods, droughts and natural disasters [6].

The two key components for sustainable development under the United Nations Sustainable Development Goals are water and energy [7]. Water and energy are considered interlinked. The water–energy nexus describes the relationship between energy and water in terms of the amount of water needed in the generation and transmission of energy, and the amount of energy needed for the collection, cleaning, transport, storage, disposal and treatment of water. Water–energy nexus has importance in literature in terms of strategic policymaking and sustainability planning for the future [8]. Climate change severely affects the water–energy nexus [9, 10].

Water is required for fuel production, extraction and refining. It is the main component in a hydropower plant and is also needed in thermo electrical cooling. It is also used in refineries and in the production of biofuels via the treatment of wastewater. Energy is required in every step on processing and treatment of water.

Fig. 1 Water–energy nexus



Energy is needed in the storage, remediation, harvesting, disposal and treatment of water. The treatment of wastewater shows the water–energy nexus in every step. Wastewater is a major resource which is not being exploited to its full potential. Wastewater treatment by-products like the produced sludge can not only be used as a manure, it can also be used in the production of energy. At each step, the treatment of wastewater leads to the production of several important resources as by-products which have several uses such as animal feed, food, manure, soil conditioners, biofuels, etc. (Fig. 1). Most importantly, the final end product of the wastewater treatment plant is clean water. New developments in technology have made the treatment of wastewater more efficient, making use of crop plants and other plant species (several aquatic plant species) for the treatment of water. The wastewater treatment using plant species is of varied types, each making use of different plant species. These help in a dual manner, treatment of wastewater and the plants receiving nutrition and irrigation. The water that is obtained after the treatment that uses plant species is almost a clean as drinking water [11, 12]. The irrigation using treated wastewater does not pose much risk to the health of any living organism. The use of wastewater for irrigation purposes is a necessity to meet the needs of the growing population.

2 Water–Energy Nexus

A nexus, according to the Merriam Webster dictionary is a connection or a link. At a fundamental level, energy and water are thought to be linked. Basic level energy generation requires water in its process and the transportation and treatment of water require energy. Water and energy are linked at every step of the way. Water is needed for the generation and transmission of energy and energy is needed in every step of processing water. There is common flow from the source of primary energy and water, the environment and the users' end.

There are several links between electricity and water which can be classified into three categories

(a) Production Links

The production category includes those functions that are linked to the environment, like production (primary and secondary), desalination and bulk water supply.

(b) Transportation Links

Water and wastewater collection, conveyance, extraction, distribution and transfer and electricity transmission and distribution are included in the transportation category.

(c) Consumption Links

The consumption category includes those functions linked to the end-users such as wastewater treatment and sale of electricity and water.

Links can occur across the three categories and are assigned to the various categories depending on the category receiving the electricity or water. For instance, in the case of a thermal power station, the water that is recycled (serves as the Consumption link) is used in the cooling of the power station (serves as Production link).

2.1 Dimensions of Water–Energy Nexus

The water–energy nexus is multidimensional, with the dimensions influencing each other, often antagonistically. The dimensions can be classified as shown in Fig. 2.

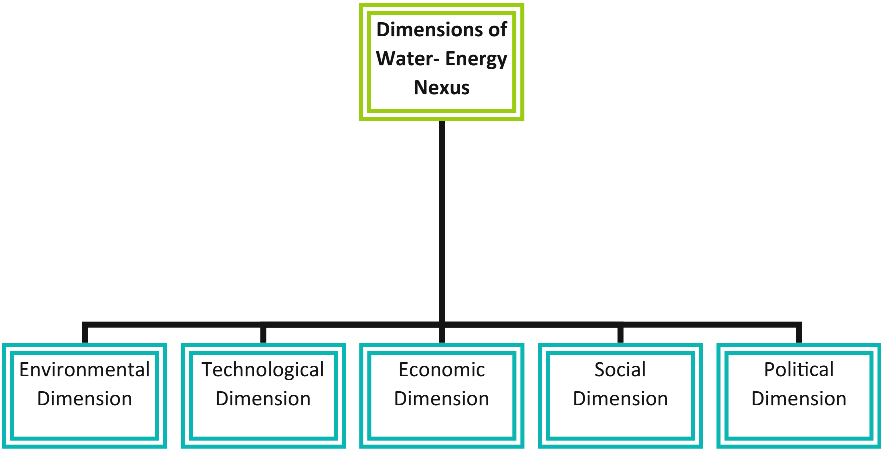


Fig. 2 Dimensions of water–energy nexus

2.1.1 Environmental Dimension

The environment is considered the start point as the environment is the source of all water and primary energy and the environmental dimension is the backdrop for many other dimensions.

Climate change is the first environmental dimension, which is being rapidly increased due to the emission of greenhouse gases by human activities. One of the biggest climate change causes is fossil fuel burning. There is the uncertainty created regarding the supplies of water in the future. This has implications on the water–energy security in the long run. The climate change mitigation policies may also increase the impact on the water for generating electricity.

The second environmental dimension is drought which has led to the focus on the water–energy nexus in the recent past. The water and energy industries are using several methods to tackle drought conditions, including sourcing alternative supplies of water, installing technologies of wastewater treatment that are advanced for recycling of water, constructing desalination plants, investing in reduced water consumption technologies. However, the consumption of electricity may be increased inevitably by some of these measures.

Policies created to protect the environment could also cause water–energy imbalances at other places, such as the stricter policies to improve ecosystem health require an improvement in the treatment of the discharged effluent from wastewater treatment plants. This would require more energy requiring treatment technologies, thereby increasing the energy cost. However, if these policies are absent, serious impacts on the environment would occur.

2.1.2 Technological Dimension

The physical links between electricity and water are described in the technological dimension. Different amounts of water are used, and different amounts of carbon are emitted by electricity generation technologies and alternative energy sources. More and more electricity is needed in the water industry as the water treatment processes such as water recycling, water transfer, desalination and groundwater extraction technologies are becoming more energy-intensive.

2.1.3 Economic Dimension

Reforms in the water and electricity industry have drawn a lot of attention towards the economic dimension. Reforms in the ownership, competitive segment, monopoly segment, pricing policies, etc., have drawn attention to the economic dimension of the water–energy nexus. The retail pricing of electricity and water has made it present in the consumption category. The subsidies and tariff structures of pricing have caused a perception in the minds of the people that water and electricity are cheap, causing overexploitation and thereby having detrimental environmental and social consequences. This is the case with India [13].

2.1.4 Social Dimension

The social attitude of the people towards water and energy impacts the water–energy nexus. The public's perception of the value of water and energy is linked to consumption. People believe that cheaper commodities are less valuable and therefore people do not save them as such.

2.1.5 Political Dimension

The political dimension largely influence which issue of the water–energy nexus gets manifested in the other dimensions. The policies for conservation and protection are created by politicians.

3 Wastewater Management Strategies

There are three stages in the wastewater treatment process as shown in Fig. 3.

1. Primary or Mechanical stage
2. Secondary stage
3. Tertiary or Advanced stage

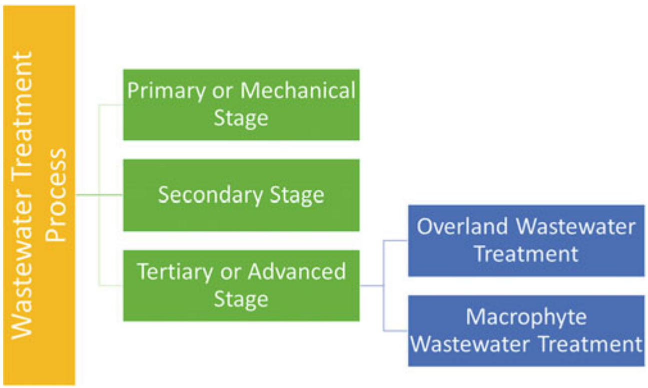


Fig. 3 Wastewater treatment process

3.1 Primary or Mechanical Stage

The raw sewage obtained directly from the source is processed in the primary stage wherein the gross, floating and suspended solids and substances are removed. The process of screening is used to trap the gross, suspended and floating solids followed by gravitational sedimentation to cause settling of the solids [14].

3.2 Secondary Stage

Dissolved organic matter that is removed in the secondary stage of treatment using microbes. The organic matter is consumed by the microbes and used as food for producing energy, which is used by the microbe for growth and reproduction. The organic matter is converted to water and carbon dioxide, inorganic matter, organic substances and new cells [15–17].

In the biological process that has high rates, microorganisms are required in high concentrations along with lesser reactor volumes compared with other processes that have low rates [18–20].

Activated sludge may be involved in secondary treatment. Microorganisms and the wastewater are taken as a suspension, called the mixed liquor, and are contained in an aeration tank or basin and are vigorously mixed by aeration devices. Oxygen is also provided [15, 21]. Industrial and municipal wastes are most commonly treated using Conventional Activated Sludge Process (CASP) [18, 22–24]. Trickling filters may also be used in the treatment process. Wooden slats, stones or plastic shapes (support media) are filled in towers or basins. Wastewater is applied to these media continuously or intermittently [25]. A biological film is formed on top of the media due to the attachment of microorganisms and the organic matter from the wastewater gets metabolized after diffusion into the biological film. Oxygen may be supplied naturally by the flow of air or forcefully by blowers. The growth of new organisms increases the biofilm thickness. Parts of the film periodically get crumbled and cast off into the liquid. Prior to their discharge into the processing of sludge, using a secondary clarifier, they are separated. Secondary effluent (clear liquid) is obtained from the secondary clarifier [25, 26]. Rotating biological contractors with slowly rotating discs of supporting media with microorganisms may also be used. These are partially submerged in the wastewater that is allowed to flow in the reactor [27–30].

3.3 Tertiary or Advanced Stage

The treatment of wastewater is made more efficient using the tertiary or advanced stage of treatment. 99% of impurities are removed in this stage. The effluent produced is almost of the status of drinking water [11, 12]. A modification to remove additional nutrients like nitrogen and phosphorus is made to the plant where the secondary treatment takes place. The use of natural processes is being preferred over that of chemicals [11, 31].

Post the primary treatment, the effluent flows into the biological treatment stage that is divided physically into five divisions or zones by weirs and baffles [24, 31]. These zones are

1. Anaerobic fermentation zone – this zone is characterized by absence of nitrogen and the levels of dissolved oxygen are low
2. Anoxic zone – this zone is characterized by low levels of dissolved oxygen and the presence of nitrates
3. Aerobic zone – This zone is well aerated
4. Secondary anoxic zone
5. Final aeration zone.

The anaerobic fermentation zone stresses phosphorus removing bacteria under low oxidation–reduction conditions thereby conditioning them. The phosphorus equilibrium is released in the bacterial cells as a result. The bacterial cells, in the aerated zone, get exposed to phosphorus and oxygen adequately and accumulate phosphorus more than the normal requirement for metabolism, thereby removing phosphorus as activated sludge. Large amounts of phosphorus are removed by the use of polyphosphate accumulating organisms (PAO) in a process called Enhanced Biological Phosphorus Removal (EBPR) [31, 32]. Overland and macrophyte wastewater treatments have been included in the tertiary treatment of wastewater.

3.3.1 Overland Wastewater Treatment

In overland wastewater treatment, the treatment is done via overland flow. The effluents are distributed across gently sloping grasslands with soils that are impermeable fairly. The wastewater is collected in ditches installed at the bottom after flowing down the slope. An essential component is water-tolerant grasses [33–36]. The type of soil, wastewater effluent quality and the near-surface environment's biochemical and physical conditions determine the wastewater application rate [37].

The crop cover forms an important part of the overland wastewater treatment process as it provides nutrient uptake, helps in the prevention of erosion of soil and forms a fixed film media where biological treatment can take place. Grasses with extensive root formation, high tolerance for moisture and growing seasons that are long are best suited for this technique. Examples include reed canary grass, ryegrass and tall fescue [38].

The surface grass helps in the removal of colloidal and suspended organic matter from the wastewater. The slope length, the temperature of the soil and application rate are all inversely related to the amount of ammonia and nitrogen that is removed. Sorption on the colloids of soil clay and precipitation in the form of insoluble complexes of aluminium, calcium and iron enable the removal of phosphorus and other trace elements [39]. Pathogens are removed without chlorination at comparable levels of secondary treatment in this technique [39, 40].

3.3.2 Macrophyte Treatment of Wastewater (Wetlands)

Maturation ponds that have emergent, submerged or floating aquatic plants are called macrophyte ponds. These ponds are used to treat effluents from stabilization ponds. During their growth, large amounts of heavy metals like copper, cadmium, zinc and mercury and inorganic nutrients, especially nitrogen and phosphorus are absorbed by the macrophytes. Due to the leaf canopy, shading of light takes place, which leads to the reduction of algal growth [41].

Floating Aquatic Macrophyte Systems

The large root systems of floating macrophyte plants account for efficient stripping of nutrients. *Spirodela, Salvinia, Lemna* and *Eichhornia* have been used and researched upon for their use in the treatment of wastewater. Several types of research have been done on water hyacinth (*Eichhornia crassipes*) [42–45]. The mass of water hyacinth doubles every 6 days in tropical regions, reducing the contents of phosphorus by 50% and that of nitrogen by 80%. Studies performed using *Ceratophyllum demersum*, a submerged macrophyte in Tamil Nadu, India have shown that the plant helped in ammonia reduction by 97%, reduction of phosphorus by 96% and BOD reduction by 95% from sewage or wastewater. The harvesting is less frequently required as the growth rate is lesser than that of water hyacinth [44].

Other than physical removal, especially by sedimentation, the removal of nitrogen and BOD and reduction of heavy metals and phosphorus also take place because of the presence of the aquatic plants which provide a living substrate for the action of microbes and uptake minerals [46]. The plants, during absorption, help in assimilation, concentration and storage of the contaminants for a small period of time and upon harvesting, result in the removal of the contaminants from the soil. The composition of the plant tissue, standing crop and rate of growth determine the aquatic macrophytes' capacity to assimilate nutrients. The rate of growth and standing crop of biomass influence the potential pollutant storage rate of a plant [41, 46].

A major problem associated with this technique is the breeding of mosquitos and flies. This problem can be partially tackled by introducing fish species (aquatic biota) that eat the larva [47]. Due to lower levels of dissolved oxygen, pH and light shading, the die-off of pathogens is poor in comparison to algal maturation ponds. These macrophytes strip effluents in the ponds of algae and nutrients and produce biomass that is harvestable. They are easily harvested and can be used in agriculture as green manure, as feed for animals, as soil conditioners. Fertilizers can be made by composting aerobically. Biogas can be made by converting in anaerobic digesters, with the residual sludge being used as soil conditioner and fertilizer [48, 49].

3.3.3 Emergent Macrophyte Treatment Systems

Raw sewage treatment and the treatment of effluents that are partially treated are being done by artificial and natural marshes and wetlands [41, 49]. Performance can be maximized in the artificial systems since conditions for optimum growth of emergent macrophytes can be managed, as compared to the natural systems where they are usually unmanaged [43].

The emergent macrophyte treatment systems have the following main features

- "Hydraulic pathways" are opened up in the gravel or soil by the growth of the macrophyte rhizomes horizontally and vertically [50].
- The surrounding soil enables treatment via anaerobic and anoxic process. Rhizosphere removes organic matter by treatment via the aerobic process. Bacterial activity removes nitrogen and BOD in the wastewater [51].
- Oxygen is transported to the rhizosphere via the atmosphere through the stems and leaves of the reeds via the rhizomes which are hollow and out via the roots [51, 52].
- Along dead stem and leaves of vegetation, the solids suspended in sewage are composted aerobically [51, 53].
- Plants remove heavy metals and nutrients by uptake [52, 53].
- Factors like climate, plant density, culture system, wastewater loading rate and factors of management limit the assimilative capacity of pollutants and the rate of growth of emergent macrophytes [50].
- Die-off chances of microorganisms that are pathogenic are increased through deposition and sieving, thereby reducing their quantity [54, 55].

Studies reveal that plants grown in wastewater systems that are enriched with nutrients have high nitrogen concentration [50]. Nutrients can be stored for periods that are longer because there are more supportive tissues in emergent macrophytes as compared to floating macrophytes. For maximum removal of nutrients, harvesting of the emergent macrophytes may not be frequently necessary, but harvesting once a year of the biomass above the ground for improved removal efficiency of nutrients [53, 56].

3.3.4 Constructed Wetlands

Pollutant loads from various sources are now being reduced by using the constructed wetland. It is an artificially designed and consists of substrates that are saturated, and contains animal life, submergent and emergent plant species and water. The conditions similar to a naturally formed wetland are stimulated for purification of water [51, 57, 58]. The quality of treatment of water is greatly improved in the artificial system. The diseases that are waterborne are significantly controlled in this system [50, 59]. The use of constructed wetlands for the treatment of wastewater started in Germany. The wastewater is fed through an inlet and is allowed to flow through a medium that is porous present under the bed horizontally till it reaches the outlet. It is then collected before being released from the outlet [11, 51, 58]. While flowing, the wastewater is acted upon by anaerobic, anoxic and aerobic (present near rhizomes and roots and add oxygen to the substrate) zones. "Hybrid constructed wetlands" constitute of different variety of wetlands combined for greater efficiency of treatment [60, 61]. For example, Horizontal flow constructed wetlands have low or no oxygen in the filtration beds and thus there is low nitrification. This can be tackled by combining it with a vertical flow system that has a high capacity to transport oxygen and thus has better nitrification. The denitrification, however, is absent or very low. A combination of constructed wetlands is used for the best treatment based on the type of pollutants to be targeted [11, 62].

3.3.5 Nutrient Film Technique

The nutrient film technique (NFT) is a system of growth that contains a modification upon the hydroponic plant growth system. Wastewater is applied in a continuous manner as a thin film upon a surface that is impermeable upon which plants are directly grown. The matter is accumulated in the traps which have large surface areas due to high production of root on top of the surface that is impermeable [63, 64]. The roots serve as filters and help in material accumulation whereas uptake of nutrients, removal of water via transpiration and algal growth retardation and protection are provided by the top growth of the plant [64, 65]. Primary treatment is provided by this technique using plants that can grow and survive in polluted condition and have roots that are large. The mechanism is characterized by conditions that are anaerobic, accumulation of sludge in large quantities, precipitation of trace metals and entrapment. Solids that are suspended and BOD of the wastewater are removed. Recovery and conversion of nutrients take place due to the production of biomass in large quantities. The polishing of wastewater occurs when the production of plants is done in nutrient-limited conditions [63–66].

4 Current Challenges in Wastewater Remediation

Legislations for the control of effluents, socio-economic conditions and regional characteristics influence the wastewater treatment processes, leading to the challenges on the treatment of wastewater. It is thus difficult to identify common challenges that would be applicable to all the situations. Some common challenges have nevertheless been shown in Fig. 4.

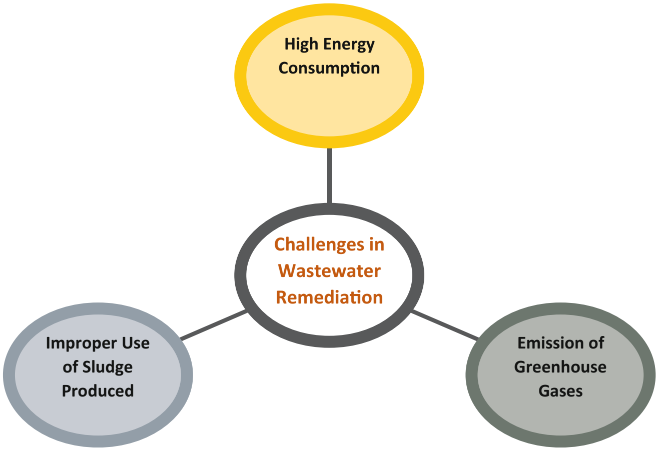


Fig. 4 Challenges in wastewater remediation

(a) Energy Consumption

The highest expense in the operation of the plants for the treatment of wastewater is the energy consumption. An estimated 2–3% of the electric power of a nation that is developed is used in the treatment of wastewater. Treatment of wastewater utilizes 0.7% of Japan's total consumption of electric power. The largest portion of electric consumption of the plant, approximately 50–60%, is utilized in the biological treatment.

(b) Sludge Production

Biological, chemical and physical treatment results in the formation of a residue called sludge. The disposal of the excess sludge poses a major challenge environmentally in the treatment process. The sludge can either be converted or utilized. In Japan, 10% of the sludge is used in agricultural lands; 13% is used for energy production by anaerobic digestion as biogas, i.e., methane; 77% is used for disposal after dewatering and incineration followed by disposal in a landfill or disposed of with no required treatment. The transformation of the sludge into biogas is feasible by anaerobic digestion since 80% of it is composed of organic carbon.

The challenge with this is that the anaerobic digestion systems are not large enough to capitalize the merits of the sludge in an adequate manner. The capital and maintenance cost of the technology is high. Moreover, harnessing the energy in this process is a difficult task.

(c) Greenhouse Gases Emission

The treatment of wastewater results in the emission of greenhouse gases such as carbon dioxide and nitrous oxide. In Japan, seven million tons-CO_2/year is emitted by the treatment of wastewater, accounting up to 0.5% of the total CO_2 emission of the country [67].

5 Technological Interventions in Wastewater Application for Irrigation

5.1 On Farm Irrigation Scheduling

A generally accepted definition of Irrigation Scheduling states that it is the process of figuring out when to irrigate and determining the amount of water needed for the production of crops that are optimal. Irrigation Scheduling enables the supply of water efficiently and effectively in order to face soil water shortages. Thus, understanding and making use of scheduling principles (in order to develop a plan for management) and then carrying out the implementation efficiently of the plan are the key components to successful irrigation [68–71].

Decisions regarding irrigation scheduling need to be based on certain aspects of the atmosphere system of the soil and the plant that are to be subjected to the irrigation. Data that is long term, that is a representation of average conditions or determined by making use of predictions that are short-term and information that is real-time can be used for developing irrigation strategies. Data on specific situations, both quantitative and qualitative, regarding soil, crop, irrigation systems, climate and management methods must be taken into consideration when tailoring irrigation scheduling procedures for that particular scenario. Conflicts and trade-offs need to be anticipated to allow for adjustments to be made in time [69, 72].

The following variables need to be kept in mind when determining irrigation scheduling strategies: the farmer's management objective, maximizing crop yield and net financial return, minimizing the cost of irrigation, minimizing pollution of groundwater, optimizing irrigation and optimizing production when there is a limited supply of water and irrigation system capacity. Usually, the most crucial factors for developing a suitable management objective are the available water supply and costs of irrigation. These two factors often lead to cases where it is optimally possible to produce almost the maximum yields from the entire irrigated area; this case is known as the land limiting case. For this case, irrigation is provided to the entire area and the appropriate depth for irrigation is, in most cases, extremely similar to that required for the production of yield in maximum quantity. Thus, water stress prevention of the crop during the season of growth is the most appropriate irrigation strategy and is the most seen traditional irrigation scheduling application [70, 71]. Where deficit irrigation is concerned, however, the management strategy is the maximization of production per unit of water applied, instead of per unit of land. One big advantage to limited irrigation is the reduction of the area allocated to dryland cropping, thereby increasing the efficiency of water used and the yield of the total farm [71, 73, 74].

Evaporation rates or the measure of the water content of the soil is used in conventional scheduling methods. Due to advancements in research, monitoring of leaf turgor pressure, sap flow and diameter of the trunk are used in scheduling methods [70, 75, 76].

5.1.1 Soil Water Monitoring

The oldest known irrigation scheduling method is by measuring moisture in the soil. The moisture content of the soil can be ascertained using a variety of methods including resistance blocks, tensiometers, gravimetric sampling or a neutron moisture meter. Time Domain Reflectometry (TDR) is a novel soil moisture monitoring method. Currently, only a few models is accessible commercially, but the neutron meter may be replaced by TDR [77]. The available water in the soil is allowed to be depleted by the crop in the root zone. The soil conditions, as a result, establish a level that is required for irrigation. Where the monitoring of soil moisture is concerned, the quantity of water that has been utilized can be a determined by calculations based on the quantity of water that would be needed to fill up the crop root zone or a lesser value or is uniformly applied by the irrigation system [69, 78, 79]. For irrigation scheduling by utilizing measurements of soil moisture, first, a soil moisture measuring site needs to be selected, followed by choosing a device that can ascertain the water content of the soil or potential. Next, points of “full” and “refill” for the soil being monitored need to be set, and a record-keeping scheme needs to be established which can be used to ascertain when irrigation is necessary and can also notify when overirrigation occurs. Once the monitoring site has been set up following the above steps, the soil water is ready to begin being monitored and being scheduled for irrigation. The biggest advantage of this method is that it is usually non-destructive. Once calibrated, the soil is only disturbed during installation.

Water released by crop evapotranspiration (ET) and the quantity of water that gets incorporated into the soil reservoir (as effective irrigation or rain) are accounted for by the water budget methods. The thought behind these methods is to take the accumulated ET losses since the last irrigation and apply an equivalent net amount of irrigation. Therefore, the cycle begins again as the evapotranspiration of the crop plants is initiated due to the recharging of the soil profile. In case complete recharge is not possible or desired, the net irrigation amount or field observations can be used to determine the new balance. However, this method may be ineffective at areas where quantitative data regarding ET of the crop from sources like a water table, etc., cannot be determined or verified [80].

Smart irrigation scheduling consists of technologies that enable farmers to know and ascertain the time and amount of watering to be done for a particular crop.

5.1.2 Monitoring the Plant

The oldest known method of irrigation scheduling is plant observation. Once individual plants start developing observable signs signalling the beginning of water stress, the crop will be irrigated. These signs range from any change in colour to leaves curling and even wilting in the afternoon. The main advantage of this is that it is extremely easy and does not require gathering of quantifiable data, but the biggest drawback to this is that the crops have already suffered a reduction of yield and growth by the time they display any of the above-mentioned signs. More advanced methods make use of tracking specific physiological states of plants like psychrometers to measure leaf water potential, pressure bombs to measure leaf water status, infrared radiation to measure canopy temperature and porometers to measure stomatal closure. A noticeable change can only be seen in these physiological states in states where stress reduces yield, thus these cannot be used routinely for scheduling irrigation [70, 76, 81].

5.1.3 Monitoring the Weather

The concept behind this is to look at the evapotranspiration demand that has been imposed meteorologically, observe any variance over time and to accordingly set irrigation quantities. Researchers and irrigators estimated, based on the weather data, the water used by a crop using evapotranspiration (ET) for years with many computer programs being developed to perform this work. By making use of weather information including daily wind run, daily solar radiation, dry and wet bulb temperatures and minimum and maximum daily temperatures, determination of the reference evapotranspiration (ETo) is done. Utilizing weather monitoring as a method of irrigation scheduling primarily involves calculating or quantifying ET in order to predict water use in the future and update the water balance of the soil in an attempt to forecast when the minimum allowable water level will be obtained. Reference crop ET (ETo or ETc) and a crop coefficient to relate water use of an actual crop are used to calculate the crop ET. While there exist a wide variety of methods that can estimate ETr for alfalfa or grass, equations that are combination-based are generally found to be the most accurate, especially when it comes to computing ETc for scheduling with short intervals common. Climatic data for wind velocity, vapour pressure, solar radiation and air temperature are required for the calculation of combination equations. The data for all of these factors is not available for the same areas; thus, easier methods to compute ETr are utilized to predict crop water use ([71, 82, 83]).

5.1.4 Limitations

Irrigation scheduling becomes particularly sensitive under conditions of limited water resources.

- In areas with conditions of water shortage, it is difficult to carry out irrigation scheduling. Appropriate knowledge is required regarding levels of salt tolerance in areas with saline conditions.
- It is difficult to incorporate the different patterns of rainfall in the irrigation calendars. This needs to be considered.
- Reliable and suitable indicators of water stress are required for deficit irrigation and yield-salinity relationship knowledge is needed for saline waters areas.

- During the operation and selection of the system of irrigation scheduling, the efficiency is to be considered, which is in turn determined by the efficiency of application and adequacy and the criteria of the design of the system.
- The cost of technology may not be affordable by the end-user.
- Not all farmers obtain the necessary knowledge on the adequate use and management of tools.
- Few farmers prefer regular irrigation since they do not understand water budgets and hydrology and lack the necessary skills (technical) to schedule irrigation [84].

5.2 Treated Wastewater Irrigation

Given the huge pressure on water resources, treated wastewater from wastewater treatment plants (WWTPs) has grown to become an invaluable resource to help in irrigation in agriculture. Arid countries such as Saudi Arabia, Peru, Jordan and Israel have been using treated wastewater for irrigation of crops for a long time [85]. Three fundamental resources can be found in wastewater: Water, nutrients and energy.

With urban settlements being the major polluting source, the treatment or collection of 80% of wastewater is not done worldwide [86]. Large amounts of wastewater are both produced and consumed by urban and peri-urban areas. Already seeing increased use in agricultural and irrigation practices, soon untreated or partially treated wastewater will transform into the only water source for several farmers in sub-Saharan Africa [87]. Wastewater contains nutrients and organic matter which improve the fertility of the soil, thereby reducing the need to apply chemical fertilizers. Therefore, farmers benefit due to an increase in yields and productivity along with faster growth cycles, while at the same time minimizing the chemical fertilizer requirements as well as additional sources of water [88] as long as they manage to stick to a set of principles for the protection of farmers and their families from health risks associated with irrigation using wastewater [89].

A big challenge when it comes to promoting irrigation in agriculture using wastewater that is treated is the concerns to health and safety of using the products since even treated wastewater is contaminated by a variety of pollutants. Traditionally, heavy metals and pathogens that cause disease have been a major concern but recently contaminants of emerging concern (CECs), especially pharmaceutical and personal care products (PPCPs) are becoming a bigger area of concern. Given that there is an upward trend in the use of PPCPs, due to healthcare advancements and populations that are ageing, and that wastewater is not completely free of these chemicals, PPCPs tend to be found in WWTPs wastewater (effluent) around the world [90–93].

Malchi et al. [94] found the presence of 3 PPCPs in 2 root vegetables (sweet potato and carrot) that had been irrigated by using wastewater that had undergone a secondary stage of treatment, and 10 PPCPs in those two root vegetables when they were irrigated with spiked (290 – 1,550 ng/L) water under field conditions. Calderon-Preciado et al. [95] discovered the presence of 6 pharmaceuticals in apple tree leaves and alfalfa crops that were irrigated with wastewater that was treated. Jones-Lepp et al. [96] conducted a field study and found only N, N-dimethylphenethylamine (DMPEA) at 48–180 ng/g (dry weight) in 4 crops that had wastewater irrigation done from a local wastewater water treatment plant. Wu et al. [97] found in 8 vegetable measurable quantities of 19 commonly occurring PPCPs under field conditions when irrigated with wastewater that was treated. Crops were irrigated with wastewater that had undergone tertiary treatment until harvest, with or without a fortification of each PPCP at 250 ng/L followed by crop samples being taken at premature and mature stages. Upon analysis, edible tissues were found to contain a frequency of 91% and 64% in all vegetables from the fortified water treatments and treated wastewater, respectively. Same amounts of PPCPs, including meprobamate, triclosan, naproxen, Dilantin, DEET, primidone, carbamazepine and caffeine were found in the edible samples from the two tissues. The edible tissue treated from fortified irrigation treatment and the treated wastewater found the following total concentrations of PPCPs in the range of 0.15–7.3 and 0.01–3.87 ng/g (dry weight), respectively. After a research on the accumulation of 19 PPCPs that occur frequently after the irrigation with wastewater that has been treated till the tertiary stage in 8 common vegetables under normal field conditions, it was found that human exposure to these PPCPs through daily consumption of these vegetables was small.

5.3 Microalgal Consortia

During the tertiary treatment phase, the phosphorus and nitrogen in wastewater are removed mainly using processes that are biological, like by nitrification and denitrification that are done after anaerobic digestion [98–102]. However, several cycles are required, and this leads to high processing costs [103]. Chemical methods may also be utilized but these are expensive and huge amounts of sludge that is contaminated and contains chemical compounds is produced which then have to be treated further [104–106].

In order to overcome these obstacles, microalgae have been considered as a tool for the treatment of wastewaters. Microalgae grow by making use of large quantities of phosphorus and nitrogen [98, 107], therefore these can effectively remove, from the wastewater, phosphorus and nitrogen. In fact, microalgae have already been reported to be highly effective (80–100%) at removing large nitrogen and phosphorus quantities from wastewaters of various places (e.g. municipal, industrial and agricultural) [108–112].

