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Mahmoud Nasr
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Cost-efficient Wastewater Treatment Technologies

Engineered Systems

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Volume 118

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Cost-efficient Wastewater Treatment Technologies

Engineered Systems

Volume Editors: Mahmoud Nasr · Abdelazim M. Negm

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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 second of two volumes that together provide a comprehensive overview of the currently 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 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 6 main themes: Part I: Introduction; Part II: Physicochemical-based Wastewater Treatment Systems; Part III: Biological-based Wastewater Treatment Systems; Part IV: Advanced and Tertiary Wastewater Treatment Systems; Part V: Wastewater Management and Sustainability; and Part VI: Conclusions and Recommendations. It consists of 22 chapters written by researchers, scientists, and experts from more than 10 countries, including Sweden, Italy, Germany, Czech Republic, Vietnam, China, Poland, Denmark, and the USA, and other countries from the Middle East/North Africa (MENA) region, representing more than 30 institutions worldwide. The book gives essential information on the engineered (mechanized) wastewater treatment technologies and demonstrates the current challenges in wastewater management and pathways toward sustainability, offering a global perspective on these topics.

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 benefit 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.

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Part I
Introduction

Introduction to “Cost-efficient Wastewater Treatment Technologies: Engineered Systems”

Mahmoud Nasr and Abdelazim M. Negm

Contents

Abstract Recently, the rise of population and expansion in urbanization and industrial and agricultural activities have been associated with the generation of huge quantities of wastewater. This wastewater carries different organic and inorganic contaminants, trace elements, and emerging pollutants that probably result in serious human health risks. Accordingly, wastewater should be subjected to adequate

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treatment processes to have a final effluent complying with the national and international disposal of regulations. The design, implementation, and operation of wastewater treatment units depend on the process, being either natural (ecological) or engineered (mechanized). This chapter represents the basic ideas of the mechanized wastewater treatment units covered by the book volume "*Cost-efficient Wastewater Treatment Technologies: Engineered Systems.*" It gives brief information on activated sludge system, trickling filter, anaerobic digestion, adsorption technology, green nanomaterial preparation and application, tertiary treatment by disinfection, emerging contaminants, and a life cycle assessment (LCA) approach. Some case studies clarifying the idea of wastewater treatment by engineered systems are demonstrated.

Keywords Environmental impacts, Mechanized systems, Recycling and reuse, Sustainability, Wastewater guidelines

1 Introduction

The population growth has recently increased exponentially, resulting in a wide expansion of the industrial, agricultural, and agro-industrial activities [1, 2]. This pattern is accompanied by the generation of large volumes of wastewater laden with organic and inorganic contaminants, dyes, heavy metals, trace elements, persistent toxic species, and micro-pollutants [3, 4]. These substances negatively affect the environmental matrices and cause various human health risks such as nausea, vomiting, stomach cramps, diarrhea, icterus, and liver toxicity [5]. Stakeholders, policymakers, and decision-makers should have enough information about the wastewater treatment technologies to attain sustainable solutions for the mitigation of environmental pollution [6, 7].

Generally, wastewater is treated using three subsequent steps, namely primary, secondary, and tertiary [8]. The primary phase (also known as the physical treatment process) includes screening, grit chamber, dissolved air flotation, and primary sedimentation units [9]. This phase is used to remove large objects (paper, wood, plastic, etc.), particulate matter (coarse gravel, glass, etc.), and floating objects (e.g., oil) [10]. This step is followed by the secondary phase, also known as the biological treatment process, where a group of microorganisms grows under certain environmental conditions such as aerobic, anaerobic, facultative, or fermentative [11]. The microorganisms tend to bio-convert the organic and nutrient pollutants into stable inorganic by-products simply separated from the wastewater [12]. Finally, the secondary treated wastewater enters a tertiary step, containing filtration, adsorption, disinfection, and/or other post-treatment units [13, 14]. Each treatment unit should be well designed and implemented to remove the desired pollutant species [15]. Moreover, the required equipment (e.g., pumps, diffusers, heaters, and control unit) should be appropriately selected to reduce the capital and operational costs.

This chapter gives general information on the engineered (mechanized) wastewater treatment systems covered by the book volume titled "*Cost-efficient Wastewater Treatment Technologies: Engineered Systems.*" The essential knowledge, skills, and practices about influent/effluent wastewater quality, design criteria, required resources (energy, water, chemicals/reagents, etc.), and initial and running costs related to wastewater treatment plants (WWTPs) are represented. The following sections of this chapter briefly describe the main technical elements of the book volume, offering cost-efficient, reliable, and practical solutions to address the emerging challenges accompanied by pollution control and resource recovery.

2 Aerobic Biological Treatment of Sewage

The biological treatment of wastewater could be maintained under an aerobic condition, where the microorganisms consume the dissolved oxygen supplied to the system for breaking down organic contaminants [12]. Other pollutants such as nitrogen and phosphorus could be subjected to the aerobic oxidation process; finally converted into stable inorganic elements [16]. A mechanical aeration device (e.g., diffuser, compressor, surface aerator, and air blowers) is used to supply the wastewater medium with the required amount of air/oxygen [17]. In activated sludge systems, this aeration technique is used to support the microorganism's metabolic activity and keep the bacterial biomass in a suspension condition, representing the mixed liquor suspended solids [18]. In this system, an aeration tank is designed and implemented to provide a suitable environment for microorganisms to convert the organic compounds into carbon dioxide and new cells in the presence of oxygen. Other aerobic-based systems such as trickling filters and bio-towers are equipped with a packing media (e.g., plastic sheets, cubic sponges, and rocks) that offer a suitable surface area to carry the bacterial biofilm. This scheme is known as an attached growth system, where a community of microorganisms able to degrade the organic contaminants is attached to the media surface. Other species located inside the media could grow under a denitrification process, consuming nitrate as an electron acceptor.

3 Anaerobic Biological Treatment of Sewage

Unmanaged disposal of organic wastes has been associated with oxygen depletion in the aquatic environment, causing special challenges in the conservation of fishes. Anaerobic digestion is a biological-based process used to convert these organic pollutants into value-added products, such as biogas, under oxygen-deficit conditions [19]. The produced biogas could be utilized as a source of energy to reduce natural gas consumption and greenhouse gas (GHG) emissions [20]. This process also contributes to the generation of biohydrogen and biofertilizers. The design and operation of anaerobic digestion plants should consider the relation between GHGs emissions and economic profit [21]. Implementation of the farm-scale biogas plants has the potential to generate ecological benefits and mitigate climate change and eutrophication. It's essential to explore the environmental, bioeconomic, and social benefits of anaerobic digestion of organic wastes for energy generation. Biogas upgradation technologies and future perspectives should be robust, economic, efficient, and easy to implement.

4 Membrane Bioreactor (MBRs) for Wastewater Treatment

Membrane bioreactor (MBR) is an attractive technology for wastewater treatment that could maintain better removals of various organic and nitrogenous pollutants from wastewater compared with the conventional systems [22]. In particular, the secondary sedimentation tank of traditional activated sludge systems is replaced by a membrane module that separates the solid phase (e.g., biomass, mixed liquor, and particulates) from the aqueous phase (wastewater). However, membrane fouling and energy demand/consumption are the main challenges for the wide implementation of the MBR technology. Fouling mitigation methods of MBR include mechanical/manual cleaning, vibratory shear enhanced process, and alternating electric field. Moreover, air scouring is employed by passing bubbles near the membrane surface to generate local shear forces that remove the fouling layer. Ceramic MBR has several benefits, including a longer lifespan, higher permeate flux, and greater ability to withstand various temperature conditions compared with the conventional membrane material [23]. The reciprocation MBR depends on the application of a particular lateral movement that generates inertial forces on the hollow fiber membrane modules. This movement is driven by a motor connected to a moving bed that carries the membrane cassettes. This configuration has positive effects on energy conservation and fouling reduction.

5 Electrochemical Methods of Wastewater Treatment

Electrochemical oxidation is a promising method used for oxidizing (degrading) organic pollutants to simple inorganic elements such as H_2O and CO_2. It could also be used for the decontamination of wastewater laden with pharmaceuticals, phenol, and organic dyes that are hardly treated by the conventional biological treatment processes [24]. Two different pathways are basically involved in the destruction of complex organic pollutants by the electrochemical oxidation process [25] (1) direct charge transfer reactions (the mediation of the electrons) between the anode surface and the organic pollutants, and (2) indirect generation of multiple electroactive species (e.g., electrogenerated active chlorine) at the anode surface. The main challenges of electrochemical oxidation include polarization (accumulation of gases on the electrode surface causing poor mass transfer), passivation (generation of polymeric and oligomeric compounds accompanied by electrode reactions), and corrosion (formation of corrosive products owing to the oxidation reactions of the anode material). The performance of electrochemical oxidation techniques depends largely on the electrode material, such as graphite, platinum, carbon, and metal oxides. For example, the RuO_2-based electrodes are effective electrocatalysts in the evolution of chlorine species for the degradation of organic compounds and microbes in wastewater. The selected electrodes should meet three requirements: (1) degradation of various types of toxic pollutants causing inhibition to microorganisms' activities, (2) high stability under anodic polarization conditions, and (3) cost-effective manufacturing process.

6 Disinfection for Pathogen Reduction

Chlorination is the most extensive and widely employed technique for the disinfection of treated wastewater [13]. However, disinfection of municipal drinking water by chlorine could generate harmful by-products, such as trihalomethanes (THMs), which cause carcinogenicity, teratogenicity, and genotoxicity [26]. The formation and control of THMs during wastewater disinfection rely on the raw water composition (e.g., organic matter and ammonia levels), operational factors, and residual chlorine [27]. Hence, wastewater effluents should be subjected to de-chlorination before their final disposal in nearby water bodies.

7 Cavitation in Wastewater Treatment

Cavitation is a phenomenon that describes the formation, growth, and subsequent collapse of microcavities, releasing large magnitudes of power in the fluid [28]. Cavitation is established by passing the liquid through a specially designed geometry of a cavitation device (hydrodynamic cavitation) or executing sound waves within a range of 16 kHz to 100 MHz to create cavitation in the solution (acoustic cavitation). The generated energy (high localized temperatures $>$5,000 K and pressures 500 atm) depends on the fluid properties, operative parameters, and device geometry (i.e., orifice plates, nozzles, and Venturi systems). Advanced oxidation processes based on cavitation (hydrodynamic and acoustic) have been used for the effective degradation of contaminants in wastewater treatment [29]. In this system, external oxidants (H_2O_2, ozone, and $Na_2S_2O_8$) are added to the cavitation system for releasing more reactive radical species. Subsequently, $HO^{\bullet}$, $^{\bullet}H$, $HO_2{}^{\bullet}$, and H_2O_2 useful for oxidation, decolorization, decomposition, bond cleavage, and mineralization are formed. The generated species also reveal a high synergism between oxidants and cavitation to maintain the ultra-fast degradation of pollutants [30]. Also, this hybrid system allows for removing highly persistent pollutants (bio-refractory, organic, and toxic contaminants) from aqueous systems under ambient conditions.

8 Improving Bioremediation Using Biosurfactants

The development of genetically engineered microbial strain, as well as optimization of a biological process parameter, is a greener approach to lower down the waste generated from various industries. Biosurfactants (or biomolecules) are active and amphiphilic compounds that can be produced at the cell surface of microorganisms such as bacteria, yeasts, and filamentous fungi [31]. Biosurfactants may be extracellular (secreted outside the cells) or intracellular (located inside the cells, requiring a cellular disruption process) [32]. Biosurfactants are characterized by biodegradability, lower toxicity, and environmental compatibility [33]. These non-conventional surface-active molecules have been applied in treating wastewater from different agricultural, domestic, and industrial sources [34]. Biosurfactants could be used for the degradation of contaminants (e.g., oil, phenol, and grease), oil-water separation, and removal of heavy metals (e.g., Zn, Cu, and Pb) under wide operational conditions (temperature, pH, and salinity). Biosurfactants could also be used to enhance the separation efficiency of the dissolved air flotation unit [35]. Advanced molecular tools should be used for biosurfactant production on an industrial and commercial scale.

9 Emerging Organic Contaminants (EOCs) Removal

Emerging organic contaminants (EOCs) are a group of pollutants of worldwide concern that enter the environmental matrices (soil, water, waste, sediment, and air) through various agro-industrial activities [36]. These contaminants tend to threaten human health and deteriorate the aquatic environment. The EOCs group is associated with several substances such as hormones, personal care products (skin, cosmetics, and fragrances), pharmaceutical drugs, pesticides, detergents, surfactants, and flame retardants. The technologies used to reduce the EOC risk groups include membrane systems, adsorption process, oxidation schemes, particular biological treatment, and/or their combinations [15]. An economic evaluation of such technologies for treating wastewater containing EOCs is essential. Moreover, it’s required to implement an international discussion board and platform agreement to avoid the release of EOCs from the industrial sector.

10 Nanotechnology for Wastewater Treatment

Due to the release of various emerging, newly, persistent, and non-traditional organic pollutants in aquatic ecosystems, access to clean water has been considered a major global challenge [37]. Nanotechnology has been used to overcome the drawbacks and limitations of conventional methods used for wastewater treatment [38]. With the advancement in nanotechnology, nanomaterials have been employed for water disinfection, contaminant removal/adsorption, and enhancement of microbial activity involved in the bio-processes [39]. Different kinds of nanomaterials, such as carbon-based nanomaterials, biodegradable polymer–nanomaterials composites, nanocomposites, hydrophilic nanoparticles, and antibacterial nanoparticles, have been used for contaminant removal from wastewater [40]. The integration of green chemistry and nanotechnology enhances the applicability of nanoparticles to remediate and improve the environment [41].

11 Biochar Synthesis and Applications to Treat Wastewater

Subjecting biomass residues to a pyrolysis process results in the generation of a carbon-rich solid material, namely biochar [28]. The physicochemical properties of biochar depend on the pyrolysis temperature that can vary from 300 to 600°C, residence time (0.5–24 h), and feedstock types (e.g., plant, food residues, and agricultural wastes) [42]. The application of biochar in different industrial and agricultural sectors is a reliable, cost-efficient, and environmentally benign approach; especially when the feedstock biomass is readily available [43]. Recently, biochar has been widely employed as a cost-effective and environmentally friendly adsorbent for wastewater treatment with high efficiency. Biochar properties could be modified (using chemical treatment, or thermal activation) to enhance its performance for adsorbing various organic and inorganic pollutants. Relatively higher pyrolysis temperature encourages the preparation of biochar with a larger surface area and micropore size distribution able to adsorb the organic contaminants mainly by hydrophobic interaction and partitioning mechanism [28]. However, some oxygen-based functional groups (e.g., carboxyl, phenolic, and lactonic) able to form binding with the heavy metals could be enriched at lower pyrolysis temperatures. More studies are required to illustrate the characterization and preparation of biochar, with demonstrating the major mechanisms involved in the removal of organic and inorganic contaminants from wastewater. Moreover, future research should aim to balance between the optimization of the biochar production process (e.g., optimum pyrolysis temperature) and the minimization of the preparation costs.

12 Life Cycle Assessment (LCA) of Wastewater Reuse

The world is facing a dual challenge of water scarcity and climate change, causing various unprecedented issues [44]. This problem reaches its peak in the arid areas, including the Arabian Gulf region, that rely on desalination using fossil fuels to raise the water resources availability and quality. Hence, the reuse of treated wastewater to cope with the water scarcity issue is an essential task. Life cycle assessment (LCA) should be performed to meet the missed opportunities and challenges associated with the full utilization of municipal recycled wastewater [45]. Life cycle assessment (LCA) includes the impacts of particulate matter (as kg PM2.5 equivalent), climate change (as kg CO_2 equivalent), fossil fuel depletion (as kg oil equivalent), human toxicity (as kg 1,4-dichlorobenzene equivalent), and metal depletion on the reuse of tertiary treated effluent for irrigation purposes [46]. The data used to construct the LCA system boundaries (from cradle-to-gate), including materials, energy/electricity requirements, and chemicals/reagents, could be collected via field visits, reports, or the literature. Specific crops able to grow by reclaimed water reuse should be defined to maintain appropriate management of high volumes of wastewater [47].

13 Conclusions

This chapter gives a brief overview of the main topics covered by the book volume titled "*Cost-efficient Wastewater Treatment Technologies: Engineered Systems.*" This volume focuses on the application of engineered and well-designed systems used for treating various wastewater types. These systems could be implemented based on the process configuration (suspended growth, attached growth, or hybrid system), feeding scheme (batch, continuous, or semi-batch), and oxidation state (use oxygen, nitrate, or sulfate as electron acceptors). As such, this work successfully represented the cost-effective, practical, and feasible systems used in the wastewater treatment plants. Evaluation of wastewater treatment performance using the life cycle assessment (LCA) tool, regarding challenges of climate change, resource scarcity, and lack of funding is addressed. The chapter outputs would attract environmental managers, researchers, and policymakers alike.

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Part II

Physicochemical-based Wastewater Treatment Systems

Adsorption: A Cost-Effective Wastewater Treatment Technology for Removal of Conventional and Emerging Organic Contaminants

Yahya Jani

Contents

Abstract Water is a vital component for sustaining life on the earth because it is interacted with all metabolic activities of all living beings (human, plants, and others). The decomposition of organic pollutants, in general, causes oxygen deficiency in water bodies that can lead to severe damages in the ecosystem. Therefore,

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cost-effective innovative methods for the purification of wastewater is always needed. One of the most important methods that has gathered attention is adsorption. This method has witnessed continuous development in the case of the selected materials as adsorbents. Low cost as well as the production of new nano-materials have been used for the decontamination of water. In this chapter, a general overview based on the information available in the literature was produced to highlight the importance of adsorption as a method for the purification of water from conventional and emerging organic compounds.

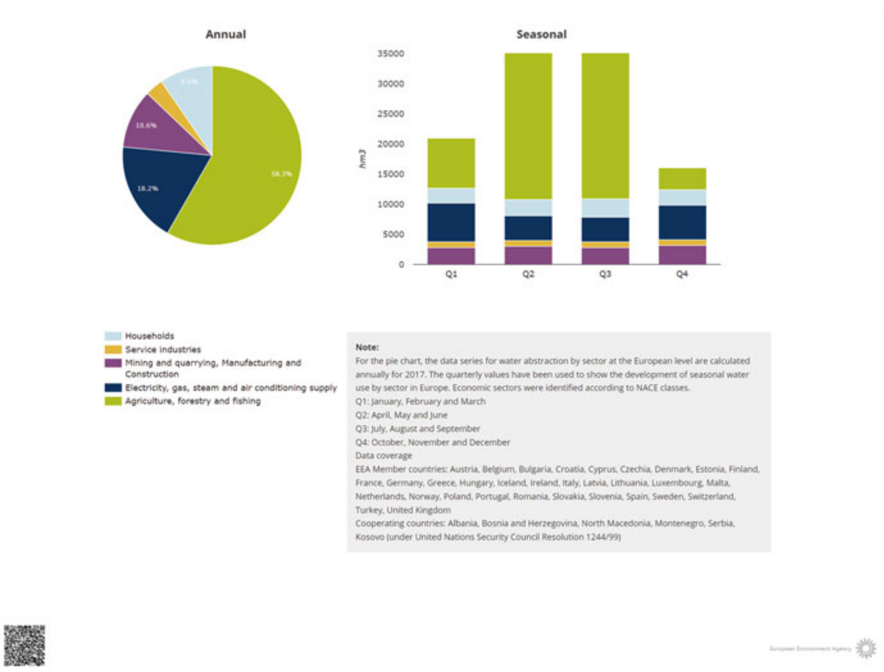
Keywords Adsorption, Organic pollutants, Wastewater, Water contamination, Water purification

1 Introduction

The development of the standard of living with population growth and climate change are crucial factors that contribute to increase the demands for most of the Earth finite natural resources, in particularly fresh water. Different parts of the world are already suffering from a shortage of fresh water resources. This fresh water represents 2–3% of the total water found on the Earth and it is the main sources for sustaining life [1]. Although, 80% of the fresh water resources is wasted in different compartments such as industrial, agriculture, and others, as shown in Fig. 1, for Europe [2]. Most of the wastewater is then discharged directly to recipients (oceans, rivers, lakes, and other bodies) mostly without treatment [1]. This practice leads to the contamination of most of the fresh water sources all over the world, highlighting the demands for treatment per discharge.

In Sweden, for instance, industrial and household wastewater were discharged directly to the nearest water body without any treatment until 1950. Environmental and health aspects concerning the treatment of wastewater were first carried out in the middle of the 1950s due to a salmonella epidemic expansion which led to the use of a biological treatment step [3]. Public health was the main driving force towards the development of the wastewater treatment plants that witnessed an increase in their number and capacity during the 1950s. Problems of oxygen deficiency initiated the use of chemical techniques to treat nutrients that was first introduced during the 1960s [3]. Local as well as global restrictions of legislations and guidelines such as the European Water Framework Directive (2000/60/EC) have led to the development of European wastewater plants by including series of physical, chemical, and biological treatment methods of wastewater before discharging to recipients.

On the other hand, water effluents from the industrial sectors have witnessed the development of different centralized and decentralized wastewater treatment systems. This was promoted by recycling as a step towards cost effectiveness especially for industries responsible for the generation of large volume of wastewater like mining industry and oil refineries. Besides, local legislations were also introduced to decrease the environmental and human health effects by industrial discharges



Note:
For the pie chart, the data series for water abstraction by sector at the European level are calculated annually for 2017. The quarterly values have been used to show the development of seasonal water use by sector in Europe. Economic sectors were identified according to NACE classes.
Q1: January, February and March
Q2: April, May and June
Q3: July, August and September
Q4: October, November and December
Data coverage
EEA Member countries: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czechia, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey, United Kingdom
Cooperating countries: Albania, Bosnia and Herzegovina, North Macedonia, Montenegro, Serbia, Kosovo (under United Nations Security Council Resolution 1244/99)

Fig. 1 Share of European fresh water used by each sector based on seasonal consumption [2]. For a high-resolution interactive image, please consult this figure at (https://www.eea.europa.eu/data-and-maps/indicators/use-of-freshwater-resources-3/assessment-4)

containing conventional and emerging organic contaminants. Various methods such as ion exchange [4], filtration [5], distillation [4], extraction [6], and adsorption are used to capture most of these contaminants before reaching to the surrounding environment. These techniques have also been employed to recycle and reuse the organic and inorganic contaminates as an input back to the circular economy.