Moreover, using microalgae for removing unwanted elements presents several advantages [113–115]

1. Through the production of fertilizers, the assimilated phosphorus and nitrogen by microalgae can be recycled.

2. Pharmaceuticals, food, animal feed and bioenergy can be produced from the resulting biomass.
3. The effluent that is discharged is oxygenated and then released into the water bodies.

Microalgal-bacterial consortia have proven to have more advantages as compared to only composed of microorganisms that are photosynthetic as they can replace treatment that is secondary and tertiary treatment of wastewater, while only the tertiary step can be replaced by the use of microalgal consortia (wastewater polishing).

The processes for the treatment of wastewater can further be improved by these systems because [116]

1. There can be a significant reduction in the associated costs with the activated sludge tank oxygenation.
2. The CO_2 that is released by the bacteria, by the action of the microalgae, gets converted to organic matter. Thus, the effect of greenhouse gases emitted by the plant can be negligible [117].

6 Future Prospects and Conclusion

Water, energy and food are inextricably linked and are considered as the basic resources for the development of social economy and maintenance of life. Due to the current rate at which the world population is increasing and due to an increase in urbanization, the water crisis is increasing. The energy crisis will also increase due to these reasons. There is a requirement for advancements in technology to make the water–energy nexus more efficient.

Globally, 90% of freshwater and 30% of energy are consumed for food production. Several new methods of irrigation have been developed for the efficient use of water. Wastewater is an excellent resource and can be used efficiently for the purpose of irrigation. The energy used in the treatment of wastewater can be reduced by the use of aquatic biota. This not only helps in the reduction of energy but also helps in providing nutrition to the growing plants. This can be used in the growing of crops. The sludge that is produced as a by-product can be used for the production of bioenergy and providing nutrition to the crops naturally. There is a huge scope for advancements in technology for the use of wastewater and its by-products. The current methods of irrigation such as irrigation scheduling require intensive advancements for the better use of the resources to obtain the maximum yield. There is a need for better research in the incorporation of microorganisms in the treatment of wastewater and further use in agriculture. New advancements in irrigation technology are required for the efficient use of water and energy.

References

1. Tian Y, Hu H, Zhang J (2017) Solution to water resource scarcity: water reclamation and reuse. In: Environmental science and pollution research, vol 24, no 6. Springer Science and Business Media LLC, pp 5095–5097
2. Zhang X, Vesselinov VV (2017) Integrated modeling approach for optimal management of water, energy and food security nexus. In: Advances in water resources, vol 101. Elsevier BV, pp 1–10
3. UNICEF (2012) Progress on drinking water and sanitation – 2012 annual report. https://data.unicef.org/resources/progress-on-drinking-water-and-sanitation-2012-update
4. Deng C, Wang H, Gong S, Zhang J, Yang B, Zhao Z (2020) Effects of urbanization on food-energy-water systems in mega-urban regions: a case study of the Bohai MUR, China. Environ Res Lett 15(4):044014
5. IEA (2012) Emissions from fuel combustion. International Energy Agency (IEA/OECD). https://www.iea.org/reports/co2-emissions-from-fuel-combustion-overview
6. Dai J, Wu S, Han G, Weinberg J, Xie X, Wu X et al (2018) Water-energy nexus: a review of methods and tools for macro-assessment. Appl Energy 210:393–408
7. Griggs D, Stafford-Smith M, Gaffney O, Rockstrom J, Ohman MC, Shyamsundar P, Steffen W, Glaser G, Kanie N, Noble I (2013) Policy: sustainable development goals for people and planet. Nature 495:305–307
8. Scott CA, Pierce SA, Pasqualetti MJ, Jones AL, Montz BE, Hoover JH (2011) Policy and institutional dimensions of the water–energy nexus. Energy Policy 39:6622–6630
9. Rothausen SGSA, Conway D (2011) Greenhouse-gas emissions from energy use in the water sector. Nature Clim Change 1:210–219
10. Lee M, Keller AA, Chiang P-C, Den W, Wang H, Hou C-H, Wu J, Wang X, e Yan, J. (2017) Water-energy nexus for urban water systems: a comparative review on energy intensity and environmental impacts in relation to global water risks. Appl Energy 205:589–601
11. Vymazal J (2009) The use constructed wetlands with horizontal sub-surface flow for various types of wastewater. J Ecol Eng 35:1–17
12. Francisca CM, Soler J, Alpendurada MF, Rui AR, Enric B, Vitor JP (2016) Tertiary treatment of a municipal wastewater toward pharmaceuticals removal by chemical and electrochemical advanced oxidation processes. Water Res 105:251–263
13. Malik RPS (2002) Water-energy nexus in resource-poor economies: the Indian experience. Int J Water Resour Dev 18(1):47–58
14. Mannie MN, Bower A (2014) Challenges in determining the correct waste disposal solutions for local municipalities - a South African overview. In: Proceedings of the 20th WasteCon conference 6-10 October 2014. Somerset West, Cape Town
15. Tilley E, Ulrich L, Luethi C, Reymond P, Zurbruegg C (2014) Compendium of sanitation systems and technologies.2nd rev edn. Swiss Federal Institute of Aquatic Science and Technology (Eawag), Duebendorf
16. Benammar L, Menasria T, Ayachi A, Benounis M (2015) Phosphate removal using aerobic bacterial consortium and pure cultures isolated from activated sludge. Process Saf Environ Prot 95:237–246
17. Dharmender Y, Vikas P, Pramod K (2016) Enhanced biological phosphorus removal in aerated stirred tank reactor using aerobic bacterial consortium. J Water Process Eng 13:61–69
18. Mang HP, Li Z (2010) Technology review of biogas sanitation. Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH, Eschborn
19. Jeon B, Nam S, Kim Y (2014) Treatment of pharmaceutical wastewaters by hydrogen peroxide and zerovalent iron. Environmental Engineering Research
20. Sinha SK, Sinha VK, Kr S, Pandey AT (2014) A study on the wastewater treatment Technology for Steel Industry: recycle and reuse. Am J Eng Res 03(04):309–315
21. Irene M, Lesage N, Sperandio M, Besierre Y (2016) Impact of sonication on activated sludge properties and consequence on PAH partitioning. Can J Chem Eng 94:244–252

22. Madoni P (1994) Microfauna biomass in activated sludge and biofilm. Water Sci Technol 29: 63–66
23. Cordi L, Assalin MR, Ponezi AN, Durán N (2012) Identification of microbiota for activated sludge acclimated by paper mill effluent Kraft E1 bioremediation. J Bioremed Biodegr 3:169
24. Mittal A (1 Aug 2011) Biological wastewater treatment. Water Today, pp 32–44
25. Wilson SP, Ouki SK, Saroj DP, Pearce PA, Bancroft L, Germain E (2015) Adopting primary plastic Trickling filters as a solution for enhanced nitrification. Water Environ Res 87(1):80–88
26. Wafler M (2008) Training materials on anaerobic wastewater treatment (ecosan expert training course). Seecon GmbH, Aarau
27. Galvaân A, Urbina P, De Castro F (2000) Characterization of filamentous microorganisms in rotating biological contactor biofilms of wastewater treatment plants. Bioprocess Eng 22:257–260
28. Tawfik H, Temmink GZ, Klapwijk B (2006) Sewage treatment in a rotating biological contactor (RBC) system. National Research Center, Water Pollution Control Dept, pp 275–289
29. Cortez S, Teixeira P, Oliveira R, Mota M (2008) Rotating biological contactors: a review on main factors affecting performance. Rev Environ Sci Biotechnol 7(2):155–172
30. Manoj RT, Sonali BP, Jyoti RM (2015) Review paper on study of rotating biological contactor for wastewater treatment process. Int J Curr Eng Technol 5(3):1539–1541
31. De la Cruz N, Esquius L, Grandjean D, Magnet A, Tungler A, De Alencastro LF, Pulgarín C (2013) Degradation of emergent contaminants by UV, UV/H2O2 and neutral photo-Fenton at pilot scale in a domestic wastewater treatment plant. Water Res 47(15):5836–5845
32. Pickford J (1987) Developing world water. Grosvenor Press, London
33. USEPA (1995) United State Environmental Protection Agency guidance for risk characterization. Science Policy Council. February 1995
34. De Godos I, Munoz R, Guieysse B (2012) Tetracycline removal during wastewater treatment in high-rate algal ponds. J Hazard Mater 229–230:446–449
35. Petrie B, Barden R, Kasprzyk-Hordern B (2015) A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. Water Res 72:3–7
36. Rafiee A, Kamyar Y, Mohammad H, Saeid P, Amirhosein M, Masud Y, Mehran K, Ramin N (2016) Assessment and selection of the best treatment alternative for infectious waste by modified sustainability assessment of technologies methodology. J Environ Health Sci Eng 14(10):1–14
37. Yaman C, Martin JP, Korkut E (2006) Effects of wastewater filtration on geotextile permeability. Geosynth Int 13(3):87–97
38. Kadlec RH, Wallace SD (2008) Treatment wetlands.2nd edn. CRC Press, Boca Raton
39. Suzanne EA, Claudia S, Sébastien FL, George T, Pierre L (2015) Potential efficiency of riparian vegetated buffer strips in intercepting soluble compounds in the presence of subsurface preferential flows. PLoS One 10(7):1–21
40. Olilo CO, Onyando JO, Moturi WN, Muia AW, Ombui P, Shivoga WA, Roegner AF (2016) Effect of vegetated filter strips on transport and deposition rates of Escherichia coli in overland flow in the eastern escarpments of the Mau Forest, Njoro River Watershed, Kenya. In: Energy, ecology and environment, vol 1, no 3. Springer Science and Business Media LLC, pp 157–182
41. Shah M, Hashmi HN, Ghumman AR, Zeeshan M (2015) Performance assessment of aquatic macrophytes for treatment of municipal wastewater. J South Afr Inst Civil Eng 57(3):18–25. Paper 1011
42. Saunders MJ, Jones MB, Kansiime F (2007) Carbon and water cycles in tropical papyrus wetlands. Wetl Ecol Manag 15:489–498
43. Vymazal J (2011) Constructed wetlands for wastewater treatment: five decades of experience. Environ Sci Technol 45(1):65–69

44. Peixoto RB, Marotta H, Bastviken D, Prast E (2016) Floating aquatic macrophytes can substantially offset open water CO2 emissions from tropical floodplain lake ecosystems. Ecosystems 19(4):724–736
45. Vymazal J (2014) Constructed wetlands for treatment of industrial wastewaters: a review. In: Ecological engineering, vol 73. Elsevier BV, pp 724–751
46. Saunders MJ, Kansiime F, Jones MB (2012) Agricultural encroachment: implications for carbon sequestration in tropical African wetlands. Glob Chang Biol 18:1312–1321
47. Rey JR, Walton WE, Wolfe RJ, Connelly CR, O'Connell SM, Berg J, Sakolsky-Hoopes GE, Laderman AD (2012) North American Wetlands and mosquito control. Int J Environ Res Public Health 9(12):4537–4605
48. UN Economic and Social Commission for Asia and the Pacific (1981). https://www.unescap.org/publications/transport-and-communications-bulletin-asia-and-pacific-no-57
49. Jensen CD, Gujarathi NP (2015) Characterization of a macrophyte microcosm as a surface water treatment system for antibiotics. Environ Prog Sustain Energy 34:1605–1612
50. Borkar RP, Mahatme PS (2015) Tidal flow constructed wetland: an overview. Int J Eng Sci 5(10):31–34
51. Ana D, David M, Gayani C, Yali L, Belinda H, Emily P, Kefeng Z, Rebekah H, Peter K, Anja R, Ze M, Bonnie G, Tracey P, Jason E (2014) Biofilters and wetlands for stormwater treatment and harvesting. Cooperative Research Centre for Water Sensitive Cities. Monash University
52. Glaister BJ, Fletcher TD, Cook PLM, Hatt BE (2014) Co-optimisation of phosphorus and nitrogen removal in stormwater biofilters: the role of filter media, vegetation and saturated zone. Water Sci Technol 69(9):1961–1969
53. Payne EGI, Fletcher TD, Cook PLM, Deletic A, Hatt BE (2014) Processes and drivers of nitrogen removal in storm water biofiltration. Crit Rev Environ Sci Technol 44(7):796–846
54. Jenny AG, Diego P, Janneth AC (2013) Effects of plants and the combination of wetland treatment types systems in pathogen removal in tropical climate condition. Ecol Eng 58:57–62
55. Chandrasena GI, Pham T, Payne EG, Deletic A, McCarthy DT (2014) E. coli removal in laboratory scale stormwater biofilters: influence of vegetation and submerged zone. J Hydrol 519(Part A):814–822
56. Shrestha RR (2005) Faecal sludge management through constructed wetland system in Nepal. Concern & quest ENPHO, Environment and Public Health Organisation, Kathmandu
57. Wong TH, Breen PF, Somes NL (1999, February) Ponds vs wetlands–performance considerations in stormwater quality management. In: Proceedings of the 1st South Pacific conference on comprehensive stormwater and aquatic ecosystem management, vol 2, pp 223–231
58. Namratha N, Harshini P, Hamsalekha S, Sindhu MS, Udayashankara TH (2016) A review on removal of phosphate and nitrate from kitchen wastewater by constructed wetlands. Int J Mod Trends Eng Res 3(3):273–276
59. Davison L, Headley T, Pratt K (2005) Aspects of design, structure, performance and operation of reed beds-eight years' experience in North-Eastern New South Wales, Australia. Water Sci Technol 51:129–138
60. Vymazal J (2005) Horizontal sub-surface flow and hybrid constructed wetland systems for wastewater treatment. Ecol Eng 25:478–490
61. Haghshenas AA, Heidarpour M, Tarkesh ES (2016) Evaluation of horizontal-vertical subsurface hybrid constructed wetlands for tertiary treatment of conventional treatment facilities effluents in developing countries. Water Air Soil Pollut 227(28):1–18
62. Weerakoon G, Jinadasa K, Herath G, Mowjood M, Dongqing Z, Soon K, Ng, Wun J (2016) Performance of tropical vertical subsurface flow constructed wetlands at different hydraulic loading rates. CSAWAC 44(8):909–1084
63. Lennard WA, Leonard BV (2006) A comparison of three different hydroponic sub-systems (gravel bed, floating and nutrient film technique) in an aquaponic test system. Aquacult Int 14(6):539–550

64. Castillo CD, Zavala LI, Ruiz VJ, Radilla GA, Nieto NJ, Romero BC, González-H C (2016) Implementation of an experimental nutrient film technique-type aquaponic system. Aquac Int 4(2):637–646
65. Danaher JJ, Shultz RC, Rakocy JE, Bailey DS (2013) Alternative solids removal for warm water recirculating raft aquaponic systems. J World Aquac Soc 44(3):374–383
66. Donde O (2017) Wastewater management techniques: a review of advancement on the appropriate wastewater treatment principles for sustainability. Environ Manag Sustain Dev 6:40. https://doi.org/10.5296/emsd.v6i1.10137
67. Hosomi M (2016) New challenges on wastewater treatment. Clean Techn Environ Policy 18: 627–628
68. Cassel DK (1984) Irrigation scheduling. Crops and soil magazine. Am Soc Agron. February, March–April
69. Heermann DF, Martin DL, Jackson RD, Stegrnan EC (1990) Irrigation scheduling controls and techniques. In: Stewart BA, Nielsen DR (eds) Irrigation of agricultural crops. Agronomy monographs no:30. ASA. CSSA, SSSA, Madison, pp 510–533
70. Jones JW (2004) Irrigation scheduling: advantages and pitfalls of plant-based methods. J Exp Bot 55(407):2427–2436
71. Martin DL, Stegman EC, Fereres E (1990) Irrigation scheduling principles. In: Hoffman GJ et al (eds) Management of farm irrigation systems. ASAE Monograph, St. Joseph, pp 155–199
72. Abdulmumin S, Bastiansen J, Smith M, Rijks D, Gbeckor-Kore NA (1990) Application of climatic data for irrigation planning and management. Training manual. FAO WMO, Rome
73. Hillel D (ed) (1982) Advances in irrigation, vol 1. Academic Press, New York
74. English MJ, Musick JT, Murty VVN (1990) Deficit irrigation. In: Hoffman GJ et al (eds) Management of farm irrigation systems. ASAE Monograph, St. Joseph, pp 631–655
75. Yazar A, Kanber R, Ozekici B (1995) Irrigation scheduling in agronomic practice. In: Pereira LS et al (eds) Sustainability of irrigated agriculture. NATO ASI series E: applied sciences, vol 312. Springer, pp 251–266
76. Fernández JE, Green SR, Caspari HW, Diaz-Espejo A, Cuevas MV (2007) The use of sap flow measurements for scheduling irrigation in olive, apple and Asian pear trees and in grapevines. Plant Soil. https://doi.org/10.1007/s11104-007-9348-8
77. Topp GC, Davis JL (1985) Time-domain reflectometry and its applications to irrigation scheduling. In: Hillel D (ed) Advances in irrigation, vol 3. Academic Press, Orlando, pp 107–129
78. Bucks D, Sammis TW, Dickey GL (1990) Irrigation for arid areas. In: Hoffman GJ et al (eds) Management of farm irrigation systems. ASAE Monograph, St. Joseph, pp 499–542
79. Evett SR (2008) Neutron moisture meters. In: Evett SR, Heng LK, Moutonnet P (eds) Field estimation of soil water content: a practical guide to methods, instrumentation, and sensor technology. International Atomic Energy Agency, Vienna
80. Harrison K (2009) Irrigation scheduling methods. The University of Georgia, Cooperative Extension Service Bulletin 974
81. Turner NC (1990) Plant water relations and irrigation management. Agric Water Manag 17(1990):59–73
82. Jensen ME, Rangeley WR, Dielman PJ (1990) Irrigation trends in world agriculture. In: Stewart BA, Nielsen DR (eds) Irrigation of agriculture crops. Agronomy 30. American Society of Agronomy, Madison
83. Allen RG, Pereira LS, Raes D, Smith M (1998) Crop evapotranspiration. FAO irrigation and drainage paper 56. FAO, FAO, Rome
84. Yazar A (2013) On-farm agricultural water management (irrigation scheduling techniques)
85. World Health Organization (WHO) (1989) Health guidelines for the use of wastewater in agriculture and aquaculture. WHO, Geneva
86. United Nations World Water Assessment Programme (WWAP) (2012) The United Nations world water development report 4: managing water under uncertainty and risk. UNESCO, Paris

87. World Health Organization (WHO) (2006) Guidelines for the safe use of wastewater, excreta and grey water. WHO, Geneva
88. Corcoran E, Nellemann C, Baker E, Bos R, Osborn D, Savelli H (eds) (2010) Sick water? The central role of waste-water management in sustainable development. A rapid response assessment. United Nations Environment Programme, UN-HABITAT, GRID-Arendal, Oslo
89. Avellán T, Ardakanian R, Perret SR, Ragab R, Vlotman W, Zainal H, Im S, Gany HA (2018) Considering resources beyond water: irrigation and drainage management in the context of the water–energy–food nexus. Irrig Drain 67:12–21
90. Gros M, Petrovic M, Ginebreda A, Barcelo D (2010) Removal of pharmaceuticals during wastewater treatment and environmental risk assessment using hazard indexes. Environ Int 36: 15–26
91. Kim SD, Cho J, Kim IS, Vanderford BJ, Snyder SA (2007) Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. Water Res 41:1013–1021
92. Sui Q, Huang J, Deng S, Chen W, Yu G (2011) Seasonal variation in the occurrence and removal of pharmaceuticals and personal care products in different biological wastewater treatment processes. Environ Sci Technol 45:3341–3348
93. Vanderford B, Snyder S (2006) Analysis of pharmaceuticals in water by isotope dilution liquid chromatography/tandem mass spectrometry. Environ Sci Technol 40:7312–7320
94. Malchi T, Maor Y, Tadmor G, Shenker M, Chefetz B (2014) Irrigation of root vegetables with treated wastewater: evaluating uptake of pharmaceuticals and the associated human health risks. Environ Sci Technol 48(16):9325–9333
95. Calderón-Preciado D, Jiménez-Cartagena C, Matamoros V, Bayona JM (2011) Screening of 47 organic microcontaminants in agricultural irrigation waters and their soil loading. Water Res 45:221–231
96. Jones-Lepp TL, Sanchez CA, Moy T, Kazemi R (2010) Method development and application to determine potential plant uptake of antibiotics and other drugs in irrigated crop production systems. J Agric Food Chem 58:11568–11573
97. Wu X, Conkle JL, Ernst F, Gan J (2014) Treated wastewater irrigation: uptake of pharmaceutical and personal care products by common vegetables under field conditions. Environ Sci Technol 48(19):11286–11293
98. Renuka N, Prasanna R, Sood A, Ahluwalia AS, Bansal R, Babu S, Singh R, Shivay YS, Nain L (2015) Exploring the efficacy of wastewater-grown microalgal biomass as a biofertilizer for wheat. In: Environmental science and pollution research, vol 23, no 7. Springer Science and Business Media LLC, pp 6608–6620
99. Sonune A, Ghate R (2004) Developments in wastewater treatment methods. Desalination 167: 55–63
100. Ruiz J, Arbib Z, Álvarez-Díaz P, Garrido-Pérez C, Barragán J, Perales J (2013) Photobiotreatment model (PhBT): a kinetic model for microalgae biomass growth and nutrient removal in wastewater. Environ Technol 34:979–991
101. Cai T, Park SY, Li Y (2013) Nutrient recovery from wastewater streams by microalgae: status and prospects. Renew Sust Energ Rev 19:360–369
102. Queiroz MI, Lopes EJ, Zepka LQ, Bastos RG, Goldbeck R (2007) The kinetics of the removal of nitrogen and organic matter from parboiled rice effluent by cyanobacteria in a stirred batch reactor. Bioresour Technol 98:2163–2169
103. Foess GW, Steinbrecher P, Williams K, Garrett GS (1998) Cost and performance evaluation of BNR processes. Fla Water Res J 11:11–13
104. Barnard JL (1975) Biological nutrient removal without the addition of chemicals. Water Res 9: 485–490
105. Malhotra SK, Lee GF, Rohlich G (1964) Nutrient removal from secondary effluent by alum flocculation and lime precipitation. Int J Air Water Pollut 8:487–500

106. Wang X-J, Xia S-Q, Chen L, Zhao J-F, Renault N, Chovelon J-M (2006) Nutrients removal from municipal wastewater by chemical precipitation in a moving bed biofilm reactor. Process Biochem 41:824–828
107. Muñoz R, Guieysse B (2006) Algal-bacterial processes for the treatment of hazardous contaminants: a review. Water Res 40(2006):2799–2815
108. González LE, Cañizares RO, Baena S (1997) Efficiency of ammonia and phosphorus removal from a Colombian agroindustrial wastewater by the microalgae *Chlorella vulgaris* and *Scenedesmus dimorphus*. Bioresour Technol 60:259–262
109. Li Y, Chen Y-F, Chen P, Min M, Zhou W, Martinez B, Zhu J, Ruan R (2011) Characterization of a microalga *Chlorella* sp. well adapted to highly concentrated municipal wastewater for nutrient removal and biodiesel production. Bioresour Technol 102:5138–5144
110. Phang S, Miah M, Yeoh B, Hashim M (2000) Spirulina cultivation in digested sago starch factory wastewater. J Appl Phycol 12:395–400
111. Sydney E, Da Silva T, Tokarski A, Novak A, De Carvalho J, Woiciecohwski A, Larroche C, Soccol C (2011) Screening of microalgae with potential for biodiesel production and nutrient removal from treated domestic sewage. Appl Energy 88:3291–3294
112. Zhu L, Wang Z, Shu Q, Takala J, Hiltunen E, Feng P, Yuan Z (2013) Nutrient removal and biodiesel production by integration of freshwater algae cultivation with piggery wastewater treatment. Water Res 47:4294–4302
113. Renuka N, Sood A, Ratha SK, Prasanna R, Ahluwalia AS (2013) Evaluation of microalgal consortia for treatment of primary treated sewage effluent and biomass production. J Appl Phycol 25:1529–1537
114. Aslan S, Kapdan IK (2006) Batch kinetics of nitrogen and phosphorus removal from synthetic wastewater by algae. Ecol Eng 28:64–70
115. Rawat I, Kumar RR, Mutanda T, Bux F (2011) Dual role of microalgae: phycoremediation of domestic wastewater and biomass production for sustainable biofuels production. Appl Energy 88:3411–3424
116. De Godos I, González C, Becares E, García-Encina PA, Muñoz R (2009) Simultaneous nutrients and carbon removal during pretreated swine slurry degradation in a tubular biofilm photobioreactor. Appl Microbiol Biotechnol 82:187–194
117. Gonçalves AL, Pires JCM, Simões M (2017) A review on the use of microalgal consortia for wastewater treatment. Algal Res 24(1):403–415

Microalgae Production Integrated with the Wastewater Treatment: A Management Approach

Luan de Souza Leite and Luiz Antonio Daniel

Contents

Abstract Microalgae are a sustainable source of high value-added bioproducts that can be used for a variety of purposes, such as energy, food, and raw materials. However, the costs incurred to microalgae production are still very high, which prevents its large-scale application from being economically viable. One widely discussed solution in recent years is the association of microalgae cultivation with wastewater treatment, in order to reduce costs related to its cultivation. In this process, the microalgae uptake nutrients (e.g., carbon, nitrogen, and phosphorus) and other substances from the wastewater, generating a treated wastewater effluent and a microalgal biomass with high economic value. After the cultivation process, the generated biomass has to be recovered from the wastewater. Harvesting is also a

L. de S. Leite (✉) and L. A. Daniel
Department of Hydraulics and Sanitation, São Carlos School of Engineering, University of São Paulo, São Paulo, Brazil
e-mail: luanleite@usp.br

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 299–324, DOI 10.1007/698_2022_862,

bottleneck process because it represents about 20–60% of the total production costs. Since there is no universal method applied to microalgae recovery, different harvesting methods have been investigated, mainly including centrifugation, filtration, flotation, and sedimentation. Thus, choosing the appropriated harvesting method is crucial for a cost-effective microalgae production. In this context, this chapter presents an overview of the microalgae production, integrated with the wastewater treatment, and the potential harvesting methods. In addition, the challenges to apply the system in Brazil are also discussed.

Keywords Biomass, Harvesting, Microalgae, Wastewater treatment

1 Introduction

Microalgae are an environmental source of high-value products with commercial applications (e.g., carbohydrates, fatty acids, food supplements, lipids, pigments, protein, and vitamins) [1]. Nevertheless, the high costs of biomass production make it economically unfeasible. Microalgae growth coupled with wastewater treatment is a promising solution to reduce the microalgae cultivation costs. Reduction higher than 50% has been projected when low-cost sources such as wastewater are used to obtain fresh water and nutrients [2]. At the same time, a sustainable wastewater treatment is proposed considering that over 80% of the world wastewater is discharged into the environment without any treatment [3].

The discharge of the untreated wastewater may have serious consequences to the environment, since the nutrients addition (e.g., carbon, nitrogen, and phosphorus), at certain concentrations, alters the water quality significantly. If the alterations affect the requested uses for the water body, such as aquatic life preservation, power generation, and water supply, this phenomenon is named eutrophication. The consequences of this phenomenon are: development of anoxic conditions; uncontrollable algae/microalgae growth; increase of the water treatment cost; cyanotoxin release in the water; and gradual disappearance of the water body [4].

According to Dodds et al. [5], around US$2.2 billion is lost per year due to the eutrophication phenomenon in the U.S. freshwaters. This value is mainly attributed to the waterfront property's economic losses and the recreational water use. The authors also cite that this value is even higher than what was estimated, because there are some gaps in the current records of the U.S. Environmental Protection Agency.

Considering the economics and environmental consequences, it is fundamental that the population's perceptions about wastewater change in order to reflect correctly its value. Wastewater is a sustainable and accessible source of water, energy, and nutrients, and the improvement in its management offers great opportunities, including recovery and reuse [3].

Microalgae indeed is a bioindicator of the nutrients presence in the aquatic environment, nevertheless these microorganisms can also be used in the bioremediation process. Several studies demonstrated the microalgae capacity to uptake the dissolved pollutants present in wastewater, mainly the nutrients carbon (C), nitrogen (N), and phosphorus (P) [6–9]. It has been reported that microalgae can also promote a total removal of nitrogen and phosphorus from the wastewater [10].

The technologies employed worldwide in the wastewater treatment plant (WWTP) produce a large sludge volume as a by-product, which requires additional treatments (e.g., dewatering, drying, and disinfection) and final disposal [11]. Costs involved in these sludge treatment are around 20–40% of the operating costs in a full-scale WWTP [12]. In this context, the microalgae application for wastewater treatment is more sustainable than traditional technologies, since it has a potential biomass with high economic value as by-product. Moreover, wastewater treatment by microalgae promotes higher nitrogen and phosphorus removal than the traditional technologies under the same conditions [13].

Despite the advantages of the wastewater treatment using microalgae, some hurdles must be reduced or overcome to make the treatment economically feasible on large-scale, such as:

- The cost associated to the microalgae harvesting is high. It represents about 20–60% of the microalgae production cost [14];
- Some locations require the use of artificial light for an efficient microalgae growth, when the natural photoperiod is not enough. However, power consumption for artificial light can represent 94.5% of the cultivation costs [15];
- The wastewater quality is subject to variation in each cultivation cycle, because it depends on the weather conditions, daily patterns, and eventual industrial wastewater discharge [16]. These conditions can reduce the process efficiency, since the N:P ratio influences the microalgae production and nutrient removal from the wastewater [17]. Moreover, toxic and new compounds can be introduced by the industrial wastewater discharge, causing serious consequences for the microalgae [18].

In this context, the present chapter presents an overview of the microalgae production integrated with the wastewater treatment, the potential harvesting methods, and the perspective to apply this treatment system in Brazil.

2 Microalgal Bioproducts

Microalgae are unicellular, autotrophic, and photosynthetic organisms, which are found in almost every aquatic environment in the planet. It consists in a very diverse group of microorganisms with different sizes, morphologies, and structures. The major microalgal classes are *Chlorophyta* (green algae), *Euglenophyta*, *Rhodophyta* (red algae), and *Phaeophyta* (brown algae) [19]. These microorganisms are the main primary producers and the most efficient photosynthetic organisms on Earth, which makes them a promising biomass for different purposes [20, 21].

Table 1 Microalgal bioproducts and their potential applications

Bioproduct	Example	Application	Reference
Biomass	–	Animal food Fertilizer Food supplement	[1]
Bioplastic	Polylactic acid (PLA) Polyhydroxyalkanoate (PHA) Polyhydroxybutyrates (PHB)	Cosmetic Medicine Packaging material	[29]
Carbohydrate	Starch Cellulose Pectin Sulfated polysaccharides Glucose	Drink industry Natural food Pharmaceutical industry	[30]
Carotenoid	Astaxanthin Lutein ß-carotenoid Lycopene Canthaxanthin Fucoxanthin	Animal food Cosmetic Food supplement Pharmaceutical industry	[31]
Enzyme	Lipase α-Galactosidase Aminopeptidase Protease Phytase Prolyl endopeptidase Superoxide dismutase (SOD)	Natural food Medicine Research	[32]
Lipid	Docosahexaenoic acid (DHA) Eicosapentaenoic acid (EPA) Glycolipids Hydrocarbons Omega-3 Phospholipds Sterol Triacylglyceride (TAG)	Biofuel Food supplement Pharmaceutical industry	[33]
Protein	Enzyme Essential aminoacids(EAAs) Mycosporine-like amino acids(MAA)	Cosmetic Medicine Research	[34]
Vitamin	Vitamin B Vitamin C Vitamin E	Food supplement Pharmaceutical industry	[35]

One of the main challenges of this century is supplying with energy, food, and raw materials to match the needs of an increasing population in the midst of global climate change [22]. In this context, microalgae stand out as a potential source of these compounds, with the advantage of being obtained without consuming fossil energy or using arable land. Moreover, microalgae productivity per hectare is higher than the traditional vascular plants [23], which demonstrate their huge potential to be produced on large-scale.

Several high-value compounds are found in the microalgal biomass, which have numerous applications as shown in Table 1. It is important to mention that most of the compounds shown are not established or not available in the market, but they already have great market opportunities. Fatty acids have an estimated annual market value of US$700 million, carotenoids of US$1,200 million, vitamins and supplement of US$68 million, and lutein of US$233 million [24].