Adsorption is regarded as one of the widely used methods to decontaminate ground and drinking water and industrial wastewater from organic and inorganic pollutants. Adsorption is defined as a selective separation of an atom or a molecule (adsorbate) from a fluid (gas or a liquid) on a solid surface (adsorbent). It is a mass transfer process based on the solute concentration difference on the interface between the fluid and the solid phases. The adsorbate is bounded on the adsorbent by physical, chemical, or physico-chemical interactions.

2 Water Contaminants

Human being activities as well as natural actions have led to tremendous changes in the ecosystem. More than ten million sites have been reported to be potentially contaminated with different compounds in the whole world [7], while three million

Table 1 Trace elements contamination in soils samples from a glasswork located at the southeastern part of Sweden analysed by X-ray fluorescence (XRF) Olympus DS-4000 (Innov-X system, USA)

Soil sample	Trace element mg/kg							
	Cr	Co	Ni	Cu	Zn	As	Ba	Pb
Mean values (30 samples)	71	251	58	108	2,482	570	1,576	5,339
Standard deviation	19	77	25	36	1,447	150	949	4,316
Swedish EPA guideline limits of contaminated soil [10]	150	35	120	200	500	25	300	400

sites have been reported in both Europe and the USA [8]. In Sweden alone, there are 80,000 potential contaminated sites with 24,500 sites confirmed a presence of different classes of contamination [9]. As an example, glass industry is responsible for the spread of many metals (like, Pb, Cd, and Sb) and metalloids (like As) to soils and ground and surface water around many of old and modern glassworks sites [10].

In the southeastern part of Sweden, for instance, around 50 glassworks are the main source of more than 500,000 tons of hazardous artistic and crystal glasses [9]. As shown in Table 1, these glasses contain circa 30% of the total weight Pb and considerable amounts of As, Sb, and others. Most of these metals have been emitted to the surrounding communities and are responsible for human health problems [10, 11]. According to Höglund et al. [12], the annual leaching from these sites to ground and surface water was estimated as 44 kg of As, 12 kg of Cd, and 165 kg of Pb. These metals represent a continuous hazard to human health and the environment due to their non-biodegradable properties. These metals have the ability to accumulate in human beings and interact with the nitrogen, oxygen, and sulphur contained in human bodies and cause damages of the peripheral central nerve system, gastrointestinal, cardiovascular, and other carcinogenic effects [13].

Furthermore, modern societies are responsible for the generation of large amounts of wastes each year, approaching 17 Gt with an estimation to reach to more than 27 Gt within the next 50 years [14]. Households, urban activities, and industries are the main contributors with different kinds of solid wastes. In Europe alone, there are between 150,000 and 500,000 close or still operating landfills and dumpsites [10, 15, 16]. These sites contain textile, pharmaceuticals, food, paper, glass, rubber, electronics, and other sorts of wastes [17, 18]. When water comes in contact with small particles of dumped or landfilled wastes, the particles acquire mobility and may transfer with water to reach to surface and ground water resources. Most of these particles have high molecular weight and complex chemical structure that are hard to degrade such as plastics [19].

Health care products and pharmaceuticals are other forms of water pollutants that are regarded as water emerging hazards [20]. Nanogram or milligram concentration of hormones, antibiotics, pain killers, and analgesics compounds may be toxic to all living organisms including human beings due to their bioaccumulation abilities, perseverance in the environment, and toxicological performance [20]. When these products enter a living body, they can inhibit the hormone receptors and hinder the metabolic process. It has been reported that conventional wastewater treatment plants are lacking the purification efficiency of these chemicals due to ageing and old used methods [21].

Adsorption, as a technique, has shown the capability to treat all of the above-mentioned types of water contaminates. Silica gel [22], zeolites [23], activated carbon [24], and low-cost adsorbents produced from waste materials have been widely used for the extraction of these pollutants from wastewater [25].

3 Types of Adsorbents

Adsorbent is a solid material used to entrap the adsorbate pollutant. This substance can be synthesized from either natural or synthetic/commercial origin as the one shown in Fig. 2. A simple, low cost, and well-known example of natural adsorbent is sand that has been widely used for the purification of water laden with metal ions [26, 27]. Metals ions in water can interact with the surface functional group of silicates (sand), leading to the separation process. On the other hand, activated carbon is the best candidate to represent a synthetic adsorbent group as it is one of the most used adsorbents in the purification and capturing of different organic and inorganic water contaminates [28]. Table 2 lists various types of adsorbents that have been broadly used in the wastewater purification processes.

Any material that acts as an adsorbent need to have suitable properties such as selectivity, adsorption capacity, pore structure, internal surface area, particle size, durability, regeneration, availability, and cost efficient among others. These factors are connected to each other; for example, durability means long function period that is connected to reduced cost. Selectivity is the ability of an adsorbent to adhere an adsorbate from a mixture of elements, which is associated with capacity; therefore, selectivity can be calculated from the capacity ratio of one pollutant to that of another pollutant at a constant fluid concentration. Capacity is a function of fluid temperature and initial concentration, and it represents the extent of adsorbate that can be adsorbed per unit mass of an adsorbent. Of course, capacity is a vital parameter to design a machine that can be used for the whole treatment process, because capacity

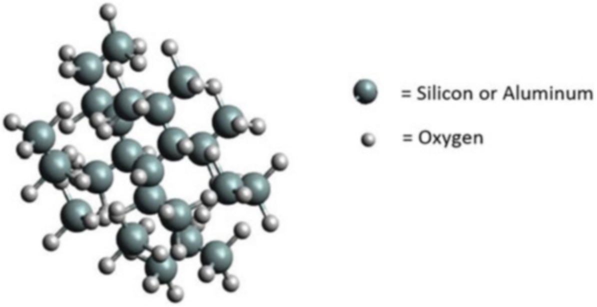


Fig. 2 Sketch of the structure of synthesis molecular sieve based on the idea presented by Barrer [29]

Table 2 Different types of water purification adsorbents with organic pollutants

Adsorbent	Adsorbates	Reference
Aluminium oxide (Al_2O_3)	Azo-monosulphate ester2,4-Dinitrophenol Azo-disulphonated Monosulphonated Polynuclear aromatic hydrocarbons Dodecylammonium chloride Phenol Alkyl sulphate esters 4-Aminoazobenzene	[30] [31] [32] [33]
Silicate (SiO_2)	Anthraquinone dye, monosulphonated p-Nitrophenol $C_6H_5.N{:}N.C_6H_4.NH_2$-p,HCl	[34]
Cellulose	Haematoxylin 2-hydroxybiphenyl p-Aminoazobenzene 2-$C_{10}H_7.SO_3H$ and Na salt 2-naphthol-6-sulphonic acid Benzidine hydrochloride 3-hydroxydiphenylamine 4,4-Diaminodiphenylmethane 2,2-Dihydroxybiphenyl Anthraquinone, disulphate ester Azo, monsulphonated Na alkylaryl sulphates	[35] [36] [37] [36] [37]
Carbon (C)	di- and tri-sulphonated aromatic compounds Glucose Phenol Sucrose n-Aliphatic acids ($>C_4$) n-Aliphatic alcohols Anthracene-1-sulphonic acid Na alkyl sulphates p-Nitrophenol	[38] [39] [40]
Wool	Benzyl alcohol Haematein Phenol derivatives (monosubstituted) p-Nitrophenol 2,4-Dinitrophenol Triphenylmethane, asym.-disulphonated Anthraquinone-2,7-disulphonic acid Naphthalene-2-sulphonic acid Na alkyl sulphates Na palmitate Sulphuric acid Aliphatic alcohols Phenylazobenzene cpds HCl	[41] [42] [43]
Rice husk	Safranin Methylene blue Methylene blue dye	[44] [45] [46]

(continued)

Table 2 (continued)

Adsorbent	Adsorbates	Reference
	Indigo Carmine Basic blue 9 Acid yellow 36 p-Chlorophenol p-Nitrophenol	[47] [48] [49] [50]
Wheat bran	Reactive blue 19 Reactive red 195 Reactive yellow 145	[51]
Tea waste	Methylene blue	[52]
Coir pith waste	Rhodamine B Acid violet Congo red	[53]
Coconut	Methylene blue 2,4,6-Trichlorophenol	[54] [55]
Orange peel	Acid violet 17 Direct Red 23 Direct Red 80 Methyl orange Methylene blue Rhodamine B Methyl violet Amino black 10B	[56] [57] [58]
Banana peel	Phenolic compounds Methyl orange Methylene blue Rhodamine B Congo red Methyl violet Amino black 10B	[59] [58]
Sunflower stalks	Methylene blue Basic red 9	[60]
Bagasse pith	Basic blue 69 Basic red 22 Acid red 114 Acid blue 25	[61]
Maize cob	2,4-Dichlorophenol Basic dyes Acid dyes	[62] [63]

specifies the needed volume to reach to desirable efficiency. Pore size defines the adsorbent potential uptake capacity and internal surface area, and it is divided into different ranges of sizes as macropores (pore size ≥500 Å), mesopores (between 20 and 500 Å), and micropores (pore size <20 Å) [64]. Pore size can have different structure based on the pore shape (straight, slit, or cylinder), size, and connectivity (crystalline, amorphous, etc.) [64]. One of the most important parameters in the design of adsorption equipment is the internal surface area that can range from

0.0005 to 3,000 m^2/g [65]. The selection of adsorbent with high internal surface area means decreasing the needed working volume, and hence, reducing the cost of the whole treatment system.

4 Thermodynamic of Adsorption

Adsorption is a mass transfer process that depends on the difference in adsorbate concentration between two different phases (liquid and solid in this chapter) and is related to the parameters effecting the mass transfer resistance like temperature, initial concentration, and pressure drop. This phenomenon can be either physical (physi-sorption) or chemical (chemi-sorption). The process is fully physical when van der Waals and electrostatic forces contribute to adsorption, and the interaction between the adsorbate and adsorbent is based on the polarization forces. Physical interaction, or the physi-sorption, is initiated with low activation energy, thus, it is weak and revisable even with multilayer adsorptions. This physi-sorption is an exothermic reaction (negative enthalpy and entropy differences) and the enthalpy is low (20 to 40 kJ/mol); therefore, it is always decreasing with increasing temperature [66].

Chemi-sorption, on the other hand, is a chemical reaction that involves strong chemical bonds and electrons transfer between the adsorbent and adsorbate. The endothermic reaction between the adsorbate and adsorbent is initiated with high activation energy because the chemi-sorption process increases with increasing temperature. The enthalpy of reaction is high (80 to 240 kJ/mol). The chemi-sorption process is slow and may be irreversible even with a monolayer reaction. Moreover, selectivity in chemi-sorption is favourable compared to the very low selectivity in physi-sorption [4].

5 Adsorption Mechanism and Kinetics

For the design of any chemical or physical based equipment such as adsorption, specific information must be available such as operating temperature, pressure, initial concentration, and flow rate [4]. This information is essential to specify, for instance, the volume of the equipment as well as operating cost, running cost, and the final cost of the whole unit operation. A key factor in all the mentioned parameters is the adsorption kinetic profile that needs to be specified through assessing the equilibrium time, rate of adsorption (chemi- or physi-sorption and desorption), and adsorption efficiency [67]. Adsorption equilibria is the time required to reach equilibrium between the rate of sorption (molecules adsorb onto the solid surface) and desorption (molecules released from the solid surface). Equilibrium data concerning water organic pollutants can be either found experimentally or available in the literature [67].

To find the rate of adsorption, different reaction models have been proposed and used for organic and inorganic water contaminants. However, most of the suggested and used models are based on the adsorption of gas–liquid systems due to the available information of the gas phase structure compared to that of liquid. Some of the eminent used models are discussed in the following sections.

5.1 Elovich Model

This model was first investigated by Zeldowitsch [68] and is based on the adsorption of CO (gas) on manganese dioxide (solid MnO_2). The Elovich model is derived to find the chemi-sorption kinetics of gases on heterogeneous surfaces. The model proposed an exponential relationship for the kinetic of the adsorption process as follows:

$$\frac{dc}{dt} = ke^{-bc} \tag{1}$$

where c is the amount of gas adsorbed (mmol/dm^3), t is the time (min^{-1}), k is the desorption constant (mmol/g min), and b initial adsorption rate (g/mmol).

By assuming the initial conditions are c is zero at t zero and c equal to c at time t this will lead to:

$$c_t = bln(kb) + blnt \tag{2}$$

The Elovich model has been widely used for fitting and describing the kinetic data of different organic compounds like the dye (Sumifix Supra Scarlet 2GF) on chitosan [69].

5.2 Pseudo-First-Order Model

This model proposes a first-order differential equation to describe the reaction kinetic of adsorption based on the solid phase capacity [70]:

$$\frac{dc_t}{dt} = k\,(c_e - c_t) \tag{3}$$

where c_t (mg/g) is the adsorption capacity at time t (min^{-1}), c_e (mg/g) is the adsorption capacity at equilibrium, and k (min^{-1}) is the rate constant.

Solving this equation with the initial conditions c_t is zero when t is zero and c_t is c_t when t is t can give

$$c_t = c_e\left(1 - e^{kt}\right) \tag{4}$$

This model equation was suitable to fit the adsorption kinetics of many organic contaminants in water. As an example, the adsorption of food azo dyes on chitosan [71].

5.3 Pseudo-Second-Order Model

In this model, the adsorption is assumed to follow a second-order behaviour to describe the chemi-sorption of elements onto solid surfaces. The pseudo-second-order model was derived based on the chemi-sorption of copper (a divalent metal) on peat [72].

$$\frac{dc_t}{dt} = k(C_e - C_t)^2 \tag{5}$$

where c_t (mg/g) is the adsorption capacity at time t (min^{-1}), c_e (mg/g) is the adsorption capacity at equilibrium, and k (g/mg min) is the rate constant.

The integration of this equation with the initial conditions $c_t = 0$ when $t = 0$ and $c_t = c_t$ when $t = t$ is giving

$$c_t = \frac{1}{\frac{1}{h_o} + \frac{t}{c_e}} \tag{6}$$

where h_o is the initial adsorption rate (mg/g min), which can be found from

$$h_o = kc_e^2 \tag{7}$$

The pseudo-second-order model has been widely used to describe the adsorption kinetics of different physical and chemical adsorption of organic and inorganic elements in water [73, 74].

6 Adsorption Isotherm Models

Most of the available theories of adsorption are based on gas–solid systems due to the accessible information of gas phase compared to that of liquid. However, for the applied science and designing and manufacturing of adsorption applications like packed beds columns [4], it is crucial to obtain the adsorption equilibrium data. For this case, semi-theoretical and empirical models have been used to fit the adsorption equilibrium capacity data like Langmuir isotherm [75, 76], Freundlich isotherm equation [77], and BET-theory [78].

6.1 Langmuir Isotherm

This isotherm is based on the dynamic equilibrium between the adsorption and desorption rates on the adsorbents surface, while the surface fractional coverage is a function of the adsorbate concentration. Langmuir isotherm was derived based on the following assumptions: only monolayer adsorption coverage occurs, a site can be occupied by one adsorbate molecule, adsorbent surface is uniform with equivalent activation energy in all sites, and a molecule ability of occupation is not effected by neighbours occupied sites [75, 76]. The mathematical derivation for this isotherm is

$$\frac{1}{q_e} = \frac{1}{q_{mK_LC_e}} + \frac{1}{q_m} \tag{8}$$

where q_e is the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g); C_e is the amount of unadsorbed adsorbate per unit mass of adsorbent is solution at equilibrium (mg/L); q_m is the adsorbent theoretical monolayer saturation capacity (mg/g); K_L is Langmuir equilibrium constant (L/g).

The Langmuir isotherm model has been widely used by different researchers to describe the adsorption isotherm of organics and inorganics contaminates in water [79].

6.2 Freundlich Isotherm

One of the most popular isotherms is the Freundlich model [77], which is an empirical equation that assumes heterogeneous adsorption. Freundlich model is based on the variation of the amount of adsorbed gas per unit mass of adsorbent. The mathematical expression of Freundlich isotherm is

$$q_e = kC_e^{\frac{1}{n}} \tag{9}$$

where q_e is the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g); k (L/g) and n (g/L) are the equation constants and their values are function of adsorbent and adsorbate at a given temperature; C_e is the amount of unadsorbed adsorbate per unit mass of adsorbent is solution at equilibrium (mg/L).

Taking the logarithm of both sides of Eq. (9) will lead to

$$\log q_e = \log k + \frac{1}{n}\log C_e \tag{10}$$

This isotherm has been widely used for the fitting of the adsorption of many organic and inorganic pollutants from water [80].

6.3 The BET Isotherm

This theory was firstly developed by Brunauer, Emmett, and Teller in 1938 [78]. It is based on the same assumptions of Langmuir isotherm with one exception which it allows multilayers adsorption on different parts of the adsorbent surface. In addition, adsorption rate is related to the frequency of molecules that strike the surface and the area of that surface. The mathematical expression for liquid–solid adsorption can be written as

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

where q_{e} is the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g); q_{BET} is the monolayer adsorption capacity (mg/g); $k_{1\&2}$ are the BET isotherm constants and based on the adsorbent and adsorbate (L/mg); c_e is the amount of unadsorbed adsorbate per unit mass of adsorbent is solution at equilibrium (mg/L).

This model has been also used to fit the adsorption of different organic and inorganic contaminants from water [81].

7 Adsorption Technology and Sustainable Development of Resources

Studies and researchers as well as field applications have shown that adsorption is a potential and suitable phenomenon for the treatment and decontamination of many organic and inorganic pollutants from water and wastewater. The technical flexibility, low energy constraint, and simple design and use are among other advantages of this phenomenon. The prospective future of nanomaterials as adsorbents have been highlighted in different applications especially water purification; for example, the adsorption of anionic dyes on nanosized alumina [82] or basic blue 3 dye on nanoscale zero valent iron [83]. The nano scale adsorption potential can give the opportunity of small-scale applications concerning drinking water and wastewater with a cost-effective purification.

Furthermore, the development and production of new green adsorbents based on wastes and byproducts from agriculture industry will add significant improvement to the effectiveness of adsorption as well as the reduction of dumped wastes by recycling these wastes back to the circular economy as new secondary materials. This will contribute towards the sustainability of natural resources by transferring these wastes to useful material for the environment and human health.

7.1 Adsorption of Emerging Contaminants

The technical development in analytical instruments has facilitated the detection of nano- and micro-gram concentrations of many elements especially personal care products, steroid hormones, pesticides, phytoestrogens, and other emerging contaminants [2]. The main source of these emerging contaminants is the industrial and municipal water sewages. It is well known that municipal wastewater treatment plants are lacking the effectiveness to control or treat these contaminants due to ageing. On the other hand, adsorption has shown the potential to decontaminate many of these emerging contaminants effectively using, for instance, activated carbon, zeolites [84], and cost-effective adsorbents [85].

8 Conclusions

In epidemic times when people health is under huge concern, clean water can be a key solution especially for hygienic or drinking purposes. Adsorption has been regarded as one of the most important methods for the purification of conventional and emerging organic pollutants in wastewater. This method has witnessing continuous development concerning adsorbents like food and agriculture wastes as cost-effective adsorbents as well as nano-adsorbents. This chapter highlights some spotlights of adsorption process as a cost-effective technique to decontaminate organic pollutants.

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Wastewater Treatment Using Biochar Technology

S. A. M. Abd El-Azeem

Contents

Abstract Water is one of the life requirements for individuals and societies, and it affects the global economy. The contamination of water is a worldwide problem that threatens the environment and poses abundant hazardous effects on the quality of water and aquatic species. Numerous techniques are known to remove the contaminants from wastewater. Biochar-based material has a novel ability to remediate wastewater due to its distinctive physicochemical properties. It has been considered a promising candidate material for the removal of pollutants through adsorption in the practical application processes. Researchers have reported numerous methods to modify the biochar to enhance their adsorption efficiency. Biochar is considered a

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cost-effective, environmentally friendly, and sustainable sorbent that has an extraordinary potential to proficiently remove potentially toxic organic and inorganic pollutants from water and wastewater. Adsorption is one of the most efficient techniques to remove pollutants from water and wastewater. These adsorption processes include several mechanisms for the removal of organic and inorganic pollutants as discussed in this chapter. Modified biochar, known also as engineered/designed biochar, has a larger surface area, high adsorption capacity, and predominant surface functional groups that gave a new type of biochar with a great application approach in different wastewater treatment plants compared to natural or pristine biochar. Additionally, the properties of biochar are depended on the type of feedstocks materials and pyrolysis conditions.

In this chapter, the currently available research regarding wastewater treatment using biochar technologies has been reviewed. Specifically, we have critically reviewed the (1) wastewater treatment; (2) production and characterization of biochar; (3) application of biochar for wastewater treatment concerning its role for removal of organic and inorganic pollutants; (4) capacity and mechanism of adsorbing hazardous pollutants from wastewater using biochar. Moreover, the economics and potential risks of biochar in wastewater treatment have been also discussed. This chapter demonstrates the predominant scientific chances for a comprehensive understanding of using biochar as an emerging technique for wastewater treatments. Finally, we also introduced some conclusions and recommendations for further work to enhance the efficiency of biochar for wastewater treatment.

Keywords Adsorption mechanism, Biochar, Pollutants removal, Wastewater treatment

1 Introduction

Water is a vital and crucial component of life since it is essential for the efficient functioning of the earth's ecosystems. Water pollution has recently increased because of rapid industrialization, urbanization, mismanaged of water resources, global warming, and rising of populations [1]. Specifically, around 80% of the global untreated wastewater is discharged and a large volume of untreated wastewater flows back into groundwater resources, lakes, polluting rivers, the environment, and oceans. Furthermore, this discharge polluted the water body with various organic and mineral (inorganic) pollutants such as dyes, heavy metals, surfactants, pharmaceuticals, pesticides, nutrients like nitrogen and phosphate, and personal care products from industries and municipalities [2]. Additionally, wastewater from urban areas is high in nitrogen and phosphorus compounds, which originate primarily from urine and industrial by-products. Most of these contaminants are extremely persistent in nature and would otherwise transform to refractory forms if left uncontrolled. The unregulated discharge of these pollutants into ecosystems is a subject of concern because of their significant negative effects [3]. Hence, wastewater treatment, reuse, and safe disposal have become critical for long-term sustainability. Wastewater treatment has recently become a difficult issue for living organisms and the biophysical environment [4]. Wastewater treatment, as one of the greatest critical concerns in environmental remediation programs, is urgently required to provide sanitary water for the ever-growing global population [5]. This finding agrees with the United Nations Sustainable Development Goals, "clean water and sanitation" required in the 2030s vision [6]. Conventional technologies are commonly applied to eliminate organic and inorganic pollutants from wastewater, these technologies include chemical precipitation, conventional coagulation/filtration, ion exchange, membrane separation, electrodialysis, and electrolysis [1]. These technologies are not only expensive, but they also produce secondary pollutants, and inadequate removal of pollutants, and they need high energy requirements. Several researchers have been received great attention for the adsorption process because of its easy operation and high efficiency. However, eco-friendly and low-cost adsorbent and efficient preparation procedures are important concerns in the adsorption process [7].

Biochar with rich carbon content is a product of thermal decomposition obtained from biomass feedstock with little or no oxygen [8]. Pyrolysis, hydrothermal carbonization, gasification, torrefaction, and microwave heating are all types of thermal decomposition that differ in thermochemical temperature and duration [9]. Biochar has some desirable properties such as high specific surface area, good ion exchange capacity, high porosity, rich oxygen functional groups, and multidisciplinary applications, indicating that it has a lot of potential in various sustainable environmental treatment applications, particularly wastewater treatment [10, 11]. It is usually produced from numerous biomass feedstocks including crop straw, municipal wastes, and industrial by-products [12]. Innovative ways for transforming organic matters into valuable materials like biochar as well as their subsequent applications have piqued interest in numerous research fields. Numerous investigators reported that biochar-based materials are extremely effective for wastewater cleanup. Modification of biochar using physical activation and chemical treatment has been applied to improve its sorption ability. Moreover, the modified biochar (engineered biochar) is highly efficient for removal of pollutants from wastewater than the unmodified biochar (pristine biochar) due to larger surface area and some other enhanced properties such as porosity, larger positive surface charge, greater surface oxygen-containing functional groups, and incorporation of surface amino functional groups [8, 13–19]. For instance, incorporating amino functional groups into the biochar surface by chemical processes or mixing biochar with amino-rich polymers (polyethylenimine and chitosan) enhances sorption ability by producing strong complexation between pollutants and the amino sites [20, 21].

Previous literatures have shown that biochar has a high adsorption capability for organic and inorganic pollutants from wastewater [22–28]. Due to the differing retention mechanisms of lead and atrazine, biochar produced from dairy manure could effectively remove both lead and atrazine at the same time with little competition [29].

Although biochar has shown to be useful in the treatment of wastewater, the potential negative effects of biochar addition should be also considered. Biochar may contain various heavy metals and other contaminants that may be released during its use in aqueous solutions, and severity of these negative effects is largely determined by the type of feedstocks used and the conversion procedure used to produce it. Thus, more research is required to investigate the stability of biochar and its relationship to the experimental conditions used during biochar production. In this chapter, we will look at some of the most recent research on biochar as a low-cost adsorbent for wastewater remediation. Specifically, the chapter covers details on the production and modification of biochar, as well as mechanisms of organic and inorganic pollutants removal from water and wastewater and some recommendations for future research.

2 Wastewater Treatment

Water is often the most misused and mispriced component in several sectors (domestic, industrial, and agricultural). Increased global population and industrialization, particularly in developing countries, have resulted in an increase in water demand and have caused the generation of wastewater that is contaminated with harmful pollutants such as oxygen-demanding substances, nutrients, pathogens, toxic inorganic and organic substances, dyes, and other cancer-causing chemicals. These pollutants caused serious problems to aquatic life and increased the algal growth and eutrophication [4]. Additionally, the amounts of these contaminants considerably differed based on the wastewater source. Furthermore, if wastewater was not correctly treated, hazardous or toxic pollutants might percolate into the ground, eventually contaminating the groundwater resources. According to United Nations World Water Development reports, almost 80% of all industrial and municipal wastewater is discharged into nature without being treated, resulting in water quality degradation either directly or indirectly [30].

Physical, chemical, and biological processes, as well as their combinations, are used in traditional wastewater treatment approaches. In brief, physical processes such as screens and filters are used to remove particles from wastewater. To remove complex pollutants, chemical and physical processes are frequently combined. Microorganisms are used in biological processes to remove and degrade toxic organic pollutants [31]. Wastewater treatment is most effective when done in phases, which usually include primary, secondary, and tertiary stages, as well as sludge treatment options [32].

Toxic compounds have been removed from water and wastewater using different treatment technologies (precipitation, coagulation/filtration, ion exchange, membrane separation, flotation, and electrochemical removal) [33]. Nevertheless, these technologies have significant problems such as partial removal, high operating and maintenance cost, and high energy requirements [33]. Several strategies for the development of cheaper and more effective technologies to remove pollutants from water and wastewater have recently been investigated. Therefore, biochar has concerned a lot of interest due to its promising role in many environmental management concerns. Many scientists in the wastewater treatment area have considered biochar-based technology because of the great requirement for lower costs, improved efficiency, and a more superficial method. Hence, biochar is a promising wastewater treatment that has been widely employed as an adsorbent to remove toxic metals, organic pollutants, and nutrients from wastewater [34].

3 Technology of Biochar

3.1 Definition

Biochar (BC) has not been provided a clear definition, but the International Biochar Initiative (IBI) (http://www.biochar-international.org/biochar), defines biochar as a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited condition [35]. The IBI divides biochar into three classes based on carbon content: Class 1 biochar (contains 60% carbon or more), Class 2 biochar (between 30 and 60% carbon), and Class 3 biochar (between 10% and 30% carbon). Biochar is a carbon-rich substance that can be produced from solid waste pyrolysis (agricultural solid waste and sludge from wastewater treatment plants). Biochar can be used as fuel and adsorbents in various ways, depending on the degree of thermochemical conversion. Other definitions of biochar include "biological charcoal" with various sizes based on the size of the initial biomass and BC is a type of carbon-rich pyrogenic materials.

Biochar is a solid substance produced from the pyrolyzing feedstock or biomass at 300–800°C under anoxic conditions. Biochar differs from charcoal and similar materials in that it is produced with the intent to be applied to soil to improve soil condition, to filter and retain nutrients from percolating soil water, and to provide carbon storage [36]. The term "pristine biochar" refers to biochar produced through slow pyrolysis of feedstock at temperatures of up to 700°C with or without oxygen ($\leq 2\%$).

3.2 Production of Biochar

Biochar production technology is quite simple and suitable for many regions of the world, but large-scale development requires optimization and economic evaluation. Figure 1 shows the simple procedure of biochar production. Firstly, raw material of feedstock is treated to several pretreatment procedures (dewatering/air drying, crushing, sieving, etc.), following which pyrolysis takes place. The final product is produced by simply treating the pyrolysis product. The main thermochemical processes used for biochar production include fast pyrolysis, slow pyrolysis

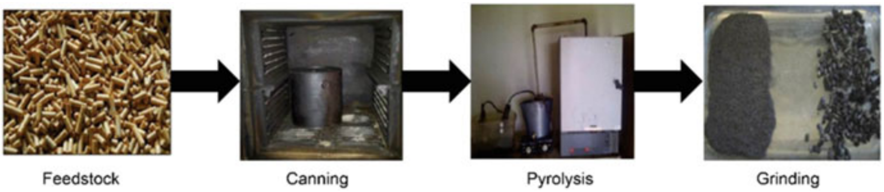

Fig. 1 Process of biochar preparation [37]

(conventional carbonization), flash carbonization, and gasification [18]. The constituents of feedstock (cellulose, hemicellulose, lignin, fat, and starch) are thermally degraded during these processes, resulting in three components: biochar (solid), bio-oil (partly condensed volatile matter), and non-condensable gases such as CO_2, CO, CH_4, and H_2. The bio-oil and gases can be captured to generate energy and the yield of biochar is determined by the pyrolysis process conditions [38]. In this regard, Ahmad et al. [39], Demirbas [40] observed that as the pyrolysis temperature increased, the biochar yield decreases. Slow pyrolysis (350–500°C and slow heating rate) produced higher yield of biochar (30%) than fast pyrolysis (600–700°C and fast heating rate) that produced 10% or less yield or gasification (700°C or above).

However, the materials should be pretreated in various ways (physical, chemical, and biological pretreatment processes) before producing biochar from various raw sources. Additionally, physical and chemical methods are used to increase the biochar's specific surface area, pore volume, surface chemistry, and functional agents [9]. Based on the pyrolysis temperature and time, the process is divided into three categories: slow, medium, and fast pyrolysis [17].

Different preparation methods of biochar affect the physical and chemical properties of biochar (yield, ash, specific surface area, pore structure, type and number of functional groups (acidic functional group, -COOH, -OH) and alkaline functional groups, and cation exchange capacity [11].

3.3 *Biochar Characterization*

The physical, chemical, and mechanical properties of biochar depend mostly on the sources and types of feedstocks, pretreatment methods, production conditions, i.e. residence time, temperature, heating rate, and reactor type, all of which significantly influence the capacity of biochar to adsorb various contaminants [34]. Biochar has a cheap cost, highly specific surface area, and a high capacity for adsorption. Modification and loading of nanoparticles onto biochar can also be used to create biochar composites. Biochar can help with nanoparticle dispersion and stability, as well as increasing the number of surface-active sites, which enhances the material's physicochemical properties. The adsorption performance and activation efficiency of biochar depend on physicochemical properties of materials that differ significantly depending on the type of feedstock and biochar production conditions.

Consequently, biochar production processes and control parameters greatly affected the physical and chemical properties of the resulting biochar [17]. The generated biochar may be classified into pristine biochars and engineered biochars (modified and composite biochars) depending on the technique and progress of the synthesis and modification procedures [16].

The physicochemical properties of biochars were greatly varied depending on pyrolysis process conditions. Hu et al. [41] revealed that pyrolysis temperature had a greater impact on biochar characteristics than pyrolysis time. When the temperature increases, biochar production decreases due to the presence of water and volatile organic compounds during the pyrolysis process [10]. The breakdown of acidic functional groups (carboxylic acids and phenols) in biomass may have resulted in a higher pH value in biochar produced at high temperature. This is accompanied by an increase in carbonization temperature and is associated to ash and mineral salts formation. For instance, Kwak et al. [42] reported that increasing the temperature of pyrolysis process led to an increase in electrical conductivity of produced biochars as a result of the decomposition of organic matter.

During the heating process, the chemical environment of the carbon in biochar is changed, resulting aromatic structures that are more resistant to microbial breakdown as compared to carbon present in most organic materials. Biochar's skeletal structure is mostly made up of carbon and minerals with varying pore diameter [43]. Micropores are responsible for surface area and high absorptive capacity, whereas mesopores are crucial for liquid–solid adsorption processes, and macropores are vital for aeration, hydrology, movement of roots, and bulk soil structure. Aromatic C-containing groups predominate in biochars generated above 350°C, which effectively adsorb heavy metals or toxic compounds. The aromatic rings' hydrogen, nitrogen, oxygen, phosphorus, and sulfur (H, N, O, P, and S) define the electronegativity of the biochar product that affecting the cation exchange capacity. Pyrolysis at temperatures exceeding 900°C induces deformation, resulting in the expansion of micropores due to the breakdown of walls between adjacent pores, resulting in an increase in surface area. As mentioned above, the nature, composition, and particle size of the feedstock and the processing parameters (temperature, heating rate, furnace residence time, and the type of pyrolytic reactor) affecting the quality of biochar or its characteristics. When compared to biochar derived from plant residues, biochar made from animal manure contains more nitrogen. Although the pore structure of biochar derived from plant materials is more structured, the fertilizer quality and heavy metal adsorption capacity of manure biochars were observed to be excellent [44]. For instance, higher heating rates and optimal feedstock-material processing temperatures improve the production of bio-oil, whereas slower rates and lower processing temperatures stimulate biochar production. Biochar composed of fixed or stable carbon, labile carbon and other volatile compounds, moisture, and ash components [44].

4 Biochar Modifications

The additions of biochar to sequester several pollutants are limited because of different parameters. The unmodified biochars have a poorer ability for contaminants removal than certain modified biochars, particularly at higher pollutant concentrations [45]. To excess the adsorption efficacy toward the removal of wastewater pollutants, several studies have been concentrated on biochar modifications through novel structures, surface characteristics improvement, and activation techniques. Increasing the surface area and porosity of biochar, enhancing the surface characteristics, and embedding other materials into the biochar matrix to generate useful biochar composites are all common modifications [19]. The activation of the initial biochar by physical and chemical techniques is referred to as the modification process. The properties of biochar are affected by the kind of activator, soaking duration, activation time, and activation temperature. Biochar can be modified in a variety of ways as described below [11]:

4.1 Physical Activation

The physical process includes treatment of biochar by gases (CO_2) and steam at the temperature above 700°C. In steam process, the partial combustion components are eliminated, and the porosity is enhanced, both of which increase the sites of sorption [19].

4.2 Chemical Oxidation and Reduction

Chemical oxidation means the oxidation of biochar surface using different oxidants such as HCl, HNO_3, H_2O_2, and H_3PO_4. This process led to an increase in oxygen-containing functional groups (i.e. -OH and -COOH), thereby increasing its hydrophilicity, enhanced adsorption capacity for polar adsorbate. For chemical reduction or alkali modification technique, the reducing agent (NaOH, KOH, and NH_4OH) was applied to reduce functional groups on the surface of biochar and enhance its non-polarity.

4.3 Metal Impregnation

The adsorption of certain heteroatoms or metal ions into the surface and pores of the biochar is referred to a metal impregnation. The specific surface area increased, and metal ions were coupled with the adsorbate to enhance the adsorption act. Iron, magnesium, silver, and zinc are common metal ions.

5 Application of Biochar for Wastewater Treatment

As mentioned above, wastewater has been a worldwide concern that is a byproduct of domestic, industrial, and agricultural activities. The quantity of pollutants from industrial wastewater and their types are substantially increasing due to the rapid development of the industry such as mining, smelting, battery manufacturing, dyes, and chemical industry [8, 9]. The contamination of agricultural wastewater is becoming increasingly serious problem because of the quick development of agricultural industry and huge amount of toxic heavy metals discharged into farmlands. Additionally, most pollutants in the domestic wastewater are nitrogen, phosphorus, and organic matter which could be utilized as nutrients for plant growth [9].

The adsorption process is preferred over other water and wastewater treatment technologies due to its lower cost, simple design, and ease of operation. Activated carbon (an all-purpose adsorbent) is commonly used to remove wide range contaminants from water and wastewater. The goal of current research is to modify carbon surfaces to improve their adsorption capability for specific contaminants. However, because of its greater costs, commercial activated carbon is not always widely used, especially in developing or poor countries. As a result, efforts are being undertaken to develop low-cost adsorbents using plentiful natural materials such as agricultural and industrial waste materials. Use of waste materials as low-cost adsorbents is desirable since it helps to reduce waste disposal costs and so contributes to environmental conservation.

Most research have recently been conducted to study the use of biochar to remove pollutants from wastewater. Because of the wide availability of feedstocks, low-cost, and promising physical/chemical surface features, biochar has a good potential to efficiently combat water pollutants. Biochar and biochar composites have been widely used in wastewater treatment to improve the efficacy of Fenton-like processes (activation of hydrogen peroxide and persulfate) as an advanced oxidation method for organics removal and wastewater decontamination [17]. Thus, biochars are regarded as a cost-effective adsorbent that is also being recognized as an environmentally friendly and effective sorbent for the removal of organic and inorganic contaminants from water and wastewater [9, 46].

5.1 Removal of Inorganic Pollutants

5.1.1 Heavy Metals

Heavy metals contamination of wastewater endangers food safety and disrupts the ecosystem. Heavy metals in wastewater have received great interest due to their potential for harming human health even at extremely low concentrations, as well as their ability to bioaccumulate and persistency in water. Surprisingly, biochar-based materials have gotten a lot of attention because of their low cost, high absorbance characteristics, and lack of environmental impact. It also has a porous structure and a high specific surface area, which allows for a considerable amount of space for heavy metals adsorption and ensures adequate interaction between the adsorbent and adsorbate. During biomass pyrolysis, several functional groups (hydroxy, phenolic hydroxyl, carboxyl, and carbonyl) are formed on biochar, and they are mostly influenced by the nature of biomass, pyrolysis temperature, and heating rates [46].

Several research have focused into the use of biochar (produced from plant and animal residues) in the removal of heavy metals from water and wastewater using an effective adsorption technique [9, 47]. The potential of biochar to adsorb heavy metals in water and wastewater is summarized in Table 1. In this regard, Dong et al. [49] found that sugar beet tailing biochar has a hexavalent chromium (Cr(VI)) adsorption capacity of 123 mg g^{-1} in an acidic condition. Biochar produced from fruit peel has been used to remove heavy metals from wastewater in previous research. For instance, Wang et al. [27] revealed that biochar derived from pineapple peel can adsorb Cr(VI), while in another recent study, Khan et al. [57] investigated the removal of Cu^{2+} and Zn^{2+} from simulated wastewater using muskmelon peel biochar. Rice husk biochar has some advantages, such as porous nature, heterogeneity, and metal ions adsorption characteristics, which make it useful for removing heavy metals from water and wastewater. This adsorption capacity was shown to be suitable for the removal of As^{3+} at 90% and Cu^{2+} at 93%, and other metals such as Cd^{2+}, Ni^{2+}, and Zn^{2+} metal ions from aqueous solutions [58].

Under 300, 500, and 700°C, tea waste biochar (TWBC) has maximal Cd adsorption capabilities of 8.90, 4.73, and 7.26 mg g^{-1}, respectively. The adsorption abilities of TWBC considerably decreased after acid washing that indicated that the soluble minerals in biochars played a key role during the Cd removal process. The functional groups at 300°C have an essential role in Cd removal, and the aromatic structure at 700°C may also play a role in Cd adsorption [59]. The pyrolysis temperature has the greatest impact on the effectiveness of Cd removal from water. For instance, Higashikawa et al. [60] showed that increasing the pyrolysis temperature during biochar preparation (sugarcane straw, rice husk, sawdust, and chicken manure + sawdust) from 350°C to 650°C resulted in higher Cd^{2+} removal from water.

Arsenic (As) is a very poisonous metal that can be found in drinking water and wastewater and is considered a human carcinogen (group I). The removal of As^{3+} and As^{5+} from water and wastewater is applied by the adsorption process using pristine (unmodified) biochar or modified biochar. In this regard, Van Vinh et al.

Table 1 Biochar utilization for heavy metals pollutants in water

Pollutant	Biochar type	Pyrolysis temperature (°C)	Effect	References
Arsenic As (III), As (V)	Waste leaves litter	800	Adsorption (endothermic and exothermic)	[48]
As (III and V) and Cd (II)	Sewage sludge digestate	350	Adsorption	[28]
Chromium	Oak wood	400–450	Sorption	[34]
Chromium	Sugar beet tailing	300	Electrostatic attraction: Reduction of Cr(VI) to Cr (III): Complexation	[49]
Lead	Dairy manure	200	Precipitation with phosphate	[50]
Lead	Sewage sludge	550	Adsorption due to cation release, functional groups complexation, surface precipitation	[51]
Lead	Sewage sludge digestate	350	Adsorption	[52]
Lead	Sawdust of white spruce Canola straw, wheat straw Manure pellet	300, 400, and 500 with and without steam activation	Adsorption, precipitation, ion exchange, and inner-sphere complexation	[42]
Copper	Crop straw	400	Adsorption due to surface complexation	[53]
Copper	Pecan shell	800	Precipitation of azurite or tenorite at pH 7, 8, and 9; sorption on humic acid at pH 6	[54]
Copper and zinc	Hardwood	450	Endothermic adsorption	[25]
Copper, cadmium, nickel, and zinc	Broiler straw Alfalfa stems	500	Adsorption onto inorganic fraction of biochar	[55]
Mercury	Soybean stalk	300–700	Precipitation, complexation, reduction	[56]

[61] observed that surface modification of biochar by $Zn(NO_3)_2$ impregnation increased the ability of As^{3+} adsorption from 5.7 mg g^{-1} to 7.0 mg g^{-1}. With biochar produced from paper mill sludge, the maximum adsorptive capacity of As^{3+} was 34.1 mg g^{-1} [14]. Because of the negative charge on modified surface biochar, pristine biochar has a lower capacity removing As^{3+} from water than modified

biochar. In aquatic environments, for example, KOH-modified sewage sludge digestate-derived biochar improved As^{5+} and Cd^{2+} sorption capacity from 1.6 μmol g^{-1} and 16.1 μmol g^{-1} to 8.5 μmol g^{-1} and 318.5 μmol g^{-1}, respectively compared to raw biochar [52]. This could be due to washing methods using ultrapure water after KOH treatment, which resulted in the release of phosphate and organic matter from the biochar, possibly leading to the oxidation of As^{3+} to As^{5+}.

Biochars can also be used to remove Pb^{2+} from wastewater. Biochars produced from fresh and dehydrated banana peels, for example, have Pb^{2+} removal efficiencies of 359 mg g^{1-} and 193 mg g^{1-}, respectively. Additionally, biochar derived from fresh dehydrated banana peels also performed well in terms of Pb adsorption [62]. Biochars produced at various process conditions from wood bark, dairy manure, tailing of sugar beet, wood from pine and rice husk have been proven successful in removing heavy metals such as Cd, Cr, Hg, and Pb from wastewater [63, 64].