The bioproduct concentration in the microalgae biomass depends on the microalgae specie and the cultivation parameters. There are strategies to increase the production of certain compound using stress conditions with abiotic factors during the microalgae cultivation, such as high light intensity, high temperature, salt addition (NaCl), nutrient starvation (nitrogen and phosphorus), and the carbon source used (organic or inorganic) [25].

Microalgae studies have been predominantly focused on biofuel production in the past few years. However, the high processing cost (extraction, purification, and conversion) required to obtain biofuels changed the research route to other microalgae bioproducts [26]. Recently, the biorefinery concept has been getting attention as a proposal to reduce the process cost and maximize the bioproduct extraction. This technique aims to extract multiple bioproducts in one stage, where several processes of biomass conversion occur simultaneously [27].

Besides the wide range of value-added compounds obtained from microalgae biomass, the costs to their production on large-scale is still too high [15]. Because of that, efforts have been made to reduce the costs at different parts of the microalgae production, which usually is divided by cultivation, harvesting, dewatering/drying, and processing/extraction. The microalgae production combined with wastewater treatment is a promising solution to overcome the costs incurred in microalgae cultivation [28], which is discussed in the present chapter.

3 Microalgae Cultivation and Operational Parameters

The efficiency of biomass production by photosynthesis depends mainly on the following factors: carbon source, cultivation system, light intensity, nutrient concentration in the medium, N:P ratio, pH, photoperiod, and temperature.

Several types of microalgae cultivation systems are reported in the literature, which differ mainly in design, construction and operation cost, weather dependence, and mixing type. The systems are usually classified by their configuration design as open or closed [36]. Closed systems, usually called as photobioreactor, despite being more expensive, have some advantages over the open systems, for instance minimization of contamination and better control of the cultivation variables [37]. There are different commercial examples of closed (e.g., airlift, bubble column, flat panel, and tubular) and open (e.g., raceway and lagoons) systems. Table 2 shows a comparison between the characteristics of these cultivation systems.

During cultivation, microalgae uptake the inorganic nutrients available in culture medium to convert into organic matter by the intracellular metabolism. The main

Table 2 Comparison between open and closed microalgae cultivation system

Parameters	Open system	Closed system
Biomass productivity	Low	High
CO_2 utilization	Low	High
Contamination and species control	Difficult	Easy
Construction cost	Low	High
Evaporation	High	Low
Light efficiency	Low	High
Maintenance	Easy	Difficult
Mixing	Low	High
Operation cost	Low	High
Operation regime	Batch/continuous	Batch/semi-continuous
Predator control	Difficult	Achievable
Temperature control	Difficult	Easy
Typical microalgae concentration (g/L)	<1	1–12
Weather dependence	High	Low

nutrients for biomass growth are nitrogen and phosphorus. Because of the energy demand, ammonia (NH_3) is the preferred inorganic nitrogen species to be incorporated by microalgae and later converted to organic nitrogen compounds [38]. Orthophosphate (PO_4^{3-}) is the elected phosphorus form since microalgae have the ability to store this nutrient. It has been observed that microalgae usually uptake a higher orthophosphate concentration than it is required for their growth [16, 39].

The N:P ratio available in the culture medium affects the biomass production and nutrient removal by microalgae. As a result, many researchers investigated the optimal N:P ratio for phytoplankton growth [40]. However, there are few studies about the N:P ratio when microalgae are cultivated in the wastewater. Choi and Lee [17] found the maximum *Chlorella vulgaris* production with domestic wastewater using the N:P ratio from 1 to 10, and nutrient removal efficiencies higher than 75%. In contrast, Fernandes et al. [7] found that *Chlorella sorokiniana* promoted total removal of inorganic nitrogen and phosphorus from black water, using N:P ratios ranging from 15 to 26. The authors also showed that nutrients adsorbed by microalgae had different tendency, with nitrogen having a slower removal compared to phosphorus.

The pH range for the most microalgae species is between 7 and 9, and the optimal range is between 8.2 and 8.7 [41]. pH control is artificially performed by chemical addition or carbon dioxide injection into the culture system. In the cultivation without carbon dioxide application, microalgae adapt to the alkaline medium and use bicarbonate (HCO_3^-) as an inorganic carbon source for the photosynthesis. Later, HCO_3^- is converted to CO_2 by carbonic anhydrase intracellular enzymes and there is a consequent release of OH^- into the medium, which justifies the high pH in these conditions [42]. The concentration of free ammonia form (NH_3) also increases with the pH, and it can be toxic to the living organisms in the environment

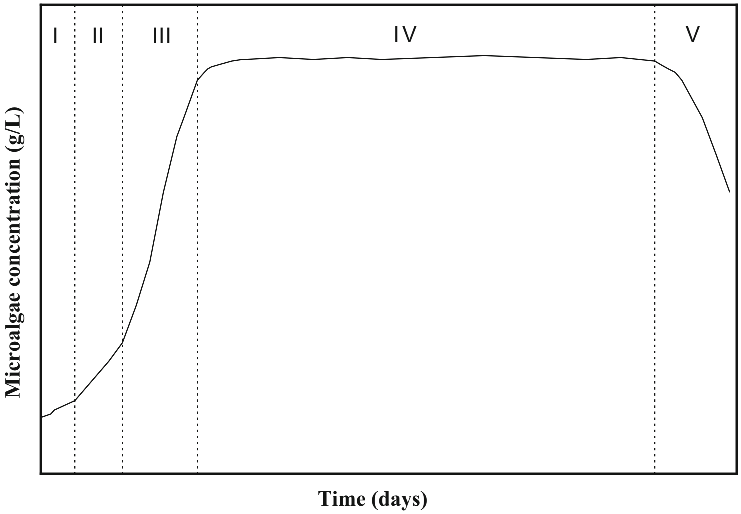


Fig. 1 Microalgae growth curve

[4]. However, studies with no pH control have not shown inhibition to the microalgae growth [43–45].

Most microalgae species have the optimal temperature range from 20 to 30°C and the light intensity from 33 to 400 μmol/m^2/s [46]. However, experimental studies show different values, which show the importance of a complete investigation of the microalgae species prior to its use on large-scale. *Chlorella sorokiniana* handle a light intensity until 2,100 μmol/m^2/s without showing photoinhibition signal [47], but intensities higher than 1,100 μmol/m^2/s do not promote any increment in O_2 production [48]. The *Chlorophyceae* class, popularly known as green microalgae, has the upper limits of temperatures from 26 to 42°C [49], and *Chlorella sorokiniana* has 38°C as the optimal temperature for biomass growth [50].

The choice of the appropriate photoperiod is important when the goal is to maximize microalgae production. Considerable biomass is lost during the dark period compared to the end of the light period, which can reach up to 20% in dry weight produced [51]. It happens because some microalgae species cannot store photoenergy to support their growth in the dark period [52]. Several optimal photoperiods are reported in the literature using different culture medium, different light intensities, and microalgae species [53, 54].

The characteristic curve of the microalgae growth is shown in Fig. 1. The microalgae growth curve can be drawn using periodic measurements of direct (cell counting) and indirect (absorbance, chlorophyll, and dry weight) methods. The absorbance is the most popular method as a result of its simplicity and fast result. Different wavelengths have been used to monitor the microalgae growth such as 650 nm [55], 678 nm [56], 680 nm [57, 58], 690 nm [59], and 750 nm [15]. However, absorbance is a dimensionless measure, which also requires another method to quantify the microalgae concentration (i.e., gram of microalgae per suspension litre). Some studies associate the absorbance with dry weight; however, it is not recommended in wastewater studies because of the variation of the wastewater characteristic in each cultivation cycle.

The microalgae growth is divided into five phases: (I) lag, (II) exponential growth, (III) linear growth, (IV) stationary growth, and (V) decline or death. It is important to mention that this division is didactic, since the phases are not clearly separated or not all occur in the cultivation studies [6, 10, 16, 45, 59]. Cultivation time is usually adopted for the microalgae growth until the stationary phase.

3.1 Wastewater Treatment

It has been estimated that there are more than 72,500 algal species distributed in the freshwater, marine, and terrestrial environments [60]. However, few species were tested for their tolerance to organic pollution. The microalgae genus more used in wastewater studies are *Chlorella* and *Scenedesmus* [17, 61–65].

Microalgae production coupled with wastewater treatment is a promising solution to overcome the high costs of the cultivation process. Reduction higher than 50% is estimated when carbon, nutrients, and water are obtained from economical sources [2]. This process can also promote a safe effluent disposal, reducing the dissolved concentrations of inorganic nutrients (N and P) and other substances initially present in the wastewater. Emerging pollutants, hormones, dyes, and metal traces can be removed during microalgae cultivation by different processes (absorption, biodegradation, or photodegradation) [18, 66].

Another positive aspect is that considerable bacterial removal is obtained during microalgae cultivation [67, 68], however the removal process is still unclear. The consortium between microalgae–bacteria can also promote the degradation of the dissolved and particulate organic matter from the wastewater [8].

Different types of wastewater have been tested for microalgae cultivation. Table 3 shows some microalgae cultivation studies using different wastewater, microalgae species, nutrients concentration, pre-treatment, and operating conditions (temperature, pH control, CO_2 application, light intensity, and photoperiod). Nitrogen and phosphorus removal from the wastewater as well as the microalgae production using different wastewater types shows the huge potential of the treatment using microalgae.

Despite carbon, nitrogen, and phosphorus, other nutrients are also essential for the microalgae growth, such as calcium, potassium, magnesium, and trace metals (nickel, manganese, and copper) [69]. Nevertheless, nutrient availability in wastewater is not the only requirement. The operating conditions (temperature, pH control, CO_2 application, light intensity, and photoperiod), discussed previously in this chapter, also contribute significantly to the microalgae growth [41].

Care should be taken with the combination of some operating parameters during cultivation, because high pH and aeration can promote ammonia removal from

Table 3 Nitrogen and phosphorous removal and biomass production using different wastewater, microalgae species, and operating conditions. Removal of nitrogen and phosphorus is given in parenthesis

Wastewater type	Pre-treatment; type	Microalgae	Influent concentration (mg/L)		Cultivation time (days)	Temperature (°C)	pH control	CO_2 injection	Photoperiod (day:night)	Light intensity (μmol/m²/s)	Biomass production (g/L)	Reference
			N	P								
Dairy industry	Dilution	*Chlamydomonas polypyrenoideum*	101.8 (97.1)	5.6 (98.0)	15	28	Yes	No	12:12	10[a]	6.3	[55]
Alcohol distillery	Centrifugation	*Chlorella sorokiniana*	15 (95.0)	773 (77.0)	4	27	Yes	No	24:00	180	10.0	[56]
Cheese whey	Filtration and dilution	*Scenedesmus obliquus*	NR	NR	13	22.5	No	No	16:8	100	4.9	[78]
Concentrated black water	UASB	*Chlorella sorokiniana*	1,070 (98.9)	73 (100)	14	37	Yes	Yes	24:00	150	12.1	[10]
Municipal	Centrifugation	*Chlorella vulgaris*	41.6 (83.0)	3.1 (100)	8	25	No	No	12:12	200	2.6[b]	[79]
Primary effluent	Filtration	*Chlorella vulgaris*	41.0 (60.2)	10.0 (34.8)	28	20	No	No	24:00	0.98[c]	2.7	[59]
Secondary effluent			62.9 (55.9)	26.0 (11.5)							1.9	
Digestated sludge			136.6 (33.6)	200.0 (25.8)							2.4	
Piggery	Sedimentation	*Chlorella vulgaris*	420.6 (89.5)	60.4 (85.3)	12	25	No	No	NR	NR	0.8	[75]
Sugarcane vinasse	Centrifugation and dilution	*Micractinium sp.*	21.6 (46.4)	12.0 (4.2)	3	37/24	Yes	Yes	12:12	400	0.5	[80]
Digested kitchen waste	Centrifugation and dilution	*Scenedesmus sp.*	118.6 (22.9)	1.0 (96.2)	8	25	No	No	24:00	60	0.5	[57]
	Filtration	*Chlorella sp.*			45	25	No	No	24:00	135	0.9	[73]

(continued)

Table 3 (continued)

Wastewater type	Pre-treatment; type	Microalgae	Influent concentration (mg/L)		Cultivation time (days)	Temperature (°C)	pH control	CO_2 injection	Photoperiod (day:night)	Light intensity (µmol/m^2/s)	Biomass production (g/L)	Reference
			N	P								
Seafood processing			121.1 (96.6)	57.3 (68.4)								
Meat processing	Filtration	*Scenedesmus obliquus*	99.5 (55.5)	106.8 (71.9)	9	27	No	No	16:8	256[d]	1.7	[58]
Municipal and piggery	UASB	*Chlorella sorokiniana*	306–186 (92.2–96.6)	10.9–19.5 (40.0–60.0)	7	30	No	No	16:8	196	0.9–1.0	[16]

Note: *NR* not reported

Light information given by

[a] W/m^2

[b] Microalgae production expressed as chlorophyll concentration (mg/L)

[c] µW/cm^2

[d] lux

wastewater by air stripping [70]. This phenomenon can reduce drastically the nitrogen concentration available in the wastewater and consequently, reduces the microalgae production and phosphorus removal because of the nitrogen limitation [16].

The turbidity and color are an intrinsic problem of using wastewater for microalgae production, which significantly interfere the light penetration into the cultivation system and consequently affects the nutrient removal and biomass productivity [71]. To reduce the dissolved and suspended solids interference in cultivation, different wastewater pre-treatments have been used before its application in the microalgae cultivation such as centrifugation [72], dilution of wastewater with water or culture medium [73], filtration [74], and sedimentation [15, 75]. However, the use of these methods on large-scale can further increase the cost of microalgae cultivation.

In this context, UASB (Upflow Anaerobic Sludge Blanket) reactor is a classic and inexpensive technology to reduce the organic load of wastewater, especially in warm weather regions. This anaerobic treatment also converts organic nitrogen into ammonia and organic phosphorus to orthophosphate (inorganic phosphorus) [76], which are the species used by the microalgae for their growth. Moreover, UASB reactor is easy to operate and do not remove nutrients efficiently [77].

Special care should be taken during the operation of microalgae cultivation in order to promote the expected system efficiency, since the following situations can occur:

- Growth of other microalgae species besides the one initially inoculated;
- Presence of microalgae predators (e.g., ciliates, copepods, and *Daphnia*) or microbial contamination (e.g., protozoan, virus, and bacteria);
- Chemical contamination by any compounds present in the wastewater, since some WWTPs (Wastewater Treatment Plant) receive industrial wastewater.

To avoid or minimize such problems, a periodic monitoring of the microalgae species, the wastewater quality, the presence of other microorganisms and the biomass growth is required. If it is necessary, the culture system has to be inoculated again with pure and adapted microalgae.

4 Microalgae Harvesting

Microalgae harvesting is the major bottleneck for microalgae production on large-scale [81]. The cost of this step may reach up to 60% of the total cost of algae production [14]. The high cost reflects the difficulties to remove the biomass from the culture medium, which is a result of the low microalgae concentration (0.5–5.0 g/L), small cell diameter (5–50 μm), and negative electrostatic surface (−20 to −35 mV) [82].

Different techniques showed efficiency to microalgae recovery, including mainly flotation, filtration, centrifugation, and sedimentation [28]. Microalgae harvesting

Table 4 Advantages, disadvantages, and the operational parameters of the major methods used in microalgae harvesting

Harvesting method	Advantage	Disadvantage	Operational parameter
Centrifugation	Easy operation High efficiency Large-scale application	Cell damage High-energy demand High installation cost	Centrifuge type Centrifugation time Velocity gradient
Filtration	High efficiency Small-scale application	Clogging High operation cost Slow process	Clogging time Flow mode Membrane material Pore size
Flotation	Easy operation High efficiency Large-scale application	Coagulant cost High-energy demand to bubble generation	Flotation velocity pH Recirculation rate Saturation pressure
Sedimentation	Easy operation High efficiency Large-scale application low energy demand	Biomass toxicity Coagulant cost	Coagulation time Flocculation time Velocity gradient pH Sedimentation velocity

efficiency is usually determined by the absorbance, because of its simplicity and fast results. Table 4 summarizes the advantages, disadvantages, and the operational parameters of the major methods used in microalgae harvesting.

These methods can be physical (e.g., centrifugation and filtration) as well as physical-chemical (e.g., flotation and sedimentation). The wastewater characteristics are more important for chemical methods, since the wastewater contains compounds and solids that can interact with microalgae and/or the separating agent (e.g., coagulants and precipitates) and also reduce the process efficiency. Moreover, the initial concentration of these wastewater compounds is highly variable because of the daily patterns, industrial wastewater discharge, and weather conditions [83].

The understanding of the interactions between the wastewater composition and the microalgae during the harvesting process is crucial to reach high efficiency. Some substances found in the wastewater can decrease or even inhibit the microalgae harvesting efficiency, such as algogenic organic matter, carbohydrates, citric acid, humic acid, and protein [84–86]. Thus, it is fundamental to evaluate the harvesting technology application for microalgae cultivated in the wastewater.

In the literature, information about harvesting efficiencies and new harvesting methods are mainly found for microalgae recovery from culture medium [87]. Besides the lack of studies, the use of information about microalgae removal from wastewater requires caution, since the wastewater quality is highly variable.

Another technical difficulty is that the harvesting studies generally did not consider operational parameters as a study variable. In general, the experiments are conducted in small volumes and the operational parameters unmentioned in the technical form, which complicates the scale-up and the method reproducibility [88–

93]. Moreover, the optimization of the operational parameters is necessary to reduce the process cost and maximize the efficiency.

Since there is no universal harvesting technique, the choice of the appropriate method should be based on the cost (e.g., installation and operational), microalgae characteristics (e.g., size and morphology), and the harvesting efficiency. More details of the major harvesting methods are discussed below.

4.1 Centrifugation

Centrifugation is a mechanical method that applies the centrifugal force for particles removal from the suspension. Different centrifuge types have been used for microalgae harvesting such as disc-stack, decanter bowl, hydrocyclone, and nozzle discharge [14]. Despite the high recovery efficiency (>90%), this method has high-energy demand and high cost involved. Moreover, centrifugation can cause damage in microalgae cells and the harvested ones (<12%) can lose their viability during the process [94]. The microalgae damage is calculated by a viability test, which is directly linked to the microalgae bioproducts release to the medium.

The current commercial production system of microalgae has been using centrifugation as the harvesting method. In this case, some strategies can be applied to reduce the overall costs. Dassey and Theegala [95] proposed a harvesting process with multiple steps, since the high flow rate passing into centrifuge reduces the microalgae recovery from the medium. The most cost-effective strategy promoted a reduction of 82% in the energy consumption when 28.5% of the microalgae were recovered with high flow rate (18 L/min). The association of filtration/flotation/sedimentation followed by centrifugation can also significantly reduce the operating costs. Fasaei et al. [81] evaluated the techno-economic performance of 28 harvesting possibilities for microalgae on large-scale. The lowest cost and energy demand was found for filtration followed by centrifugation.

4.2 Filtration

Filtration is a method used to separate solids from liquid by passing the suspension through a porous barrier capable of trapping the solids. This technique can be used in two operating modes: cross-flow and dead-end. The difference between them is based on the feeding mode. In the dead-end filtration the flow is applied perpendicular to the membrane surface, while in the cross-flow filtration the flow is tangential [96]. Cross-flow filtration was developed to reduce the fouling problem due to the microalgae accumulation on the membrane surface and inside the membrane porous, which reduce considerably the operating time [97].

Filtration is classified by the size of the membrane pore used in the process such as macrofiltration (>10 μm), microfiltration (0.1–10 μm), ultrafiltration

(0.02–0.2 μm), and reverse osmosis (<0.001 μm) [98]. Microalgae cell diameter is usually between 5 and 50 μm [82], which explains the high number of studies using microfiltration [99–101].

The solids presence in the wastewater complicates the filtration application as a harvesting method, which reduces the operating time and increases the operational costs. Moreover, filtration could be more expensive than centrifugation on large-scale [14].

4.3 Flotation

The traditional flotation method is based on the microbubbles generation to promote the rising of microalgae floc to the system surface, where the biomass is accumulated and removed [102]. Flotation system is labeled by the air type addition in the system, which can be trough pressurization (dissolved air flotation, DAF) or diffuser (dispersed air flotation, DiAF).

Flotation is more efficient for microalgae recovery than sedimentation, considering the same operational parameters (pH, coagulant dosage, mixing time, and velocity gradient) for both methods [103]. Moreover, gravitational dewatering promoted by flotation shows a thicker biomass than sedimentation [104].

The flotation process is usually preceded by coagulation and flocculation, which promotes the mixing between the microalgae and chemical compound for the subsequent floc formation [105]. In the coagulation process, different types of coagulants (e.g., natural, metal salts, and synthetic) are commonly used [88, 106–108], while pH-modulation followed by flotation is poorly explored [109, 110].

The DAF is the flotation type more used to microalgae harvesting and shows high efficiencies [111–113]. Furthermore, DAF is also an efficient process to improve wastewater quality by reducing chemical organic demand, phosphorus, pathogenic protozoan cysts, suspended solids, and turbidity [114, 115].

In order to reduce the cost related to microbubble generation, several alternative flotation methods have been proposed. For instance, the use of bioflocculant [116], aluminum electrolysis [107, 117], and hydrogen generation with cyanobacteria cultivation [118].

4.4 Sedimentation

The sedimentation method is usually reported in the microalgae studies as flocculation because of the prior floc formation before the sedimentation. The terminology of sedimentation types used in literature is not unique, which makes the reader sometimes confused. According to Branyikova et al. [119], sedimentation can be caused by: autoflocculation caused by extracellular polymeric substances, bioflocculation that involves other microorganisms, chemical flocculation by coagulant use, and spontaneous or forced alkaline flocculation.

Sedimentation stands out as a low-cost process and can concentrate the microalgae suspension up to 100 times [120]. Different sedimentation types have demonstrated high microalgae harvesting efficiencies, but also have some disadvantages that should be considered for their selection. Coagulants, popularly used in wastewater and water treatment (e.g., aluminum sulfate, ferric chloride), can contaminate the harvested biomass and complicate the bioproduct extraction [91]. Autoflocculation induced by the production of extracellular polymeric substances is a slow process and mainly depends on the presence of some substances on the cell surface such as glycoproteins [121]. Bioflocculation, which often use other microorganisms to promote flocculation, can also cause biomass contamination [122].

Considering the wastewater characteristics, sedimentation by alkaline flocculation shows a promising method. In this process, the high pH leads to chemical precipitation of calcium and/or magnesium salts, which promotes the microalgae harvesting by electrostatic interaction [92]. Moreover, this method is low-cost and non-toxic, and wastewater has the appropriate species concentrations for the precipitates formation [123]. The cost of alkaline flocculation is based on the base price used to increase the pH (pH 9–12), plus the additional cost to reduce the wastewater pH to meet the current legislation and then to be disposed.

5 Brazilian Perspective

Only 46% of all wastewater produced in Brazil is treated. The situation is even more critical in the Northern region, where 21.7% of the wastewater is treated [124]. Thus, a lot of work is required to universalize the sanitation to all population.

In this context, wastewater treatment using microalgae may be an attractive solution to promote a sustainable process. However, some limitations must be overcome in Brazil, especially regarding the nutrients concentration. The typical nitrogen and phosphorus concentration in the Brazilian centralized wastewater systems is around 45 and 7 mg/L, respectively [4]. Microalgae cultivation in these low nutrient concentrations is unattainable, not only in regards to the economy, but also the practicality and sustainability [66].

One possible solution is to nutritionally enrich the wastewater from Brazilian WWTPs with another wastewater type, which has higher nitrogen and phosphorus concentrations [125]. Piggery wastewater have high concentrations of organic matter, nitrogen, and phosphorus [126], which makes it a potential candidate. Timely, Brazil occupied the fourth in pork production and export worldwide, producing around 3.75 million tons in 2017 [127].

The discharge of the piggery wastewater has been an environmental problem in Brazil, because it is sometimes directly discharged into water bodies. The use of piggery wastewater for microalgae cultivation was evaluated by several studies

Table 5 Efficiency of *Chlorella sorokiniana* recovery from municipal and piggery wastewater using different harvesting methods and operational parameters

Harvesting method	Coagulant agent	Operational parameter	Efficiency (%)	Reference
DAF (coagulant) MC = 0.6 g/L pH 7	10 mg/L Zetag 8,185	Velocity gradient = 500 1/s Mixing time = 30 s Flotation velocity = 8 cm/min	98.4	[108]
	75 mg/L Tanfloc SG		94.5	
	500 mg/L $Al_2(SO_4)_3$		95.4	
	1,000 mg/L $FeCl_3$		96.7	
DAF (alkaline flocculation) MC = 0.6 g/L pH 8.6	pH 12 (using NaOH)	Velocity gradient = 500 1/s Mixing time = 30 s Recirculation rate = 20% Flotation velocity = 12 cm/min	96.5	[110]
Sedimentation (alkaline flocculation) MC = 0.5 g/L pH 9	pH 12 (using NaOH)	Velocity gradient = 250 1/s Mixing time = 10 s Settling time = 7 min	97.8	[130]

Note: Microalgae concentration (MC)

[125, 126, 128]. It is important to mention that the direct use of piggery wastewater is not recommended due to its high organic load. Thus, the mixture of piggery and municipal wastewater becomes an attractive solution both environmentally and economically.

Another advantage of the municipal and piggery wastewater is the dilution of the piggery wastewater. However, the wastewater proportion in the mixture should be optimized, since the piggery is very concentrated in terms of organic matter (>7,000 mg/L of total solids) and nutrients (>300 mg/L of nitrogen and >400 mg/L of phosphorus) [129]. The volume of piggery wastewater can represent more nutrient concentration, but also more turbidity and color in the final mixture for the microalgae cultivation.

A pilot study was carried out in Brazil by Leite et al. [16] using piggery and municipal wastewater for microalgae production during 4 weeks. The system consisted of an UASB as pre-treatment and *Chlorella sorokiniana* cultivation in three flat panel photobioreactors. High organic matter removal was reached by UASB treatment (>92% of chemical oxygen demand removal), even with a large variation of the wastewater characteristics. *Chlorella sorokiniana* concentration reached about 1 g/L, with an average efficiency removal of 100% for ammonia, 46–56% for dissolved inorganic carbon, and 40–60% for orthophosphate. The authors also discussed possible solutions to improve microalgae production and the wastewater treatment.

After the great results obtained from the cultivation studies, the authors tested different methods for microalgae harvesting from the mixture wastewater (Table 5).

Sedimentation and flotation were tested because they are consolidated technologies in wastewater treatment and applicable on large-scale. All methods presented high efficiency (>94.5%) at the optimal operational conditions and improved the wastewater quality. The complexity of the wastewater composition showed no interference in the harvesting process, even working with sensible methods like alkaline flocculation [110, 130]. These results show the great potential of the mixture wastewater for microalgae production and also can serve as guidelines for the application on large-scale in Brazil.

6 Future Prospective

As shown in this chapter, microalgae production coupled with wastewater treatment has a great potential to be applied on large-scale. However, hurdles and limitations must be reduced or overcome to make the treatment economically viable. In this context, technology development is essential to increase the biomass productivity and to reduce the process cost.

Despite the numerous studies, most of the reported cultivation experiments have been carried out in small-scale under controlled condition. The current investigations are usually focused on closed photobioreactor operating in batch mode during a short time period. Then, little information is available about the scale-up process, growth of other microalgae species, presence of microalgae predators, and possible contamination by chemical compounds present in wastewater. These are essential data on microalgae cultivation in long-term period.

Microalgae harvesting is the major bottleneck for microalgae production, due to the microalgae characteristics. Most studies on the harvesting method have been carried out with microalgae grown in culture medium and require validation to be applied into biomass grown in wastewater. Also, it is fundamental that the studies consider operational parameters as a study variable and also report the technical information to scale up the process and to allow the method reproducibility.

Thus, research is still needed for the development of technology in improving the cost-effectiveness of the microalgae cultivation coupled with wastewater on large-scale.

7 Conclusion

The microalgae are sources of high-value bioproducts, which motivates studies to enable the microalgae production on large-scale. Microalgae production coupled to the wastewater treatment is an interesting and sustainable alternative to reduce the costs regarding the cultivation process, since the nutrients (e.g., carbon, nitrogen, and phosphorus) and water are available cheaply. In this process, the microalgae uptake nutrients and other chemical dissolved substances, promoting simultaneously the wastewater treatment and biomass production.

Besides the benefices for wastewater use as culture medium, its composition complexity complicates the harvesting process, since the presence of solid and some compounds can reduce the efficiency or even inhibit the microalgae recovery by some methods. This fact endorses the importance of the harvesting method assessment for every wastewater type before its application.

Thus, the wastewater treatment integrated to the microalgae production becomes a promising alternative to overcome the high costs; however, there are still many challenges to make the system economically viable on large-scale.

References

1. Coppens J, Grunert O, Van Den Hende S, Vanhoutte I, Boon N, Haesaert G, De Gelder L (2016) The use of microalgae as a high-value organic slow-release fertilizer results in tomatoes with increased carotenoid and sugar levels. J Appl Phycol 28:2367–2377. https://doi.org/10.1007/s10811-015-0775-2
2. Slade R, Bauen A (2013) Micro-algae cultivation for biofuels: cost, energy balance, environmental impacts and future prospects. Biomass Bioenergy 53:29–38. https://doi.org/10.1016/j.biombioe.2012.12.019
3. WWAP (2017) The United Nations World Water Development report 2017. Wastewater: the untapped resource, Paris
4. Von Sperling M (2014) Introdução à qualidade das águas e ao tratamento de esgotos.4th edn. Editora UFMG, Belo Horizonte. https://doi.org/10.3390/s150922234
5. Dodds WK, Bouska WW, Eitzmann JL, Pilger TJ, Pitts KL, Riley AJ, Schloesser JT, Thornbrugh DJ (2009) Eutrophication of U. S. freshwaters: analysis of potential economic damages. Environ Sci Technol 43:12–19. https://doi.org/10.1021/es801217q
6. Caporgno MP, Taleb A, Olkiewicz M, Font J, Pruvost J, Legrand J, Bengoa C (2015) Microalgae cultivation in urban wastewater: nutrient removal and biomass production for biodiesel and methane. Algal Res 10:232–239. https://doi.org/10.1016/j.algal.2015.05.011
7. Fernandes TV, Suárez-Muñoz M, Trebuch LM, Verbraak PJ, Van de Waal DB (2017) Toward an ecologically optimized N:P recovery from wastewater by microalgae. Front Microbiol 8:1742. https://doi.org/10.3389/fmicb.2017.01742
8. Foladori P, Petrini S, Andreottola G (2018) Evolution of real municipal wastewater treatment in photobioreactors and microalgae-bacteria consortia using real-time parameters. Chem Eng J 345:507–516. https://doi.org/10.1016/j.cej.2018.03.178
9. Mennaa FZ, Arbib Z, Perales JA (2019) Urban wastewater photobiotreatment with microalgae in a continuously operated photobioreactor: growth, nutrient removal kinetics and biomass coagulation–flocculation. Environ Technol 40:342–355. https://doi.org/10.1080/09593330.2017.1393011
10. Fernandes TV, Shrestha R, Sui Y, Papini G, Zeeman G, Vet LEM, Wijffels RH, Lamers P (2015) Closing domestic nutrient cycles using microalgae. Environ Sci Technol 49:12450–12456. https://doi.org/10.1021/acs.est.5b02858
11. de Souza Leite L, Matsumoto T, Albertin LL (2018) Mathematical modeling of thermal drying of facultative pond sludge. J Environ Eng 144:04018079. https://doi.org/10.1061/(ASCE)EE.1943-7870.0001427
12. de Souza WG (2012) Pós-secagem natural de lodos de estações de tratamento de Água e esgoto sanitários. Universidade de São Paulo, São Paulo

13. Wang L, Liu J, Zhao Q, Wei W, Sun Y (2016) Comparative study of wastewater treatment and nutrient recycle via activated sludge, microalgae and combination systems. Bioresour Technol 211:1–5. https://doi.org/10.1016/j.biortech.2016.03.048
14. Molina Grima E, Belarbi EH, Acién Fernández FG, Robles Medina A, Chisti Y (2003) Recovery of microalgal biomass and metabolites: process options and economics. Biotechnol Adv 20:491–515. https://doi.org/10.1016/S0734-9750(02)00050-2
15. De Francisci D, Su Y, Iital A, Angelidaki I (2018) Evaluation of microalgae production coupled with wastewater treatment. Environ Technol 39:581–592. https://doi.org/10.1080/09593330.2017.1308441
16. de Souza Leite L, Hoffmann MT, Daniel LA (2019) Microalgae cultivation for municipal and piggery wastewater treatment in Brazil. J Water Process Eng 31:100821. https://doi.org/10.1016/j.jwpe.2019.100821
17. Choi HJ, Lee SM (2015) Effect of the N/P ratio on biomass productivity and nutrient removal from municipal wastewater. Bioprocess Biosyst Eng 38:761–766. https://doi.org/10.1007/s00449-014-1317-z
18. Norvill ZN, Shilton A, Guieysse B (2016) Emerging contaminant degradation and removal in algal wastewater treatment ponds: identifying the research gaps. J Hazard Mater 313:291–309. https://doi.org/10.1016/j.jhazmat.2016.03.085
19. Heimann K, Huerlimann R (2015) Microalgal classification: major classes and genera of commercial microalgal species. In: Handbook of marine microalgae. Biotechnology advances, pp 25–41. https://doi.org/10.1016/B978-0-12-800776-1.00003-0
20. Acreman J (1994) Algae and cyanobacteria: isolation, culture and long-term maintenance. J Ind Microbiol 13:193–194. https://doi.org/10.1007/BF01584008
21. Krienitz L, Huss VAR, Bock C (2015) *Chlorella*: 125 years of the green survivalist. Trends Plant Sci 20:67–69. https://doi.org/10.1016/j.tplants.2014.11.005
22. Posten C, Chen SF (2016) Microalgae biotechnology. Springer. https://doi.org/10.1016/0014-5793(73)80708-2
23. Randrianarison G, Ashraf MA (2017) Microalgae: a potential plant for energy production. Geol Ecol Landscapes 1:104–120. https://doi.org/10.1080/24749508.2017.1332853
24. Markou G, Nerantzis E (2013) Microalgae for high-value compounds and biofuels production: a review with focus on cultivation under stress conditions. Biotechnol Adv 31:1532–1542. https://doi.org/10.1016/j.biotechadv.2013.07.011
25. Liang M-H, Wang L, Wang Q, Zhu J, Jiang J-G (2018) High-value bioproducts from microalgae: strategies and progress. Crit Rev Food Sci Nutr:1–19. https://doi.org/10.1080/10408398.2018.1455030
26. Brennan L, Owende P (2010) Biofuels from microalgae – a review of technologies for production, processing, and extractions of biofuels and co-products. Renew Sustain Energy Rev 14:557–577. https://doi.org/10.1016/j.rser.2009.10.009
27. Singh B, Bauddh K, Bux F (2015) Algae and environmental sustainability. Springer. https://doi.org/10.1007/978-81-322-2641-3
28. Kadir WNA, Lam MK, Uemura Y, Lim JW, Lee KT (2018) Harvesting and pre-treatment of microalgae cultivated in wastewater for biodiesel production: a review. Energ Conver Manage 171:1416–1429. https://doi.org/10.1016/j.enconman.2018.06.074
29. Rahman A, Miller CD (2017) Microalgae as a source of bioplastics. Elsevier. https://doi.org/10.1016/B978-0-444-63784-0.00006-0
30. Chen CY, Zhao XQ, Yen HW, Ho SH, Cheng CL, Lee DJ, Bai FW, Chang JS (2013) Microalgae-based carbohydrates for biofuel production. Biochem Eng J 78:1–10. https://doi.org/10.1016/j.bej.2013.03.006
31. Gong M, Bassi A (2016) Carotenoids from microalgae: a review of recent developments. Biotechnol Adv 34:1396–1412. https://doi.org/10.1016/j.biotechadv.2016.10.005
32. Brasil B dos SAF, de Siqueira FG, Salum TFC, Zanette CM, Spier MR (2017) Microalgae and cyanobacteria as enzyme biofactories. Algal Res 25:76–89. https://doi.org/10.1016/j.algal.2017.04.035

33. Roux JM, Lamotte H, Achard JL (2017) An overview of microalgae lipid extraction in a biorefinery framework. Energy Procedia 112:680–688. https://doi.org/10.1016/j.egypro.2017.03.1137
34. Sathasivam R, Radhakrishnan R, Hashem A, Abd Allah EF (2019) Microalgae metabolites: a rich source for food and medicine, Saudi. J Biol Sci 26:709–722. https://doi.org/10.1016/j.sjbs.2017.11.003
35. Koyande AK, Chew KW, Rambabu K, Tao Y, Chu D-T, Show P-L (2019) Microalgae: a potential alternative to health supplementation for humans. Food Sci Human Wellness 8:16–24. https://doi.org/10.1016/j.fshw.2019.03.001
36. Razzak SA, Hossain MM, Lucky RA, Bassi AS, De Lasa H (2013) Integrated CO_2 capture, wastewater treatment and biofuel production by microalgae culturing – a review. Renew Sustain Energy Rev 27:622–653. https://doi.org/10.1016/j.rser.2013.05.063
37. Singh RN, Sharma S (2012) Development of suitable photobioreactor for algae production – a review. Renew Sustain Energy Rev 16:2347–2353. https://doi.org/10.1016/j.rser.2012.01.026
38. Jia H, Yuan Q (2016) Removal of nitrogen from wastewater using microalgae and microalgae-bacteria consortia, cogent. Environ Sci 2:1–15. https://doi.org/10.1080/23311843.2016.1275089
39. Eixler S, Karsten U, Selig U (2006) Phosphorus storage in *Chlorella vulgaris* (*Trebouxiophyceae*, *Chlorophyta*) cells and its dependence on phosphate supply. Phycologia 45:53–60. https://doi.org/10.2216/04-79.1
40. Geider RJ, La Roche J (2002) Redfield revisited: variability of C:N:P in marine microalgae and its biochemical basis. Eur J Phycol 37:1–17. https://doi.org/10.1017/S0967026201003456
41. Pahazri NF, Mohamed R, Al-gheethi AA, Mohd AH (2016) Production and harvesting of microalgae biomass from wastewater: a critical review, environ. Technol Rev 5:39–56. https://doi.org/10.1080/21622515.2016.1207713
42. Raven JA, Cockell CS, De La Rocha CL (2008) The evolution of inorganic carbon concentrating mechanisms in photosynthesis. Philos Trans R Soc B Biol Sci 363:2641–2650. https://doi.org/10.1098/rstb.2008.0020
43. de Godos I, Blanco S, García-Encina PA, Becares E, Muñoz R (2009) Long-term operation of high rate algal ponds for the bioremediation of piggery wastewaters at high loading rates. Bioresour Technol 100:4332–4339. https://doi.org/10.1016/j.biortech.2009.04.016
44. Vadlamani A, Viamajala S, Pendyala B, Varanasi S (2017) Cultivation of microalgae at extreme alkaline pH conditions: a novel approach for biofuel production. ACS Sustain Chem Eng 5:7284–7294. https://doi.org/10.1021/acssuschemeng.7b01534
45. Zhang Q, Wang T, Hong Y (2014) Investigation of initial pH effects on growth of an oleaginous microalgae *Chlorella* sp. HQ for lipid production and nutrient uptake. Water Sci Technol 70:712–719. https://doi.org/10.2166/wst.2014.285
46. Singh SP, Singh P (2015) Effect of temperature and light on the growth of algae species: a review. Renew Sustain Energy Rev 50:431–444. https://doi.org/10.1016/j.rser.2015.05.024
47. Cuaresma M, Janssen M, Vílchez C, Wijffels RH (2009) Productivity of *Chlorella sorokiniana* in a short light-path (SLP) panel photobioreactor under high irradiance. Biotechnol Bioeng 104:352–359. https://doi.org/10.1002/bit.22394
48. Cazzaniga S, Osto LD, Szaub J, Scibilia L, Ballottari M, Purton S, Bassi R (2014) Domestication of the green alga *Chlorella sorokiniana*: reduction of antenna size improves light-use efficiency in a photobioreactor. Biotechnol Biofuels 7:1–13. https://doi.org/10.1186/s13068-014-0157-z
49. Kessler E (1985) Upper limits of temperature for growth in *Chlorella* (*Chlorophyceae*). Plant Syst Evol 151:67–71. https://doi.org/10.1007/BF02418020
50. Franco MC, Buffing MF, Janssen M, Lobato CV, Wijffels RH (2012) Performance of *Chlorella sorokiniana* under simulated extreme winter conditions. J Appl Phycol 24:693–699. https://doi.org/10.1007/s10811-011-9687-y
51. Edmundson SJ, Huesemann MH (2015) The dark side of algae cultivation: characterizing night biomass loss in three photosynthetic algae, *Chlorella sorokiniana*, *Nannochloropsis*

salina and *Picochlorum* sp. Algal Res 12:470–476. https://doi.org/10.1016/j.algal.2015.10.012

52. Janssen MGJ (2002) Cultivation of microalgae: effect of light/dark cycles on biomass yield. Wageningen University
53. Khoeyi ZA, Seyfabadi J, Ramezanpour Z (2012) Effect of light intensity and photoperiod on biomass and fatty acid composition of the microalgae, *Chlorella vulgaris*. Aquac Int 20:41–49. https://doi.org/10.1007/s10499-011-9440-1
54. Krzemińska I, Nawrocka A, Piasecka A, Jagielski P, Tys J (2015) Cultivation of *Chlorella protothecoides* in photobioreactors: the combined impact of photoperiod and CO_2 concentration. Eng Life Sci 15:533–541. https://doi.org/10.1002/elsc.201400174
55. Kothari R, Prasad R, Kumar V, Singh DP (2013) Production of biodiesel from microalgae *Chlamydomonas polypyrenoideum* grown on dairy industry wastewater. Bioresour Technol 144:499–503. https://doi.org/10.1016/j.biortech.2013.06.116
56. Solovchenko A, Pogosyan S, Chivkunova O, Selyakh I, Semenova L, Voronova E, Scherbakov P, Konyukhov I, Chekanov K, Kirpichnikov M, Lobakova E (2014) Phycoremediation of alcohol distillery wastewater with a novel *Chlorella sorokiniana* strain cultivated in a photobioreactor monitored on-line via chlorophyll fluorescence. Algal Res 6: 234–241. https://doi.org/10.1016/j.algal.2014.01.002
57. Yu Z, Song M, Pei H, Han F, Jiang L, Hou Q (2017) The growth characteristics and biodiesel production of ten algae strains cultivated in anaerobically digested effluent from kitchen waste. Algal Res 24:265–275. https://doi.org/10.1016/j.algal.2017.04.010
58. Hu X, Meneses YE, Stratton J, Wang B (2019) Acclimation of consortium of micro-algae help removal of organic pollutants from meat processing wastewater. J Clean Prod 214:95–102. https://doi.org/10.1016/j.jclepro.2018.12.255
59. AlMomani FA, Örmeci B (2016) Performance of *Chlorella vulgaris*, *Neochloris oleoabundans*, and mixed indigenous microalgae for treatment of primary effluent, secondary effluent and centrate. Ecol Eng 95:280–289. https://doi.org/10.1016/j.ecoleng.2016.06.038
60. Guiry MD (2012) How many species of algae are there? J Phycol 48:1057–1063. https://doi.org/10.1111/j.1529-8817.2012.01222.x
61. Hong J, Kim O, Kim H, Jo S, Cho H, Yoon H (2016) Mass cultivation from a Korean raceway pond system of indigenous microalgae as potential biofuel feedstock. Oil Gas Res 2:1–6. https://doi.org/10.4172/2472-0518.1000108
62. Kim S, Lee Y (2013) Effects of pH and aeration rates on removal of organic matter and nutrients using mixotrophic microalgae. J Korean Soc Water Wastewater 27:69–76. https://doi.org/10.11001/jksww.2013.27.1.69
63. Mattos ER, Singh M, Cabrera ML, Das KC (2012) Effects of inoculum physiological stage on the growth characteristics of *Chlorella sorokiniana* cultivated under different CO_2 concentrations. Appl Biochem Biotechnol 168:519–530. https://doi.org/10.1007/s12010-012-9793-6
64. Posadas E, Morales M, Gomez C, Acién FG, Muñoz R (2015) Influence of pH and CO_2 source on the performance of microalgae-based secondary domestic wastewater treatment in outdoors pilot raceways. Chem Eng J 265:239–248. https://doi.org/10.1016/j.cej.2014.12.059
65. Shchegolkova N, Shurshin K, Pogosyan S, Voronova E, Matorin D, Karyakin D (2018) Microalgae cultivation for wastewater treatment and biogas production at Moscow wastewater treatment plant. Water Sci Technol 78:1–12. https://doi.org/10.2166/wst.2018.088
66. Mohd Udaiyappan AF, Abu Hasan H, Takriff MS, Sheikh Abdullah SR (2017) A review of the potentials, challenges and current status of microalgae biomass applications in industrial wastewater treatment. J Water Process Eng 20:8–21. https://doi.org/10.1016/j.jwpe.2017.09.006
67. Ansa EDO, Lubberding HJ, Gijzen HJ (2012) The effect of algal biomass on the removal of faecal coliform from domestic wastewater. Appl Water Sci 2:87–94. https://doi.org/10.1007/s13201-011-0025-y

68. Slompo NDM, Quartaroli L, Fernandes TV, da Silva GHR, Daniel LA (2020) Nutrient and pathogen removal from anaerobically treated black water by microalgae. J Environ Manage 268:2–8. https://doi.org/10.1016/j.jenvman.2020.110693
69. Cavet JS, Borrelly GPM, Robinson NJ (2003) Zn, Cu and Co in cyanobacteria: selective control of metal availability. FEMS Microbiol Rev 27:165–181. https://doi.org/10.1016/S0168-6445(03)00050-0
70. Zhang L, Lee YW, Jahng D (2012) Ammonia stripping for enhanced biomethanization of piggery wastewater. J Hazard Mater 199–200:36–42. https://doi.org/10.1016/j.jhazmat.2011.10.049
71. Marcilhac C, Sialve B, Pourcher AM, Ziebal C, Bernet N, Béline F (2014) Digestate color and light intensity affect nutrient removal and competition phenomena in a microalgal-bacterial ecosystem. Water Res 64:278–287. https://doi.org/10.1016/j.watres.2014.07.012
72. Kuo CM, Chen TY, Lin TH, Kao CY, Lai JT, Chang JS, Lin CS (2015) Cultivation of *Chlorella* sp. GD using piggery wastewater for biomass and lipid production. Bioresour Technol 194:326–333. https://doi.org/10.1016/j.biortech.2015.07.026
73. Gao F, Peng YY, Li C, Yang GJ, Deng YB, Xue B, Guo YM (2018) Simultaneous nutrient removal and biomass/lipid production by *Chlorella* sp. in seafood processing wastewater. Sci Total Environ 640–641:943–953. https://doi.org/10.1016/j.scitotenv.2018.05.380
74. Zhang L, Cheng J, Pei H, Pan J, Jiang L, Hou Q (2018) Cultivation of microalgae using anaerobically digested effluent from kitchen waste as a nutrient source for biodiesel production. Renew Energy 115:276–287. https://doi.org/10.1016/j.renene.2017.08.034
75. Wang M, Yang Y, Chen Z, Chen Y, Wen Y, Chen B (2016) Removal of nutrients from undiluted anaerobically treated piggery wastewater by improved microalgae. Bioresour Technol 222:130–138. https://doi.org/10.1016/j.biortech.2016.09.128
76. Metcalf E, Eddy H (2003) Wastewater engineering: treatment and reuse.4th edn. McGraw-Hill, Boston
77. Von Sperling M, Freire VH, Chernicharo CAL (2001) Performance evaluation of a UASB-activated sludge system treating municipal wastewater. Water Sci Technol 43:323–328. https://doi.org/10.2166/wst.2001.0698
78. Girard JM, Roy ML, Ben Hafsa M, Gagnon J, Faucheux N, Heitz M, Tremblay R, Deschênes JS (2014) Mixotrophic cultivation of green microalgae *Scenedesmus obliquus* on cheese whey permeate for biodiesel production. Algal Res 5:241–248. https://doi.org/10.1016/j.algal.2014.03.002
79. Delgadillo-Mirquez L, Lopes F, Taidi B, Pareau D (2016) Nitrogen and phosphate removal from wastewater with a mixed microalgae and bacteria culture. Biotechnol Rep 11:18–26. https://doi.org/10.1016/j.btre.2016.04.003
80. Santana H, Cereijo CR, Teles VC, Nascimento RC, Fernandes MS, Brunale P, Campanha RC, Soares IP, Silva FCP, Sabaini PS, Siqueira FG, Brasil BSAF (2017) Microalgae cultivation in sugarcane vinasse: selection, growth and biochemical characterization. Bioresour Technol 228:133–140. https://doi.org/10.1016/j.biortech.2016.12.075
81. Fasaei F, Bitter JH, Slegers PM, van Boxtel AJB (2018) Techno-economic evaluation of microalgae harvesting and dewatering systems. Algal Res 31:347–362. https://doi.org/10.1016/j.algal.2017.11.038
82. Sukenik A, Shelef G (1984) Algal autoflocculation – verification and proposed mechanism. Biotechnol Bioeng 26:4–9. https://doi.org/10.1002/bit.260260206
83. Chys M, Demeestere K, Nopens I, Audenaert WTM, Van Hulle SWH (2018) Municipal wastewater effluent characterization and variability analysis in view of an ozone dose control strategy during tertiary treatment: the status in Belgium. Sci Total Environ 625:1198–1207. https://doi.org/10.1016/j.scitotenv.2018.01.032
84. Beuckels A, Depraetere O, Vandamme D, Foubert I, Smolders E, Muylaert K (2013) Influence of organic matter on flocculation of *Chlorella vulgaris* by calcium phosphate precipitation. Biomass Bioenergy 54:107–114. https://doi.org/10.1016/j.biombioe.2013.03.027

85. de Souza Leite L, Daniel LA, Pivokonsky M, Novotna K, Branyikova I, Branyik T (2019) Interference of model wastewater components with flocculation of *Chlorella sorokiniana* induced by calcium phosphate precipitates. Bioresour Technol 286:121352. https://doi.org/10.1016/j.biortech.2019.121352
86. Vandamme D, Beuckels A, Vadelius E, Depraetere O, Noppe W, Dutta A, Foubert I, Laurens L, Muylaert K (2016) Inhibition of alkaline flocculation by algal organic matter for *Chlorella vulgaris*. Water Res 88:301–307. https://doi.org/10.1016/j.watres.2015.10.032
87. Deconinck N, Muylaert K, Ivens W, Vandamme D (2018) Innovative harvesting processes for microalgae biomass production: a perspective from patent literature. Algal Res 31:469–477. https://doi.org/10.1016/j.algal.2018.01.016
88. Kurniawati HA, Ismadji S, Liu JC (2014) Microalgae harvesting by flotation using natural saponin and chitosan. Bioresour Technol 166:429–434. https://doi.org/10.1016/j.biortech.2014.05.079
89. Pérez L, Luis Salgueiro J, Maceiras R, Cancela Á, Sánchez Á (2017) An effective method for harvesting of marine microalgae: pH induced flocculation. Biomass Bioenergy 97:20–26. https://doi.org/10.1016/j.biombioe.2016.12.010
90. Rakesh S, Saxena S, Dhar DW, Prasamna R, Saxena KA (2014) Comparative evaluation of inorganic and organic amendments for their flocculation efficiency of selected microalgae. J Appl Phycol 26:399–406. https://doi.org/10.1007/s10811-013-0114-4
91. Ummalyma SB, Mathew AK, Pandey A, Sukumaran RK (2016) Harvesting of microalgal biomass: efficient method for flocculation through pH modulation. Bioresour Technol 213: 216–221. https://doi.org/10.1016/j.biortech.2016.03.114
92. Vandamme D, Foubert I, Fraeye I, Meesschaert B, Muylaert K (2012) Flocculation of *Chlorella vulgaris* induced by high pH: role of magnesium and calcium and practical implications. Bioresour Technol 105:114–119. https://doi.org/10.1016/j.biortech.2011.11.105
93. Wu Z, Zhu Y, Huang W, Zhang C, Li T, Zhang Y, Li A (2012) Evaluation of flocculation induced by pH increase for harvesting microalgae and reuse of flocculated medium. Bioresour Technol 110:496–502. https://doi.org/10.1016/j.biortech.2012.01.101
94. Heasman M, Diemar J, Connor WO, Sushames T, Foulkes L (2000) Development of extended shelf life microalgae concentrate diets harvested by centrifugation for bivalve molluscs – a summary. Aquacult Res 31:637–659. https://doi.org/10.1046/j.1365-2109.2000.318492.x
95. Dassey AJ, Theegala CS (2013) Harvesting economics and strategies using centrifugation for cost effective separation of microalgae cells for biodiesel applications. Bioresour Technol 128: 241–245. https://doi.org/10.1016/j.biortech.2012.10.061
96. Nagy E (2019) Membrane materials, structures, and modules. In: Nagy E (ed) Basic equations mass transport through a membrane layer2nd edn, Elsevier, pp 11–19. https://doi.org/10.1016/b978-0-12-813722-2.00002-9
97. Sharma KK, Garg S, Li Y, Malekizadeh A, Schenk PM (2013) Critical analysis of current microalgae dewatering techniques. Biofuels 4:397–407. https://doi.org/10.4155/bfs.13.25
98. Milledge JJ, Heaven S (2013) A review of the harvesting of micro-algae for biofuel production. Rev Environ Sci Biotechnol 12:165–178. https://doi.org/10.1007/s11157-012-9301-z
99. Rios SD, Clavero E, Salvadó J, Farriol X, Torras C (2011) Dynamic microfiltration in microalgae harvesting for biodiesel production. Ind Eng Chem Res 50:2455–2460. https://doi.org/10.1021/ie101070q
100. Sun X, Wang C, Tong Y, Wang W, Wei J (2013) A comparative study of microfiltration and ultrafiltration for algae harvesting. Algal Res 2:437–444. https://doi.org/10.1016/j.algal.2013.08.004
101. Ahmad AL, Mat Yasin NH, Derek CJC, Lim JK (2012) Crossflow microfiltration of microalgae biomass for biofuel production. Desalination 302:65–70. https://doi.org/10.1016/j.desal.2012.06.026
102. Laamanen CA, Ross GM, Scott JA (2016) Flotation harvesting of microalgae. Renew Sustain Energy Rev 58:75–86. https://doi.org/10.1016/j.rser.2015.12.293

103. Edzwald JK (1993) Algae, bubbles, coagulants, and dissolved air flotation. Water Sci Technol 27:67–81. https://doi.org/10.2166/wst.1993.0207
104. Rubio J, Souza ML, Smith RW (2002) Overview of flotation as a wastewater treatment technique. Miner Eng 15:139–155. https://doi.org/10.1016/S0892-6875(01)00216-3
105. Edzwald JK (2010) Dissolved air flotation and me. Water Res 44:2077–2106. https://doi.org/10.1016/j.watres.2009.12.040
106. Ndikubwimana T, Chang J, Xiao Z, Shao W, Zeng X, Ng I, Lu Y (2016) Flotation: a promising microalgae harvesting and dewatering technology for biofuels production. Biotechnol J 11:315–326. https://doi.org/10.1002/biot.201500175
107. Shi W, Zhu L, Chen Q, Lu J, Pan G, Hu L, Yi Q (2017) Synergy of flocculation and flotation for microalgae harvesting using aluminium electrolysis. Bioresour Technol 233:127–133. https://doi.org/10.1016/j.biortech.2017.02.084
108. de Souza Leite L, Hoffmann MT, Daniel LA (2019) Coagulation and dissolved air flotation as a harvesting method for microalgae cultivated in wastewater. J Water Process Eng 32:100947. https://doi.org/10.1016/j.jwpe.2019.100947
109. Besson A, Guiraud P (2013) High-pH-induced flocculation-flotation of the hypersaline microalga *Dunaliella salina*. Bioresour Technol 147:464–470. https://doi.org/10.1016/j.biortech.2013.08.053
110. de Souza Leite L, dos Santos PR, Daniel LA (2020) Microalgae harvesting from wastewater by pH modulation and flotation: assessing and optimizing operational parameters. J Environ Manage 254:109825. https://doi.org/10.1016/j.jenvman.2019.109825
111. Kwon H, Lu M, Lee EY, Lee J (2014) Harvesting of microalgae using flocculation combined with dissolved air flotation. Biotechnol Bioprocess Eng 19:143–149. https://doi.org/10.1007/s12257-013-0433-y
112. Wiley PE, Brenneman KJ, Jacobson AE (2009) Improved algal harvesting using suspended air flotation. Water Environ Res 81:702–708. https://doi.org/10.2175/106143009x407474
113. Zhang X, Hewson JC, Amendola P, Reynoso M, Sommerfeld M, Chen Y, Hu Q (2014) Critical evaluation and modeling of algal harvesting using dissolved air flotation. Biotechnol Bioeng 111:2477–2485. https://doi.org/10.1002/bit.25300
114. Marchioretto MM, Reali MAP (2001) Ozonation followed by coagulation/flocculation and flotation as post-treatment of the effluent from an anaerobic baffled reactor treating domestic sewage. Water Sci Technol Technol 43:99–106. https://doi.org/10.2166/wst.2001.0474%0A
115. Santos PR, Daniel LA (2017) Dissolved air flotation as a potential treatment process to remove *Giardia* cysts from anaerobically treated sewage. Environ Technol 38:2392–2399. https://doi.org/10.1080/09593330.2016.1262461
116. Lei X, Chen Y, Shao Z, Chen Z, Li Y, Zhu H, Zhang J, Zheng W, Zheng T (2015) Effective harvesting of the microalgae *Chlorella vulgaris* via flocculation – flotation with bioflocculant. Bioresour Technol 198:922–925. https://doi.org/10.1016/j.biortech.2015.08.095
117. Zhang D, Yu Y, Li C, Chai C, Liu L (2015) Factors affecting microalgae harvesting efficiencies using electrocoagulation-flotation for lipid extraction. RSC Adv 5:5795–5800. https://doi.org/10.1039/c4ra09983d
118. Feng Q, Chen M, Wang W (2016) Study on the harvest of oleaginous microalgae *Chlorella* sp. by photosynthetic hydrogen mediated auto-flotation for biodiesel production. Int J Hydrogen Energy 41:16772–16777. https://doi.org/10.1016/j.ijhydene.2016.07.142
119. Branyikova I, Filipenska M, Urbanova K, Ruzicka MC, Pivokonsky M, Branyik T (2018) Physicochemical approach to alkaline flocculation of *Chlorella vulgaris* induced by calcium phosphate precipitates. Colloids Surf B Biointerfaces 166:54–60. https://doi.org/10.1016/j.colsurfb.2018.03.007
120. Vandamme D, Foubert I, Muylaert K (2013) Flocculation as a low-cost method for harvesting microalgae for bulk biomass production. Trends Biotechnol 31:233–239. https://doi.org/10.1016/j.tibtech.2012.12.005

121. Salim S, Kosterink NR, Tchetkoua Wacka ND, Vermuë MH, Wijffels RH (2014) Mechanism behind autoflocculation of unicellular green microalgae *Ettlia texensis*. J Biotechnol 174:34–38. https://doi.org/10.1016/j.jbiotec.2014.01.026
122. Ummalyma SB, Gnansounou E, Sukumaran RK, Sindhu R, Pandey A, Sahoo D (2017) Bioflocculation: an alternative strategy for harvesting of microalgae – an overview. Bioresour Technol 242:227–235. https://doi.org/10.1016/j.biortech.2017.02.097
123. Cole AJ, Neveux N, Whelan A, Morton J, Vis M, de Nys R, Paul NA (2016) Adding value to the treatment of municipal wastewater through the intensive production of freshwater macroalgae. Algal Res 20:100–109. https://doi.org/10.1016/j.algal.2016.09.026
124. Instituto Trata Brasil, Dados de esgoto no Brasil (2020) http://www.tratabrasil.org.br/saneamento/principais-estatisticas/no-brasil/esgoto
125. Ganeshkumar V, Subashchandrabose SR, Dharmarajan R, Venkateswarlu K, Naidu R, Megharaj M (2018) Use of mixed wastewaters from piggery and winery for nutrient removal and lipid production by *Chlorella* sp. MM3. Bioresour Technol 256:254–258. https://doi.org/10.1016/j.biortech.2018.02.025
126. Kunz A, Steinmetz RLR, Ramme MA, Coldebella A (2009) Effect of storage time on swine manure solid separation efficiency by screening. Bioresour Technol 100:1815–1818. https://doi.org/10.1016/j.biortech.2008.09.022
127. Associação Brasileira de proteina animal (2018) Annual Report, São Paulo
128. Franchino M, Tigini V, Varese GC, Mussat Sartor R, Bona F (2016) Microalgae treatment removes nutrients and reduces ecotoxicity of diluted piggery digestate. Sci Total Environ 569–570:40–45. https://doi.org/10.1016/j.scitotenv.2016.06.100
129. Sánchez E, Borja R, Travieso L, Martín A, Colmenarejo MF (2005) Effect of organic loading rate on the stability, operational parameters and performance of a secondary upflow anaerobic sludge bed reactor treating piggery waste. Bioresour Technol 96:335–344. https://doi.org/10.1016/j.biortech.2004.04.003
130. de Souza Leite L, Daniel LA (2020) Optimization of microalgae harvesting by sedimentation induced by high pH. Water Sci Technol:1–10. https://doi.org/10.2166/wst.2020.106

Reuse of Agriculture Drainage Water – Case Studies: Central Valley of California and the Nile Delta in Egypt

Mohamed Galal Eltarabily

Contents

Abstract Agricultural drainage water (ADW) is mainly the excessive water that runs off the agricultural field at the low end of furrows, border strips, basins, and flooded areas during or after surface irrigation. It can be reclaimed and beneficially reused for the irrigation of fields at lower elevations without any treatments and pumping. In many cases, the runoff can be collected and stored in lined ponds (e.g., with a membrane liner) for later reuse. In contrast, the stored water should not be allowed for infiltration into groundwater aquifers when it has a high chemical content. In this chapter, we will (1) discuss the reuse of ADW in large agricultural regions in California, such as the Central Valley (2) summarize the different strategies for ADW reuse and its practices in the Nile Delta of Egypt. The conclusion of the chapter is presented and recommendations for the long-term usage of ADW.

M. G. Eltarabily (✉)
Civil Engineering Department, Faculty of Engineering, Port Said University, Port Said, Egypt

Kearney Agricultural Research and Extension Center, University of California, Parlier, CA, USA
e-mail: eng_m_trabily@eng.psu.edu.eg; meltarabily@ucdavis.edu

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 325–344, DOI 10.1007/698_2022_863,

Also, the assessment of the long-term impact of using drainage water from the environmental aspect is summarized.

Keywords Agriculture, Central Valley, Drainage water reuse, Irrigation, Nile Delta, Non-conventional water sources, Salinity

Abbreviations

ADW	Agricultural drainage water
B	Boron
BCM	Billion cubic meter
BOD	Biological oxygen demand
C_e	Coefficient of evaporation
dS/m	Decisiemens per meter
EC	Electrical conductivity
E_V	Annual evaporation rate
MALR	Ministry of Agriculture and Land Reclamation
mg/L	Milligrams per liter
mmho/cm	Millimho per centimeter
MWRI	Ministry of Water Resources and Irrigation
Ppm	Parts per million
SAR	Sodium adsorption ratio
Se	Selenium
TDS	Total dissolved solids

1 Introduction

With increasing world population, the gap between water supply and demand is widening. The Non-conventional ways of conserving water are now applied through the reuse of wastewater of agriculture and industry [1]. While agricultural drainage water, ADW is treated before using for irrigation purposes in developed countries where standards are applied, it is not always strictly adhered in developing countries. ADW refers to irrigation tailwater at the lower ends of basins, furrows, border strips, and flooded areas. ADW reuse practices vary significantly around the world. It ranges from the use of untreated wastewater in regions where wastewater treatments are limited to the usage of highly treated recycled water in the more developed regions. In either case, both food and non-food crops are commonly irrigated [2].

Across all contexts, water scarcity is the common motivation for agricultural reuse [3]. ADW generally has a high load of organic matter (high biological oxygen demand, BOD). The reuse of ADW can pose positive benefits to the farmers' community, where it helps to improve soil organic content, cation exchange capacity, soil moisture-holding capacity, and soil nutrient content and productivity. In the cases where ADW contains high levels of salts and nutrients, mixing with lower-salinity water can make it safe for irrigation reuse [4]. Agricultural practices under the semi-arid climatic conditions in Central Valley of California need intensive, frequent irrigation and well-designed subsurface drainages to prevent salt accumulation in the surface soils. The discharging from the groundwater in the San Joaquin Valley–Central California (Fig. 1) altered the mechanism of the groundwater flow and the distribution of chemicals in the groundwater [5].