The efficiency of biochar in removing heavy metals from water is depended on pyrolysis temperature and the type of biomass used. In this regard, Islam et al. [65] investigated the sorption capacity of papermill sludge (PMS) and rice straw (RS) biochars (treated with N_2 and CO_2 as purging gas,) for Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+}. They found that PMS biochar had higher adsorption affinities for the removal of Cu^{2+}, Ni^{2+}, and Pb^{2+} in an aqueous solution, whereas RS biochar had higher adsorption capacity for Cd^{2+}, indicating that the highest adsorption was related to metal specific. Biochar's specific surface area and pore volume were also increased because of the modification of biochar. For instance, Yin et al. [66] observed that the maximum adsorption capacity of cadmium from aqueous solution on $MgCl_2$-modified biochar (using *Pennisetum* sp. straw) was 763.1 mg g^{1-} that was 11.2 times higher than that of the pristine biochar. Batch adsorption experiments revealed that the Cd^{2+} adsorption data of $MgCl_2$-modified biochar are highly fitted to the Langmuir isothermal and pseudo-second-order kinetic models, indicating a chemical adsorption has played a significant role in the system.

5.1.2 Nitrogen and Phosphorus

Wastewaters are rich in nitrogen (N) and phosphorus (P) compounds. The concentration of N and P in agricultural, industrial, and domestic wastewater is rapidly increasing due to human activities and anthropogenic features. Increasing the amount of soluble N and P in water encouraged the growth of weeds and algae, both of which have negative environmental impacts. In the water system, inorganic N and P are often found as NH_4-N, NO_3-N, and PO_4^{3-}. These two elements are the primary causes of eutrophication in water. Water eutrophication is mainly occurred by the action of two or three different nutrients, such as NH_4^+, NO_3^-, and PO_4^{3-}, which might change depending on the season and the trophic status of water [67]. In this regard, Zeng et al. [68] reported that the coexistence of NH_4-N, NO_3-N, and PO_4^{3-} produces water blooms, whereas the coexistence of NH_4^+, NO_3^- has no effect on water bodies. Moreover, the coexistence of NH_4-N and PO_4^{3-} stimulates phytoplankton more than the coexistence of NO_3-N and PO_4^{3-}. Water eutrophication is a serious global environmental problem that causes the degradation of the water ecosystem and the damage of the self-purification capacity of water.

On the other hand, inorganic contaminants have been successfully removed from water bodies using aluminum oxide, fly ash, zeolite, activated carbon, and synthetic materials. However, the use of activated carbon, ion exchange resin, and zeolite as adsorbents requires expensive raw materials and economical adsorbent such as biochar is needed [69]. Biochar's multifunctional properties have increased interest in its removal of N and P from water and wastewater. Table 2 contains a list of references that describe the use of biochar to remove inorganic contaminants (N and P) from water and wastewater. Biochar has recently been used to be a new type of adsorbent for the removal of N and P from water and wastewater. In this regard, Yin et al. [77] reviewed the use of biochar in the removal of inorganic N (NH_4^+, NO_3^-) and P (PO_4^{3-}) from water due to the impact of actual properties of biochar on N/P adsorption as well as the possible adsorption mechanisms. They concluded that the adsorption of N and P on biochar is controlled by the collaborative interactions of several processes (physical and chemical). The physical adsorption is correlated to the porous structure and wide surface area of biochar, while chemical adsorption is related to the biochar types, the type and quantity of functional groups, and the compositions of biochar. Ion exchange and electrostatic adsorption between biochar surface functional groups and N are the main processes for N adsorption, whereas P adsorption is depended on the content and morphology of metallic compounds. Furthermore, the conditions of the adsorption solution exert effects on N and P adsorption. For instance, the adsorption of NH_4^+ using hydrous bamboo biochar was investigated by Fan et al. [78]. Their results showed that hydrous bamboo biochar is an adequate adsorption capacity for NH_4^+, with a maximum of 6.38 mM g^{-1}. The adsorption process was enhanced at higher ionic strength conditions and pH value was around 6.5, indicating that physical reactions possibly made contributions to the adsorption process such as electrostatic interactions, specific chemical bonds and surface precipitation to ammonium adsorption. This adsorption process was an endothermic and spontaneous adsorption process. Additionally, Hu et al. [41] investigated the relationship between NH_4^+ adsorption and physicochemical properties of biochars produced from various types of fruit peel (orange, pineapple, and pitaya), which were synthesized at 300, 400, 500, and 600°C with residence times of 2 h and 4 h. They demonstrated that the maximum adsorption abilities of NH_4^+ were related to biochars of orange peel (4.71 mg g^{-1}) and pineapple peel (5.60 mg g^{-1}), which produced at 300°C for 2 h. Moreover, the maximum adsorption of NH_4^+ (2.65 mg g^{-1}) was observed when used pitaya peel biochar that produced at 400°C for 2 h. Surface complexation, cation exchange, and electrostatic attraction were the most common adsorption processes.

Biochar modification is significant for increasing the ability of modified biochar for phosphate ion adsorption from wastewater. In this regard, Ajmal et al. [13] compared the efficiency of original (pristine) and modified biochars (magnetic modification) for removing PO_4^{-3} from wastewater. They observed that the ability of magnetic biochar for sorption process was twofold (25–28 mg g^{-1}) than that of

Table 2 Removal of inorganic N and P from water and wastewater by pristine and engineered biochar

Biomass feedstock	Treatment temperature, °C	Production method	Target pollutants	Initial concentration	Adsorption capacity	References
Oak wood Greenhouse waste Municipal waste Presscake from AD Oak wood Greenhouse waste Municipal waste Presscake from AD	400–450 400–450 400–450 400–450 600–650 600–650 600–650 600–650	Pyrolysis	NH^{4+}	1,000 mg NH_4^+ l^{1-}	129.4 ± 34.8 mg g^{1-} 118.2 ± 26.9 mg g^{1-} 137.3 ± 0.6 mg g^{1-} 105.8 ± 11.5 mg g^{1-} 123.5 ± 28.7 mg g^{1-} 99.3 ± 28.5 mg g^{1-} 128.3 ± 6.7 mg g^{1-} 136.2 ± 18.1 mg g^{1}	[70]
Wood biochar Rice husks biochar	600	Slow pyrolysis for a retention time of 10 h	NH^{4+}-N	1,400 mg N l^{1-}	44.64 ± 0.60 mg g^{1-} 39.8 ± 0.54 mg g^{1-}	[69]
Cassava peel	500	Bentonite powder and cassava peel mixed in water	NH^{4+}	200 mg NH_4^+ l^{1-}	Maximum 23.67 mg NH_4^+ g^{1-}	[71]
Oak sawdust Oak sawdust	300 300	Pyrolysis feedstock impregnated with $LaCl_3$	NH^{4+} NH^{4+}	25.7 mg NH_4^+ l^{1-}	3.12 mg NH_4^+ g^{1-} 4.13 mg NH_4^+ g^{1-}	[72]
Peanut shells/corn-cobs/cotton stalks	300/450/600	Low pyrolysis temperatures	NH^{4+}	50 mg NH_4^+ l^{1-}	15.8–17.6 mg NH_4^+ g^{1-}	[73]
Oak sawdust Oak sawdust	600 600	Pyrolysis feedstock impregnated with $LaCl_3$	NO_3^- NO_3^-	20.0 mg NO_3 l^{1-}	2.81 mg NO_3 g^{1-} 8.7 mg NO_3 g^{1-}	[72]
Peanut shells Sugar beet tailings	600	Feedstock impregnated with MgO (MgO nanoflakes)	NO_3^-	20.0 mg N l^{1-}	95 mg g^{1-}	[74]
Walnut shell and sewage sludge	600	Pyrolysis for 3 h with different ratios of the two feedstocks	PO_4^{3-}	50 mg l^{1-}	303.5 mg g^{1-} for pure sewage sludge biochar	[75]
Wood and rice husks	600	Pyrolysis magnetic modification by co-precipitation of Fe^{2+}/Fe^{3+} ions	PO_4^{3-}	10 g l^{1-}	25–28 mg g^{1-}	[13]
Oak wood Greenhouse waste	400–450 400–450	Pyrolysis	PO_4^{3-}	400 mg PO_4^{3-} l^{1-}	5.5 ± 19.0 mg P g^{1-} 18.7 ± 1.9 mg P g^{1-}	[70]

Municipal waste Presscake from AD Oak wood Greenhouse waste Municipal waste Presscake from AD	400–450 400–450 600–650 600–650 600–650 600–650				11.9 ± 4.3 mg P g^{1-} 7.8 ± 1.4 mg P g^{1-} 3.6 ± 6.1 mg P g^{1-} 9.1 ± 6.5 mg P g^{1-} 14.3 ± 0.6 mg P g^{1-} 30.0 ± 24.9 mg P g^{1}	
Cotton stalk	350	Biochar granulation and modification by ferric oxides	PO_4^{3-}	20 mg PO_4^{3-} l^{1-}	0.963 mg PO_4^{3-} g^{1}	[76]
Peanut shells Sugar beet tailings	600	Feedstock impregnated with MgO (MgO nanoflakes)	PO_4^{3-}	1,600 mg P l^{1-}	835 mg g^{1-}	[74]

the unmodified biochar (12–15 mg g^{-1}). Furthermore, the sorption of PO_4^{-3} on magnetic biochar is regulated by simultaneous mechanisms (electrostatic attraction, surface precipitation, and complexation), but this sorption mainly depends on electrostatic attraction for the original biochar. In addition, Kizito et al. [69] found that pristine and modified rice husk and wood biochar can adsorb NH_4^+-N from piggery manure anaerobic digestate slurry and can be employed as nutrient filters prior to discharge into water streams. The adsorption of NH_4^+-N was increased with increase as contact time, temperature, pH and increased the concentration of NH_4^+-N, but it decreased as biochar particle size was increased. The sorption process was also endothermic, following Langmuir ($R^2 = 0.995$ and 0.998) and pseudo-second-order kinetic models ($R^2 = 0.998$ and 0.999). The sorption of ammonium in aqueous solution increased when biochar was produced at a low pyrolysis temperature [73].

5.2 Removal of Organic Pollutants

Antibiotics are crucial group of pharmaceuticals, and their utilization in medicine has been growing at an increasing rate each year. Antibiotics are carcinogenic, endocrine inherent nature, and are categorized based on their chemical structure, biological activity, and mode of action. Antibiotic pollution has resulted in an increase in the number of antimicrobial resistant bacteria in the environment. Unfortunately, even little amounts of these compounds in the wastewater cause serious processing problems because they are extremely difficult to remove from wastewater and necessitate highly effective techniques for removal. The concentration of antibiotics in wastewater ranges from μg l^{1-} to ng l^{1-} [79]. The adsorption process is a low-cost and effective method for removing of pharmaceutical compounds from various sources of wastewater.

Similarly, with the ability of biochar as adsorbent for removal of heavy metals and inorganic N and P from wastewater, the ability of biochar to removal of pharmaceutically active compounds (PhACs) such as antibiotics from wastewater has been reported in the previous literatures [16, 22, 23, 79]. Engineered biochars (physically, chemically, and biologically modified biochar) and their composites have also piqued interest as a means of increasing pharmaceuticals adsorption efficiency. The utilization of antibiotics and their relationship with environmental contamination and their removal using biochar-based materials have been reviewed by Krasucka et al. [16]. In this regard, Wang et al. [80] investigated the adsorption of tetracycline (TC) from aqueous solution using biochar that produced from pyrolysis of rice straw at 300, 500, and 700°C. They found that the adsorption of TC was more effective onto biochar produced at higher temperatures than at lower temperatures. The relative increase of TC adsorption from 300°C to 700°C is 250%. Similarly, increasing the temperature of pyrolysis process from 400°C to 600°C increased the adsorption of TC by 25% in swine manure biochar modified with H_3PO_4 [24] and pinewood (an increase from 600°C to 800°C promoted TC adsorption by 56%) [81]. These results were linked to increase biochar porosity during pyrolysis process at higher temperatures. In addition, the interaction between the aromatic rings on antibiotic and biochar is responsible for the high efficiency. The ring structure of the antibiotic molecule promotes π–π EDA interactions that are mainly responsible for TC adsorption onto biochar [24]. As the synthesis temperature increase, biochar increases the degree of graphitization on its surface, the number of arene rings participating in the binding of π–π EDA to the TC molecule, and thus the major fraction of this form of interaction in the adsorption process. The binding of TC with modified biochar may be influenced by hydrophobic interactions, hydrogen bonding, and electrostatic interactions [82].

Sulfonamide antibiotics (sulfamethoxazole and sulfapyridine) are also used to prevent and control infectious diseases in human and animals. In this regard, Xie et al. [83] found that pinewood biochar pyrolysis at 500°C had a higher sulfonamides adsorption than that produced at 400°C. This is attributed to the improved π–π electron–donor–acceptor interaction with the carbon surface of biochar (500°C) due to the higher degree of graphitization. At pH 4, the maximum adsorption capacity of chlortetracycline from wastewater onto sugarcane bagasse biochar was 16.96 mg g^{1-}, while at pH 5, the highest adsorption efficiency of chlortetracycline onto corn cob biochar was accomplished with a maximum adsorption of 12.39 mg g^{1-} [84].

6 Adsorption Mechanism by Biochar

Because of its advantages of cheaper cost, simple operation, good selectivity, and use of readily accessible renewable adsorbents, the adsorption technique has been widely used to remove organic and inorganic pollutants for a long time among various water and wastewater treatment systems, [5]. For the removal of many types of pollutants from water and wastewater, a universal adsorbent (activated carbon) and other materials such as clays, waste, oxides and hydroxides, and synthetic materials are usually used. However, there is a significant difficulty with their use in terms of high production costs, environmental unfriendliness, inconsistent performance, and regeneration issues. Therefore, use of waste materials as low-cost adsorbents is desirable due to their contribution to waste disposal cost reduction, and thus environmental conservation [9, 47, 85, 86]. Specifically, biochar is expected to be a high-efficiency, low-cost adsorbent with properties like activated carbon. It is also being accepted as an environmentally friendly and effective sorbent for reducing organic and inorganic pollutants, making it a tool for reducing the toxic pollutants pose on the worldwide environment [87]. The adsorption mechanisms vary corresponding to the properties of both biochar and contaminants. Pristine biochar and modified biochar (engineered and composites biochar) have a significant potential for practical uses as adsorbents for the removal of various pollutants due to their good pore structure, large specific surface area, and rich surface functional groups. In this chapter, we will go through the major mechanisms in the removal of organic contaminants, heavy metals, and other pollutants by biochars (Figs. 2 and 3).

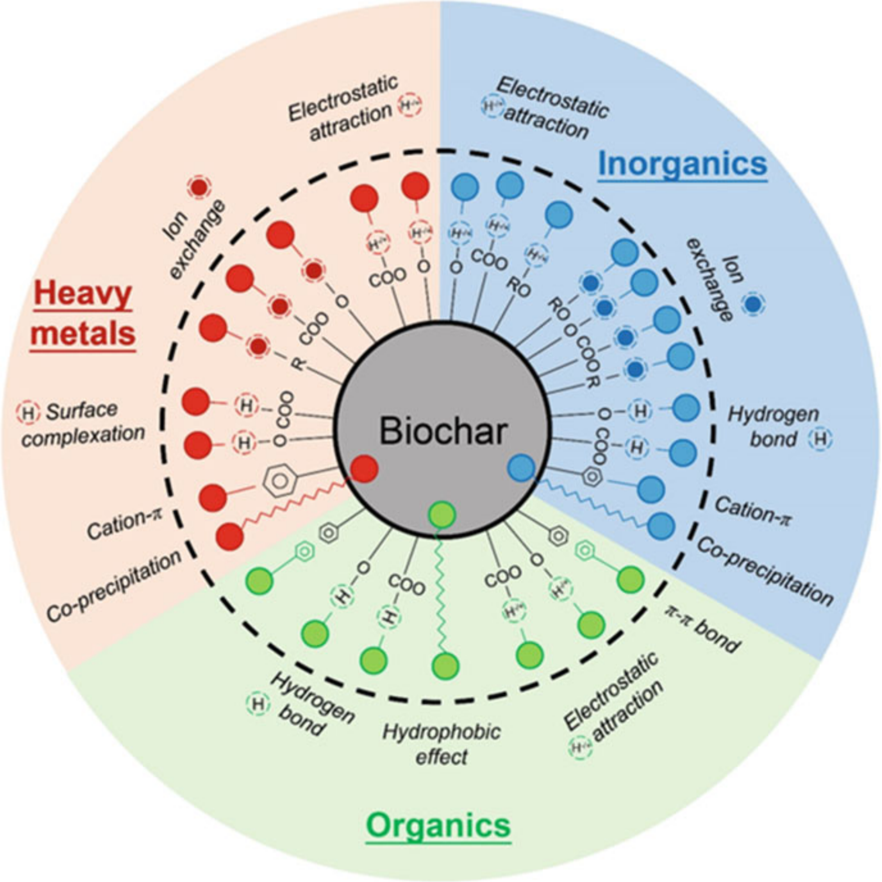

Fig. 2 Adsorption mechanisms of biochar for heavy metals, organic pollutants, and inorganic pollutants [17]

The two basic types of adsorption mechanisms are physisorption and chemisorption. The first mechanism is mostly based on biochar's physical properties, whereas the second mechanism consist of numerous processes such as precipitation, electrostatic interaction, ionic exchange, and complexion with functional groups [87]. The pH value, mineral content, porosity, functional groups on the surface, chemical structure, active sites, particle size, stable molecular structure, and specific surface area are all factors that affect physisorption and chemisorption mechanisms [87, 88]. Therefore, more details about these two mechanisms affecting the adsorption of the target pollutants will aid in producing specific biochars for specific pollutants.

The adsorption mechanism of biochar is significantly depended on the properties of biochar or modified biochar including mineral and organic structure in feedstock, surface functional groups, surface electrical properties, nanomaterials, porous

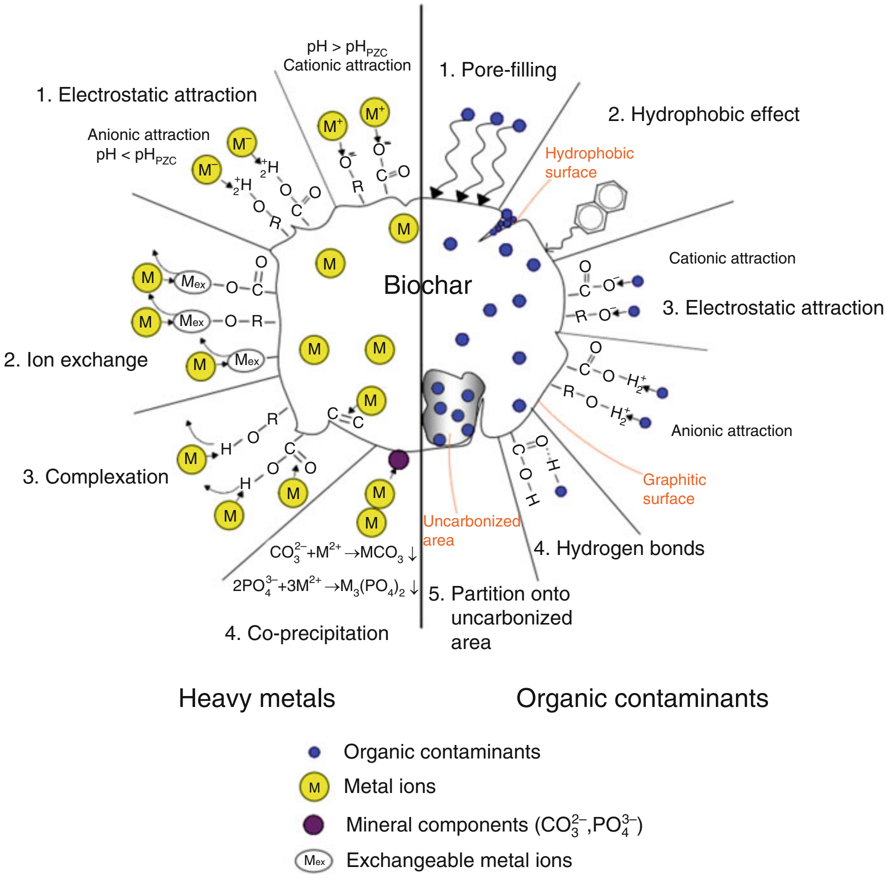

Fig. 3 Sorption mechanisms of organic pollutants and heavy metals on biochar [8]

structure, and the types of target pollutants (type and properties of pollutants), in addition the coexisting components in wastewater [8, 86]. Furthermore, the removal processes of heavy metals from water and wastewater using biochar varied based on the valence state of the target metal at various solution pH [89]. The following are four hypothesized biochar processes for removing heavy metals from water and wastewater: (1) electrostatic attraction of heavy metals with surface of biochar; (2) ion exchange on biochar surface between heavy metals and alkali or alkaline earth metals or protons; (3) complexation with π electron-rich domain or surface functional groups; (4) co-precipitation to form insoluble compounds [63, 89, 90]. Biochar's adsorption activity for various agricultural pollutants varies greatly. In agricultural wastewater, the interactions between heavy metals and biochar-based functional materials include some mechanisms such as hydrogen bonding, intermolecular interaction, electrostatic interactions, surface complexation, ion exchange, hydrophobic interactions, precipitation, inner-sphere complexes, π–π interaction, and/or cation-π bonding [86]. The existing acidic function groups (phenolic-OH and carboxyl C=O) were strongly related with the increase of NH_4^+ adsorption. Increasing basic functional groups on lanthanum biochar (La-biochar) improved NO_3^- and PO_4^{3-} adsorption, and PO_4^{3-} was also potentially related to the formed La_2O_3 [72]. Yin et al. [66] reported that the removal of Cd^{2+} by $MgCl_2$-modified biochar was mostly known to the mechanisms in this order: $Cd(OH)_2$ precipitation (73.43%) > ion exchange (22.67%) > Cd^{2+}-π interaction (3.88%), with negligible contributions from functional group complexation, electrostatic attraction, and physical adsorption.

Previous research confirmed that biochar formed from biomaterials has promising ability to remove organic pollutants [91]. Generally, the main mechanisms of organic contaminants sorption by biochar are pore-filling, hydrophobic effect, electrostatic interaction, and hydrogen bonds, that varying due to the physicochemical properties of the contaminants and biochar.

7 Economic and Environmental Benefits of Biochar in Wastewater Treatment

A few published literature for studying the cost-benefit biochars production from different materials. The use of biochar as adsorbent in the sorption of contaminants in wastewater treatment is regarded a significant economic factor due to the cheap prices of biochar production ($ 350- $ 1,200 ton^{1-}) compared to activated carbon ($ 1,100–1700 ton^{1-}) [92]. The cost of producing biochar varies based on the type of feedstocks or raw materials used, as well as collection and transportation, supply, distribution, and handling, the conversion technique, temperature, labor costs, and recycling and lifetime concerns. The lack of more information on all parameters of the biochar production led to difficulties in calculating the biochar's economic cost. In this regard, Haeldermans et al. [93] observed techno-economic analysis of biochar production plants for conventional (CPS) and microwave (MWP) pyrolysis using six different residue streams. They observed that minimal biochar selling prices in CPS range from € 436 ton^{1-}to € 863 ton^{1-}, and between € 564 ton^{1-} and € 979 ton^{1-} in MWP, indicating that CPS is more practicable than MWP. Another interesting factor is labor cost in biochar production, which is extremely high in the United Kingdom and the United States (about $ 5,000 ton^{1-}) and comparatively low in Philippines and India ($ 90 ton^{1-}). For instance, Kulyk (2012) estimates the cost of biochar to be between $ 50 and 200 ton^{1-}. The cost of biochar, according to the United States Biochar Initiative, is $ 500 ton^{1-}. Furthermore, Shackley et al. [94] provide a range of values for biochar production costs ranging from $ 0 to 682.54 ton^{1-}of biochar, based on the feedstock, the cost of pyrolysis unit, and other factors; a zero value here represents the assumption that the profitable of biochar production, and thus the biochar production cost is zero. Biochar's cost-effectiveness can be improved by utilizing a less expensive feedstock and more efficient production technique. However, due to applying the modifications and additional components in biochar, the

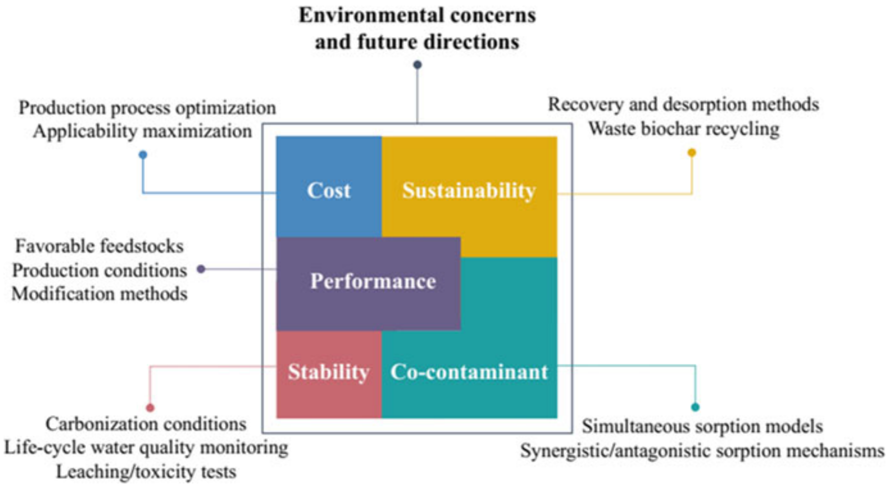

Fig. 4 Environmental interests and biochar research directions in the future [8]

production costs of modified biochar (Engineered biochar) increased. Consequently, future studies should focus on calculating the cost of producing engineered biochars to compare them to raw/pristine biochars. Figure 4 briefly illustrated the potential environmental concerns and propositional future research directions on proposed concerns.

Recycling of waste into biochar is of great environmental importance. This approach is consistent with recent trends of sustainable development and circular economy. In 2015, United Nations members adopted “The 2030 Agenda for Sustainable Development.” Two of 17 main objectives of the agenda are: (1) Goal 11 Makes cities and human settlements inclusive, safe, resilient, and sustainable through decreasing the adverse per capita environmental impact of cities, including by paying special attention to air quality and municipal and other waste management, (2) Goal 12 ensures sustainable consumption and production patterns through sustainable waste management including their prevention, reduction, recycling, and reuse. Nevertheless, it should be considered the possible threats and restrictions resulting from the utilization of these type of feedstocks [6].

Biochar is promoted as a long-term, sustainable, and easy-to-monitor method for global warming mitigation. Biochar has a lot of potential in terms of reducing global warming. Pyrolyzing feedstocks into biochar and storing it in the soil – often known as “carbon negative” farming – helps to keep carbon out from circulation for thousands of years, which would otherwise be released by decomposing biomass. Converting biomass into biochar yields a recalcitrant compound and diverts carbon from a fast biological cycle into a slower biochar cycle. Production of bioenergy with biochar carbon storage helps in producing carbon-negative energy [36]. Additionally, data reveals that storing C in biochar reduces the emission of 0.1–0.3 billion tons of CO_2 year^{-1} that economically may result in a reduction of cost for CO_2 offset [95]. Modified biochar has a better efficiency than other biochars as well as organic and inorganic sorbents, making it a highly suitable source as a low-cost and effective material for remediation of contaminated wastewater.

8 Conclusions and Future Work

In this chapter, we gave an overview of the extensive application of biochar in wastewater remediation and to remove popular and promising organic and inorganic pollutants. The production of biochar was discussed, and it gave the reader informative knowledge about the biochar modification (engineered biochar) to improve its performance and their importance for pollutants removal from wastewater. The modification of biochar increased the surface area, porosity, reaction activity, surface sorption sites, and forming functional groups as well as using engineered biochar as an adsorbent to remove inorganic and organic contaminants, nitrogen and phosphorus from wastewater. The complicated adsorption processes are demonstrated as a foundation of studies on biochar sorption behavior. The adsorption mechanism of biochar is significantly depended on the properties of biochar or modified biochar including mineral and organic structure in feedstock, surface functional groups, surface electrical properties, nanomaterials, porous structure, and the types of target pollutants (type and properties of pollutants) as well as the coexisting components in wastewater. On the one hand, electrostatic attraction (between heavy metals and biochar surface), ion exchange (between heavy metals and alkali or alkaline earth metals or protons on biochar surface), complexation with π electron-rich domain or surface functional groups, and precipitation to form insoluble compounds are some of the multiple mechanisms for removing inorganic pollutants (heavy metals). Pore-filling, hydrophobic effect, electrostatic interaction, and hydrogen bonds, on the other hand, are the key processes of organic pollutants sorption by biochar, which vary depending on the contaminants and biochar's physicochemical properties. Biochar application's environmental concerns are explored in terms of cost performance, stability, co-contaminant, and sustainability. Modification of biochar (Engineered biochar) led to an increase in their production costs because of the used modifications and additional components. Thus, future research should focus on estimating the cost of producing engineered biochars to compare them to raw/pristine biochars. Future study is being proposed to facilitate biochar more applicable.

Comparative research is really suggested to control the cost-effectiveness of biochar compared to other physical, chemical, and biological techniques that developed for the treatment of polluted waters and wastewaters. Additional studies are required to find ecotoxicological and environmental consequences of magnetic biochar after recycled. Economic analyses are also required to indicate the cost-effectiveness of such novel biochar. Conditions of biochar production can affect the presence of some environmental pollutants (polycyclic aromatic hydrocarbons, volatile organic compounds). Therefore, we required identical methods for quantitative analysis of these compounds in the biochar structure especially under environmentally relevant conditions. Additional research is needed to combine technologies like solar power technology with the pyrolysis process to produce biochar and reducing the operating costs. More studies are required to investigate the economic parameters of biochar production and application of the remediation of polluted waters and wastewaters. Only a few social studies have proven that using biochar is socially acceptable. However, further studies are required to have a comprehensive conclusion on this subject [96]. The treatments of biochar will certainly increase the production cost as compared with traditional activated carbon. Hence, future research should aim to get a balance between optimizing the production process and maximizing biochar's applicability to reduce costs [8].

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Part III

Biological-based Wastewater Treatment Systems

Biotechnology for Green Future of Wastewater Treatment

Marwa Darweesh, Amina M. G. Zedan, Antar El-Banna, Heba Elbasiuny, and Fathy Elbehiry

Contents

Abstract A scarcity of water supply and inadequate wastewater treatment combined with intensified industrial activity have led to increased contamination in lakes, rivers, and other water bodies in developing countries. Nevertheless, some common techniques for wastewater treatment are not practicable for developing countries. The biotechnological approach is considered an important tool for wastewater treatment. The biological method is the method of choice for nutrient removal from wastewater because of its low cost and environmentally friendly. Also, it can be respected as a dynamic force for integrated environmental protection that leads to

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sustainable development. In this chapter, we show the useful tools of biotechnology to wastewater treatment such as activated sludge, membrane bioreactors, media filters, anaerobic treatment, biosorption, biocatalysts, soil biotechnology, and hydroponic system that are feasible in the context of the developing countries in addition to the role of the genetic engineering in this context.

Keywords Biotechnology, Developing countries, Wastewater treatment

1 Introduction

Population growth and the diversification of its activities have resulted in an exponential increase in the generation of liquid and solid wastes in recent years. Wastewater is 99.9% water, while the other 0.1% is what causes concern. That 0.1% includes other materials that make up only a small portion of wastewater. However, these materials can be highly concentrated in water to endanger public health and the environment [1]. In developing countries, only a small quantity of the wastewater that comes from sewered communities is treated. The shortage of financial support is often the reason for the deficiency of wastewater treatment; however, it is also because of the ignorance of low-cost processes of wastewater treatment and the economic benefits of reusing treated wastewater [2].

Over 50% of the world's rivers, lakes, and coastal waters are dangerously polluted by untreated agricultural, domestic, and industrial wastewaters, and they have high numbers of fecal bacteria. This untreated wastewater causes major environmental damage and affects human health. Thus, wastewater should be treated for reducing the spread of excreta-related diseases and for mitigating water pollution and the consequential damage to aquatic biota. Therefore, effective wastewater treatment needs to be recognized, as an environmental and human health imperative [2]. There are a large number of technologies applied for wastewater treatment, and these have their advantages or disadvantages [3]. However, wastewater treatment within developing countries focuses on the treatment of sludge and disposal without respecting water treatment. Households are the most common wastewater type linked to combined discharges to sewage systems and then the septic tanks, commerce, industries, and storm water as in Fig. 1 [4].

Nowadays green technology processes are applied for wastewater treatment. Nonconventional and conventional methods are particularly selected based on the characteristics of wastewater to be treated [5].

An important part of wastewater treatment is a biological treatment that is recently identified as biotechnology. Microorganisms are isolated, subsequently chosen, mutated, and genetically engineered for effectual wastewater bioremediation. This can be operated in situ and ex situ treatments of contaminated wastewater. Biotechnology-based wastewater treatments involve bioaugmentation, bioreactors,

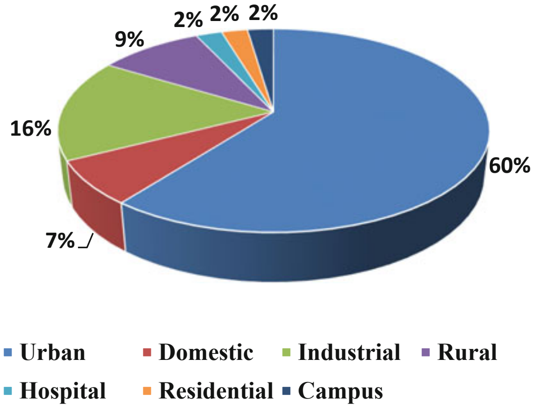

Fig. 1 Wastewater types in developing countries (as Gallego-Schmid and Tarpan, [4] found in the literature)

bioremediation, and phytoremediation. Treatment of wastewater can be done by aerobic, anaerobic, or mixing of both techniques [1].

2 Water Scarcity and the Need for Wastewater Treatment

Water is a scarce natural resource on our planet. The scarcity of water and pollution remain major challenges in urban settlements and rural areas in many developing countries. This is likely to increase with the increase in the number of the world's population, especially in countries where the rate of urbanization is at a faster rate. Because of rapid industrialization, the water pollution problem increased worldwide. These industries use large quantities of potable water for various industrial purposes and release them in the form of wastewater as a by-product [2, 6]. In addition to population growth, climate change, urbanization, and the expansion of agricultural activities and other industrial activities are among the factors that contribute to the scarcity of water in several countries throughout the world. With the population flow, urban areas in several developed countries face many social and environmental challenges. These include the lack of housing, poor sanitation, and deficiency of adequate energy sources, leading to limited access to fresh water [7].

The wastewater generated by different sources has major environmental concerns because it contains various hazardous pollutants, and the release of wastewater into the ecosystem leads to several harmful effects on both flora and fauna. Although it is not possible to stop releasing wastewater into the environment, it is feasible to overcome its harmful effects by treatment using various methods. The conventional treatment processes have been successfully applied sometime before, but these methods have many limitations [6]. Since viable alternatives, biological treatments are becoming more accepted day by day; they are eco-friendly, cost-effective, and energy-saving solutions for wastewater treatment. Biological wastewater treatment aims to remove the major contaminants from different wastewaters and enable disposing of them safely without posing threats to the public health and environment and to recycle them for many purposes [6, 8].

3 Green Technologies for Wastewater Treatment

The term “green technology of wastewater” indicates the adoption of ecological and sustainable approaches in wastewater treatment. Also, environmentally friendly materials, novel technologies, biotechnology, and new options for green chemistry should be utilized. There are different green methods for wastewater treatment such as mesoporous materials, nanocomposites and magnetic nanoparticles, catalysts, photo-Fenton, photocatalysis, electrochemical approach, and adsorption [9, 10]. Thus, green wastewater technology includes the development and expansion of the practices, processes, and applications that improve or replace the current technology and enable society to meet their requirements. Conversely, these alternative technologies substantially decrease the human impacts on the globe amid environmental scarcity and ecological risks. Developing clean alternate technologies to replace those that have negative impacts on health and environment and improving human manufacturing and expenses behavior to decrease the pollution resulted from releasing the waste release and contamination [10].

4 Biotechnology and its Role in Preventing Environmental Pollution

Biotechnology has been used increasingly to wastewater treatment for decades. This technology involves the manipulation of whole organisms; populations of organisms and nucleic components hold much promise for improving the quality of water and wastewater. Biotechnology provides various tools for manipulating the main processes of wastewater treatment. Also, biotechnology is “the integrated use of biochemistry, microbiology, and engineering sciences to achieve the technological utilization of the capacities of microorganisms and cultured tissue cells” [1, 11].

Bioaugmentation: A practice of introducing specific microorganisms to a system that enhances the desired activity to concentrate or accumulate specific compounds. It is achieved by adding oxygen, water, and nutrients [1, 11].

Bioremediation: The use of naturally occurring or genetically modified microorganisms to break down or degrade hazardous substances into less or non-toxic substances.

Bioreactors: Closed containers in which microorganisms are maintained under controlled conditions to create or destroy specific species [1, 11].

Phytoremediation: The use of vegetative species for the remediation of polluted sites/water bodies [1, 11].

5 Biotechnology in Wastewater Treatments in Developing Countries

In developing countries, wastewater treatments have recently improved; however, it is still a high priority and sustainability challenge. The methods based on biotechnology in wastewater treatments are activated sludge (AS), oxidation ponds, trickling filters, biofilters, and anaerobic treatment. Moreover, biotrickling filters, solid waste composting techniques, and biosorption are biotechnology applications examples in environmental engineering. It is essential in all methods to find appropriate microorganisms that will breakdown organic substances as well to accomplish the treatment steps in favorable conditions [12].

(a) *Activated sludge (AS)*: AS is a widely used biotechnique in wastewater treatment with the lowest cost among present techniques. The AS floc currently is primarily comprised of highly hydrophilic polar material and the zoogloea on AS floc has a strong adsorption capacity of pollutants. When heavy metals, organic pollutants, and other pollutants get close to the AS floc, they are adsorbed. Their adsorption is dependent on the characteristics of bacteria and the pollutant's attraction to organisms. This adsorption process involves both physical and chemical processes like complexation, ion exchange, coordination, non-polar micro-precipitation, oxide reduction, enzymatic mechanism, and electrostatic adsorption. It is found that the effects of AS were highly great on dyes, heavy metals, antibiotics, hepatic gas, and nanoparticles. It is also proven that the existence of extracellular polymers in sludge and the ions in sewage increased microbial adsorption [13].

(b) *Anaerobic treatment*: Anaerobic treatment of wastewater is primarily focused on the removal of organic carbon after treatment of N, P, and infectious propagules. Anaerobic bioprocesses are realized to have advantages compared with the physicochemical techniques due to their cost-effective and eco-friendly nature. Anaerobic digestion is an attractive method for sludge treatment. It has the following advantages: considerable reductions in solids, BOD and COD, nitrates and phosphate, production of biogas, and bio-fertilizer. The method has a cheap operating cost [14]. Upflow anaerobic sludge blanket (UASB) reactors can be used to treat sulfur-rich wastewater [1]. This process produces fewer quantities of biological excess sludge with high treatment efficiency, low capital costs, no oxygen requirements, methane production, and low nutrient requirements. Anaerobic digestion performs poorly at low temperatures and therefore needs to be linked to low-value heat recovery processes [1]. Also, anaerobic digestion of swine wastewater with acclimatized exogenous granular sludge was much better than with indigenous anaerobic sludge, tenth-day COD removal efficiency of 85% and 37%, respectively [15]. The better performance of acclimatized exogenous granular sludge was ascribed to the more efficient breaking down of volatile fatty acids and a stronger tolerance to the ammonia inhibition of swine wastewater [15].

(c) *Membrane bioreactor (MBR)* is the acronym for water and wastewater treatment processes which integrates a biological process with a membrane separation step. In general, membrane filtration is aimed at retaining biomass and other suspended materials to produce a clarified and disinfected permeate [16]. Membrane technology has got increasing significance in separation processes as a result of its advantages of modularity, easy to scale-up, lower footprint, and easy to incorporate with another process. A membrane bioreactor (MBR) has been counted as an attractive strategy for solving the limitations of the conventional AS process, such as poor sludge quality, biological instability, and low concentration of mixed liquor suspended solids [17]. MBR is used to efficiently removal COD and remove minor pollutants. MBR can be a suitable option to treat wastewater from different industrial and domestic sources. Although some present water treatment alternatives exceed the cost and energy efficacy of MBR technology, the potential advancements in bioreactor design and the efficiency of pollutant removal can make an MBR system a smart opportunity for wastewater treatment in nearby future [18]. Almost all the studies that tried to use MBR for polluted surface water treatment introduced activated sludge into the MBR system, which led to membrane fouling. To avoid this fouling problem of the membrane, an attached growth MBR could be an alternative technological solution wherein the immobilized microbes on the carrier could assist to keep biomass in the reactor which provides a good biodegradation rate [19]. Also, sequencing-batch membrane bioreactor (SMBR) could effectively remove antibiotics in swine wastewater and thus potentially reduce their ecological risk, SMBR could remove N60% of organic matter and nutrients [20].

(d) *Media filters (trickling filters)*: Biological trickling filter (BTF) processes have been successfully used for domestic wastewater treatment through the last few decades. The systems typically consist of a fixed bed of gravel, rocks, or plastic media where wastewater flows downward, and a layer of microbial biofilm grows on the media. The pollutants removal from the wastewater stream includes absorption and adsorption processes of organic and some inorganic compounds like nitrite and nitrate ions by microbial biofilm layer in aerobic conditions. As the biofilm layer gets thick, it ultimately sloughs off into the effluent and then forms a part of the secondary sludge. Usually, a clarifier (sedimentation tank) is needed to separate and remove the secondary sludge in the BTF effluents [21]. Biotrickling filtration has shown to be low cost-effective and efficient for removing volatile organic compounds. Microorganisms are the main component of BTFs, and the choice of certain strains has a significant influence on their effectiveness [22]. Also, the two-stage trickling filter can be applied as a low-cost desulfurization method to perform biogas purification and N elimination [23] (Fig. 2).

(e) *Rotating biological contactors (RBCs)*: A RBC is a fixed aerobic and anaerobic biological treatment film. It is commonly operated as a secondary treatment method of domestic and industrial wastewater. In RBC, disc biomass is liable for degrading the organic materials. RBC consists of a different size glass container (reactor) and chains of circular discs of polymer materials such as polyethylene,

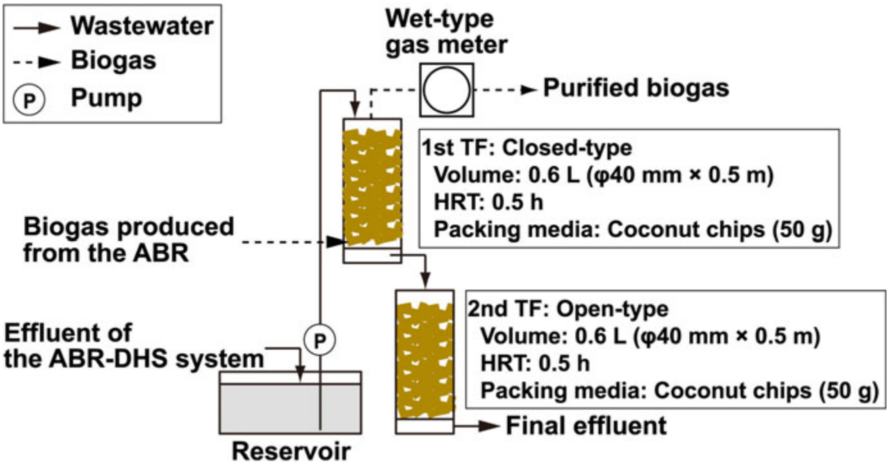

Fig. 2 Schematic diagram of the two-stage TF system. Source: [23]

polystyrene, acrylic plastic, and polyvinyl chloride. These discs are immersed in wastewater and rotated across it by a variable-speed electric motor. RBC consists of single or multiple stages. There are many parameters influencing the performance of RBCs such as wastewater temperature, organic loading, biomass, hydraulic loading, RBC media, rotational speed, dissolved oxygen levels in addition to medium submergence. RBC as a biological method offers many advantages such as cheapness, simplicity, process stability, and eco-friendly operations and also has a high interfacial area created in the rotating disc for establishing good contact between the pollutants and microbial species. Also, RBC increases the efficiencies of phenol removal by more than 56% [24].