The management of the high volumes of ADW in San Joaquin Valley is highly challenging, where ADW has a considerable amount of selenium, Se and Boron, B, as well as the high level of salinity. ADW cannot be directly disposed into the surface water bodies or discharged to groundwater aquifer because of the environmental hazards of Se to wildlife and environment. In this case, the ADW is collected and stored in evaporation ponds for Se, B, and salts accumulation [6].

There is an increasing trend towards the reuse of ADW with poor quality for agricultural production in San Joaquin Valley. It can serve two purposes; one is to dispose of ADW that would otherwise be costly to be treated and pumped again to the fields, and the other is to utilize this drainage water for irrigating salt-tolerant crops without significant reduction on the yield. Consequently, the successful adoption of a practical agricultural drainage water reuse strategies in Central Valley of California requires integrated management practices related to the irrigation schemes with poor-quality waters, crop selection, and monitoring groundwater and soil for the fate of toxic elements in agricultural production systems [7].

Egypt lies in aridity climate conditions at the end of the longest river all over the world. It has a negative water balance where its total annual water supply accounts for approximately 57.7 billion cubic meters, BCM (from the Nile, rainfall along the Mediterranean coast, and the deep groundwater), and the annual demand is around 72.4 BCM. This 25% difference between the demand and supply comes from the reuse of agricultural drainage water multiple times where pumps lift the water from drains and discharge it back into irrigation canals for reuse. The main problem is that when water infiltrates through soil and drainage networks, it is combined with salts and agricultural drainage, such as chemical fertilizers, which finally adversely affect the soil properties [8]. Therefore, two water are mixed together (the freshwater in irrigation canals, and the drainage water from agriculture) following two strategies; the governmental scale, where official mixing of the water occurs at the pumping stations, and the unofficial practices (farm-scale) by the local growers. This second practice by the local farmers leads to having low-quality resultant water, which later adversely affects the crops and the groundwater quality [9].

The ability of the selected crops which can survive in the drainage water reuse system depends on many plant parameters. Some of these parameters are varieties and population, stage of growth (initial, development, mid-season, and late-season), type of irrigation (drip, sprinkler, and furrow), and bed arrangements [10]. When the drainage water is reused to irrigate different fields, respectively, its quality becomes increasingly poor until reaching the last field. Thus, it is imperious to select higher salinity tolerant crops for the latter stage of the drainage water reuse system. The

Fig. 1 San Joaquin Valley–Central California

selection of the crops is based on two substantial criteria, which are the economic viability of the plant and the lowest maintenance requirements for the field [11].

2 Agricultural Drainage Water Reuse

Reuse of agricultural drainage water is essential to keep the balance between the water requirements and water supply for both the short and long-term. In arid regions and areas that suffer from the limitation of water resources, the reuse of agriculture drainage water is applied for supplemental compensation where strategies for the reuse have evolved. However, the crops type and patterns are determined based on the quality of the used drainage water. Drainage water with high salinity cannot be used for the irrigation of salt-sensitive crops while it could be flooding salt-tolerant forages, and it will be successful. A framework summarizes the uses of drainage water from agriculture is presented in Fig. 2.

2.1 *Reuse for Crop Irrigation*

Agricultural drainage water reuse for crop irrigation mainly depends on the ions' concentrations and salinity. Drainage water with lower ionic concentrations is safe for plant growth and could provide the plant with the essential nutrients' requirements. When the drainage water contains plenty of salts, the ions accumulate in the soil, increase the osmotic pressure, limit the plant water uptake. The critical factor that controls the reuse of the drainage water for crop irrigation is how to drain salts away from the root system of the plant and to control the salinity levels based on crop tolerance. With more usage of drainage water, it becomes saltier and thus leads to keep monitoring and management for achieving sustainability of the system.

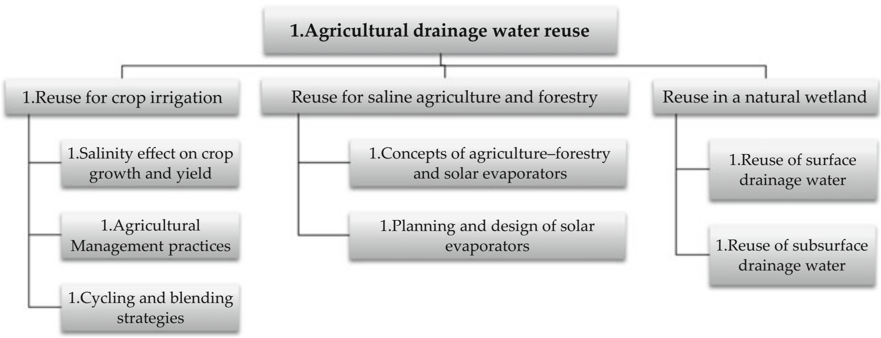


Fig. 2 Framework of agricultural drainage water reuse

2.1.1 Salinity Effect on Crop Growth and Yield

On the other hand, when salinity level in the drainage water that is used for irrigation increases beyond the threshold level of the crops, a significant decline of yield inevitably occurs. In this case, the designer or the farm advisor should compare the reduction with a control case (with non-saline irrigation water) for decision if the system is beneficial or not. The salinity tolerant is represented based on the threshold salinity (a) and the slope (b) of the yield decline and calculated from Eq. (1).

$$Y_r = 100 - b\,(\mathrm{EC}_e - a) \tag{1}$$

where EC_e is the soil salinity in Deci siemens per meter (1 dS/m = 1 mmho/cm = 640 mg/L).

2.1.2 Agricultural Management Practices

The main objective of using agriculture drainage water for irrigation is to reduce the cost of water (when the value of water is high), drainage, nutrients (in the form of fertilizer saving), and achieving a maximum profit with reaching a highest possible yield. When drainage of the tailwater is limited because of topography restrictions, serious salinity hazards on crop growth will happen, and substantial, intensive management plans should be considered for achieving suitable irrigation and cropping strategies. The greater the salinity of the drainage water, which is used as irrigation water, the greater application of the required water because of the needed water fraction for leaching requirements. Thus, the accumulation of salts in the soil depends on the amount of residual water after the plant's need, which is available for leaching the salts.

Crops irrigated with a sprinkler system are susceptible to injury not only from soil salinity but also from the absorbed salts through the wetted leaf surfaces from water drops; however, this is not the case with waxy leaves. When the reused ADW contains high salinity levels, the flood irrigation would be the first preferable irrigation system, then the drip irrigation and lastly sprinklers. When irrigation water is frequently applied through drips, continuous leaching of salts from the root area occurs in addition to supplementary leaching during the rainfall season. Salinity in root zone estimates is weighted based on a typical pattern of root distribution of 40:30:20:10 to account for the water uptake at the different depths. Thus, leaching requirements (LR) can be simply estimated from Eq. (2) by [12] as follows:

$$\mathrm{LR} = \mathrm{EC}_w/5\,(\mathrm{EC}_e) - \mathrm{EC}_w \tag{2}$$

where LR is the minimum leaching requirements for controlling salts within the EC_e tolerance, EC_w is the salinity of the applied irrigation water (in dS/m), and EC_e is the average soil salinity.

2.1.3 Cycling and Blending Strategies

Some other management techniques could improve yield when saline drainage water is used as irrigation water for crop production. Some of these management techniques are using seeds of considerable size and weight, use more vigorous varieties of cultivars, increasing crop density, planting on sloped beds to accumulate salts away from the lines. On the other hand, fertilizer applications would be reduced while the applied drainage water always has plenty of essential nutrients for plants. The sodium (Na) content in the soil is another essential factor that we should consider it because the high sodium concentration decreases soil permeability and leads to prevention or insufficient leaching of salts. The suitability of water and soil is measured using the sodium adsorption parameter (SAR).

Cyclic strategies for using drainage water of different salinities is the most common practice among agricultural drainage water reuse practices. Different mixing ratios between freshwater and saline drainage water can be successfully applied to crops during different growth stages (where salinity tolerant is different) or can be used with crop rotations between tolerant and sensitive crops. Most of crops are sensitive to salinity during the seedling and germination stages while they are more tolerant of salinity during the later growth stage. Some critical practices during irrigation should also be considered. Increasing the number of irrigation cycles (irrigate more frequent) during the sensitive growth stages and irrigate less frequently with higher salinity levels of irrigation water during the salt-tolerant stages of plant growth. Other factors affecting the cyclic strategy of drainage water reuse such as the climate conditions, heterogeneity of soil along with the depth which affects the salt accumulation, and the actual root density and distribution parameters. In addition to its low salinity, the blended water has low toxic ions, which means it is environmentally friendly when the final disposing of the drainage water occurs.

2.2 Reuse for Saline Agriculture and Forestry

2.2.1 Concepts of Agriculture-Forestry and Solar Evaporators

The agriculture-forestry system manages the drainage water as a source of reuse instead of direct disposal into evaporation ponds, rivers, or lakes. While agriculture-forestry produces biomass, it also significantly reducing the final volume of non-reusable drainage water, which could be disposed into rivers during their seasonal high flows. Solar evaporators are preferable from the wildlife safety aspect

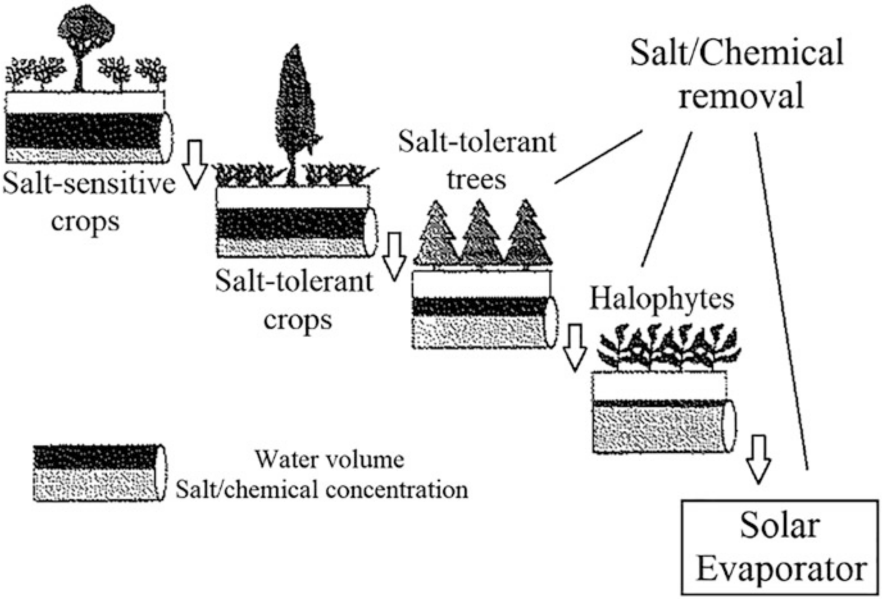


Fig. 3 Agriculture-forestry and salt management systems [7]

where trees create wildlife habitats, reduce air pollution, and enhance the overall environmental quality. The agriculture-forestry systems have been developed and applied in California for salt management of irrigated farmland through two objectives: (1) to reduce the volume of drainage water, which is discharged directly on the farm and (2) to utilize the drainage water as a resource to produce profitable marketable crops.

The productive use of ADW through the agriculture-forestry system and its disposal into the solar evaporators has been developed and widely applied in California. The agriculture-forestry system for the subsequent reuse and reduction of drainage water volume can be performed through the water flow from salt-sensitive crops to salt-tolerant trees then to more salt-tolerant halophytes and finally, to a solar evaporator (Fig. 3). The primary function of this system is to subsequently reuse the water until the final disposed water could not be used anymore. The salt-tolerant trees are used to consume and evaporate large volumes of drainage water, which act as biological pumps. Trees biomass could generate electricity and bio-chemical or biofuel. After that, halophytes are planted as food potentials or industry. With going through each successive stage in the system, the salinity is increased, and the water volume is decreased.

In the agriculture-forestry system, almost 80–85% of ADW that was initially applied at the first stage to grow salt-sensitive crops is subsequently reused to produce salt-tolerant crops. The remaining percentage of the water volume (15–20%) with the high concentration of salts evaporates into the solar evaporators. The solar evaporator's design consists of a leveled area lined with impermeable liner on which the crystallized salt is collected. A correlation between the daily amount of discharged drainage water into the solar evaporator and the daily evaporation rates is performed to prevent the water ponding.

2.2.2 Planning and Design of Solar Evaporators

The agriculture-forestry system in California is operating for subsequent reuse of drainage water. At the same time, salt removal utilizes the drainage water with 7,000 mg/L as an initial salt concentration, following the irrigation of salt-tolerant crops. This technology offers management options for the salt crystallization in relatively small areas on farms or the discharge of the reduced volume of drainage water (brine) into natural sinks or solar ponds. Salt crystallization in solar evaporators supplies salt to the market with required salts through its short-/long-term storage on farms or the designated landfills [7].

Additionally, the system for subsequent reuse of drainage water is efficiently reducing Se levels. The average Se concentration is 0.5 mg/L in drainage water, which could be applied to trees, and 0.9 mg/L in the reduced volume of drainage water applied to halophytes. Selenium is subsequently reduced through the volatilization and is also taken up by halophytes and trees. Selenium removal by trees is mainly positioned in the leaves. Successful experiments for this system achieved when Se could be transferred through the harvesting of halophytes and then used this forage safely for cattle feeding.

The design of solar evaporators is fundamental to the development of the integrated agriculture-forestry system. The size (area) of the solar evaporator is a function of the annual evaporation rates, which depend on the farming region's location. The solar evaporator's area is calculated by Eq. (3) as follows:

$$A_e = 1000\,\mathrm{DW}_h/E_\mathrm{V} \times C_e \tag{3}$$

where A_e is the area of the solar evaporator (m^2), DW_h is the drainage water discharged from halophytes into the solar evaporator (1,000 m^3), E_V is the annual evaporation rate (m), and C_e is the coefficient of evaporation, for reduced evaporation of saline water.

2.3 *Reuse in a Natural Wetland*

Agricultural drainage water could also be utilized for wetland or wildlife habitat irrigation after addressing the following questions:

1. Is a sufficient volume of the water available, and what constitutes are existing in the water?

2. What vegetation could be grown using this drainage water and where it is from surface or subsurface drainage water?
3. What are the associated environmental impacts on wildlife, and is the wetland sustainable or not?

2.3.1 Reuse of Surface Drainage Water

Surface drainage water is derived only from surface drains or tailwater sources. The main question is whether the water contains applied fertilizers and pesticides or not. In the areas where powerful environmental safeguards exist, and restrictions are followed when applying the pesticide, there is little risk associated with the reuse of surface runoff or tailwater drainage water. For example, rice field drainage water accounts for a large percentage of the water supply for managed natural wetlands in Sacramento Valley in California, where it is generally safe for reuse. Most of surface derived drainage water is utilized to flood wetlands in the early autumn. In the rice-growing sectors, the fields are drained in the early autumn or late summer. These drainage patterns concur with the wintering grounds of waterfowl's autumn migration.

Ideally, the habitat of the winter waterfowl is flooded to a depth of 20–50 cm. Based on soil type, seepage, and evaporation rates, the drainage water required for the initial flooding will be ranged from 500 to 1,500 m^3/ha. Whenever local supplies of surface derived drainage water are available, water is used to maintain ponds from October to March of the following year. In warm climates, the consumptive use (the annual evaporation) is approximately 2,500 m^3/ha, which causes a further increase of salt concentrations in the wetland outflow.

The typical native marsh plants grown with surface agricultural drainage waters include pale smartweed (*Polygonum lapathifolium*), swamp timothy (*Heleochloa schoenoides*), and hardstem bulrush (*Scirpus fluviatilis*). These plants are grown under plenty of soil moisture content. Water is applied in the autumn and held until the warm temperature of the soil exists, which occurs in March or April in the Central Valley. When the soil begins to warm, ponds are drained to be in mudflat conditions, and this stimulates seed germination. In some areas, seed germination does not require additional water until the autumn flood up period. However, where summer months are hot and dry, one or more irrigations will be required between July and early August in order to provide an optimal seed production.

2.3.2 Reuse of Subsurface Drainage Water

The reuse of the subsurface saline ADW for wetlands management can pose a substantial challenge and can generate severe problems. Thus, it could affect wildlife and habitat reductions. Although subsurface drainage water is free from pesticides or herbicides, it sometimes contains naturally derived toxicants or trace elements such as salts and nitrates. Prior to planting and seedling, a careful analysis of subsurface agricultural drainage water is required. The provision of a sufficient volume of flow-through water is essential to minimize the concentration of toxic elements due to evaporation.

However, because of the high vulnerability of food-chain and processing, most wetland managers and decision-makers intentionally refuse to use subsurface agricultural drainage water, which contains high levels of trace elements. The potential costs of clean up or remediation of a contaminated wetland dictate a conservative approach. The primary consideration is the management of water salinity and soil. Maintaining of the salt balance between applied water and the soil/water interface is key to the production of salty water native marsh plants. General in California, water with total dissolved solids, TDS level of 2,500 mg/L or less is preferable for wetland management. Occasionally, water with a TDS level as high as 5,000 mg/L can be used only for short periods of applications.

In late winter, ponds are drained to discharge the drainage water and accumulated salts. Ponds are then refilled with new freshwater as profoundly as practicable. After about 14 days, the water is drained for the second time. The drainage cycle is repeated about two to three times before the cycle is totally completed. This process removes the salts in the surface water through the evaporation process and allows for the rebalancing of the soil moisture contents.

3 Strategies for Agricultural Drainage Water Reuse in Egypt

The reuse of drainage water offers a further illustration of how humans modify the cycle of water through Egypt. Agricultural drainage water reuse strategies follow the hydro-social cycle, which offers a framework for highlighting the intersection between water flows and the social processes. Rather than seeing water as a substance that circulates independently of society, the hydro-social cycle recognizes each storage component and flow as moderated by social, political, economic, and cultural relations that, in turn, are shaped in part by the flow of water. Instead of water only cycling from precipitation (over the East African source regions of the Nile) to surface flow (through the Nile and over the fields), to infiltration (through the soil), and back into the atmosphere via transpiration (through the crops) or evaporation from a drainage outlet (the Mediterranean), the reuse of drainage water adds an extra loop to the cycle (Fig. 4).

About 71% of the farmers in the Nile Delta find insufficient water in the irrigation canals during summer months because of the intense pressure on the water supplies [14]. The drainage water reuse helps make up these shortages by enabling farmers to irrigate their fields. Additionally, the budget from the reuse of agricultural drainage water could help in providing the required water for the land reclamation projects in the desert, where the government pursues an ambitious strategy to expand the cultivated land by 3.1 million acres by the end of the year 2030 [15]. Two factors

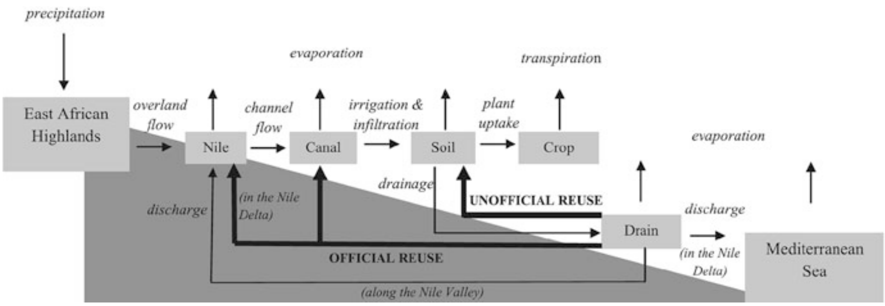


Fig. 4 The Nile's hydro-social cycle [13]

that are governing the reuse process are quality and quantity. Quality means water must be at a certain standard before it can be used for irrigation. At the same time, quantity affects the relative volumes of clean and polluted water, (which determines the nature of the resultant mixture). The significance of the hydro-social cycle concept not only comes from what it tells us about where the water goes but also about what the water will be.

The "hydro" cycle is dynamic (not static). Social, political, and economic relations determine who within the farming population is able to access drainage water for reuse and who is not. The most fortunate farmers are those who have no need for drainage water in the first place as they have enough good quality irrigation water. Among the vast majority of the farmers who do not have sufficient water, they stay in line with government reuse pumping stations to supplement their canal supplies. Besides, any farmer with the money to buy or rent a pump and land near a drain can access drainage water "unofficially." However, the process of drainage water reuse reworks relations of power and influence by impacting the volume and quality of water each farmer could receive and thereby setting the parameters of agricultural possibility. The better the quality of water a farmer is able to access for irrigation, the higher the yields and profits he will achieve.

Average salinity in the main drains in the irrigation and drainage network of Egypt, measured in parts per million (ppm), is 565 ppm but can reach up to 6,000 ppm in northern parts of the Delta [16]. It is possible to irrigate with saline water and still maintain excellent levels of production (the so-called biosaline agriculture), but this requires careful land management practices [17]. So, for most farmers, saline irrigation water means lower yields. In studies conducted by the Egyptian Ministry of Water Resources and Irrigation (MWRI), for example, irrigation with saline water (1,000 ppm) produced yields up to 29% lower than freshwater irrigation. Yield declines were most marked for sensitive crops, like maize, in comparison to more tolerant crops, like cotton and wheat, which can cope with a higher salinity [18].

To understand where the drainage water comes from, we have to look at the irrigation and drainage network system of the Nile Delta of Egypt. About 60% of Egypt's cultivated land is served by a subsurface drainage system comprising a network of pipes just over a meter below the ground surface [19]. The rest of the land is crisscrossed by drainage ditches, which border each field of the Nile Delta's land. Drainage water from the surface and subsurface systems meet in the open branch drains, which channel water into the main drains.

Drainage is, therefore, a converse flow to irrigation. Whereas the irrigation network channels water from a single source (the Nile River) to multiple points of the outlet (the fields), the drainage network transfers water from multiple sources (the fields) to a single point of the outlet (the drain). The majority of drains in the northern part of the Delta are wide and full of dark and polluted water [20]. Salinity is always high, on average, over 2,800 ppm. The main drains discharge a total of approximately 12.5 BCM of water a year, either directly into the Mediterranean Sea or into the coastal lakes of Mariut, Edku, Burullus, and Manzala [21].

3.1 Official Reuse

The Egyptian Ministry of Water Resources and Irrigation (MWRI) initiated the program of agricultural drainage water reuse and constructed large pumping stations on the main drains of the Nile Delta [22]. Until 1984, 2.9 BCM of drainage water was discharged again into the main canals and the Nile's two branches for reuse in agriculture [23]. In 2011, MWRI expanded the network of pumping stations (Fig. 5), and the official reuse of ADW reached 7.5 BCM, which means almost 10% of Egypt's water need meets by the drainage water reuse [24].

On the other hand, farmers play an active role in companying government responsibility through the MWRI program to establish the pumping stations in their areas. Although the enormous efforts from the government side, some farmers still have the concept that the drainage water is "a very bad thing," and the drainage water is not only a substandard source of water for irrigations but also a symbol of marginality. The hydro-social cycle that affecting the water quality depends on many factors such as the type and quality of the original drainage water before mixing, the volume of the freshwater (the mixing ratio), and the place of mixing.

3.1.1 Salinity Threshold

The future of ADW in Egypt's national water resources plan for 2017 by [22] does not consider the salinity as a factor restricting the reuse of the drainage water. These estimates of high reuse potential (Fig. 6) support the vision of the Egyptian government for agricultural expansion into the desert. However, some other reports adopted 1,600 ppm as a salinity threshold, which leads to 8.9 BCM maximum potential reuse [25]. Other salinity thresholds could be adopted based on crop and soil type.

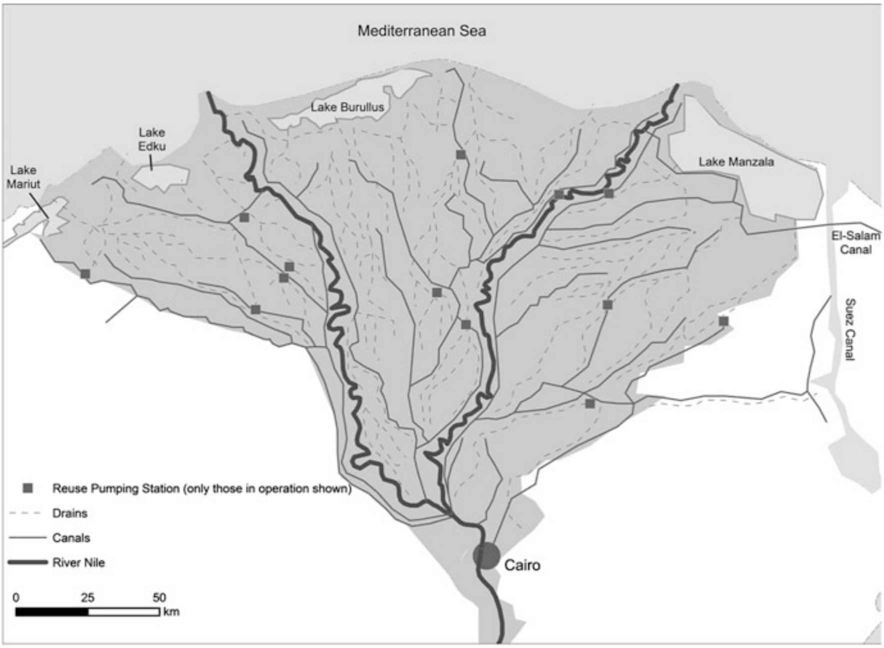


Fig. 5 Drainage outlets and reuse pumping stations in the Nile Delta [13]

3.1.2 Mixing Ratios

The quality of the drainage water after the reuse depends on how much freshwater was mixed in with it. The mixing ratio of one to one is cited as “rule of thumb” which means one-part irrigation should be mixed with one-part drainage water [26]. This rule was originated from the El-Salam project, one of the massive governmental reuse projects where the freshwater (originated from Damietta branch of the Nile) mixes an equal proportion of the drainage water from two main drains [27]. The generated mixed water was discharged through a syphon under the Suez Canal and El-Sheikh Zaid canal into the desert of the Sinai Peninsula for land reclamation (Fig. 7). About 6.21×10^5 feddans of reclaimed lands (2.21×10^5 and 4×10^5 feddans west and east of Suez Canal, respectively) are irrigated by 2.3 BCM per year. 2.11 BCM/year is from the Damietta branch, which is equal to the drainage portion from Bahr Hadus drain, 1.905 BCM/year, and El-Serw drain, 0.435 BCM/year [29].

Unlike El-Salam Canal, the mixing ratio is 1:1, and it could reach 5:1 of the canal to drainage water in cases of the high salinity of the drain water. Thus, MWRI applies different mixing ratios according to practical contexts for each pumping station for water ruse. It is clearly saying that the quality of the resultant mixed water is the main governing factor to decide the specified mixing ratio when the salinity of the mixed water reaches 1,000 ppm.

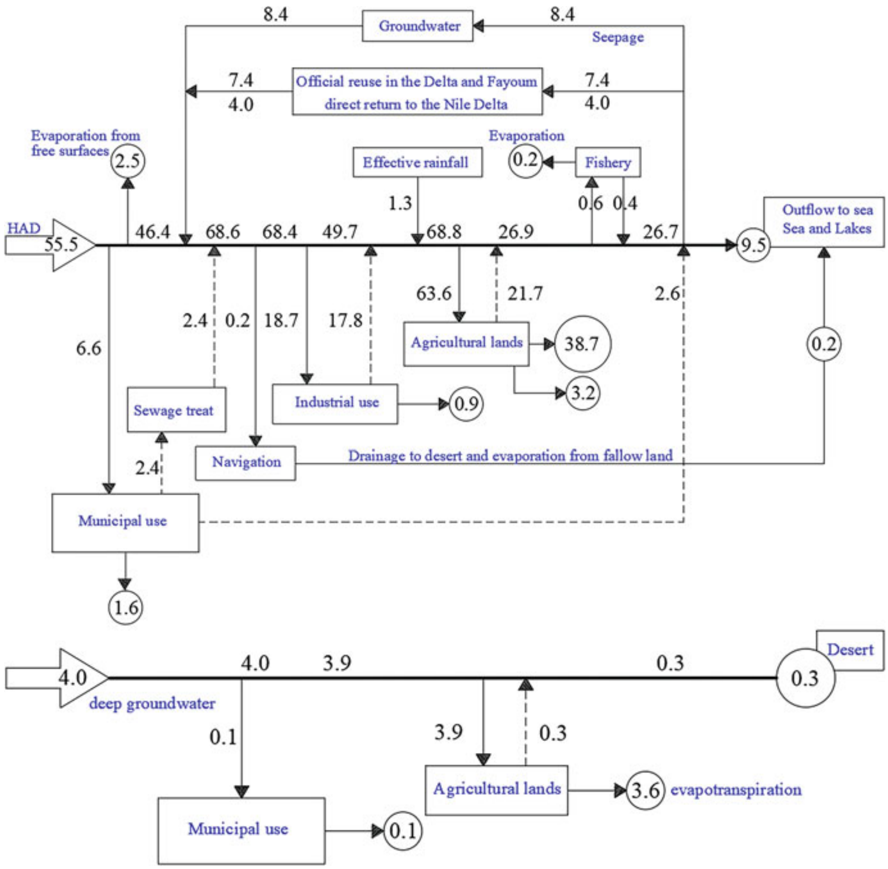


Fig. 6 Water balance of Egypt including agricultural water reuse for Nile system and Desert in 2017 (redrawn after [22])

3.1.3 Mixing Location

The process of agricultural drainage water reuse depends on the place where the mixing of the two sources of the water occurs. MWRI has traditional practices of recycling the water from the main drains where pumping stations lift the water and discharge it into a main canal or branch of the Nile (Fig. 8). Recently, the MWRI starts the “intermediate drainage reuse” practice, which is led by the regional irrigation directorates where water from branch drains is collected and discharged into tail ends of the branch canal. Unlike the main drainage reuse (from main drains), which MWRI accounts for recycling in their national budget and each directorate’s water supply, the intermediate reuse is localized only with the response to the scarcity.

The local farmers are allowed to operate their small pumps when there is no water existing at the ends of the branch canals. The pumps, in this case, will not

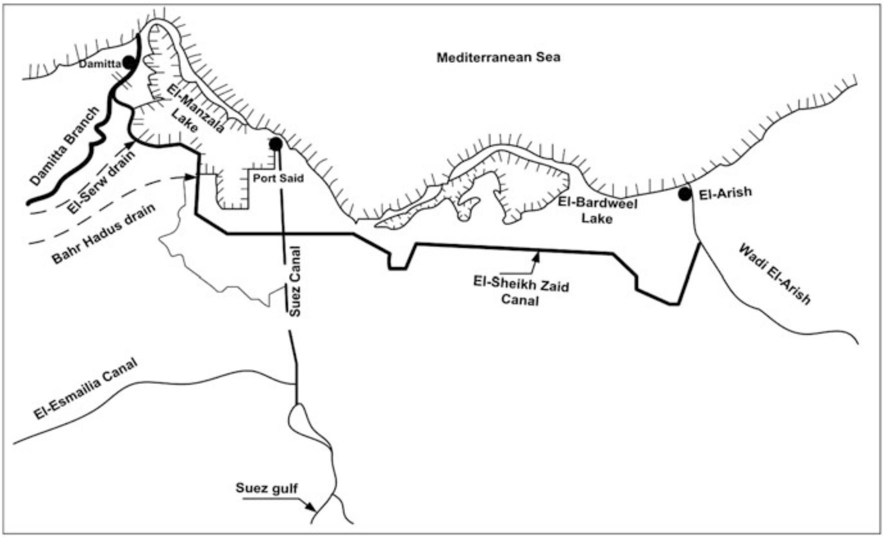


Fig. 7 El-Salam Canal project layout map [28]

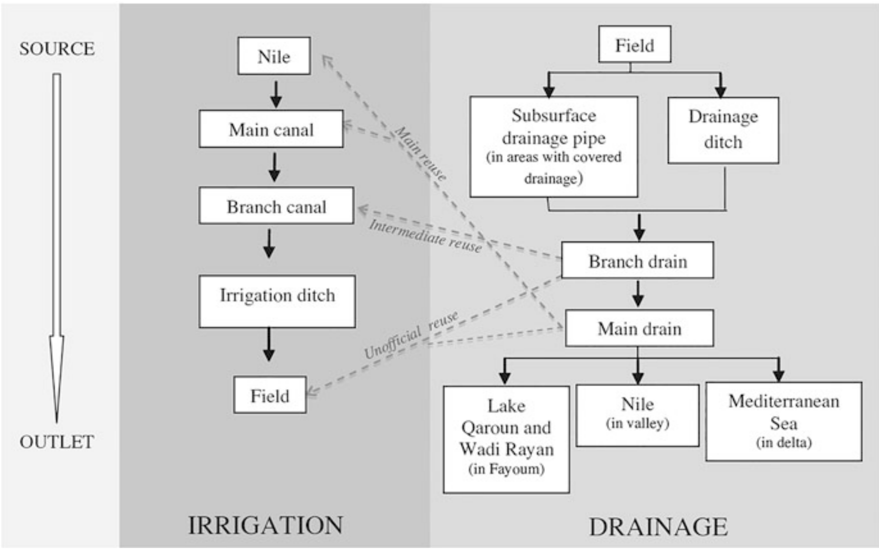


Fig. 8 Egypt's irrigation and drainage systems and points of mixing [13]

continuously operate because the branch canal that they are going to directly discharge the collected drainage water in it has a limited hydraulic capacity, and the drain itself sometimes does not have sufficient water for collecting. In most of the farmland in the Nile Delta, local farmers operate the pumps for about 10 h a day, or just during the 4 months of the summer, where the pressure on canal water is highly intensive. MWRI started to define the branch drains in which farmers could collect water from them based on the water quality thus, specifies the point of mixing water, e.g., before the drain joins another more contaminated and high saline main drain [30].