(f) *Biosorption of heavy metals by microorganisms (fungi and bacteria)*: Recently, heavy metals pollution is one of the most serious environmental problems. Mechanisms of metal removal commonly include ion exchange, physical adsorption, complexation, chelation, and micro-precipitation. Biosorption is defined as the pollutants' passive uptake by dead or inactive biomaterials through several physicochemical methods. Biosorption includes many metabolism-independent processes that take place principally in the cell wall. The mechanisms responsible for metal binding vary based on the biomass type. Bacteria, fungi, algae (fresh and marine), animals and fruits skin, plant residues, biopolymers, and active sludge are examples of commonly used biosorpents for metal ions removal. It is worth noted that the majority of the published researches in biosorption worked on the removal capacity of a specific biosorbent toward one metal in synthetic solution under laboratory conditions. It was shown a good removal efficiency of these biosorbents toward different metals. Biosorption is considered one of the cost-effective biotechnologies for the treatment of high volume and low concentration complex wastewaters having heavy metal(s) in the order of 1–100 mg L^{-1} [25–27].

Fungi are well-acknowledged for tolerating and detoxifying heavy metals contaminated effluents. The biomass of fungi is usually used as biosorbents of heavy metals as polysaccharides in their cell wall enhance biosorption [28]. One of these biosorbents is *Saccharomyces cerevisiae* as is a natural, low-cost, and abundant sorbent and has the potential to be utilized as biosorpent of very low concentrations of Pb and Cd. This is useful in reducing the contaminations of foodstuff and drinking water with green technologies [29]. Chen et al. [30] reported that the resistant strains to Cu (II) and Ni (II) *(Aspergillus niger, Aspergillus awamori, and Aspergillus flavus)* were isolated from their contaminated habitats and have better suitability and application in bioremediation of heavy metals from the wastewater and sludge [31]. Moreover, *rhizobial* strain may play a role in stimulating metal uptake of the nodulated plant [30]. Also, Pseudomonas and Bacillus are broadly used to remove heavy metals from soil and wastewater because of their high metal binding affinities. Bacterial functional groups like carboxyl, hydroxyl, amide, sulfonate, and phosphonate groups are mostly concerned with the metal's uptake process from aqueous solutions [28].

(g) *Biocatalysts*: Biocatalysts are catalysts based on native enzymes. They received considerable attention because they showed relatively higher wastewater treatment efficiency and are considered a potential alternative to conventional methods. Therefore, it can be applied as a secondary or primary treatment. Enzymatic biodegradation presents high specificity, selectivity, and catalytic activity, mild reaction conditions, and few byproducts formation [32]. Industrial enzymes as protease, lipase, amylase which are non-toxic, complex, biodegradable protein molecules are commercially employed as biocatalysts in different industries such as detergent, paper, pharmaceuticals, textile, leather, food, beverages, biofuels, and in environmental applications. Usually, these biocatalysts are created by the cultivation of particular microorganisms that have activity against particular substrates. Thus, biocatalyst production with many activities is now required for working in complex substrates. Biocatalysts could be yielded by biomass anaerobic digestion such as food and agricultural processing wastes [33]. Biocatalysts give a persistent reduction for the microenvironment, and it is showing a good correlation with dye degradation in the anaerobic system [34]. Also, a multi-hydrolytic biocatalyst was used for pre-treatment of municipal waste activated sludge as the sludge has various complex organic molecules and thus this pre-treatment would assist to increase the usability of the enormous quantity of sludge for industrial purpose. The enzymatic pre-treatment of the sludge at improved conditions led to an increase of sCOD (32%), sProtein (53.57%), and sCarbohydrate (76.71%). Thus, a low-cost multi-purpose biocatalyst could be well produced from organic solid wastes and used to enhance the treatment of municipal waste activated sludge [33].

(h) *A soil biotechnology system*: Soil biotechnology (SBT) is a green technology for treating the wastewater effectively, eco-friendly, and less costly which uses the granular media such as soil, sand, and gravels or biological media such as bacteria, earthworms, and plants. Thus, this technology is useful comparing with the conventional wastewater treatment systems. This technology can maintain better socioeconomic and environmental benefits and thus is usually considered to be one of the most promising technologies to treat wastewater. It has many advantages such as its low cost, low energy demand, simple operation, minimum maintenance, low noise, and free of odor. It can also be used for the removal of heavy metals. The low maintenance cost, use of treated effluent, its environmental impact, and social acceptance are the main advantages of this technology [35, 36]. Arvindbhai and Vyas [37] reported that the overall efficacy of COD in the treated petrochemical wastewater from the soil biotechnology was decreased 81 to 82% (at 6 h detention time) and 88 to 91% (at 12 h detention time). It provides primary, secondary, and tertiary treatments all in one unit in a single evergreen facility opened to the atmosphere. The treated water over the soil biotechnology can be used for groundwater recharging, irrigation, construction, industrial processes, flushing, gardening, road/car wash, etc.

(i) *A bio-hedge water hyacinth* is an improved constructed wetland water hyacinth system using bio-hedges to phytoremediation of wastewater. The bio-hedge is an advanced form of shallow pond water hyacinth system in which plastic meshes type structures (bio-hedges) were provided to achieve higher biomass concentrations. The bio-hedge process is supposed to have many advantages over types of water hyacinth and elective ponds. In this system, the elimination of high pollutants can be achieved with simple and cheap tools. This exceptional process provides a pronounced cell mass content and microbial activity in treating wastewater. The particular arrangements of the bio-hedge system hinder the related problems of odor and insects because of the effective transfer of O across the root zone in addition to the short retention time (14 h). Thus, the bio-hedge system performance can offer quantitative advantage provided rather smaller footprints and lower capital cost. Water hyacinth can be used for wastewaters with higher levels of suspended solids. Bio-hedge water hyacinth is a suitable eco-technology process due to improved biofilm formation, reduced footprint, energy savings, and increased quality effluent [38, 39] (Fig. 3).

(j) *Hydroponic system*: Hydroponics is defined as the technique of plant cultivation without soil using only water and dissolved nutrients. It presents many advantages, including faster growth, high productivity, easy handling, and greater efficiency in water use [40]. The hydroponic system use for municipal wastewater treatment has a lot of advantages and it is more sustainable than another conventional biological system of wastewater treatment. It needs less space and can work with any type and volume of flows. This helps to eliminate human risks from parasites and transferable diseases consequently the reduction of weeds and soil-borne diseases. Moreover, the system does not need a particular drainage system making it cheaper for producing crops. Hydroponics can support the growth of almost several plant species and many types of planter beds can be applied ranging from channels, containers, pipes, etc. The system has proven to have many advantages through field crop production such as the accelerating of plant growth rate from 30 to 50% than a plant grown under similar conditions in the soil. Furthermore, the required land for crop production in the hydroponic wastewater treatment and reuse system is eliminated. Also, the risk of soil

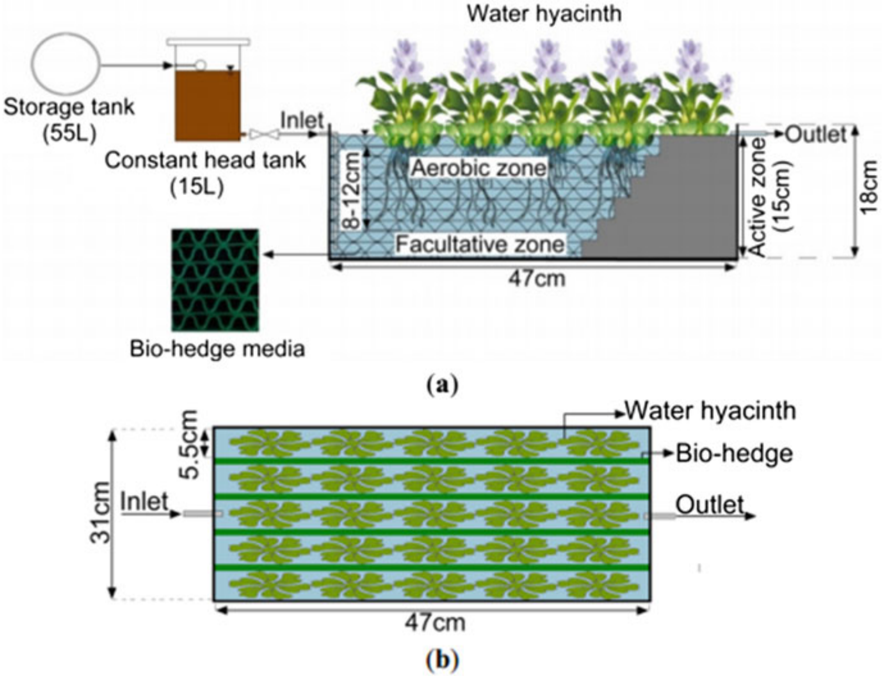

Fig. 3 Schematic diagram of the bio-hedge water hyacinth. Source [38]

contamination by salts and solids accumulations as a result of effluent reuse is reduced. Nevertheless, there are some limitations related to high setup cost and the technology can be quite demanding for small scale systems [41]. The system proved to be a cheaper method of wastewater treatment and its applications may offer an alternative to the problems of wastewater treatment in areas where modern systems are either unavailable or cost-ineffective. The removal of these contaminants is statistically significant. The removal of ammonia, nitrite, nitrate, total P, and fecal coliforms reached 87%, 96%, 99%, 87%, and 92%, respectively [42].

6 Genetically Engineered Microorganisms and Removal of Xenobiotic Compounds

There are a lot of technique including genetic engineering microorganism to improve treatment of wastewater and removing xenobiotic compounds, a definition of xenobiotics includes compounds which released in every compartment of the environment by the action of peoples and thus occur in a concentration which is higher than natural [43].

6.1 These Techniques Include

6.1.1 Gene Transfer

Gene transfer also called lateral gene transfer [44] where microorganisms may obtain genetic information from any related or phylogenetically populations in the community by horizontal gene transfer. Gene transfer in microbial includes transduction, conjugation [45, 46], and natural transformation. Cabezon et al. [47] reported that bacterial conjugation is one of the main mechanisms for horizontal gene transfer. Most genes correlated to the biodegradation of xenobiotics are found on catabolic plasmids. The first degradation plasmids of organic xenobiotics were reported just about three decades ago, since then many of such catabolic plasmids have been reported in the literature. Catabolic plasmids are generally rather large (>50 kb) and genetic reports have indicated that such catabolic plasmids have complete sets of transfer and catabolic genes. In a microbial population, plasmid-encoded catabolic pathways confer a further advantage for assistance horizontal transfer of the genes of catabolic, this contributes to a quick adaptation of bacteria and fungi to new aromatic pollutants existing in a particular ecosystem. Examples of catabolic plasmids, Pseudomonas sp. contain pVI150 catabolic plasmid. P. fluorescens contains CF600 and pL6.5 catabolic plasmids, R. eutropha JMP134 contains pJP4 catabolic plasmid, P. putida NCBI 9816–4 contains pDTG1 catabolic plasmid, P. putida R1 contains SAL1 catabolic plasmid, pPS12–1 in Burkholderia sp. and Alcaligenes sp. contains pSAH catabolic plasmid, which are implicated in the biodegradation of phenol, naphthalene, toluene, 3-chlorobenzoate, salicylate, tetrachlorobenzene, and 2-aminobenzoate sulfonates, respectively [48]. Furthermore, NAH7 and pWW0 from gammaproteobacterial Pseudomonas putida strains are IncP-9 conjugative plasmids that carry the genes for degradation of naphthalene and toluene, respectively [49].

Burlage et al. [50] have reported that pAC25, pSS50, pBRC60, and pJP4 catabolic plasmids carry genes that degradation of chloroaromatic. Shintani et al. [51] reported that plasmid pCAR3 is a carbazole-degradative plasmid from Sphingomonas sp. strain KA1. Retrospective studies indicated that mobile genetic elements play a major function concerning the in situ proliferate and yet de novo construction of pathways for catabolic in microorganisms, allowing microbial communities to rapidly adapt to new xenobiotics [52].

The formation of novel pathways occurs by the employment of catabolic genes or gene segments from different organisms into a new suitable host. This was later confirmed by the detection of relics genes precursor encoding the degradation of toluene, chlorobenzene-degradation flanking gene clusters were detected in two independently isolated bacterial strains [53, 54]. Horizontal gene transfer has allowed for the insertion of the transposon for TN4371 biphenyl from R. oxalatica, which circulated genes for biphenyl degradation [55]. Horizontal transfer of catabolic genes will improve bacterial adaptability and this could elucidate the heterogeneity between different E. coli strains belong to their ability to mineralize aromatic compounds [56].

Gene transfer from one organism to another has been applied for metal bioremediation. Genetic engineering can redesign microorganisms, consequently, biological metal sequestering systems are more tolerant to ambient conditions and they have a higher intrinsic capability and specificity, for example, the genetically engineered strain of E. coli JM109, which expresses a Hg^{2+} transport system and metallothionein used for removal Hg^{2+} from contaminated solutions or wastewater that are resistant to widespread treatments. The potential application of JM109 would be to eliminate Hg^{2+} from Hg^{2+}-contaminated soil and particulates by washing them with a Hg^{2+} chelator, then regenerating the chelator by passing the solution through a reactor containing the JM109 strain [57].

Genetically engineering bacteria such as E. coli and Moraxella sp. can accumulate up to 25-fold more cadmium or mercury than the wild type strain resulting from expressing a metal-binding peptide EC20 (with 20 cysteines) intracellularly or on the cell surface [58–60]. Expression of a metal-binding peptide (EC20 with 20 cysteines) in *Pseudomonas putida* 06909 not only enhanced cadmium binding but also removed the cellular toxicity of cadmium. More importantly, inoculation of sunflower roots with the engineered *Pseudomonas putida* 06909 resulted in a noticeable decrease in cadmium phytotoxicity also a 40% augment in cadmium accumulation in the plant root. Because of significantly improved growth characteristics of both the engineered *Pseudomonas* and plant, the use of this strain with organic-degrading capabilities may be a hopeful strategy to remediate contaminated sites with heavy metals [61].

6.1.2 Genome Rearrangements

Microorganisms live in nature as members of mixed and complex communities. The microbial communities in bioreactors of industrial wastewater have a new metabolic pathway and this phenomenon occurs in native ecosystems. The microorganisms compete for different carbon sources in these bioreactors and always have to evolve new metabolic abilities for survival. So, industrial bioreactors are a rich source of new biocatalysts [62]. To grow and survive in toxic environments, bacteria have evolved a difficult range of mechanisms at the molecular and cellular levels, including membranes, catabolic enzymes, responsible genes, protein synthesis machinery, and so on [63].

Genome rearrangements are a phenomenon observed in microorganisms concerned with the biodegradation of aromatic hydrocarbons, for instance, Clc-catabolic genes (genes are specialized for the degradation of chlorocatechols) appear to translocate as a separate DNA part from one plasmid to another. These DNA parts carrying the catabolic genes of plasmids pAC27 and pJP4 somewhat look like transposons (transposable genetic elements). Such catabolic modules have been reported for other catabolic genes and plasmids such as the lac and transposons [64]. A. calcoaceticus and P. putida contain groups of genes encoding pathways of ortho-cleavage. These genes were seen to be different from each other and similar genes of other microorganisms, possibly as a consequence of genomic DNA rearrangements in the related loci [64, 65]. Oltmanns et al. [66] isolated three 1,4DCB-growing microorganisms from sewage samples and river water as well as the construction of 1,4DCB-growing microorganisms by mating a benzene-growing strain with other strains that degrade chlorocatechol. The majority of the aromatic catabolic genes from E. coli are strictly connected to mobile genetic elements that could help their mobilization. So, the maopaa and mhp genes are located at chromosomal sites that are rich in IS30 and IS2 insertion elements. Furthermore, the presence of REP and BIME sequences within the hpa and mhp clusters, respectively, perhaps also contributes to the genetic rearrangements and spread of these clusters [56].

6.2 Genetic Engineering and Induction of Mutation Are Tools for Gene Activation

Recent progress in biotechnology has made novel opportunities for research in genetic engineering about biodegradation. The principle of engineering a microbial metabolism to break toxic compounds in water and soil is an appealing opportunity for remediating heavily polluted soil and wastewater. To utilize this component of microbial metabolism that results in polychlorinated biphenyls and polycyclic aromatic, hydrocarbons degradation requires a greater depth of understanding of the genes at play in the system. Identifying and targeting the genetic elements which control xenobiotic biodegradation in microorganisms can allow scientists to better attribute elements of the xenobiotic degradation mechanism to precise enzymatic activity. With this type of control, it would be possible to modify the process, upregulating the production of enzymes responsible for xenobiotic degradation [67]. To increase the ability of microorganisms to degrade xenobiotics, microbe improvement by gene manipulation should be accomplished. Gene manipulation can be classified into four categories: mutagenesis, DNA recombinant-based editing, posttranscriptional manipulation by gene silencing with RNA interference (RNAi), and endonuclease-based editing. Induction of mutation or genetic engineering of microorganisms has been reported in the literature. Bacillus amyloliquefaciens was exposed to diverse doses of gamma radiation and mutants isolated. The isolated mutants were grown on diverse polycyclic aromatic hydrocarbons. The results indicated that mutant MAM-62 (4) showed higher growth on the four polycyclic aromatic hydrocarbons sources especially on benzo-a-anthracene and pyrene when compared with wild type. This study indicated that B. amyloliquefacians wild type (MAM-62) was different from its mutant (MAM-62 (4)) in their intermediates and pathways [68].

Gene expression rate can be activated by the insertion of genetic elements that have been observed in the operons that are related to the degradation of aromatic compounds. The examples for this are, (1) constructing a mixture pathway in *Pseudomonas* strains for 2-chlorotoluene biodegradation via toluene dioxygenase to generate 2-chlorobenzyl alcohol, (2) the TOL higher pathway to alter 2-chlorobenzyl alcohol to 2-chlorobenzoate, and (3) modified ortho-cleavage pathway to mineralize 2-chlorobenzoate [69]. Walker and Keasling [70] reported that introducing the Flavobacterium- opd gene ATCC 27551 and the genes of p-nitrophenol degradation from *Pseudomonas* sp. ENV2030 into KT2440 strain for *P. putida* to construct a parathion-degrading pathway. As well, introducing the genes encoding the 2,4-dinitrotoluene (2,4-DNT) degradation pathway from *Burkholderia* sp. strain DNT into *Pseudomonas fluorescens* ATCC 17400, which could completely degrade 2,4-DNT was also reported [71]. In addition, it was also reported the using of *E. coli* as a host for cloning and expressing the genes encoding a novel partial reductive pathway for 4-chloronitrobenzoate and nitrobenzene from *Comamonas* sp. strain CNB-1 [72]. Chen et al. [73] reported cloning of catechol 2,3-dioxygenase (C23O) gene, responsible for the conversion of catechol to 2-hydroxy-muconic semialdehyde due to cleavage of aromatic C–C bond at the meta-position of dihydroxylated aromatic substrates, from P. aeruginosa ZD 4–3 in the E. coli expression system.

7 Conclusion

The need for water supply under increasing water contamination and water scarcity requires a practical solution, especially in developing countries. In this regard, adopting green technologies mean the direction toward sustainable approaches in wastewater treatments. Biotechnology is a promising way for achieving that. It is the integrated use of many sciences, i.e. biochemistry, microbiology, and engineering sciences to utilize the microorganism’s capacities and cultured tissue cells. Activated sludge among other biotechnological methods is widely used in wastewater treatment with the lowest cost. It is effectively adsorbed pollutants from wastewater. Additionally, anaerobic treatment has some advantages compared to the physicochemical techniques due to their cost-effective and eco-friendly nature. Membrane bioreactors, media filters, rotating biological contactors, biosorption by microorganisms, biocatalysts, and other techniques are also used as biotechnological methods. Furthermore, genetic engineering microorganisms are used also to improve wastewater treatment and remove the xenobiotic compound. Although there are many biotechnological methods to treat wastewater, there is a need to develop and adopt new other biotechnological methods that have many advantages in this regard.

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Wastewater Treatment Applications by Using Trickling Filter as a Low Energy Consumption Solution: Case Studies Worldwide

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Contents

Abstract The increasing environmental pollution because of wastewater generating in industry and municipal urban increases the need for sustainable and cost-effective treatment solutions. This helps to face many challenges in wastewater treatment applications and minimize treatment cost and energy consumption in the treatment phase. Therefore, the application of trickling filter technologies for years ago has provided valuable service in overcoming the above challenges. They have proven to be simple to operate, reliable, energy-efficient, and meet the treatment levels required for many discharge purposes.

This study demonstrates several applications of the trickling filters. These technologies were designed to treat different types of wastewater under different operational applications in different climate conditions. The operating experiences

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generally show in detail a high rate of efficiency removal of organic content (BOD, COD), nitrogen (TN, NH4), total suspended solids TSS, etc., as a secondary treatment level. Even Trickling Filter is a simple technology, there is a lack of mathematical design and operation experience, as trickling filter mechanics are poorly understood. Therefore, some design criteria, including operation, low energy requirements, and high treatment efficiency were demonstrated and summarized in this Chapter.

Besides, the trickling filter application in this study shows low energy consumption, compared with the activated sludge system solution. Therefore, the case studies in this chapter were considered as the best practice of trickling filter application especially in a hot dry climate where such experience is limited.

Keywords Biodeck plastic filter media, Biofilm, Biological treatment, Denitrification, Design, Nitrification, Operation, Trickling filter

1 Introduction

A trickling filter is an old wastewater treatment technology using a biofilm system that depends on the biological treatment process in wastewater treatment. The trickling filter treatment process has been used in wastewater technology since the turn of the century [1]. Trickling filter usually consists of a cylindrical container/ structure and is filled with special packing elements (e.g., plastic elements, stones, textile, etc.). The wastewater trickles evenly over the packing, which is covered with a thin biofilm. The treatment process depends on the surface contact between the biofilm and wastewater [2]. Therefore, the microorganisms ideally process the dissolved water constituents into water and carbon dioxide for BOD reduction and nitrification of nitrogen compounds [3]. In order to prevent any clogging of the trickling filter due to excessive bacterial growth and solids, a certain flow rate and recirculation rate of wastewater are necessary as a rinsing agent [4]. Therefore, the recirculation rate of treated wastewater may be important to keep the bacteria wet, to increase the oxygen demand also to increase wastewater treatment efficiency in the treatment unit. Depending on the inflow wastewater organic load and the bio-filter filling material, it may be necessary to determine the optimum recirculation rate [5]. The required oxygen for the BOD reduction and nitrification stage is taken up by the wastewater when the trickling filter trickles out of the air. This happened because of the ventilation as the filter material is connected to the atmosphere from the top and bottom of the treatment unit [6]. Generally, the normal ambient air is sufficient for the bacteria, artificial ventilation is rarely required. When the wastewater flows through the trickling filter, groups of bacteria dissolve and contaminate the drain water with undissolved particles. These are separated in downstream clarifiers or sieves. This makes the trickling filter working in its full capacity to increase treatment efficiency and to avoid any clogged by coarse substances and other particles [7]. A trickling filter system usually consists of a good pretreatment stage, the trickling filter body as a biological treatment stage by biofilm system, and a final sedimentation tank. Typically, trickling filter components are: distribution system, trickling filter construction, filter media, underdrain system, and support material.

1.1 Treatment Process of Trickling Filter

A trickling filter is a biological treatment technology by biofilm. It needs very good pretreatment efficiency to keep the biofilm in biological treatment as the second stage works in its full capacity. In the biological stage, there is a reduction of the levels of BOD and ammonia within the wastewater to levels that can be discharged into watercourses or reused it for irrigation purposes, without compromising the condition of the receiving waters [8]. Therefore, the trickling filter application under several organic and hydraulic loads depending on several designs and operating factors was requested to test its efficiency. Wastewater supply can operate by gravity feed mode without using any additional energy. Therefore, the application of a trickling filter with an appropriate topographic layout of filters can save energy consumption and capital cost. There is the only aerobic water treatment process that offers this advantage. The organic loading rates applied to secondary filters are typically between 0.2 kg BOD/m^3/day and 1.0 kg BOD/m^3/day – depending on the required effluent quality after the GEA-Water company. The application of this filter gives high-level treatment efficiency and nitrification rate to meet tighter ammonia discharge consents. This type of treatment by biofilm system with the nature and type of biomass that establishes itself within tertiary nitrification filters produces fewer amounts of sludge. According to this effective application of the filter, and due to combining of many operation factors like long retention times, crossflow structure, and high specific surface area, this produces high treatment efficiency and nitrification rate with low ammonia concentrations in the effluent [9].

1.2 Typical Application Area

Trickling filters can be designed to treat municipal, domestic, and industrial wastewater in many conditions, to meet stringent standards of treated water discharged into water bodies or/and for irrigation purposes [10]. Therefore, they are the ideal process for good and cost-effective add-on stage either to decrease the organic load in the biological treatment as secondary or advanced treatment stages to meet the discharge standards dictated by legislation and to meet future needs of treatment efficiency and low layout and treatment cost [3].

Also many industrial wastewaters can be treated by using such kind of technologies, although many industrial wastewaters in general are characterized by special details like temperature, salinity different PH values, high and hard organic load

[11]. Trickling filter technology can treat wastewater by producing a small Sludge quantity and high energy efficiency. In addition to saving of volume plant by using large biofilm service area and easy operation/supervision. In addition, the filters are particularly efficient to reduce wastewater temperature through the filter bodies as an additional effect of requiring partial treatment to meet consents for discharge into municipal sewers.

There are many types of filter media applied to produce BOD reduction, nitrification, and denitrification but the replacement of existing rock filter media by plastic media is one of the cost-effective high treatment levels; this is due to the open media structure and design in addition to high effective surface area [12]. Therefore, applying plastic media designed by several companies in Germany increases around 3 times the organic load and up to 10 times the hydraulic flow than to rock media. Depending on the above, many replacements of filter media in treatment plants increase the treatment efficiency by increasing the surface area and material of filter media as an effective solution.

High treatment efficiency can be achieved by using high rate trickling filters by increasing the surface area of connection between wastewater and biofilm on the filter media. They are normally designed to reduce the BOD loads between 50% and 70%. This is by applying organic loading rates of 1.0 kg BOD/m^3/day up to 5.0 kg BOD/m^3/day. The energy input is less than 0.2 Kwh per kg reduction in BOD. It was recommended by several researches that vertical flow media structure has the optimal structure to steadily expel the excess sludge and for good ventilation or aeration [13].

In modern technologies, the trickling filter is composed of plastic media filter of PP or PVC material. The influent pump station pumps wastewater through an overhead sprayer onto the filter bed to distribute it under control of speeds, where bacteria and other microorganisms have formed a biofilm on the filter media surfaces. In normal case the trickling filter is operated by natural ventilation system as no need to build an aeration system (Fig. 1).

1.3 State of Research and General Design Criteria

Germany and other countries have many years of experience in trickling filter technology applications to adapt to climate change. The resulting design specifications ensure adequate treatment performance and, as a rule, safe operation in these regions. However, since biological processes are strongly temperature-dependent, it is reasonable to assume that the design approaches applicable to temperate climates are only suitable to a limited extent at high temperatures and may lead to over-dimensioning with regard to wastewater treatment by biofilm systems in hot climates [14]. The design approaches most commonly used in the literature for the design of single-stage trickling filters with and without nitrification are based on long-term experience or empirical mathematical equations, which were obtained from the observation of performance curves and degradation processes in the trickling filter.

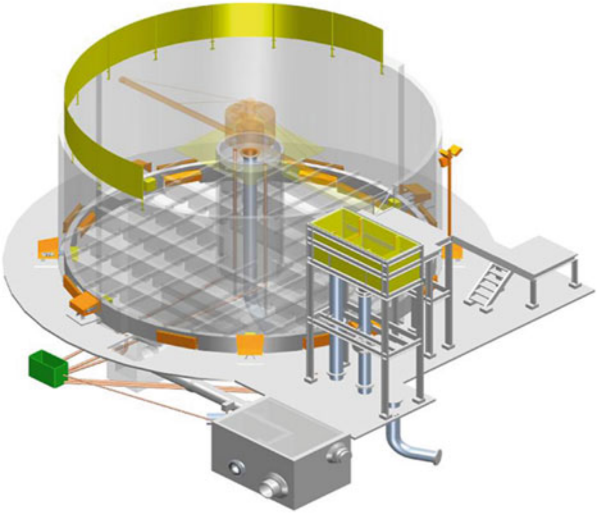

Fig. 1 Components of trickling filter and its profile. (**a**) Trickling filters components; (**b**) Profile of trickling filter

The German design specifications can be found in the worksheet ATV-DVWK-A 281 [15]. The European standard EN 12255-7 [16] applies in Europe, which is available in different languages but only provides very general information. In the United States, similar approaches are published in two fact sheets by the US, which applied by the Environment Protection Agency [17, 18].

2 Materials and Methods

2.1 Parameters Analysis

The locations of trickling filters in this study (as biological wastewater treatment applications) are selected in a goal-oriented manner, so that the approaches proposed in this study of trickling filter as wastewater technology in different countries can be systematically checked and promoted. Therefore, an inventory data evaluation is also provided for this study from 2 different trickling filter systems with sufficient data. Good data quality can be evaluated systematically in detail to present the treatment efficiency of the trickling filter as cost-effective solutions for different applications, rehabilitation purposes in different scales and different climates.

WWTPs	The aim of study
Trickling filter: Managua	Operation of WWTP-Managua in the higher load range (BR: 1.2 kg BOD/m^3 day) of municipal wastewater, and it is installed in 6 parallel nitrification trickling filter units

(continued)

WWTPs	The aim of study
	Evaluation of treatment performance of the trickling filters to meet the designed limitation was an important issue to ensure the treatment efficiency
Trickling filter: Al Awir: Dubai	The wastewater treatment plant in Dubai has 15 trickling filters to treat municipal wastewater of Dubai. One of the existing trickling filters was converted by GEA Water Technologies after the performance of the systems filled with filter material was unsatisfactory. Therefore, the optimization of aeration, water distribution, and improvements of notification were done, under specific operations (not only with regard to nitrification but also for improving the ventilation in the hot season)

This study evaluates the treatment efficacy of two different trickling filter types. The filter media used technical solution for hot climate as an effective cost solution. All parameters were tested (biochemical oxygen demand (BOD), total suspended solids (TSS), chemical oxygen demand (COD), total nitrogen concentrations) to monitor the operational factors and treatment efficiency. The physical, chemical, and biological parameters are monitored for each trickling filter effluent in this study and were also determined for evaluation. This leads to more reduction in concentrations of ammonia-nitrogen, nitrite-plus nitrate nitrogen, total phosphate, and BOD concentration in tow trickling filters for different places and climates. The existing data could be queried and included in the comparison with other results. The selected trickling filters were implemented, designed, and tested by GEA Water Technologies. Influent and effluent flowrates, BOD, COD, TN, TSS concentrations, and temperatures were collected from the above trickling filter plants where they were obtained.

2.2 Background Theory; Design BOD and Nitrifications Trickling Filters

Especially in emerging and developing countries, cost-effective wastewater treatment technologies are needed to be reliable in operation and also to be used by less skilled personnel. On the other hand, treatment systems must be robust which have easy operation and maintenance. They should have a low cost–benefit ratio as well as flexibility and good expansion options. All of these approaches (German ATV-DVWK-A 28, European standards EN 12255-7, and U.S. EPA 832) assume that the organic load is decisive for the treatment performance of a trickling filter. Depending on the desired treatment goal and the filling material, permissible surface loads are recommended, from which the trickling filter volume can be calculated. A major disadvantage of these approaches is that the influence of different climatic conditions, in particular the temperature, is not taken into account when determining the volume. Experience has shown, however, that an increase in temperature leads to an increase in the growth rate of the microorganisms and thus to an increase in treatment performance. Since the above design data are based on experience in temperate climates, their use can lead to oversized systems in hot climate effects. Therefore, concepts cannot be easily transferred to regions where there are other climatic conditions under the premise of high economic efficiency. Other mathematical model approaches for the design of trickling filters take the temperature into account, but the deviations between the models are considered at high temperatures. The Velz equation [19] is important with regard to trickling filters for the BOD reduction. In general, the previous mathematical model approaches to assess the temperature effect may only be used to a limited extent. Incorrect dimensioning cannot be ruled out. The existing design approaches can basically be divided into two groups. On the one hand, there are design approaches that contain empirical values from the observation of existing systems. This group includes the design approaches of ATV-DVWK worksheet A 281 (ATV 2001, BS EN 12255-72006, U.S. EPA 832-F-00-0142000 & U.S. EPA 832-F-00-0152000a). On the other hand, some approaches based on mathematical or empirical equations, such NRC equation [20], the Velz equation [5], and the Approach [21], are used in Trickling Filter calculation.

Due to the often large fluctuation ranges of these values, a relatively high degree of freedom can be expected when using this information to dimension a new trickling filter. BS EN 12255-72006, U.S. EPA 832-F-00-0142000, and U.S. EPA 832-F-00-0152000a summarize typical load and operating values of existing trickling filter systems. In some cases, the specific surface and empirically determined filling material constants are taken into account. Some of the algorithms are limited to the solved BOD. This can lead to a large volume deviation. The ATV-DVWK worksheet A 281 [15] does not contain a design algorithm but specifies room loads. Possible influencing factors such as different material structures, the influence of the fill level, and others are not taken into account or are excluded by being guided by the worst case. By using this approach, hardly any volume deviations are to be expected. Worksheet A 281 contains information on recirculation, area loading, and washing power. Designing trickling filter systems for complete carbon removal with or without nitrification using worksheet A 281 thus enables a safe but not optimized dimensioning. A plausibility checks with the information in BS EN 12255-72006, U.S. EPA 832-F-00-0142000, and U.S. EPA 832-F-00-0152000a is definitely recommended. Highly loaded trickling filters are not taken into account in worksheet A 281 because the maximum permissible volume loads contained therein are limited for operational safety reasons. If heavily loaded trickling filters are designed for partial cleaning, the information in BS EN 12255-72006 and U.S. EPA 832-F-00-0142000a can be used. Since the design approaches based on empirical values are based on findings from regions with temperate climates, they must be used critically in hot climates. Due to the strong influence of temperature on the biochemical and physical processes in the trickling filter, over-dimensioning can be expected at higher wastewater temperatures [4]. The influence of temperature is only taken into account in approaches that are based on mathematical or empirical equations. However, due to the relatively little experience with systems at high temperatures, there is great uncertainty when adjusting the temperature coefficients. A suboptimal dimensioning cannot, therefore, be ruled out.

The NRC approach was designed exclusively for the design of random media-filled trickling filters for BOD removal completely or partially. According to [22], a high organic load elimination effort can be achieved by trickling filter technologies, this is by over-dimensioning trickling filters. The temperature can be taken into account by correcting the treatment performed using the formula kT = k20 · Θ (T-20). However, a correct interpretation cannot be guaranteed.

The Velz equation [19] is available for the design of plastic-filled trickling filters for complete or partial BOD removal. The influence of temperature can be also determined by the above formula, the formula with a correction of the empirical coefficient k20 must be taken into account. A major disadvantage of this approach is that the coefficient k20 is filler-specific. An incorrect assumption for k20 can lead to considerable volume deviations. In addition to DWA 281, the approaches of Okey and Albertson [20] are available for the design of trickling filter systems for nitrification. Boller and Gujer developed a design algorithm for downstream trickling filters [23]. It can thus be summarized that the previous design approaches can lead to considerable deviations in the design of trickling filter systems, especially at high temperatures. With regard to the design of denitrification trickling filters, reference can be made to [15]. In international plant construction, especially in wastewater treatment plants, suppliers of important process engineering components are very often involved in the design of the components by both the customer and the treatment plant. In most cases, the process is only analyzed on a random basis. Therefore, it needs more applications and researches to analyze more factors to find climatic boundary conditions and to test its behavior especially in hot climate conditions, etc. [7]. The influence of temperature is very clear for BOD reduction and nitrification which can be determined [11]. Therefore, demonstration of trickling filters worldwide as successful case studies in large- and small-scale plants intends to create a knowledge base that reliably presents the objective advantages of trickling filters technology in the respective fields of application [24]. This makes it easier to communicate such solutions to customers. In order to use the design approaches and operating recommendations for trickling filters. which was obtained from semi-engineering under country-specific influencing factors, i.e. primarily in warm Climates. It is important to be a reliable basis for practical application and to enable the recommendations to be updated, and to be economically advantageous solutions. This was needed to compare the dimensioning according to the existing standards [25]. Therefore, several trickling filters were selected, which have different boundary conditions with regard to the climatic conditions and the operating range and mode of operation of trickling filters, to be demonstrated according to the operational boundary conditions and practical operating methods, as well as treatment efficiency factors. These will be successful case studies and experience collection for operators.

3 Trickling Filters Case Studies

3.1 Trickling Filter-Managua

3.1.1 Full-Scale System and Design

Wastewater Treatment plant of Managua was designed in 6 trickling filters as in Fig. 2 to treat municipal wastewater type. About 135,000 PE are connected to the treatment plant to the date June 2013 and the number of connected households is increasing but not as fast as the prognosis for 2025. The Water type into wastewater treatment plant of Managua is municipal waste water: WWTP-Managua received about 69% domestic, 26% commercial areas & offices, and 5% industrial wastewater after pretreatment. The industry is mainly food industry, e.g. Pepsi and Cola, etc. The first step is a screening of the water with screens size of 6 mm spacing. Then the water goes through a grease and sand trap followed by primary sedimentation in 9 lamella tanks.

The pretreated wastewater is pumped over 6 trickling filter each of them is 35 m dimeter, 5.1 m filter media depth, 5000 m^3 volume, and total volume is 30,000 m^3. Trickling filters design based on modified Velz equation proved as reliable.

3.1.2 Operation and Treatment Performance

The 9 primary sedimentation tanks were designed to remove 19% BOD and 50% TSS. The primary stage shows high treatment efficiency more than required, that it removes 25–28% BOD and 65–70% TSS. The designed filter plastic media type is: FB 10.27 with a surface area of 100 m^2/m^3 from the German supplier GEA GmbH. The organic loading into the TF is 1.46 kg/m^3/d but the operational situation to the study time is more like 0.45–0.85 kg/m^3/d Managua trickling filters show high treatment efficiency in BOD, COD reduction and nitrification rate of the effluent of the treatment plant in 2012. The effluent values are approximately: 15–40 mg/l;

Fig. 2 Wastewater treatment plant of Managua: 6 trickling filters

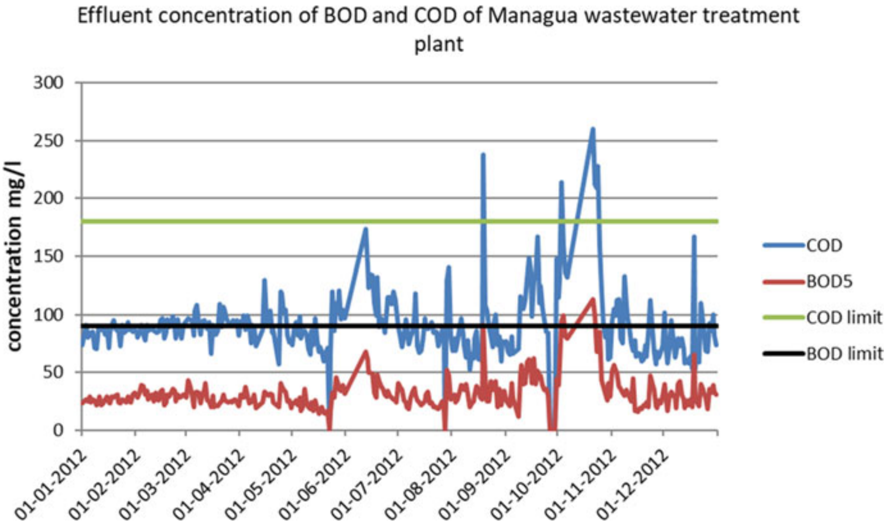

Fig. 3 Effluent of COD, BOD by trickling filter Managua during operation time-2012

BOD (limit requested 90 mg/l), 45–80 mg/l; COD (limit requested 180 mg/l), 18–40 mg/l TSS (limit requested 80 mg/l) (Fig. 3). Nitrification: With good nitrification rate, the influent ammonia concentration is 15–20 mg/l and in the effluent 5–8 mg/l. Phosphorus elimination at the treatment plant is just biological elimination by the trickling filters. The inflow concentration of total phosphorus is between 3 and 4 mg/l and about 50% of that is removed in the treatment plant. The maximum amount of recirculation possible is 704 l/s, this is controlled by the frequency of the pump. It turns out that it is regulated by a gate that separates the incoming water to the TFs from the TF effluent, letting effluent flow to the influent channel when recirculation is necessary. The recirculation is evenly distributed over all the trickling filters in operational period. Recirculation is used when the incoming flow is below 1,290 l/s. However, it is controlled by a flow meter in the pumping station to the trickling filter.

As a recommendation, denitrification stage might be necessary to avoid any eutrophication in the future. This can be done in additional denitrification tanks; in case the effluent discharge will be pumped into lake Managua about 200 m from the shore.

Effluent quality of treated wastewater by trickling filters was far better than requested of COD <180 mg/l, BOD <33 mg/l, it was achieved COD <80 mg/l and BOD <14 mg/l and TSS to 150% reduction with high quality standard.

3.1.3 Result and Economic Aspect

To demonstrate the economic aspect and energy saving by implementing trickling filter technology, energy demand was calculated of the municipal wastewater treatment cost of WWTP-Managua by using trickling filter against activated sludge system for the same wastewater to compare the energy consumption in the two cases to find out the energy saving in kwh for BOD removal and its cost in euro. Tables 1 and 2 present energy/cost saving by using trickling filter in comparison with activated sludge treatment for the same treatment efficiency [26].

The benefit of trickling filter application for WWTP-Managua was low-cost solution by low energy demand and high cost saving against activated sludge plant, in addition to high process reliability and simple control equipment.

3.2 Case Study of Trickling Filters-Al Aweer-Dubai

3.2.1 Full-Scale System and Design

The WWTP-Al Aweer has 15 trickling filters filled with random media. Over 2010, GEA has retrofitted one trickling filter with structured media BIOdek®. The Al Aweer Sewage Treatment Plant (STP) is currently the only wastewater treatment plant serving Dubai City. Both domestic wastewater and sewage are collected by sewers and pumped to the treatment plant site, about 25 km away from the city center. The plant provides tertiary treated effluent for reuse in irrigation and treated sludge converted to manure for use as a soil conditioner and fertilizer. Al Aweer Sewage Water Treatment Plant consist of 15 trickling filter for nitrification. One of these filters uses GEA 2H structured media (Figs. 4 and 5).

Process treatment description: First stage is mechanical treatment which consists of seven screens followed by grit removal.