3.2 Unofficial Reuse

The Ministry of Water Resources and Irrigation is not the only party responsible for the recycling of drainage water in Egypt. Pumps are a common sight in rural areas and have been ever since low-cost diesel pumps became widely available. In most of Nile Delta's lands, the farmers sit the pumps on the banks of canals and lifting the water to their field and start irrigation. However, some of these canals on which farmers operate their pumps are not canals but drains. Farmers, though, have no trouble telling them the difference between the canal and the drain. Farmers do not need data, however, to know the times and places in which water is acceptable for use and when and where it is not. They turn directly to the drains to irrigate their fields when the irrigation canals are empty. This is the practice of what MWRI terms "unofficial reuse."

Since farmers only turn to drainage water when their canals are empty, they do not have the option of mixing the drainage water with freshwater before reuse. Instead, they apply the drainage water immediately to their fields. As the water moves directly from drain to field, it does not directly affect water quality in the canals. But it does pass through the soil and thus directly affects soil salinity. Recently, unofficial reuse of drainage water has been expanded because of the increasing pressure on the limited canal supplies. This pressure comes in part from farmers' crop choices, where most of them have turned towards profitable but water-intensive crops like rice, leading to increased water demand [31].

In addition, agricultural expansion through desert reclamation has led to mounting claims on irrigation supplies, leaving some farmers with no option but to use drainage water [32]. Unofficial reuse of drainage water is illegal, but local officials make little effort to enforce the ban. They recognize that farmers only turn to drainage water when their irrigation water supply is insufficient. It is difficult to gauge how much drainage water farmers are recycling back into the irrigation system. The amount each farmer takes is relatively small, but the aggregate impact is tremendous. The Ministry estimates unofficial reuse to be between 2 BCM and 3 BCM a year [24]; other sources [23] suggest it could be as much as 4 BCM.

4 Conclusion and Recommendations

Irrigation management is essentially the most important strategy for reducing the volume of freshwater applied and drainage water produced in any agricultural region worldwide. Since salts are imported from the central California soils with irrigation water, a means of ultimately isolating salts from productive agricultural soils is required for sustainability. Otherwise, salts will accumulate. The long-term concern regarding reusing drainage water is that it may lead to an excessive salinity accumulation, as well as it contributes to the soil quality deterioration, e.g., permeability and tilth. The consequence can be impermeable and crusted soils with poor stand establishment. Furthermore, leaching salts from topsoils by subsurface tile-drainage systems will be essential when the soil–plant system becomes salt saturated. Monitoring programs for soil salinity should be implemented for understanding the complexity of salinity's spatial variability and its dynamic nature.

These practices of drainage water reuse are instrumental to the state. The recycling of drainage water adds to the volume of water that the ministry has the power to govern and distribute. This helps justify the government's politically motivated agricultural expansion goals. It also helps meet demand, easing relations with the regional irrigation directorates. Practices of drainage water reuse, therefore, are part of what makes it possible for the state to claim control over Egypt's water. Selecting plant species that are suitable for the different components of the drainage-water reuse systems will always be complicated by drainage-water compositions, trace elements, field variability, specific cultivation, and irrigation practices.

References

1. Cosgrove WJ, Loucks DP (2015) Water management: current and future challenges and research directions. Water Resour Res 51:4823–4839. https://doi.org/10.1002/2014WR016869
2. Khalid S, Shahid M, Natasha I, Sarwar T, Shah AH, Niazi NK (2018) A review of environmental contamination and health risk assessment of wastewater use for crop irrigation with a focus on low and high-income countries. Int J Environ Res Public Health 15:895. https://doi.org/10.3390/ijerph15050895
3. Sheikh B, Nelson KL, Haddad B, Thebo A (2018) Grey water: agricultural use of reclaimed water in California. J Contemp Water Res Educ 165:28–41. https://doi.org/10.1111/j.1936-704X.2018.03291.x
4. Banuelos G, Lin Z (2006) Reuse of agricultural drainage water in central California: Phyto sustainability in soil with high levels of salinity and toxic trace elements. Geol Soc Lond Spec Publ 266:79–88. https://doi.org/10.1144/GSL.SP.2006.266.01.07
5. Hanak E, Lund J, Arnold B, Escriva-Bou A, Gray B, Green S, Harter T, Howitt R, MacEwan D, Medellin-Azuara J, Moyle P, Seavy N (2017) Water stress and a changing San Joaquin Valley. Public Policy Institute of California. https://www.ppic.org/content/pubs/report/R_0317EHR.pdf
6. Tanji K, Davis D, Hanson C, Toto A, Higashi R, Amrhein C (2002) Evaporation ponds as a drain water disposal management option. Irrig Drain Syst 16:279–295. https://doi.org/10.1023/A:1024877630332

7. Shannon MC, Cervinka V (1997) Drainage water re-use. In: Madramootoo C, Johnston WR, Willardson LS (eds) Management of agricultural drainage water quality. Food and Agriculture Organization of the United Nations, FAO, Rome
8. Eltarabily MG, Negm AM, Savvedra OC (2015) Effects of di-ammonium phosphate on hydraulic, compaction, and shear strength characteristic of sand and clay soils. Arabian J Geosci 8:10419–10432. https://doi.org/10.1007/s12517-015-1959-4
9. Eltarabily MG, Negm AM, Yoshimura C, Savvedra OC (2017) Modeling the impact of nitrate fertilizers on groundwater quality in the southern part of the Nile Delta, Egypt. Water Supply 17(2):561–570. https://doi.org/10.2166/ws.2016.162
10. Easton ZM, Bock E, Collick AS (2017) Factors when considering an agricultural drainage system, vol 208. University, V.S., Communications and Marketing, College of Agriculture and Life Sciences, Blacksburg
11. Shrivastava P, Kumar R (2015) Soil salinity: a serious environmental issue and plant growth-promoting bacteria as one of the tools for its alleviation. Saudi J Biol Sci 22(2):123–131. https://doi.org/10.1016/j.sjbs.2014.12.001
12. Rhoades JD (1974) Drainage for salinity control. In: Van Schilfgaarde J (ed) Drainage for agriculture. Agronomy monograph no. 17. SSSA, Madison, pp 433–461
13. Barnes J (2014) Mixing waters: the reuse of agricultural drainage water in Egypt. Geoforum 57: 181–191. https://doi.org/10.1016/j.geoforum.2012.11.019
14. El-Zanaty F (2001) Knowledge, attitudes, and practices of Egyptian farmers towards water resources: national survey 2001, EPIQ Water Policy Reform Program. Report no. 7. Prepared by El-Zanaty & Associates for the Agricultural Policy Reform Project, USAID, Cairo
15. MALR (2009) Sustainable agricultural development strategy towards 2030. Ministry of Agriculture and Land Reclamation (MALR) Committee on Agricultural Research and Development in Cooperation with the Food and Agriculture Organization of the United Nations, Cairo, January 2009
16. Brown P, El Gohary F, Tawfic M, Hamdy E, Abdel-Gawad S (2003) Nile river water quality management study, Egypt water policy reform project, report no. 67. USAID, Ministry of Water Resources and Irrigation, June 2003
17. Abdelly C, Öztürk M, Ashraf M, Grignon C (2008) Biosaline agriculture and high salinity tolerance. Birkhäuser Verlag, Basel
18. Abdel-Dayem S, Abdel-Gawad S, Fahmy H (2007) Drainage in Egypt: a story of determination, continuity, and success. Irrig Drain 56(S1):S101–S111. https://doi.org/10.1002/ird.335
19. El-Bably A (2002) Advanced and integrated approaches for crop tolerance to poor quality irrigation water in Egypt. In: Zdruli P, Steduto P, Kapur S (eds) 7. International meeting on soils with Mediterranean type of climate (selected papers). CIHEAM Bari, pp 363–378 (Options Mediterraneans; n. 50)
20. Eltarabily MG, Negm AM, Yoshimura C, Abdel-Fattah S, Savvedra OC (2018) Quality assessment of southeast Nile delta groundwater for irrigation. Water Resour 45:975–991. https://doi.org/10.1134/S0097807818060118
21. Zhu Z, Elassiouti I, Khattab A, Azim R (1998) National policy for drainage water reuse. Agricultural Policy Reform Program, USAID, Ministry of Public Works and Water Resources, Report no. 8, June 1998
22. MWRI (2005) National water resources plan for Egypt–2017. Report prepared through the National Water Resources Plan Project, Ministry of Water Resources and Irrigation, Cairo. http://extwprlegs1.fao.org/docs/pdf/ egy147082.pdf
23. Van Achthoven T, Merabet Z, Shalaby K, van Steenbergen F (2004) Balancing productivity and environmental pressure in Egypt: towards an interdisciplinary and integrated approach to agricultural drainage. Agriculture & Rural Development Working Paper No. 13. Washington, DC, The World Bank
24. Ismail A (2011) Egyptian drainage water reuse practices and measures to alleviate the risk of failure. Second Arab Water Forum, November 20–23, 2011. Cairo

25. JICA (2016) The project for drainage water quality control for irrigation in middle Nile Delta in the Arab Republic of Egypt. Japan International Cooperation Agency (JICA), Sanyu Consultants Inc. Final report, March 2016. https://openjicareport.jica.go.jp/pdf/12252839_01.pdf
26. FWMP (2002) Drainage water reuse, ministry of water resources and irrigation, Fayoum water management project (FWMP). Technical report no. 29. May 2002
27. Allam M, Allam G (2007) Water resources in Egypt: future challenges and opportunities. Water Int 32(2):205–218. https://doi.org/10.1080/02508060708692201
28. Fleifle A, Allam A (2016) Remediation of agricultural drainage water for sustainable reuse. In: Negm A (ed) The Nile Delta. The handbook of environmental chemistry, vol vol 55. Springer, Cham. https://doi.org/10.1007/698_2016_119
29. Donia NS (2012) Development of El-Salam Canal automation system. J Water Resour Prot 4: 597–604. https://doi.org/10.4236/jwarp.2012.48069
30. APP (2005) In proceedings of the workshop on the intermediate reuse of drainage water. Organized by the Advisory Panel Project (APP) on Water Management, Cairo, 23rd June 2005
31. Barnes J (2014) Cultivating the Nile: the everyday politics of water in Egypt. Duke University Press, Durham. https://doi.org/10.1215/9780822376217
32. Barnes J (2012) Pumping possibility: agricultural expansion through desert reclamation in Egypt. Soc Stud Sci 42(4):517–538. https://doi.org/10.1177/0306312712438772

Policy, Laws, and Guidelines of Wastewater Reuse for Agricultural Purposes in Developing Countries

R. Malisa-van der Walt and A. Taigbenu

Contents

Abstract In developing countries, an estimated 65% of freshwater withdrawals are currently utilised in agricultural activities that are predominately related to irrigation. As climate change continues to threaten the availability of freshwater, there is a growing need to explore alternative irrigation water sources and treated municipal wastewater reuse has emerged as a viable option. Having been in practice for the past 5,000 years, municipal wastewater reuse continues to be perceived as an innovative water management approach to augment water supplies in water scarce regions.

R. Malisa-van der Walt (✉) and A. Taigbenu
School of Civil and Environmental Engineering, University of Witwatersrand, Johannesburg, South Africa
e-mail: utilitas@iafrica.com

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 345–368, DOI 10.1007/698_2022_864,

Presently several developed countries, confronted with water scarcity, have made significant progress in tapping into this resource. Strong institutional frameworks (policies, regulations, and guidelines) have significantly contributed to the progress. However, in developing countries, particularly Africa, treated municipal wastewater reuse remains an untapped resource, despite climate change projections indicating a decline in rainfall and greater uncertainty of its occurrence, while demand for freshwater is expected to increase in the coming decades. Furthermore, freshwater shortages are exacerbated by flows of untreated municipal wastewater, industrial effluents, and other pollutant sources into natural water bodies. Researchers have alluded to lack of institutional frameworks that comprehensively address and pronounce on the "What", "Where", "When", "Who", and "How" to deploy treated municipal wastewater reuse in agriculture. Through systematic literature review and document analysis of policies, regulations, and guidelines of selected case study countries in Africa, Asia, Latin America, Europe, and North America, this chapter presents a review of the developments in the reuse of treated municipal wastewater in irrigated agriculture. With an objective to unearth impediments in tapping into treated municipal wastewater reuse as an alternative water source for irrigated agriculture in Africa, we present recommendations for improvement of the current landscape. The study established that a well formulated legislative framework is vital for putting in place appropriate policies, regulations, and guidelines to enable successful adoption of projects which use treated wastewater for agricultural activities by farmers. Imbedded in such a framework should be a robust and comprehensive institutional arrangement of relevant departments which work collaboratively, and with skilled human personnel who have capabilities of engaging with relevant stakeholders and addressing technical issues of wastewater collection, transport, treatment, and reclamation, as well as being able to proffer economically viable wastewater reuse projects. Best practices of treated wastewater reuse in agriculture from the State of California and Spain, used as case studies from the USA and EU, should be adapted and refined to local conditions by countries which lag in this practice.

Keywords Developing countries, Guidelines, Irrigated agriculture, Municipal wastewater reuse, Policies, Regulations

1 Introduction

Researchers continue to reverberate how rapid and continuous population growth, coupled with urbanisation, and increased human economic activities, have resulted in freshwater demands surpassing supplies [1]. The United Nations (UN) report of 2015, predicting a global water deficit of 40% by 2030 [2], corroborates the looming freshwater crisis. The ramifications have an adverse effect on green water availability. Researchers estimate an average of 65% of freshwater withdrawals to be channelled towards agriculture globally [3]. Hence, strategies to mitigate water shortage-related risks in agriculture are highly topical. These include investigations into treated municipal wastewater reuse. Presently terrestrial water is the main freshwater source for agricultural production, and the main objective of these investigations is optimisation of water usage to achieve reduction in freshwater withdrawals intended for agricultural activities.

Several developed countries, where water scarcity is a threat to economic activities, have made significant progress in tapping into treated municipal wastewater reuse in irrigated agriculture. This has largely been achieved through putting in place policies, laws, regulations, and guidelines that explicitly articulate treated municipal wastewater reuse procedures and processes in irrigated agriculture. Consequently, stakeholders have been capacitated to efficiently implement the practice [4]. Whereas in developing countries, particularly Africa, treated municipal wastewater reuse in irrigated agriculture continues to be widely unplanned, and untreated wastewater is deployed. Several reasons are documented which include the absence of country specific policies, regulations, and guidelines that explicitly articulate and promote deployment of treated municipal wastewater reuse in irrigated agriculture [5].

Hence, this study reviewed the literature and government documents on developments of policies, laws, regulations, and guidelines that address treated municipal wastewater reuse in irrigated agriculture. In the global North, the State of California in the United States of America (USA) is selected as the case study, taking cognisance of its water scarcity experiences, adverse climate change impacts, uneven spatial distribution of water resources, coupled with its pioneering publication of regulations and standards on treated municipal wastewater reuse in irrigated agriculture in 1918 [6]. This document has shaped global municipal wastewater reuse discourses. Spain is selected in the Europe Union (EU) due to its asymmetrical distribution of water resources and first position ranking in deployment of treated municipal wastewater reuse in irrigated agriculture among EU member states [7]. In the global South, Mexico in Latin America has made significant progress in deploying wastewater reuse in irrigated agriculture, hence its selection as a case study. In Asia, China is selected, considering the complex water management issues arising from pollution of natural water bodies emanating from extensive economic activities. Furthermore, China is ranked first place globally for reported usage of untreated municipal wastewater in irrigated agriculture. In Africa, Egypt in North Africa is among countries that are making progress in the deployment of treated municipal wastewater reuse in irrigated agriculture [8]. While sub-Saharan Africa lags with limited data on municipal wastewater reuse in irrigated agriculture, the only available data depict several hectares of land in South Africa under untreated municipal wastewater irrigation, hence its selection as a case study in the region.

The main objective of this study is to unearth ways to improve and encourage treated municipal wastewater reuse in irrigated agriculture in Sub-Saharan Africa. In carrying this review, the following questions guided the study:

What policies, laws, and guidelines exist in support of municipal wastewater reuse in selected case studies?

What are the challenges in the development and implementation of institutional frameworks (policies, legislation, and guidelines) for municipal wastewater reuse in irrigated agricultural?

2 Methodology

The study employed case study research methodology recommended by [9] for an in-depth exploration of the research questions in the delimited areas. With planned treated municipal wastewater reuse in irrigated agriculture as the unit of analysis, the development of institutional frameworks (policies, laws, and guidelines), pertaining to this unit, is considered the main objective. The study conducted a systematic qualitative analysis of literature and government documents, perceived by [10], to be a suitable technique for policy content analysis.

3 International Guidelines on Municipal Wastewater Reuse in Irrigated Agriculture

Research indicates gaps in the uniformity of policy development and formulation of regulations and guidelines that create an enabling environment for wide deployment of municipal wastewater reuse in several global South regions [11]. Citing absence of universal guidelines and standards, stakeholder confidence in deployment of wastewater reuse globally is significantly eroded [12]. However, there are non-binding guidelines published by international organisations such as World Health Organisation (WHO), Food and Agriculture Organisation (FAO), and International Organisation for Standardization (ISO) that may be of value to global South countries where treated municipal wastewater reuse in irrigated agriculture is in its infancy or non-existent.

The first international organisation to publish guidelines on municipal wastewater reuse for irrigated agriculture was WHO in 1973. The published document was entitled "Reuse of effluents: methods of wastewater treatment and health safeguards". Its main objectives were to protect public health and to ensure safe application of wastewater reuse and excreta handling in agriculture. However, the document fell short in achieving these objectives as it did not explicitly articulate preventative measures on public health risks associated with wastewater reuse in agriculture and lacked any backing from epidemiological studies. Following extensive epidemiology research, the 1973 WHO guidelines were updated in 1989 and a document entitled "Health guidelines for the use of wastewater in agriculture and aquaculture" was published. This document focused on microbiological threshold levels permissible in irrigated agricultural, and prioritised public health and environmental protection [13]. The current WHO guideline, published in 2006, entitled "Safe use of wastewater, excreta, and greywater" is well informed by extensive research. Issues pertaining to public health are dealt with explicitly through assessment of health risk, health-based targets, and health protection measures. Monitoring and system assessment measures are articulated, and consideration is given to social, cultural, financial, and environmental policy aspects [14]. The WHO guidelines highlight the parasites in humans as the key risk factor and their removal to be paramount.

The FAO followed WHO and published its guidelines in 1987 which were updated in 1999 focusing on effluent quality standards for different uses. The threshold levels of trace elements permissible in irrigation of specific crops is delineated. However, regarding microbial requirements, the guidelines are less restrictive when municipal wastewater reuse is deployed, particularly in unrestricted irrigation category, while proposing stricter water quality levels for fruit trees irrigation, requiring faecal coliforms to be as low as <200/100 mL. Importantly, the physico-chemical parameters of FAO guidelines have informed the set standards, criteria, guidelines, and regulations of several organisations and state agencies [15].

In 2010, upon Israel's request titled PC 253, the first ISO standard for wastewater reuse in irrigated agriculture was issued. This was followed by Japan's proposition which was to be established along with Israel's and China's, titled TC 282, in 2015. WHO guideline (2006), Australian national water reuse regulations (2006), Israeli regulations for agricultural irrigation (1978,1999, and 2005), and California Code of Regulations (Title 22, division 4, Chapter 3, water recycling criteria (2000)) were the reference materials used in the establishment of the ISO standard. In 2015, the ISO 16075 series on guidelines for deployment of treated municipal wastewater in irrigated agriculture was released.

4 Development of Policies, Regulations, and Guidelines in Municipal Wastewater Reuse in Irrigated Agriculture

Despite treated municipal wastewater reuse gaining momentum globally, the absence of binding universal policies, regulations, and guidelines curtails its wide application. Consequently, several countries have developed theirs that are country specific, prioritising public health and environmental protection. The geographic, economic, and social landscapes actuate the development of these policies, regulations, and guidelines. Accordingly, there are disparities in permissible threshold levels of microbial and physio-chemical parameters [16]. In this regard, developed countries have had several years of experience in developing their regulations and guidelines.

Albeit development of regulations and standards for water reuse in the USA being the responsibility of the states, the Environmental Protection Agency (EPA) has also developed comprehensive water reuse guidelines that work in tandem with those formulated by states and any agencies involved in water reuse projects, to mitigate any incoherence between the federal government and the states [17].

4.1 State of California

The State of California is acknowledged globally for pioneering publication of treated municipal wastewater reuse regulations and guidelines in 1918. These regulations are explicit and comprehensive, delineating stringent restrictions on wastewater reuse parametric threshold levels permissible in irrigation for specific crops, and specifying the irrigation technique to be deployed. While many states in the USA sought what to do with the effluents from their wastewater treatment plants due to the enactment of the Clean Water Act (CWA) by Congress in 1972, that requires the Environmental Protection Agency (EPA) to set minimum standards on effluents from those plants, the State of California was well ahead with water recycling projects. To institutionalise and strengthen treated municipal wastewater reuse practices, the State of California Legislature enacted the Wastewater Reuse Law (WWRL) of 1974 [18]. From the published 1918 guidelines to the water quality standards and treatment reliability criteria that are contained in the California Department of Public Health (CDPH) Water Recycling Criteria (Title 22, Division 4, Chapter 3 of the California Code of Regulations), California has had over a century of safe use of treated municipal water for the irrigation of food crops. These standards and guidelines have been dynamic over time with improved wastewater treatment technologies, increased knowledge of the behaviour of pathogens and their impacts on human health, and changes in agricultural and irrigation practices. A recent review of these CDPH water recycling criteria by the National Water Research Institute [19] provided the data of the annual wastewater being recycled from 1989 that are presented in Fig. 1, while the three highest users of recycled water are agriculture (37%), landscape irrigation (17%), and groundwater recharge and seawater intrusion barrier (19%). With the CWA at the federal level and the WWRL in the state, coupled with the Title 22 of the California Code of Regulations, extensive wastewater reclamation projects were implemented [20]. These projects attracted huge funding from state and federal grants and included farms with large acres of land irrigated with treated wastewater.

The role of institutions in the successful deployment of wastewater reuse in irrigation in the case of California cannot be underestimated. The CDPH, State Water Resources Control Board (SWRCB) and the nine Regional Water Quality Control Boards (RWQCBs) are involved in the recycling of treated wastewater.

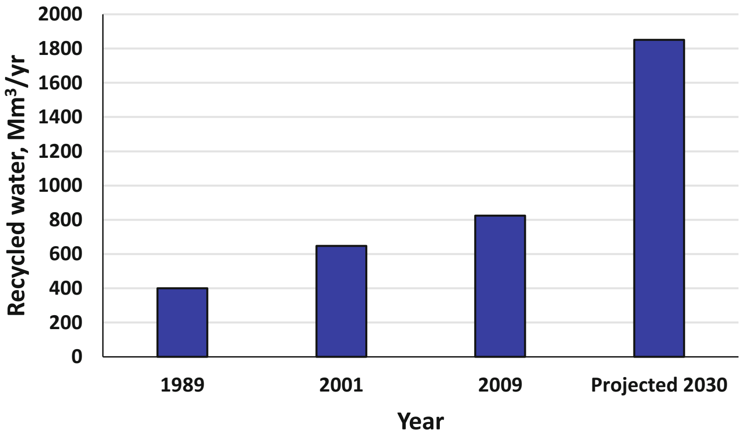


Fig. 1 Treated wastewater in the State of California. Source: [19]

While the State and Regional Water Boards oversee the environmental health of the waters of the State, the SWRCB administers water rights. The CDPH plays the role of establishing public health criteria for wastewater reclamation, including groundwater recharge, and reviewing of all proposals for such projects in the State. There is a memorandum of understanding among these agencies that ensures corporation and collaboration in achieving successful projects. While champions may be required to achieve successful farm projects in which treated wastewater is deployed for irrigation, the overarching policies, regulations, and guidelines executed through these mandated institutions ensure that success is replicated from one project to another. This approach sets precedence for global South countries in leapfrogging to achieving such successful farm projects.

4.2 European Union

The potential of treated municipal wastewater reuse in the EU has continued to gain recognition, necessitating its embeddedness within EU's Water Framework Directive (WFD). The acknowledgement by the EU of the importance of treated municipal wastewater reuse found expression in the European Innovation Partnership on water of 2012 that supports innovative solutions to water challenges, along with the report by the European Commission (COM, 2012 – 673) that provides a blueprint on how to safeguard Europe's water resources. The WFD promoted the establishment of legal frameworks among member states to ensure the protection of public health, the environment, and natural water bodies within their jurisdictions. Spain, one of EU's member states, is regarded as the pacesetter in treated municipal wastewater reuse among the states [7], and for this reason, we explore the Spanish legal framework development for treated municipal wastewater reuse in irrigated agriculture.

4.2.1 Spain

The use of treated municipal wastewater in agriculture in Spain started in 1970 from a wastewater plant in Las Palmas [21]. This practice was extended to other cities and regions before the enactment of the Water law in 1985 and Spain joining the EU in 1986. These years of 1985 and 1986 were notable with respect to wastewater reuse in agriculture. The Water law of 1985 established that "the Government shall fix the basic conditions for the water reuse based on the purification process, its quality and the planned uses" (Article 101) and served as the basis for regulations and guidelines for wastewater reuse. With Spain joining the EU in 1986, the regulations and guidelines had to be modified to align with the EU environmental directives contained in the WFD and other directives for habitats, birds, marine, and floods. The strategy for Spain to align with EU directives required authorisation for effluents from wastewater plants that ensured that there are mitigation measures against impacts on the environment, coupled with penalties for noncompliance. Between 1986 and 2007, there were pieces of legislation that were enacted and repealed, culminating in the Royal Decree 1620/2007 which established that "the Government shall establish the basic conditions for the water reuse, specifying the quality required for treated wastewater based on their expected uses". This is the current piece of legislature that regulates the reuse of wastewater for agricultural production. It contains permissible microbiological and physio-chemical parameters of treated wastewater used to irrigate crops that could be eaten raw, those not eaten raw, those which might undergo industrial processes, pastureland for milk or meat producing animals, tree crops where the treated water does not encounter the fruits that can be consumed by humans, ornamental flowers, nurseries and greenhouses, silo fodder, cereals, and oilseeds. In essence, the regulations and guidelines are comprehensive and mirror those of the State of California. The total volume of treated wastewater that is reused in Spain varies significantly depending on the sources of the data, and it is between 370 and 500 Mm^3/year [21], and the distribution of its use is presented in Fig. 2. The fact that the highest user of treated wastewater is agriculture underscores its importance to the Spanish economy.

As previously stated, pieces of legislation do not exist in a vacuum. They require institutions and adequate human capacity to translate them into successful wastewater reuse projects. In the case of Spain, the Spanish Ministry of Agriculture, Food and Fisheries together with the Ministry of Health issued the Royal Decree 1620/2007 legal framework. Project proposals for treated wastewater use in agriculture must be approved by public health authorities to ensure that they comply with the provisions of the decree in terms of technical and water quality aspects, and that there are in place self-monitoring and risk management programmes [22].

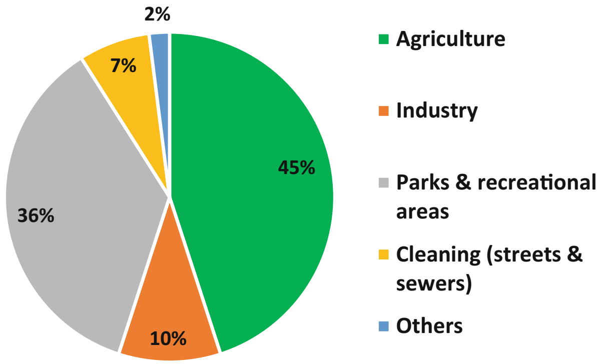


Fig. 2 Users of treated wastewater in Spain. Source: [21]

4.3 Mexico

In Latin America, Mexico has made significant progress in treated municipal wastewater reuse in irrigated agriculture. The success of Mexico can be attributed partly to its policy process and detailed regulations and standards. The policy process which dates to the 1857 Constitution in the colonial era under the Spanish Crown, followed by the 1957 Constitution that empower the Federal Congress to enact laws that pertain to waters under its jurisdiction, current water legislation is derived from the Nation Water Law enacted in 1992 [23]. However, with specific reference to treated wastewater reuse in irrigated agriculture in Mexico, this has been informed by publications and revisions of several standards and regulations from 1991 to the publication of NOM-001-ECOL-1996 and NOM-003-ECOL-1997 guidelines. The former specifies permissible limits for pollutants for water reuse activities, as well as the characteristics of effluent discharge into national water bodies, while the latter specifies the conditions, such as sampling criteria, testing and disposal, and the maximum permissible limits of physio-chemical and microbiological parameters, for various treated wastewater reuse activities [24].

One of the strategies that the Mexican government is prioritising to optimise water usage and avert compromising crop production is treated municipal wastewater reuse in irrigated agriculture. To realise this strategy the Mexican government adopted the 2007–2012 National Water Program (Conagua Programa Nacional Hidrico, 2007–2012). Following which in April 2014, another programme PNH was launched for the period 2014–2018 (Conagua Programa Nacional Hidrico 2014–2018). The main objective of these programmes is to strengthen integrated and sustainable water management, with an emphasis on treated municipal wastewater reuse and treatment of municipal wastewater to fit-for-purpose standards (Conagua PNH, 2014–2018). It was during the implementation and assessment of these programmes that wide application of treated municipal wastewater reuse across the agricultural sector was reported (The Mexican National Development Plan 2013–2018). It is worth noting that the government directed significant funding to municipal wastewater treatment infrastructure for Mexico to realise these positive developments. An increase of wastewater treatment investments of 132% between 2007 and 2011 was reported [25]. By 2012, over 90% of the population was connected to the wastewater network. Mexico is ranked first place in Latin America in terms of volume of treated wastewater reuse in irrigated agriculture, with a consumption of 1,640 Mm^3/year [26]. Despite several lingering challenges, Mexico has continued to be a pacesetter in deployment of treated municipal wastewater reuse in irrigated agriculture in Latin America.

4.4 China

For the past three decades, China has experienced rapid economic growth that has significantly altered its socio-economic landscape but with considerable adverse consequences on its water resources. Consequently, natural water bodies are remarkably polluted. An estimated one-third of lakes and rivers are highly polluted to a degree that the water cannot be utilised for human consumption [27]. Exacerbating the mismatch between the population size and water resources availability, are reports indicating 20% of the world's population residing in China and yet only 7% of the world's freshwater resources is in China [28]. Albeit China's 1st position ranking in untreated municipal wastewater in irrigated agriculture globally, since 1958, the Chinese government has promoted treated municipal wastewater reuse. This has been advanced through its inclusion in the national key scientific and technological projects of the 7th (1986–1990), 8th (1991–1995), and 9th (1996–2000) Five-Year plans. At the inception of these projects the main drawback was the absence of infrastructure for collection and treatment of municipal wastewater, resulting in the reported wide application of untreated wastewater in irrigated agriculture. Between the 10th (2001–2005) Plan and the 12th (2011–2015) Plan, considerable increase was experienced in the amount of wastewater discharge (increase in domestic wastewater discharge from 26.1 billion tons in 2004 to 48.5 billion tons in 2013), reclaimed water (increase from 1.3 billion tons in 2011 to 2.4 billion tons in 2013), and the number of treatment plants (5,364 municipal wastewater treatment plants in 2013). However, in 2013, it was reported that the amount of reclaimed water was still abysmally low at 5% of the total domestic wastewater produced, indicating a huge potential for domestic wastewater reuse in China [29].

The policy and regulatory framework are very important for China to realise its enormous potential in treated wastewater reuse to address its water scarcity, social and economic challenges. The developments of these frameworks are presented in Table 1, while the regulations and standards issued for various wastewater reclamation and reuses can be found in [29]. These include the regulations and standards issued by the Ministry of Construction and Standardization Administration for the engineering of municipal treatment plants (GB 50334-2002) and the reuse of urban reclaimed water (GB/T 18920-2002). These were accompanied by water quality standards issued by different government agencies for various wastewater reuses (GBT 18921-2002 – environment reuse), (GBT 18920-2002 – miscellaneous urban

Table 1 Chinese wastewater reclamation and reuse policies at national level. Source: [29]

Government sectors	Wastewater reclamation and reuse policies	Wastewater reclamation and reuse policies prescriptions
The State Council	The 12th Five-year Comprehensive and Emission Reduction (2011); The 12th Five-year National Urban Sewage Treatment and Recycling Facilities Construction Plan (2012)	1. Adopting reasonably the price of reclaimed water which should be lower than that of conventional water, providing the privileged policies of tax and fee reduction for reclaimed water producers 2. Encourage reclaimed water to be used in industries, carwash, urban facilities, and landscaping, forcing certain water users to use reclaimed water
MOHURD MOST	The interim Procedures of Reclaimed Water Facilities Management in Urban (1995); The Regulation of Saving Water Management in Urban (1998); The Policy of Wastewater Reclamation and Reuse Technology in Urban (2006); the 12th Five-year Development Plan of National Science and Technology (2011)	1. Using actively reclaimed water, issuing the technology policy of wastewater reclamation and reuse 2. Considering preferentially the landscaping use of reclaimed water, using the secondary effluent from municipal wastewater treatment plants in agriculture irrigation 3. Making policies to encourage wastewater reclamation and reuse by related central and local governments, offer financial supports for wastewater recycling by local government 4. Establishing gradually reasonable water price system and water utilisation structure
MEP GAQSIQ	The 12th 5-year National Environmental Protection Regulation and Environmental Economic Policy Construction plan (2011), Series water quality standards for different reclaimed water reuse	1. Making the water quality standards for different reclaimed water uses
MOF NDRC	The Notice of Implementing the policy without value-added Tax for Reclaimed Water and Others (2008), The Notice of Suggestion about Supporting the Investment and Financing Policy of the Circular Economy Development (2011)	1. Reaching to wastewater reuse rates of 20–25% for the cities with water scarcity in North China and 10–15% for coastal areas of South China in 2015 2. Encouraging wastewater reclamation and reuse to increase water resource development efficiency

MOHURD, MOST, MEP, GAQSIQ, MOF, and NDRC mean the Ministry of Housing and Urban–Rural Development, the Ministry of Science and Technology, the Ministry of Environmental Protection, General Administration of Quality Supervision, Inspection and Quarantine, the Ministry of Finance, and the National Development and Reform Commission reuse), (GBT 19923-2005 – industrial reuse), GB20922-2007 – farmland irrigation reuse), and (GB/T 25499-2010 – green space irrigation reuse). In support of the issuance of these regulations and standards on reclaimed water by the Chinese government, significance investments were made for the construction of wastewater treatment and reclamation projects to the tune of 30.4 billion CNY the 12th Five-year National Urban Sewage Treatment and Recycling Facilities Construction Plan. Despite all these efforts treated municipal wastewater reuse is still in its infancy and confronted with several challenges that limits its deployment [30].

4.5 Africa

On the African continent the study reviewed Egypt in the north and South Africa in the sub-Saharan Africa.

4.5.1 Egypt

Egypt is an arid country estimated to cover an area of one million square kilometres, and for the past 50 years has continuously experienced a rapid population growth from a population of 19 million in 1949 to 83.5 million in 2012. It is projected that the population of Egypt will be 100 million by 2025 [31]. This exponential population growth poses significant challenges to Egyptian authorities in managing their water resources. Presently, the Nile River is the major source of water, with Egypt receiving an annual fixed share of 55,500 Mm^3, which meets about 80% of its demand, and 95% of the Egyptian population resides along the banks of the Nile valley and delta – an area which constitutes only 4% of the country land. Coupled with low rainfall of at most 200 mm annually, Egypt's freshwater challenges require innovative initiatives to augment water supplies, one of which is the use of treated municipal wastewater in agriculture – a sector that contributes 11.1% to its GDP and employs about 23.8% of its labour force [32]. Egypt is ranked 1st in volumes of treated wastewater reuse in irrigated agriculture in Africa. The Egyptian National Water Plan of 2017 projects a possibility of an annual deployment of 1.4 billion m^3 of treated wastewater in irrigated agriculture. The legislative framework for treated wastewater reuse in agriculture is still deficient in many respects related to very restrictive standards, unclear institutional arrangement, lack of technical expertise, and low reliability of the quality of treated water due to poor design and maintenance of wastewater treatment plants. It is reported that only 40% of the wastewater treatment plants provide secondary treatment, while the rest provide only primary treatment, thereby limiting the amount for reuse in irrigated agriculture [33]. There are some decrees that specifically address reuse of wastewater: Decree 44/2000 (addresses restricted irrigation for the safe use of wastewater on selected crops, and the water quality requirements for unrestricted and restricted irrigation), Decree 603/2002 (prohibits irrigation of traditional field crops with treated or untreated wastewater and limits reuse to timber and ornamental trees, taking into account the protection of the health of agriculture workers), Decree 171/2005 (reviews the standards for the reuse of treated effluents and sludge in agriculture, with standards for reuse in agriculture presented in ECP (Egyptian Code of Practice) 501/2005), and Decree 1038/2009 (prohibits use of treated or untreated wastewater to irrigate food crops).

The institutions involved with water reuse in agriculture are the Ministry of Water Resources and Irrigation (MWRI), Ministry of State for Environmental Affairs (MSEA), Ministry of Water and Wastewater Utilities (MWWU), Ministry of Health and Population (MOHP), and Ministry of Agriculture and Lands Reform. The institutional framework is relatively complete and highly centralised, with the involvement of users and the private sector realised in the implementation of projects and through various public agencies and companies. However, there are still major gaps in the legislative framework and institutional arrangement that considerably curtail the reuse of treated wastewater in irrigated agriculture in Egypt.

4.5.2 South Africa

Following independence in 1994, the South African Legislature enacted the National Water Act (NWA) No 36 of 1998. Within the Act, wastewater reuse for irrigation is considered a controlled activity which involves “irrigation of any land with waste or water containing waste generated through any industrial activity or by a waterwork” (Section 37 (I) (a)). Although the National Water Strategy 1 (NWRS1) of 2004 and National Water Strategy 2 (NWRS2) of 2013 constitute the legal instrument for implementing the NWA and promote reclamation and reuse of wastewater for prudent management of water resources, the only existing regulations and guidelines for deployment of treated wastewater for irrigated agriculture are found in the Government Gazette 36820, Notice 665 of September 6, 2013. It provides standards on the microbiological and physio-chemical parameter limits of the quality of irrigation water based on the volume of wastewater utilised. The standards are for irrigation with volumes of wastewater of 2,000 m^3/day or 500 m^3/day or 50 m^3/day. The institutional arrangement for enforcing these regulations and guidelines has been vested on the Minister of Water Affairs. Although there is no data on the volume of treated wastewater being recycled for farm irrigation, there are a few active farm projects which use the practice.

Although the NWRS2 alluded to reclamation of water gaining social acceptance and proving to be technically viable, however, contradictory aspects of the laws such as the National Water Act (Act 36 of 1998), the National Environmental Management Act (Act 107 of 1998), the National Environmental Management: Waste Act (Act 59 of 2008), and the Water Services Amendment Act (Act 30 of 2004) render water reclamation to be complex. Furthermore, municipalities are legislatively permitted to enact by-laws on wastewater reuse, that may result in multiple legal frameworks, further complicating the process as confidence among stakeholders is eroded. Despite a formal government water management strategy that includes water reuse, deployment of wastewater reuse is not significantly implemented in South Africa. There is a gap in formulation of legal frameworks that comprehensively address treated municipal wastewater reuse in irrigated agriculture at national and provincial levels [34].

5 Challenges in Implementing Municipal Wastewater Reuse for Agriculture

Globally, the main barriers to reuse of municipal wastewater, particularly in irrigated agriculture, can be encapsulated as institutional, technical, economic and implementation in nature. In the global north extensive research in addressing these barriers continues and are at advanced stages, and these can be leapfrogged by global south countries. The State of California in the USA and Spain in Europe are precedent, and their progress have been highlighted.

5.1 Institutional Arrangements

In the previous section of this chapter, we had discussed the legislative framework of the case study countries. Universally, there are no binding international legal frameworks for municipal wastewater reuse in irrigated agriculture. Guidelines on wastewater reuse vary considerably, and institutions are either non-existent or dysfunctional. In the USA, guidelines and regulations of states work in tandem with those of the EPA at federal level. Similarly, the environmental directives of the EU serve to guide the activities of its member states. In developing countries supra-municipal wastewater management is not practised, and an overarching root cause of challenges is the involvement of multiple ministries without well-defined roles in treated municipal wastewater reuse projects [35] reported on Mexico having challenges emanating from lack of co-responsibility and effective communication among ministries responsible for treated municipal wastewater reuse in irrigated agriculture. In China, [36] cite incomplete regulations, lack of supporting policies and laws that enforce reclaimed water reuse, coupled with inconsistent wastewater reuse standards as major drawbacks in deployment of treated municipal wastewater reuse in irrigated agriculture.

Egypt also experiences institutional arrangement challenges emanating from the involvement of multiple ministries without well-defined responsibilities and most working in silos, coupled with the lack of political will and policies which explicitly articulate treated municipal wastewater in irrigated agriculture. In South Africa, enacting the Water Services Act of 1997 and the National Water Act No 37 of 1998 to make provision for treated municipal wastewater reuse in irrigated agriculture, the institutional arrangement that entrusts a water services authority with the full responsibility for development of by-laws that govern its deployment discourages and erodes confidence among stakeholders [34]. In essence the absence of national and provincial legal frameworks that explicitly articulates treated municipal wastewater reuse in irrigated agriculture is a major drawback in South Africa.

5.2 Technical Issues

Technical issues in the deployment of treated municipal wastewater reuse in irrigated agriculture start being addressed with effective collection and treatment of the wastewater. This is followed by the reclamation process to treat the effluent from the wastewater treatment work (WWTW) to required standard of its envisaged use. Technical issues vary according to the level of development of a region or country or political jurisdiction. In places such as the State of California, issues related to effective collection and treatment of municipal wastewater have been comprehensively addressed. Current efforts are directed at reclamation processes, and presently the focus is on removal of specific salts with a view of mitigating their adverse effects on the soil, natural receiving water bodies, and crop production. Several treatment technologies have and continue to be developed. The oversight provided by the EU through its directives enables member states to operate their wastewater treatment plants (WWTPs) so that their effluents are compliant. Through planned programmes like the National Plan of Sanitation and Water Treatment (NPSD) Spain had, as at 2010, achieved 84% full compliance with Directive 91/271/EEC, while there are on-going construction and upgrades of WWTPs [21].

In the global north there are increasing concerns on the prevalence of "contaminants of emerging concern" (CECs) in municipal wastewater, whose main source include pharmaceuticals and personal-care products [37]. The challenge CECs poses is that of non-regulatory system and their unknown long-term effects on the environment. In addition, there is consensus among scientists that reclaimed wastewater releases antibiotic-resistant bacteria. These findings render both municipal wastewater treatment and reclamation processes highly complex and expensive [38].

In the global south issues on basic sanitation infrastructure development are prevalent. The Mexican government has made considerable progress in developing its WWTW infrastructure and to adopt treatment technologies that treat the effluent to standards stipulated in NOM-001-ECOL-1996 and NOM-003-ECOL-1997. However, the stringent restrictions, particularly irrigation of vegetables, fruits, and root crops eaten raw, render deployment of treated municipal wastewater reuse in irrigated agriculture economically not feasible. Most farmers are not prepared to invest in high quality wastewater treatment technologies to meet the required water quality standards.

Following the decision by the Chinese government to promote treated municipal wastewater reuse, challenges pertaining to collection and treatment of municipal wastewater received significant consideration, coupled with hi-tech research and development in water reclamation technologies. Presently there are several technologies available to produce effluent with quality standards that meet the intended use. However, the challenge remaining is that public institutions lack the financial capacity to meet the high capital and maintenance costs of these treatment technologies.

Egypt continues to battle with issues pertaining to sewerage networks and treatment facilities, impacting adversely on the effective and efficient collection of municipal wastewaters. There are reports of large volumes of untreated wastewater flowing into natural water receiving bodies [39]. Furthermore, the current large centralised municipal wastewater treatment arrangements are not feasible for effluent reuse in irrigated agriculture. This is due to disparities in operations of several WWTPs resulting in differences in effluent quality produced by these plants, thereby complicating any plans of standardised effluent reuse. In addition, most residents are yet to be connected to the sewerage network.

As already aforementioned in this study, effective collection and treatment of municipal wastewater is the basis for deployment of reclaimed water in irrigated agriculture. However, in South Africa [40] reported 90% of WWTW being non-compliant on more than three effluent determinants. As a result, poorly treated effluents are flowing into natural water bodies, causing huge environmental challenges, and hampering any plans for deployment of treated municipal wastewater reuse in irrigated agriculture. The high population densities in low-income communities further present two major challenges in deployment of treated municipal wastewater reuse. Firstly, sewerage networks are not well developed or absent. Secondly most water service authorities lack the financial and technical capacity to institute treated municipal wastewater reuse projects.

5.3 Economic Feasibility

Deployment of treated municipal wastewater reuse projects highly depends on its economic feasibility, that usually consists of weighing the costs and benefits. One huge operations and maintenance cost is energy consumption which usually accounts for 30% to 55% of the total cost [41]. This cost component has become a major determinant in assessing economic feasibility because of global energy shortfalls. Hence, it becomes necessary to explore cheaper and cleaner sources of energy for treated municipal wastewater reuse projects. Another cost component of concern is the cost of managing challenges that emerge during the water reuse process.

Comprehensive costing of reclaimed water continues to be problematic as multiple and evolving wastewater components need consideration. Apart from the capital cost of infrastructure development of the treatment, storage and distribution, there are additional costs that include operation and maintenance, economic and environmental externality costs that are usually ignored because, in many instances, there are challenges in their quantification and water authorities are unwilling to internalise them. Therefore, it is imperative to formulate a costing structure that takes cognisance of regeneration costs and the management of reclaimed water, to establish incentives that encourage maximum usage of treated municipal wastewater. Farmers are persuaded when authorities introduce financial incentives for reclaimed water usage, while providing assurances that it complies with water quality standards that guarantee the safety of their agricultural products.

The EU funding model, whereby only 50% up-front costs for municipal wastewater reuse projects could be secured through grants and the balance from the water reuse project as stipulated in the WFD, raises the issue of sustainability due to the non-guaranteed nature of wastewater reuse pricing that depends on the demand and supply scenarios. Another option to encourage reclaimed water uptake by farmers is introduction of subsidies. However, subsidies also present another challenge in that they only cover planning, technical assistance, research, and construction costs, but do not factor in externalities such as financial, social, and environmental burdens of effluent disposal to the environment.

Challenges in Mexican funding model for municipal wastewater reuse projects emanate from variable and non-transparent federal water budget [42], posing planning and implementing challenges on treated municipal wastewater reuse initiatives by local authorities. Furthermore, the arrangement of regional and local spheres of government coordinating and mobilising water infrastructure investments and then negotiating with CONAGUA at national level for approval of sanitation funding is complicated and places limitation on their economic viability. In addition, the arrangement of CONAGUA collecting revenue and channelling it into the federal fiscus, after which only 38% of the proceeds are transferred to local authorities for construction, operations, and maintenance cost of wastewater treatment plants limit deployment of treated municipal wastewater reuse in irrigated agriculture. The lack of well-structured water pricing to foster uptake of reclaimed water by farmers exacerbates the situation.

In China, variability in funding impacts adversely on development of water reclamation facilities that in turn influences the level of success in the deployment of treated municipal wastewater reuse projects. Chinese reclaimed water pricing is not comprehensive, with the current pricing only taking cognisance of the economic and operational costs of the treatment facilities [43]. The financial challenges in Egypt emanate from the public institutions not being adequately funded to meet the high capital and operational costs for treatment and reticulation infrastructure of municipal wastewater facilities. Treated municipal wastewater pricing is still a contested matter in Egypt. Whereas in South Africa, the absence of financial backing from both national and provincial governments curtails deployment of treated municipal wastewater reuse by water service authorities. In addition, there is no tariff structure for treated municipal wastewater reuse in irrigated agriculture. Neither are there any incentives to encourage treated wastewater uptake by farmers.

5.4 Implementation Procedures

To advance treated municipal wastewater reuse, the State of California instituted a water recycling funding program (WRFP) under the State Water Resources Control Board. The programme sets out to promote the beneficial use of treated municipal wastewater and provides funding and technical assistance to agencies and other stakeholders in support of water recycling projects and research. This programme has significantly contributed to the success of municipal wastewater reuse projects. In view of water management challenges being dynamic, constant monitoring and evaluation of these projects is imperative to ensure improvement in their implementation, and this is imbedded in the WRFP. In Spain, there are several well-designed projects on treated municipal wastewater reuse in agriculture, an example is the Rincón de León WWTP-WRP.

Mexican treated municipal wastewater reuse model draws on integrated water resources management (IWRM) principles which emphasise stakeholder engagement and public participation. To this end, water users' associations, comprising several groupings of stakeholders, were organised. However, water authorities refer to them as civil society, which limits the participation of these associations in water decision-making processes at local level, as their contributions are not recognised by law [44]. In some instances, agreements on treated municipal wastewater reuse in irrigated agriculture are concluded between farmers and the authorities without consulting the local communities and water users' associations. As a result, public knowledge is not considered in the planning and implementation of these projects [45].

Currently in China, perceptions on wastewater reuse are mixed [30, 46], with a high awareness of reclaimed water ruse and acceptance of non-potable use but considerable concern of the potential public health risks, particularly for agricultural irrigation. Consequently, adoption of wastewater reuse is relatively low but there are indications, with looming water crisis in China and enhanced wastewater treatment technologies, that water reuse will grow significantly in the future.

In Egypt, the implementation process is largely centrally controlled by government water authorities, with minimal stakeholder engagement and public participation. There are a few on-going wastewater reuse projects, but they fall far short of Egypt's potential. Presently in South Africa, there are no significant treated municipal wastewater reuse projects. The national government has entrusted the local governments with development of by-laws for treated municipal wastewater reuse and deployment. However, a major drawback in this arrangement is that public trust in the water services providers is low due to the failure in basic collection and treatment of wastewater. In addition, there is low public awareness on water issues such as freshwater availability, adverse impacts of climate change, and the benefits of treated municipal wastewater reuse.

6 Conclusions and Recommendations

Albeit reported disadvantages in deployment of treated municipal wastewater in irrigated agriculture, the advantages cannot be disputed. This study established several advantages that include increased freshwater availability, sustainable use of water resources, reduced freshwater withdrawals, and an economically viable alternative water source. Agricultural advantages include reduction in crop production costs following reduction in quantities of fertilisers applied, coupled with higher reliability as an alternative water source, thereby enhancing employment in the agricultural sector and contribution to the GDP, along with increased food security. There is also improvement in environmental protection following reduction in nutrient loads to natural water receiving bodies. Hence, deployment of treated municipal wastewater as an alternative water resource in sub-Saharan Africa should receive serious consideration and attention, commencing with institutional arrangements that promote it.

From the global north, this study has established that the effective and systematic involvement of a supranational or regional body in deployment of treated municipal wastewater in irrigated agriculture enhances its deployment. An example is the EU that adopted the WFD from which directives are issued to address specific water matters including deployment of treated municipal wastewater in irrigated agriculture among member states. These directives work in tandem with the national policies, regulations, and guidelines of member states.

In the USA, although each state is fully responsible for formulation and publication of its water legal frameworks for all types of water, the federal government plays its role, through the EPA, in supporting the institutional frameworks of the states. The institutional arrangements of both the EU and the federal US government have proven to enhance uniformity in water management in the respective regions, by fostering confidence and institutional support among stakeholders in management of treated municipal wastewater in irrigated agriculture. In addition, platforms like NORMAN in Europe, ensure interdisciplinary knowledge exchange, in research and development of treated municipal wastewater reuse in irrigated agriculture.

At national level (Spain) and state level (State of California) the study established that the legal frameworks of treated municipal wastewater reuse in irrigated agriculture explicitly articulate the “What”, “Where”, “When”, “Who”, and “How”. Spain has institutionalised supra-municipal management entities to directly or indirectly, through competent entities, manage the operations and maintenance of WWTPs to ensure uniformity and compliance with the EU directives.

In developing countries, uncoordinated multiple ministerial involvement without clear roles, policy gaps, inconsistent guidelines, and incomplete regulations curtail reuse of treated municipal wastewater in agriculture. However, in Mexico, there have been major institutional reforms that have led to the drafting of legislative framework that articulates treated municipal wastewater reuse, coupled with the political will, expressed through the national administration, that have given recognition to treated municipal wastewater as a viable alternative water source. Whereas

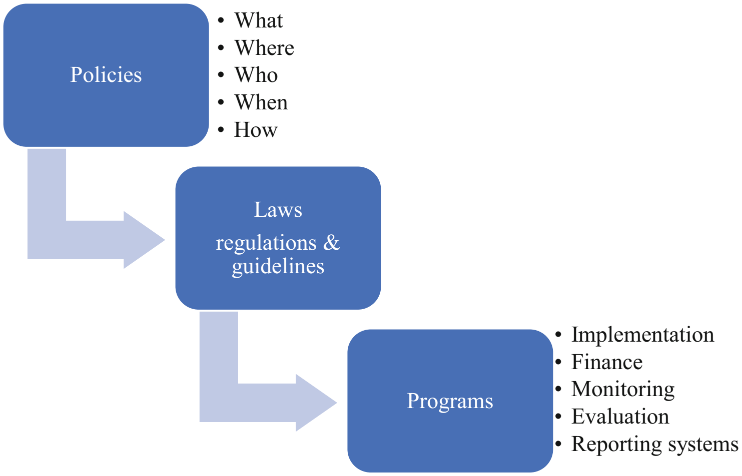


Fig. 3 Enabling institutional processes for effective deployment of treated municipal wastewater reuse in irrigated agriculture

in China, there are prevalent institutional challenges that do not promote widespread deployment of treated wastewater in agriculture.

In Africa, Egypt in north Africa was considered, and due to the absence of a regional body, Egypt is fully responsible for its water management. The study established flaws in institutional arrangements emanating from uncoordinated multiple ministries responsible for treated municipal wastewater reuse in irrigated agriculture. Policy gaps and lack of stringent regulations and guidelines continue to be problematic. Hence, we recommend a fewer number of ministries with roles and responsibilities enshrined in law to be involved in deployment of treated municipal wastewater reuse. The regulations and guidelines should match the Egyptian socio-economic landscape. In the absence of a regional body, we recommend formation of a network like NORMAN in the EU that could tap on the expertise from other north African countries to foster knowledge sharing.

Southern Africa Development Community (SADC) is the regional body in Sub-Saharan Africa and comprises 14 member states, with the majority falling in the lower-middle income category. In view of the disparities in economic landscape of SADC member states, the role of SADC in deployment of treated municipal wastewater reuse in irrigated agriculture is imperative. We recommend that SADC be effectively involved in drafting of legislative frameworks and designing of programmes that encourage treated municipal wastewater reuse in irrigated agriculture in the region. These statutes should work in tandem with national water statutes.

South Africa was considered in the Sub-Saharan Africa and the study established policy gaps, outdated regulations, and guidelines. Hence, there is an urgent need for drafting of legislative framework that match the South African socio-economic landscape for the deployment of treated municipal wastewater reuse in irrigated agriculture. We recommend effective engagement of relevant government departments and water services authorities with farmers and other stakeholders to implement projects which reuse treated municipal wastewater to conserve scarce water resources. In addition, at national level we recommend supra-municipal management entities to manage WWTP either directly or indirectly utilising highly competent private entities, to depoliticise water management, eliminate skills shortage, and improve accountability. Figure 3 delineates the recommended enabling institutional processes for deployment of treated municipal wastewater reuse in irrigated agriculture for SADC and its member states.

The technical basis for deployment of treated municipal wastewater reuse is effective collection and treatment of wastewater. In the global north, the State of California has effectively dealt with these basics, along with development of tertiary treatment technologies to produce effluent quality with stipulated standards for reuse. In the EU, compliance with the WFD directives on municipal wastewater effluent standards is imperative before reclamation. Several member states are compliant, albeit Spain is yet to achieve 100% compliance, it has made progress with the deployment of treated municipal wastewater reuse in irrigated agriculture. Spanish authorities continue to conduct extensive research on water reclamation technologies to achieve improved economic efficiency, lower energy cost, and reduced volumes of waste disposed into the environment.

The global north is aware of the growing concern of CECs, and treatment technologies for their removal continues to receive extensive research. While these technologies can be imported by global south countries, affordability and appropriateness are still an issue.

Since deployment of treated municipal wastewater reuse is still in its infancy in Africa, we recommend regional research and development units that can provide technical and innovative solutions relevant to regional concerns. These research units should network with other research organisations in the region from both private and public sectors in a systematic manner. Furthermore, the lack of infrastructure for provision of basic sanitation in African countries, particularly in high-density impoverished communities, should be addressed as a matter of urgency. The experience in Egypt to resort to decentralised wastewater treatment systems is well documented as the way forward for African countries. Such decentralised systems become the hub for modular deployment of treated municipal wastewater reuse in irrigated agriculture.

The study established that the global north has adopted well-structured funding mechanisms for initiatives such as deployment of treated municipal wastewater reuse in irrigated agriculture, along with feasible water pricing structures which favour farmers' uptake. However, in the global south, the lack of fully developed water and sanitation infrastructure, low budgetary allocations, and lack of political will make for limited investments in treated municipal wastewater reuse projects. Mexico, on realising the importance of treated municipal wastewater reuse, the government directed significant financial support towards the development of water and sanitation infrastructure, resulting in reported progress. However, there are persistent challenges on comprehensively structured funding from the national government, and lack of a water pricing regime that favours uptake of reclaimed water. A similar trend was observed in China and Egypt. In South Africa, we recommend financial support in the form of subsidies from the national and provincial government to farmers to invest in treated municipal wastewater reuse projects, along with a water pricing regime which favours the uptake of treated municipal wastewater by farmers.

The implementation of treated municipal wastewater reuse projects should be joint responsibility of local, provincial, and national governments in collaboration with farmers and the private sector. By designing programmes and identifying case studies which can be monitored and evaluated within specific timelines, documentation of issues which promote success or lead to failure will be valuable resource material for implementation of future projects. Reporting to a supra-regional body is highly recommended to upscale and out scale such successful projects. To enhance uptake of treated reuse activities among farmers, we recommend effective stakeholder engagements and public participation to earn the trust of end users and the public and be able to manage public perceptions on treated municipal wastewater reuse. In conclusion, education of the end users and the public on the reuse activities is imperative.

Acknowledgements The authors gratefully acknowledge the financial support of the University of the Witwatersrand Research Office towards the carrying out of this study.

References

1. Ahmadalipour A, Moradkhani H, Castelletti A, Magliocca N (2019) Future drought risk in Africa: integrating vulnerability, climate change, and population growth. Sci Total Environ 662: 672–686
2. UN (2015) World water development report. Water Sustain World. http://www.unesco.org/new/en/natural-sciences/environment/water/wwap/wwdr/2015-water-for-a-sustainable-world/. Accessed Aug 2020
3. Chen B, Han MY, Peng K, Zhou SL, Shao L, Wu XF, Wei WD, Liu SY, Li Z, Li JS, Chen GQ (2018) Global land-water nexus: agricultural land and freshwater use embodied in worldwide supply chains. Sci Total Environ 613:931–943
4. Shoushtarian F, Negahban-Azar M (2020) Worldwide regulations and guidelines for agricultural water reuse: a critical review. Water 12:971
5. Kellis M, Kalavrouziotis IK, Gikas P (2013) Review of wastewater reuse in the Mediterranean countries, focusing on regulations and policies for municipal and industrial applications. Global NEST J 15(3):333–350
6. Null SE, Prudencio L (2016) Climate change effects on water allocations with season dependent water rights. Sci Total Environ 571(2016):943–954
7. TYPSA (2013) Updated report on wastewater reuse in the European Union. Report for DG ENV, European Commission, Brussels
8. El-Zanfaly HT (2015) Wastewater reuse in agriculture: a way to develop the economies of arid regions of the developing countries. J Environ Protec Sust Develop 1:144–158
9. Yin RK (2003) Designing case studies. Qual Res Methods:359–386
10. Vogel B, Henstra D (2015) Studying local climate adaptation: a heuristic research framework for comparative policy analysis. Glob Environ Chang 31:110–120

11. Hanjra MA, Blackwell J, Carr G, Zhang F, Jackson TM (2012) Wastewater irrigation and environmental health: implications for water governance and public policy. Int J Hyg Environ Health 215(3):255–269
12. Qadir M, Wichelns D, Raschid-Sally L, McCornick PG, Drechsel P, Bahri A, Minhas PS (2010) The challenges of wastewater irrigation in developing countries. Agric Water Manag 97:561–568
13. WHO (1989) Health guidelines for the use of wastewater in agriculture and aquaculture: report of a WHO Scientific Group. Geneva, (Technical Report Series No 778)
14. WHO (2006) WHO guidelines for the safe use of wastewater excreta and greywater, vol 1. World Health Organization
15. FAO (1999) Wastewater treatment and use in agriculture. http://www.fao.org/docrep/T0551E/T0551E00.htm. Accessed 12 Sept 2020
16. Brissaud F (2008) Criteria for water recycling and reuse in the Mediterranean countries. Desalination 218:24–33
17. US EPA (2012) Guidelines for water reuse. US Environmental Protection Agency, Anchorage
18. Brown EC, Weinstock N (1980) Legal issues in implementing water reuse in California. Ecology LQ 9:243
19. NWRI (2012) Review of California's water recycling criteria for agricultural irrigation. Publication Number NWRI-2012-03
20. Christian-Smith J, Allen L, Cohen MJ, Peter Schulte P, Smith C (2010) California farm water success stories. Pacific Institute
21. Jodar-Abellan A, López-Ortiz MI, Melgarejo-Moreno J (2019) Wastewater treatment and water reuse in Spain: current situation and perspectives. Water 11
22. Navarro T (2018) Water reuse and desalination in Spain – challenges and opportunities. Journal of Water Reuse and Desalination 08(2):153–168
23. Hernandez A (2003) Water Law in the Republic of Mexico 11 U.S.-Mex. L.J. 15
24. Ramos AV, Gonzalez ENA, Echeverri GT, Moreno LS, Jiménez LD, Hernández SC (2019) Potential uses of treated municipal wastewater in a semiarid region of Mexico. Sustainability 11:2217
25. CONAGUA (2010) Conagua presenta alternativas para lograr la sustentabilidad hídrica en el Valle de México. https://www.cmic.org.mx/comisiones/Sectoriales/infraestructurahidraulica/normatividad/Boletines%20de%20CONAGUA/2010/Mayo%2020
26. Jiménez B (2006) Irrigation in developing countries using wastewater. Int Rev Environ Strat 6(2):229–250
27. Gleick PH (2009) China and water. The world's water 2008–2009: the biennial report on freshwater resources, pp 79–100
28. Shao W, Yang D, Hu H, Sanbongi K (2009) Water resources allocation considering the water use flexible limit to water shortage – a case study in the Yellow River Basin of China. Water Resour Manag 23(5):869–880
29. Lyu S, Chen W, Zhang W, Fan Y, Jiao W (2016) Wastewater reclamation and reuse in China: opportunities and challenges. J Environ Sci 39:86–96
30. Zhu Z, Dou J (2018) Current status of reclaimed water in China: an overview. J Water Reuse Desalin 8(3):293–307
31. Abdel-Lateef EM, Hall JE, Farrag MAA, Farrag AA (2011) AgroEconomic studies on wastewater reuse in developing marginal areas in West Delta, Egypt. Int J Water Res Arid Environ 1(2):110–115
32. Plecher H (2020) Employment by economic sector in Egypt. https://www.statista.com/statistics/377950/employment-by-economic-sector-in-egypt/. Accessed 1 Nov 2020
33. National Report (2013) Review and analysis of status of implementation of wastewater strategies and/or action plans, national report – Egypt. Sustainable water integrated management (SWIM) – support mechanism
34. Adewumi JR, Ilemobade AA, Van Zyl JE (2010) Treated wastewater reuse in South Africa: overview, potential and challenges. Resour Conserv Recycl 55(2):221–231

35. Gilabert-Alarcón C, Salgado-Méndez SO, Daesslé LW, Mendoza-Espinosa LG, Villada-Canela M (2018) Regulatory challenges for the use of reclaimed water in Mexico: a case study in Baja California. Water 10(10):1432
36. Liu S, Persson KM (2013) Situations of water reuse in China. Water Policy 15(5):705–727
37. Schwarzenbach RP, Escher BI, Fenner K, Hofstetter TB, Johnson CA, von Gunten U, Wehrli B (2006) The challenge of micropollutants in aquatic systems. Science 313(5790):1072–1077
38. Berendonk TU, Manaia CM, Merlin C, Fatta-Kassinos D, Cytryn E, Walsh F, Burgmann H, Sorum H, Norstrom M, Pons MN (2015) Tackling antibiotic resistance: the environmental framework. Nat Rev Microbiol 13(5):310–317
39. Abdel-Shafy HI, Mansour MS (2013) Overview on water reuse in Egypt: present and future. J Sustain Sanit Pract 14:17–25
40. Ntombela C, Funke N, Meissner R, Steyn M, Masangane W (2016) A critical look at South Africa's green drop programme. Water SA 42(4):703–710
41. Melgarejo J, Prats D, Molina A, Trapote A (2016) A case study of urban wastewater reclamation in Spain: comparison of water quality produced by using alternative processes and related costs. J Water Reuse Desalin 6:72–81
42. OECD (2013) OECD Making water reform happen in Mexico http://www.oecd-ilibrary.org/fr/governance/making-water-reform-happen-in-mexico_9789264187894-en
43. Chu J, Chen J, Wang C, Fu P (2004) Wastewaters reuse potential analysis: implications for China's water resources management. Water Res 38(11):2746–2756
44. Mendoza-Espinosa L, Victoria Orozco-Borbón M, Silva-Nava P (2004) Quality assessment of reclaimed water for its possible use for crop irrigation and aquifer recharge in Ensenada, Baja California, Mexico. Water Sci Technol 50(2):285–291
45. Leach WD, Pelkey NW (2001) Making watershed partnerships work: a review of the empirical literature. J Water Resour Plan Manag 127(6):378–385
46. Chen W, Bai Y, Zhang W, Lyu S, Jiao W (2015) Perceptions of different stakeholders on reclaimed water reuse: the case of Beijing, China. Sustainability 7:9698–9710

Part V
Conclusions and Recommendations

Updates, Conclusions, and Recommendations for "Cost-efficient Wastewater Treatment Technologies: Natural Systems"

Mahmoud Nasr and Abdelazim M. Negm

Contents

M. Nasr (✉)
Environmental Engineering Department, Egypt-Japan University of Science and Technology (E-JUST), Alexandria, Egypt

Sanitary Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, Egypt
e-mail: mahmoud-nasr@alexu.edu.eg; mahmoud.nasr@ejust.edu.eg

A. M. Negm
Water and Water Structures Engineering Department, Faculty of Engineering, Zagazig University, Zagazig, Egypt

Mahmoud Nasr and Abdelazim M. Negm (eds.),
Cost-efficient Wastewater Treatment Technologies: Natural Systems,
Hdb Env Chem (2023) 117: 371–386, DOI 10.1007/698_2022_910,

Abstract Recently, increasing population growth has been accompanied by considerable progress in industrialization and urbanization along with expanded agricultural production. These main developments and improvements have resulted in generating huge amounts of wastewater containing various organic and inorganic compounds. Consequently, the wastewater treatment processes, either natural-based or mechanized-based, have been technically improved to maintain pollution reduction and cost-saving. According to the environmental and economic conditions, some areas prefer the application of decentralized and cheaper treatment processes (low operation and maintenance costs) that can also be used for ecological purposes like recreational and gardening. These advantages fit the application of the natural-based systems for wastewater treatment. This chapter gives the updates, conclusions, and recommendations covered by the book volume "Cost-efficient Wastewater Treatment Technologies: Natural Systems." These topics are well defined so that the effluent of the ecological-based wastewater treatment systems could meet the strict national and international regulations.

Keywords Ecological wastewater remediation, Environmental-friendly system, Non-mechanized units, Phytoremediation, Recycle and reuse in irrigation, Water quality regulation

1 Introduction

Recently, the considerable increase in population growth has caused a fast development of various agricultural, agro-industrial, and industrial practices [1]. These activities are accompanied by the release of large quantities of wastewater, carrying several organic and inorganic compounds/pollutants [2]. The generated wastewater also contains pharmaceuticals and personal care products, and different persistent elements, emerging contaminants, and organic micropollutants [3]. Once these contaminants are released into the environment, they tend to deteriorate the aquatic life and human health [4]. Moreover, the main wastewater-related symptoms and diseases include nausea, anemia, vomiting, confusion, headache, diarrhea, liver failure, and abdominal pain [5]. In this context, policymakers, experts, and scientists are expending significant efforts to develop proper wastewater treatment technologies that are cost-efficient, environmentally friendly, and practical [6].

The wastewater treatment plants (WWTPs) can be designed, installed, and operated based on the available natural resources such as biomasses of plants, algae, and microorganisms [7]. These elements are included in simply constructed ecological systems, such as natural wetlands [8], stabilization ponds [9], and infiltration/ecological lands [10], where on-site wastewater treatment processes occur. Natural systems for treating wastewater could also be classified into soil-based, wetland, and aquatic systems, representing significant alternatives to the mechanical treatment techniques [11]. In these systems, pollutant removal via the biological and metabolic pathways occurs naturally, with very low (or even no) external energy sources, mechanical apparatus, and manpower [12]. The natural treatment systems also offer ecological and environmentally sustainable applications, and they maintain an essential scenario for climate change adaptation [13]. Several removal mechanisms, such as filtration, precipitation, adsorption, sedimentation, degradation, nitrification/denitrification, oxidation, and disinfection, are involved in the non-mechanized systems of wastewater treatment [14]. These processes could be employed to recover various resources (e.g., water, energy, and nutrients), finding multiple recycling and reuse applications in the agricultural sector [15]. Because these ecological techniques utilize natural aeration via macrophyte transmission and atmospheric reoxygenation, they attempt to overcome the high costs of artificial aeration in several conventional WWTPs [12]. However, the selection of the most suitable alternative natural technique for wastewater treatment relies on multiple criteria such as influent characteristics, site area and geometrical shape, initial investment, season variation, geographical location, and hydrogeological risk [16]. Hence, additional studies are essential for exploring the advantages, benefits, limitations, and challenges of these natural/ecological systems.

The key information and findings of this book volume highlight the main advantages, including simplified construction, green technology, reusability and recyclability, suitability for recreational activities, and adaptation to elevated CO_2, delivered from the natural wastewater treatment systems. To highlight the previously mentioned idea, the following sections briefly describe the main updates, conclusions, and recommendations of this book volume.

2 Waste Stabilization Ponds (WSPs)

2.1 Updates of Waste Stabilization Ponds (WSPs)

Waste stabilization ponds (WSPs) are simply constructed basins used for the treatment of wastewater by entirely natural processes, involving algae–bacteria beneficial interaction [9]. As such, bacteria consume oxygen to break down (stabilize) the complex organic compounds into simple products and CO_2; in turn, algae utilize CO_2 for biomass growth and O_2 generation [7]. The WSPs are operated under aerobic, anaerobic, and/or facultative conditions (connected in either series or parallel) to reduce various pollutants associated with organic matter, nutrients, heavy metals, and pathogenic organisms in wastewater [17].

2.2 Conclusions of Waste Stabilization Ponds (WSPs)

- With adequate design and operation, WSPs could sufficiently treat wastewater, and the effluent discharge could comply with the reuse regulations and standards.
- When land is available, most developing countries could implement the WSP technology for wastewater treatment due to its reliability and cost-effectiveness, especially in warm climates.
- Having a WSP effluent with physicochemical and bacteriological properties, which comply with the national and international standards, is an essential task that requires adequate design, operation, monitoring, and maintenance steps. Any flaws in these steps not only endanger the functioning of WSPs, but also cause health risks to the population utilizing the treated water.

2.3 Recommendations of Waste Stabilization Ponds (WSPs)

- Investigate the final effluent applicability for reuse in agriculture and aquaculture, focusing on the required construction cost and energy utilization.
- Investigate the effects of design criteria and organic loading on the biochemical routes involved in WSPs.
- Perform periodic monitoring and assessment on WSPs operation, including microorganisms (e.g., algae and bacteria).
- Overcome the gap existing between the created computational and hydrodynamic WSP design models and their actual application.
- Understand the mechanisms, chemical reactions, and pathways involved in pollutant removal by WSPs and enhance the efficiency of heavy metal and micropollutant removals.

3 Microalgae for Phycoremediation

3.1 Updates of Microalgae for Phycoremediation

Phycoremediation is used to remove nitrogen, and phosphorus species from wastewater by microalgae in either open pond systems (e.g., raceway) or photobioreactors [18]. It could also be employed to reduce some emerging trace pollutants in organic-enriched waste streams [1]. The operation of algal systems depends on several factors such as light intensity, temperature, pH value, CO_2 amount, and nutrient availability [7]. Moreover, the generated algal biomass is a reasonable feedstock that can be converted to bioenergy via various techniques such as pyrolysis, gasification, anaerobic (co)digestion, and fermentation [19].

3.2 Conclusions of Microalgae for Phycoremediation

- Because algal biomass contains adequate fractions of carbohydrates, proteins, and lipids, it can be utilized to generate biogas by anaerobic digestion, bioethanol and/or biohydrogen by fermentation/photofermentation, bio-oil by pyrolysis, and gases by gasification and hydrothermal liquefaction.
- A dual benefit of pollution minimization and energy production could be obtained from microalgae cultivation in wastewater.
- Microalgae have become a sustainable feedstock for obtaining high-value products such as biodiesel, bioethanol, bio-H_2, and bio-CH_4, motivating the delivery of further studies on the large-scale application.
- Bioenergy production coupled with wastewater phycoremediation has a great potential in terms of operational cost reduction, making the complete algal system economically viable.

3.3 Recommendations of Microalgae for Phycoremediation

- Further investigations are still needed for the development of microalgae production integrated with wastewater treatment to improve the cost-effectiveness of the entire process.
- Life cycle assessment, life cycle energy assessment, and life cycle carbon emissions assessment of microalgae production to fulfill the needs of energy, food, and raw materials are required.
- New, low-cost, and efficient cultivation and harvesting techniques of algal biomass should be developed.
- Investigate the application of microalgae to remove various emerging contaminants.

- The main factors influencing the operation of microalgae systems should be optimized to deliver the highest biomass productivity.

4 Anaerobic Treatment of Sewage

4.1 Updates of Anaerobic Treatment of Sewage

The anaerobic-based systems are used to break down the organic contaminants via the action of bacteria and other microorganisms under an oxygen-deprived condition [20]. Anaerobic treatment technologies experience lower energy consumption (no electricity is needed for oxygenation), nutrient requirement, and sludge generation than the aerobic treatment systems [21]. Anaerobic digestion of organic wastes undertakes multiple sequential stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis [19]. Some lagoons and pools are covered by high-density polyethylene membrane and operated under an anaerobic environment to degrade complex organic pollutants [22].

4.2 Conclusions of Anaerobic Treatment of Sewage

- Severely damaged and out of service WWTPs could be recovered and updated by converting the original Imhoff tank (based on settling particulate matter) into an anaerobic hybrid filter (AHF) unit.
- The upgraded WWTP with new AHF is robust and easy to operate and characterized by low energy consumption. Moreover, the final effluent could fulfill the international regulations for disposal in the aquatic environment.

4.3 Recommendations of Anaerobic Treatment of Sewage

- More studies are required for the adaptation and optimization of combined anaerobic hybrid filter/trickling filters/settling system to treat industrial wastewater with complex organic compounds.
- Designing the anaerobic hybrid filter should consider the concentration of mixed liquor that meet the required design criteria, such as food-to-microorganisms ratio and sludge age.
- Investigate the capability of fixing a packing media with a larger specific surface area, allowing for the inoculation of dense microbial organisms and utilization of the slowly biodegradable organic matter.

5 Adsorption Technology in Wastewater Treatment

5.1 Updates of Adsorption Technology in Wastewater Treatment

Recently, various researchers have employed the adsorption process for water and wastewater treatment to have a final effluent that complies with the permissible standards [23]. This mass transfer process involves the accumulation of contaminants (also known as adsorbate) at the interface of two phases, such as liquid/solid interface (the solid phase is termed adsorbent) [24]. The adsorption process could be either physisorption (i.e., the interaction has a physical nature) or chemisorption (the attraction forces occur due to chemical bonding) [25]. Several modeling techniques, regarding isotherm studies (Langmuir, Brunauer, Emmett, and Teller (BET), and Freundlich), and kinetic studies (pseudo-first-order and pseudo-second-order), have been commonly used to describe the adsorption process [26].

5.2 Conclusions of Adsorption Technology in Wastewater Treatment

- The adsorption of pollutants is promoted via various mechanisms, including pore-filling, complexation, ion exchange, and hydrogen bonding [27].
- The adsorbent material should be (1) efficient in removing various contaminants, (2) characterized by high adsorption rate and capacity, and (3) featured by high selectivity for multiple pollutants.
- Some advanced, low-cost, and unconventional adsorbents are prepared from agricultural and industrial wastes and residues [28].
- The surface features and properties of adsorbent material could be modified by applying proper chemical and/or thermal treatment techniques.

5.3 Recommendations of Adsorption Technology in Wastewater Treatment

- Further adsorption-related studies are required to define the operating condition necessary to maintain effective pollutant removal.
- The accuracy and certainty of various adsorption models, including isotherm, kinetic, and thermodynamic studies, to predict the adsorption performance should be demonstrated.
- Perform life cycle assessment of waste materials to obtain reliable, applicable, and cost-effective adsorbents.
- Application of adsorption process to real industrial wastewater effluents.

- Developing statistical and mechanistic modeling approaches and computational fluid dynamics to understand the adsorption mechanisms appropriately.
- Enhance regeneration studies for the recovery of valuable compounds.
- The scaling up of adsorption columns and prediction of breakthrough curves should be considered in future studies.

6 Green Nanomaterial for Environmental Remediation

6.1 Updates of Green Nanomaterial for Environmental Remediation

Green nanomaterial is prepared from environmentally benign solvents, reducing agents, and stabilizing additives, ensuring the green chemistry concept [29]. For instance, green nanoparticles could be synthesized via mixing the plant extracts with a precursor solution within several minutes, giving a final zerovalent state [30]. The prepared green nanomaterial is further characterized for crystalline structure, surface and texture morphology, composition, and thermal stability [31]. After that, the nanoparticle/nanocomposite could be used to provide a safe and clean water supply via photocatalysis, nanofiltration, and nanosorbent [4].

6.2 Conclusions of Green Nanomaterial for Environmental Remediation

- Various plant extracts have been used as an efficient resource for iron nanoparticle synthesis, showing various benefits from laboratory scale to commercial applications.
- This green nanotechnology enjoys biosynthesis of more stable, eco-friendly, and non-toxic nanoparticles, with less waste production [32].
- Green nanoparticle/nanocomposite has found successful applications for degradation of dyes and pollutants, removal of heavy metals, treating wastewater, and possessing good antibacterial activity.

6.3 Recommendations of Green Nanomaterial for Environmental Remediation

- Considering the broad applications of green iron nanoparticles, a detailed study is required for determining the life cycle assessment and circular economy aspects.

- Additional pilot studies are required to validate the industrial-scale application of nanotechnology.
- Developing additional green routes, which are more rapid, simpler, and much easier, for fabricating metal-based nanoparticles.

7 Deactivation of Waterborne Pathogens in Natural Eco-Systems

7.1 Updates of Deactivating Waterborne Pathogens in Natural Eco-Systems

Waterborne pathogens include bacteria, protozoa, viruses, and helminths, resulting in high morbidity and mortality worldwide [33]. The human health risks associated with waterborne pathogens include diarrhea, cholera, gastrointestinal diseases, and systematic illnesses [34]. The removal of waterborne pathogens at WWTPs is highly dependent on the temperature, type of the treatment process, and disinfection technologies (e.g., chlorine, ultraviolet, and ozone) [35]. Indeed, most of the standard techniques for monitoring and detecting waterborne pathogens require massive economic costs [36]. Hence, it is essential to develop practical and affordable techniques for assessing the waterborne diseases and defining the related treatment processes.

7.2 Conclusions of Deactivating Waterborne Pathogens in Natural Eco-Systems

- Plasma technology is an effective modern oxidation process used for inactivating waterborne pathogenic microorganisms.
- Cold plasma could also be utilized as a non-thermal emerging technology to eliminate persistent organic pollutants from wastewater [37].
- Non-thermal plasma offers a potential future for the oxidation of pollutants, which currently pose a significant health danger to the environment, due to its promising environmental adaptability and operation.
- The decomposition of organic compounds could be further improved via the addition of heterogeneous catalysts that promote the formation of strong oxides such as $^{\bullet}OH$, O_3, and H_2O_2.

7.3 Recommendations of Deactivating Waterborne Pathogens in Natural Eco-Systems

- Conventional WWTPs should be upgraded to eliminate the waterborne pathogens and emerging contaminants of concern.
- More studies are required to understand the oxidation mechanism of non-thermal plasma by detecting the produced amount of O_3 and H_2O_2 and the captured free radical scavengers.
- Essential types of research are needed for the installation, application, and modification of the plasma-based systems at large-scale WWTPs.
- The treated effluent after the plasma reactor should be investigated using quantitative microbial risk assessment (QMRA) for reuse and human consumption.
- Further development is needed to design plasma reactors for maintaining good water quality from an industrial perspective.

8 Treated Wastewater Reuse for Irrigation

8.1 Updates of Treated Wastewater Reuse for Irrigation

Recently, the recovery of water, nutrients, and energy from wastewater for further application in irrigation has been considered an essential strategy [38]. The effluents of wastewater treatment systems could be utilized in agriculture to compensate for water shortages [39]. Moreover, some plants tend to uptake portions of the nitrogen and phosphorus elements from treated wastewater for enhancing their growth conditions [40]. Furthermore, the organic pollutants of wastewater could be bio-converted via anaerobic digestion into biogas suitable to share the energy required to operate the farmlands (crop production and harvesting) [41].

8.2 Conclusions of Treated Wastewater Reuse for Irrigation

- The WWTPs could be adequately managed to obtain main resources (i.e., water, energy, and nutrients), having essential agricultural and agro-industrial applications.
- By-products of wastewater treatment (e.g., treated effluent, and generated biomass, sludge, and algae) could be employed to enhance the development of social economy and maintenance of life.
- The use of plants (phytoremediation) provides the dual benefits of wastewater treatment and plant biomass harvesting for bioenergy generation.
- Recently, macrophytes have been employed for treating wastewater via artificially constructed wetlands and nutrient film techniques.

- Reclaimed (or recycled) water could be a viable non-conventional water resource for landscape irrigation, showing a great potential for improving agricultural soils.
- Some halophytes and salt-sensitive crops could be used for salt management of irrigated farmland, and the disposal of this system is applicable for operating solar evaporators.
- Government policymakers have recently imposed more restrictions to limit/avoid the unofficial reuse of drainage water associated with the increasing pressure on the limited canal supplies.

8.3 Recommendations of Treated Wastewater Reuse for Irrigation

- Further research is required to assess and evaluate the presence of harmful pollutants and heavy metals in irrigation water, especially when receiving pharmaceutical and personal care products.
- The use of wastewater as an important resource for reducing the requirement of freshwater and energy in irrigation should be investigated.
- There is a need for better research in adopting efficient irrigation technologies, such as the irrigation scheduling method, to save the required water and energy inputs.
- Although technical problems related to the treatment and reuse of wastewater for irrigation have been progressively solved during the recent decades, regulations, social acceptance, and economic issues still need to be addressed.
- Comprehensive monitoring and assessment of the soil-plant system subjected to reclaimed water should be carried out to avoid further environmental and health risks.
- Monitoring of the soil physicochemical properties should be implemented for understanding the salinity's spatial variability and its dynamic behavior.
- The plant species appropriate for operating various drainage-water reuse systems should be carefully selected.

9 Agricultural Drainage Water (ADW) Management

9.1 Updates of Agricultural Drainage Water (ADW) Management

Recently, the management of agricultural drainage water (ADW) has been used to overcome the critical gap between water supply and demand [42]. The primary aim of ADW management is to minimize the quantity of freshwater utilized in irrigation while sustaining enough crop production [43]. Appropriate monitoring, analysis, assessment, and evaluation of ADW should be performed to fulfill the requirement of wastewater reuse standards for irrigation.

9.2 Conclusions of Agricultural Drainage Water (ADW) Management

- Various edge-of-field technologies such as constructed wetlands, bioreactors, and filtration units were successfully employed for removing nitrogen and phosphorus pollutants from drainage water
- The performance, reliability, and stability of the ADW treatment systems vary according to the biogeochemical, hydrogeochemical, and hydrological features.
- Accurate treatment and reuse strategies of ADW are required to mitigate the high concentrations of heavy metals and salinity.

9.3 Recommendations of Agricultural Drainage Water (ADW) Management

- Computational techniques and numerical models should be considered for defining the optimum conditions for the application of tile-drained agricultural catchments.
- Perform long-term monitoring of the water and nitrogen mass balance in tile-drained agricultural lands.
- The size of the mixing ratio between ADW and irrigation water should be accurately determined, particularly in the case of high-strength wastewater.

10 Conclusions

This chapter highlights the major updates and conclusions extracted from the book volume "Cost-efficient Wastewater Treatment Technologies: Natural Systems." In addition, a set of recommendations for future studies that aim at delivering benefits from treating wastewater by natural, ecological, and environmentally friendly systems are included. The chapter findings would assist environmental managers, scientists/researchers, and policymakers in selecting cost-effective, eco-friendly, and practical ecological technologies of wastewater remediation.

Acknowledgments The editors who wrote this chapter would like to thank the authors of the chapters for their efforts during the different phases of the book including their inputs in this chapter. The first author acknowledges Nasr Academy for Sustainable Environment (NASE). The second author acknowledges the support of the Science, Technology, and Innovation Authority (STIFA) of Egypt in the framework of the grant no. 30771 for the project titled "A Novel Standalone Solar-driven Agriculture Greenhouse—Desalination System: That Grows its Energy and Irrigation Water" via the Newton-Mosharafa Funding Scheme Call 4.

References

1. Ansari F, Ravindran B, Gupta S, Nasr M, Rawat I, Bux F (2019) Techno-economic estimation of wastewater phycoremediation and environmental benefits using Scenedesmus obliquus microalgae. J Environ Manage 240:293–302
2. Fawzy M, Nasr M, Helmi S, Nagy H (2016) Experimental and theoretical approaches for Cd (II) biosorption from aqueous solution using Oryza sativa biomass. Int J Phytoremediation 18(11):1096–1103
3. İlyasoglu G, Kose-Mutlu B, Mutlu-Salmanli O, Koyuncu I (2022) Removal of organic micropollutans by adsorptive membrane. Chemosphere 302:134775
4. Bayat F, Didar T, Hosseinidoust Z (2021) Emerging investigator series: bacteriophages as nano engineering tools for quality monitoring and pathogen detection in water and wastewater. Environ Sci Nano 8(2):367–389
5. USEPA (2009) Targeted National Sewage Sludge Survey Sampling and Analysis Technical Report. United States Environmental Protection Agency, Washington
6. Nasr M, Shmroukh A (2020) Gray-to-green infrastructure for stormwater management: an applicable approach in Alexandria City, Egypt. In: Negm A (ed) Flash floods in Egypt. Advances in science, technology & innovation (IEREK interdisciplinary series for sustainable development). Springer, Cham, pp 369–379. https://doi.org/10.1007/978-3-030-29635-3_16
7. Ahmad Ansari F, Nasr M, Guldhe A, Kumar Gupta S, Rawat I, Bux F (2020) Techno-economic feasibility of algal aquaculture via fish and biodiesel production pathways: a commercial-scale application. Sci Total Environ 704:135259
8. Nasr M, Ismail S (2015) Performance evaluation of sedimentation followed by constructed wetlands for drainage water treatment. Sustain Environ Res 25(3):141–150
9. Achag B, Mouhanni H, Bendou A (2021) Improving the performance of waste stabilization ponds in an arid climate. J Water Clim Change 12(8):3634–3647
10. Nasr M (2019) Environmental perspectives of plant-microbe nexus for soil and water remediation. In: Kumar V, Prasad R, Kumar M, Choudhary D (eds) Microbiome in plant health and disease. Springer, Singapore, pp 403–419. https://doi.org/10.1007/978-981-13-8495-0_18
11. Omidinia-Anarkoli T, Shayannejad M (2021) Improving the quality of stabilization pond effluents using hybrid constructed wetlands. Sci Total Environ 801:149615
12. Partyka M, Bond R (2022) Wastewater reuse for irrigation of produce: a review of research, regulations, and risks. Sci Total Environ 828:154385
13. Nakum J, Bhattacharya D (2022) Various green nanomaterials used for wastewater and soil treatment: a mini-review. Front Environ Sci 9:724814
14. Vagheei R (2021) Upgrading of waste stabilization ponds using a low-cost small-scale fine bubble diffused aeration system. Water Sci Technol 84(10–11):3104–3121
15. Abdulla H, El-Shatoury S, El-Shahawy A, Ghorab S, Nasr M, Trujillo M (2019) An integrated bioaugmentation/electrocoagulation concept for olive mill wastewater management and the reuse in irrigation of biofuel plants: a pilot study. Environ Sci Pollut Res 26(16):15803–15815
16. Jin L, Sun X, Ren H, Huang H (2023) Hotspots and trends of biological water treatment based on bibliometric review and patents analysis. J Environ Sci 125:774–785
17. Mahapatra S, Samal K, Dash R (2022) Waste stabilization pond (WSP) for wastewater treatment: a review on factors, modelling and cost analysis. J Environ Manage 308:114668

18. Ansari F, Nasr M, Rawat I, Bux F (2021) Artificial neural network and techno-economic estimation with algae-based tertiary wastewater treatment. J Water Process Eng 40:101761. https://doi.org/10.1016/j.jwpe.2020.101761
19. Ezz H, Ibrahim M, Fujii M, Nasr M (2021) Dual biogas and biochar production from rice straw biomass: a techno-economic and sustainable development approach. Biomass Convers Bioref
20. Long S, Liu X, Chen J, Zhao L, Pavlostathis S (2022) Effect of tetracycline on bio-electrochemically assisted anaerobic methanogenic systems: process performance, microbial community structure, and functional genes. Sci Total Environ 837:155756
21. Nasr M, Elreedy A, Abdel-Kader A, Elbarki W, Moustafa M (2014) Environmental consideration of dairy wastewater treatment using hybrid sequencing batch reactor. Sustain Environ Res 24(6):449–456
22. Passos R, Dias D, von Sperling M (2022) Simple mid-depth transverse baffles to improve bacterial disinfection in a shallow maturation pond–performance evaluation and CFD simulation. Environ Technol 43(10):1437–1445
23. Fawzy M, Nasr M, Abdel-Rahman A, Hosny G, Odhafa B (2019) Techno-economic and environmental approaches of Cd2+ adsorption by olive leaves (Olea europaea L.) waste. Int J Phytoremediation 21(12):1205–1214
24. Fawzy M, Nasr M, Adel S, Helmi S (2018) Regression model, artificial neural network, and cost estimation for biosorption of Ni(II)-ions from aqueous solutions by Potamogeton pectinatus. Int J Phytoremediation 20(4):321–329
25. Fawzy M, Nasr M, Nagy H, Helmi S (2018) Artificial intelligence and regression analysis for Cd(II) ion biosorption from aqueous solution by Gossypium barbadense waste. Environ Sci Pollut Res 25(6):5875–5888
26. Kumi A, Ibrahim M, Fujii M, Nasr M (2020) Synthesis of sludge-derived biochar modified with eggshell waste for monoethylene glycol removal from aqueous solutions. SN Appl Sci 2(10):1696
27. Kumi A, Ibrahim M, Fujii M, Nasr M (2022) Petrochemical wastewater treatment by eggshell modified biochar as adsorbent: a techno-economic and sustainable approach. Adsorpt Sci Technol 2022:2323836
28. Kumi A, Ibrahim M, Nasr M, Fujii M (2020) Biochar synthesis for industrial wastewater treatment: a critical review. Mater Sci Forum 1008:202–212
29. Raza A, Altaf S, Ali S, Ikram M, Li G (2022) Recent advances in carbonaceous sustainable nanomaterials for wastewater treatments. Sustain Mater Technol 32:e00406
30. Omran B, Baek K-H (2022) Valorization of agro-industrial biowaste to green nanomaterials for wastewater treatment: approaching green chemistry and circular economy principles. J Environ Manage 311:114806
31. Tee G, Gok X, Yong W (2022) Adsorption of pollutants in wastewater via biosorbents, nanoparticles and magnetic biosorbents: a review. Environ Res 212:113248
32. Fito J, Kefeni K, Nkambule T (2022) The potential of biochar-photocatalytic nanocomposites for removal of organic micropollutants from wastewater. Sci Total Environ 829:154648
33. Deepnarain N, Nasr M, Kumari S, Stenström T, Reddy P, Pillay K, Bux F (2020) Artificial intelligence and multivariate statistics for comprehensive assessment of filamentous bacteria in wastewater treatment plants experiencing sludge bulking. Environ Technol Innov 19:100853. https://doi.org/10.1016/j.eti.2020.100853
34. Pilevar M, Kim K, Lee W (2021) Recent advances in biosensors for detecting viruses in water and wastewater. J Hazard Mater 410:124656
35. Wang M, Zhu J, Mao X (2021) Removal of pathogens in onsite wastewater treatment systems: a review of design considerations and influencing factors. Water 13(9):1190
36. Jaiswal M, Hussain J, Gupta S, Nasr M, Nema A (2019) Comprehensive evaluation of water quality status for entire stretch of Yamuna River, India. Environ Monit Assess 191(4):208
37. Gururani P, Bhatnagar P, Bisht B, Kumar V, Joshi N, Tomar M, Pathak B (2021) Cold plasma technology: advanced and sustainable approach for wastewater treatment. Environ Sci Pollut Res 28(46):65062–65082

38. Khairy S, Shaban M, Negm A, Eldeen O, Ramadan E (2022) Drainage water reuse strategies: case of El-bats drain, Fayoum governorate, Egypt. Ain Shams Eng J 13(5):101681
39. Shaaban N (2022) Water quality and trophic status of Lake Mariut in Egypt and its drainage water after 8-year diversion. Environ Monit Assess 194(6):392
40. Ansari F, Singh P, Guldhe A, Bux F (2017) Microalgal cultivation using aquaculture wastewater: integrated biomass generation and nutrient remediation. Algal Res 21:169–177
41. Gupta S, Kumar N, Guldhe A, Ansari F, Rawat I, Nasr M, Bux F (2018) Wastewater to biofuels: comprehensive evaluation of various flocculants on biochemical composition and yield of microalgae. Ecol Eng 117:62–68
42. Schneider R, Stisen S, Højberg A (2022) Hunting for information in streamflow signatures to improve modelled drainage. Water 14(1):110
43. Jorge C, Almeida M, Brito R, Covas D (2022) Water, energy, and emissions nexus: effect of inflows in urban drainage systems. Water 14(6):868