Table 1 Energy demand for BOD removal by application of trickling filterers and activated sludge treatment technologies for WWTP-Managua

Energy demand/BOD removal	
Calculated for Managua trickling filter	For comparison: typical average energy demand for activated sludge plant
0.21 kwh/kg BOD removed	0.6 kwh/kg BOD removed

Table 2 Cost saving by application of trickling filter comparing with sludge activated sludge for WWTP-Managua

Annual energy saving by trickling filter	Annual energy cost saving by trickling filter
36,700 kg/day 360 days (0.6–0.21) kwh/kg day	(0.1 Euro/kwh)
5.492,155 kwh	550.000 Euro

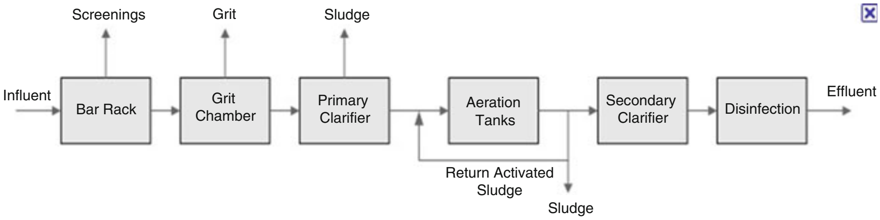

Fig. 4 Waste water treatment process of the wastewater treatment plant-Al Aweer-Dubai

Fig. 5 Existing filter media filling in trickling filter before re-habitation WWTP-Alaweer

The second step of process treatment is the Preparation tank then the primary settling tanks. The primary effluent passes through the aeration tanks where only BOD is removed. The ammonia is treated with biological filters followed by the tertiary settling tanks. After sand filters the effluent is chlorinated and supplied to the city for horticulture irrigation. However, the primary and the biological stage sludge are thickened with polymer and fed to the anaerobic digesters. The anaerobically digested sludge is dewatered with centrifuges and sent for thermal drying and windrow drying. The dried product is used for horticulture by the city and the general public. Trickling filters in 2009 with their structured cross fluted media. Inflow data into GEA-nitrification trickling filter: inflow is 33,000 m^3/day per filter: BOD 12.5 mg/l, TSS 12.7 mg/l, TN-NH4 30.5 mg/l. Even with the random media, efficient nitrification was not taking place because of some of operation problems.

3.2.2 Improvement Trickling Filter Performance

Furthermore, few problems were observed which proved to be obstacles for the efficient working of the trickling filters. The operation problems being faced are as follows:

- No even biofilm formation
- Algae growth

Fig. 6 The random media being used in the trickling fitters

- Ineffective distribution s/m
- Ineffective ventilation

The rehabilitation of one trickling filter was requested to improve the nitrification efficiency and test it under specific operations. Therefore, it was necessary to replace the filling random by GEA plastic fixed media and improve the ventilation process via the hot summer.

The aim of this rehabilitation is to improve the nitrification capacity as the old system was not able to meet the limitation in the outlet. Therefore, it was necessary to replace existing random media filling by new media type and design. It was designed to install two kinds of filter media with different surface area. The media filling types for the rehabilitation filter are BIOdek TKP619/TKP612 with total volume of 2,503 m^3 which is pp: plastic media produced in Germany and installed at WWTP-Al Aweer in Dubai (Fig. 6) (Welded at the WWTP without solvent).

The first specific surface area: 185 m^2/m^3 on the top part of the trickling filter 150 m^2/m^3, and the below layers specific surface area is 240 m^2/m^3 with media depth of 2.75 m filled in the existing trickling filter of 34.1 m diameter.

On the other hand, to improve the ventilation over very hot summer months; the existing situation was the trickling filter has only side-openings for forced ventilation as the natural ventilation is not possible because of the hot summer. So the forced ventilation pressed air at too high level into the filter.

This was changed by GEA 2H Water Technologies GmbH to the new situation; therefore, the air is blown into the discharge canal below the media as a good solution for improving the forced ventilation which improves also the treatment efficiency. However, and after some changes by GEA, air is distributed under the media support (Fig. 7). Open support and media structure (horizontal media section is to 95% open for air flow) achieve very good oxygen supply to biofilm.

Old Situation: side-openings for forced ventilation

New Situation: the air is blown into the discharge canal below the media

Fig. 7 Old and new situations for the aeration in the trickling filter over hot months at Al Aweer WWTP-Dubai. *Old Situation*: side-openings for forced ventilation; *New Situation:* the air is blown into the discharge canal below the media

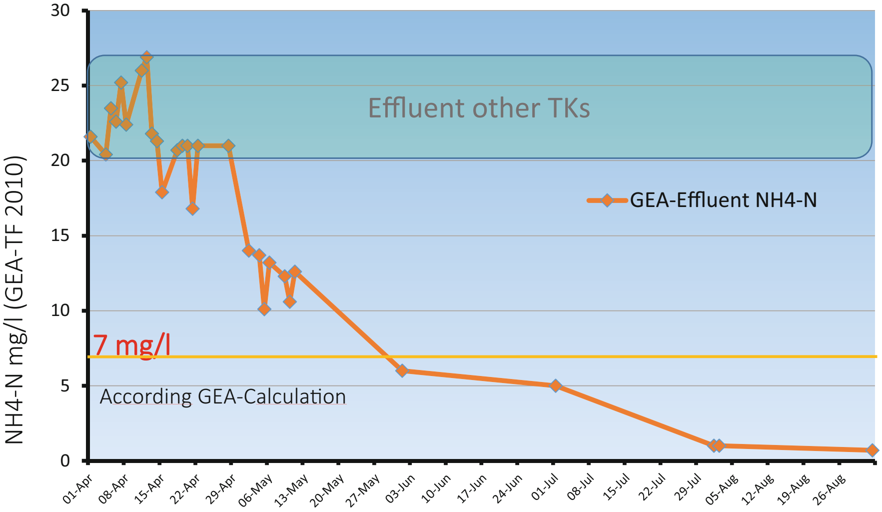

Fig. 8 Nitrification efficiency of modified trickling filter before and after rehabilitation

3.2.3 Improving Nitrification Rate/Result

Trickling filter commissioning was in November 2010 by GEA to insure the improvement of nitrification rate after some changes/rehabilitation of an old trickling filter by replacement of the filling media and improvement in the aeration via hot season. The new operation, design shows a very high nitrification rate. The result is clear in Fig. 8 which indicates to the effluent from BIOdek Filter is <1 mg/l NH4-N in comparing with the other filters effluent values (the improving in nitrification is very clear in Fig. 8). The Data from April to August (operation time after rehabilitation) were tested and received from the customer WWTP-Dubai. So GEA proposes to replace one of the 15 trickling filters with structured media as a substitute to the random media and was able to insure the efficiency of structured media over random media for nitrification, also vertical structured media was recommended to improve the ventilation via operation time.

4 Conclusions and Recommendation

Trickling filter plants for wastewater treatment (BOD and nitrogen elimination) are characterized by simple operation management, low maintenance costs, and a long service life. This is not only advantageous for modern trickling filter application, but also especially for the possibility of combining it with other technologies. They have a low energy consumption, as no energy is required for the oxygen supply and distribution required for nitrification. There are no operational problems such as bloating sludge, floating sludge, or foam formation. In addition, there is no need for returned sludge for treatment process at all, and circulations rate is needed sometimes for an operational issue. Based on the criteria mentioned above, the worldwide use of such systems is recommended.

Incidentally, other processes in the trickling filter are influenced by the temperature, some of which can have opposite effects, like the diffusion of oxygen and other nutrients into the biofilm, the oxygen solubility, the ventilation, or the biofilm strength. In particular, for planning or adapting the operating parameters – hydraulic loading, ventilation, flushing power – there are no robust design regulations.

Therefore, the existing trickling filter concepts in the EU-countries cannot be transferred directly to other countries where different climatic conditions prevail.

A major disadvantage of these approaches is that the influence of different climatic conditions, in particular temperature and hot dry climate, is not taken into account in the volume determination of trickling filters.

Because of specific operations under several circumstances and poor experience of trickling filter operation in many counties, capacity building and intensive training in O&M operation and maintenance are highly need. These enable operators to test the media under several circumstances, operational and design situations, wastewater types, deferent loads, and different climate effects.

Acknowledgments The two case studies were implemented by the GEA Water Technologies-Germany. The author was involved in above projects' implementation, operation and providing capacity building and technical skills in O&M via and after her work for the GEA-Germany as a Project Engineer. The author presents the study applications as successfully case studies of trickling filter applications especially in hot dry climate. Trickling filter Managua was financed by KFW.

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Advanced Configuration for Efficient Membrane Bioreactors

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Contents

Abstract Membrane bioreactors (MBRs) for wastewater treatment are being extensively studied and optimized to achieve the following: (a) higher pollutant removal efficiency, (b) better fouling control, (c) lower energy consumption, or (d) higher

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energy production in MBRs. These efforts have led to the development of a number of alternative advanced configurations of MBR. This chapter presents a review of non-conventional MBR systems, the directions being pursued to develop them further, and a discussion on how these systems can improve the efficiency and other aspects of wastewater treatment.

The chapter highlights new advances in MBRs, specifically in Self-Forming Dynamic Membrane Bioreactors (SFDMBRs) and Electro Membrane Bioreactors (eMBRs). This chapter also presents designs and configurations of novel MBR systems developed for energy production, notably Anaerobic Membrane Bioreactors (AnMBR) and MBR coupled with Bioelectrochemical Systems (MBR-BES) that may be used for simultaneous wastewater treatment and energy harvesting. A comparison of the performances of these advanced MBR systems in terms of conventional and emerging contaminant removal, fouling mitigation, and energy production rates is also provided.

Another part of the chapter examines the economic feasibility of practical applications of advanced configurations of MBR. Particular attention is given to the specific energy demand of the advanced MBRs. Finally, the chapter discusses the challenges encountered in using non-conventional MBRs and their future prospects.

Keywords Anaerobic membrane bioreactors, Bioelectrochemical systems, Electro membrane bioreactors, Self-forming dynamic membrane bioreactors

Abbreviations

A/O-DMBR	Anoxic-oxic dynamic membrane bioreactor
AHL	*N*-Acyl homoserine lactone
AMX	Amoxicillin
Anammox	Anaerobic ammonium oxidation
AnDMBR	Anaerobic dynamic membrane bioreactor
AnFCMBR	Anaerobic fluidized bed ceramic membrane bioreactor
AnFMBR	Anaerobic fluidized membrane bioreactor
AnMBR	Anaerobic membrane bioreactor
AnOMBR	Anaerobic forward osmosis membrane bioreactor
ARB	Antibiotic resistant bacteria
ARG	Antibiotic resistant genes
BES	Bioelectrochemical systems
CAS	Conventional activated sludge
CNT-HFM	Carbon nanotube hollow-fiber membrane
COD	Chemical oxygen demand
CZ	Carbamazepine
DFC	Diclofenac
DM	Dynamic membrane
EC	Emerging contaminant
eMBR	Electro membrane bioreactor

EPS	Extracellular polymeric substances
EPSp	Protein fraction of EPS
GAC	Granulated activated carbon
MBR	Membrane bioreactor
MEC	Microbial electrolysis cell
MFC	Microbial fuel cell
MMBR	Moving bed membrane bioreactor
MPBR	Membrane algae photobioreactor
MRC	Microbial nutrient recovery cell
NH_4^+-N	Ammonium-Nitrogen
NO_3^-	Nitrate
OMBR	Osmotic membrane bioreactor
PAC	Powdered activated carbon
PPCP	Personal care products
PVDF	Polyvinylidene fluoride
QQ	Quorum quenching
QS	Quorum sensing
SFDMBR	Self-forming dynamic membrane bioreactor
SMP	Soluble microbial products
SMX	Sulfamethoxazole
SS	Stainless steel
TCS	Triclosan
TEP	Transparent exopolymer particles
TMP	Transmembrane pressure
TOC	Total organic carbon
TrOC	Trace organic contaminants
TSS	Total suspended solids

1 Introduction

The use of MBRs in wastewater treatment has been extensively studied. MBRs are reactors that combine biodegradation and membrane filtration for pollutant removal [1]. This technology is an improvement of the conventional activated sludge (CAS) process since it eliminates the use of secondary clarifier to separate sludge from wastewater. The membrane filtration action leads to 100% retention of sludge in the reactor, leaving the effluent practically free from solids and pathogenic microorganisms [1–3].

Conventional MBRs have been shown to be efficient for removing conventional pollutants such as Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Total Suspended Solids (TSS), Total Phosphorus, and Total Nitrogen [4–7]. The potential of MBR technology has also been demonstrated in the removal of emerging contaminants, notably pharmaceutical products and other organic pollutants [6, 8], endocrine disrupting compounds [9], antibiotic resistant bacteria (ARB), and antibiotic resistant genes (ARG) [10] from wastewater.

Other advantages of MBR include smaller footprint, longer solids retention time, and no requirement of additional chemicals. However, membrane fouling is a major limitation of MBRs. Membrane fouling results from the mass transport, adsorption, and accumulation of fouling substances on the membrane surface [11]. This phenomenon manifests itself as the increase of transmembrane pressure (TMP) and reduction of permeate flux.

To optimize the potential of MBRs for wastewater treatment applications, studies are being conducted to improve its performance. These studies focus both on further enhancement of pollutant removal and mitigation of membrane fouling.

Efforts to improve the MBR performance have led to the development of advanced configurations of such reactors. In addition to the goal of achieving optimum pollutant removal and fouling alleviation, new developments have aimed to reduce costs due to membrane material and energy requirements.

The focus of this book chapter is accordingly given to advanced membrane bioreactors, notably the AnMBRs, SFDMBRs, eMBRs, and MBR-BES.

2 Recent Advances in Membrane Bioreactors

2.1 Self-Forming Dynamic Membrane Bioreactors

The SFDMBRs make use of the biofilm layer, which is formed on the surface of a support material, as membrane filter. The support material has a relatively larger pore size (10–200 μm) compared to the ultra-filters and micro-filters (0.01–0.4 μm) used in conventional MBRs [12, 13].

In this type of MBR, the biofilm layer formed as a result of the degradation of organic matter in wastewater has a lower pore size than the support material on which it builds [13]. This makes the accumulated permeable biofilm act as an effective filtration layer [11, 14].

One advantage of the SFDMBR is that it makes use of a low-cost filter material as a support and of the biofilm as a membrane instead of expensive ones used in conventional MBRs [15]. The materials commonly used as support for self-forming dynamic membranes (SFDMs) are nylon mesh, polyester mono-filamentous mesh, polypropylene mono-filamentous mesh, and woven and nonwoven fabrics. These aspects of SFDMBRs design are summarized in Table 1. Another advantage of the SFDMBR is its lower filtration resistance compared to that of the conventional MBR [15].

The SFDMBR is different from the biofilm MBRs, in which inert support materials such as biofilm carriers carbon fibers are mainly used to provide additional surface area for the attachment of microorganisms. On the other hand, the biofilm or dynamic membrane (DM) layer in the SFDMBR mainly acts as the filtration layer due to its porous structure [13].

Table 1 Aerobic, anaerobic, and anammox SFDMBRs used in recent studies

Reactor type	Biological condition	Support material	Pore Size of support material, μm	Wastewater treated	DM formation time	Scale	Reference
Continuous-flow submerged SFDMBR	Aerobic	Nonwoven fabric	100	High-strength pyridine wastewater (synthetic)	15 days	Laboratory-scale	[16]
Integrated fixed-film activated sludge (IFAS) and SFDMBR	Aerobic	Nylon mesh	50	Real municipal wastewater	n.r.	Laboratory-scale	[17]
Submerged SFDMBR	Aerobic	Nylon mesh	20; 50	Real municipal wastewater	n.r.	Laboratory-scale	[18]
Submerged SFDMBR	Aerobic	Nylon woven fabric mesh	55	Real industrial wastewater	n.r.	Pilot-scale	[19]
Submerged SFDMBR	Aerobic	Nylon mesh	80	Real municipal wastewater	3 days	Pilot-scale	[20]
Submerged SFDMBR (with agitator)	Aerobic	Polyester flat-sheet mono-filamentous mesh	30	Synthetic wastewater	14 min	Laboratory-scale	[21]
Submerged SFDMBR (with recycle permeate line at first part of operation)	Aerobic	Polyester monofilament mesh filter	30	Synthetic wastewater	5 min	Laboratory-scale	[22]
Submerged SFDMBR	Aerobic	Nylon mesh	25	Synthetic wastewater with COD of 180 mg/L	n.r.	Laboratory-scale	[14]
Submerged SFDMBR succeeding an anoxic tank	Aerobic (at submerged SFDMBR)	Nylon 6 woven mesh	20.71 ± 4.60	Synthetic wastewater	With permeate flux of 1 m^3/m^2/day: 7 days; With permeate flux of 2 m^3/m^2/day: 3 days	Laboratory-scale	[23]

(continued)

Table 1 (continued)

Reactor type	Biological condition	Support material	Pore Size of support material, μm	Wastewater treated	DM formation time	Scale	Reference
Submerged SFDMBR and submerged SFDMBR with powdered activated carbon (PAC)	Aerobic	Nylon mesh	75	Real domestic wastewater with COD of 110.6–204.4 mg/L	Submerged SFDMBR: 5–20 min Submerged SFDMBR with PAC: 5 min	Laboratory-scale	[24]
Submerged SFDMBR	Aerobic	Polyester non-woven fabric (0.20 kg/m^2)	Not specified	Synthetic wastewater with COD of 300 ± 5 mg/L	Approximately 10–100 min (dependent on mean diameter and relative hydrophobicity of sludge particles)	Laboratory-scale	[25]
Submerged SFDMBR	Aerobic	Dacron mesh	100	Real municipal wastewater with COD of 97.9–371.7 mg/L	15–30 min	Laboratory-scale	[13]
Anaerobic dynamic membrane bioreactor (AnDMBR) using external crossflow filter	Anaerobic	Polyamide/nylon monofilament woven mesh	200	Synthetic high-strength municipal wastewater with COD of 900 mg/L	n.r.	Laboratory-scale	[26]
Submerged AnDMBR succeeding an anaerobic reactor	Anaerobic	Acrylonitrile butadiene styrene filament	100	Synthetic anthraquinone textile dye wastewater	n.r.	Laboratory-scale	[27]
Upflow anaerobic sludge blanket (UASB) with side-stream crossflow filter	Anaerobic	Nylon 6 woven mesh	26; 38; 54; 61; 74	Synthetic wastewater with COD of 320 mg/L	60–90 min	Laboratory-scale	[12]

External AnDMBR; Submerged AnDMBR	Anaerobic	Polypropylene monofilament woven fabric	10	Synthetic wastewater with COD of 20,100 ± 310 mg/L	External AnDMBR: 20 days Submerged AnDMBR: 10 days	Laboratory-scale	[28]
Submerged AnDMBR	Anaerobic	Polyester non-woven fabric	30	Synthetic municipal wastewater with COD of 361 ± 20 mg/L	40–55 min	Laboratory-scale	[15]
Submerged anaerobic ammonia oxidation (anammox) SFDMBR	Anammox	Nylon woven mesh	20–25	Synthetic wastewater with 100–730 mg NH_4^+- N/L	7–8 days	Laboratory-scale	[29]
Side-stream anammox SFDMBR	Anammox	Polyamide/ nylon mesh	200; 52 (starting day 32 of experiment)	Synthetic wastewater with 50 mg NH_4^+/L and 50 mg $NO2^-$/L	<5 min	Laboratory-scale	[30]
Submerged anammox SFDMBR	Anammox	Nonwoven fabric	100	Synthetic wastewater with 25–500 mg NH_4^+-N/L	n.r.	Laboratory-scale	[31]

Note: *n.r.* Not reported

It is important that the biofilm or the DM layer also contributes to pollutant degradation. In a study by Wu et al. [32], the DM was found to remove a portion of COD, colloids, and total and organic nitrogen from wastewater. Fan and Huang [13] found that the DM in an SFDMBR contributed 37.0% removal of dissolved organic carbon (DOC) from municipal wastewater. This removal was attributed to two mechanisms: *i)* rejection of large molecules by the formed DM, and *ii)* removal of small molecules through degradation of organic carbon by the microorganisms in the DM as the permeate passed through the biological layer.

The quality of permeate from an SFDMBR is comparable to that of the permeate from the conventional MBRs. In the study by Sabaghian et al. [22], the COD and ammonium-nitrogen (NH_4^+-N) removals from a synthetic wastewater using an aerobic SFDMBR were 92% and 98%, respectively. In another aerobic SFDMBR treating synthetic municipal wastewater, COD removal achieved was 98% [21]. The SFDMBR has also been studied to treat real wastewaters such as domestic wastewater [24], dairy wastewater [33], and real canning and winery wastewaters [34].

2.1.1 Dynamic Membrane Structure and Formation

The formation of the DM is a critical process in terms of pollutant removal from the wastewater and of obtaining a stable amount and quality of permeate from the SFDMBR. Fan and Huang [13] suggested that the DM is composed of two sublayers, the cake and gel layers. Results of their study revealed that the cake layer is composed of sludge flocs that are similar to the flocs suspended in the bulk wastewater. The particles in the cake layer are easily detached from the module once it is removed from the suspension. On the other hand, the gel layer is tightly attached to the surface of the support material. It has been shown to be composed of mainly extracellular polymeric substances (EPS), making the layer permeable. The pore size of the gel layer has been reported to be at a range of <0.10–0.50 μm [13, 23]. Its structure makes the gel layer the primary DM component that rejects the fine particles in the wastewater. Aside from the structure of the DM, its formation time is an important consideration in the operation of SFDMBRs. In previous studies on SFDMBRs for wastewater treatment (Table 1), the DM formation time was reported to be at a range of 5 min to 20 days. A shorter formation time of stable DM is needed to prevent sludge flocs loss and to reduce amount of low effluent quality produced during the start-up period [35].

Several factors influence the formation and performance of the DM, including (a) support material, (b) bulk sludge properties, (c) aeration/gas sparging rates and mechanisms, and (d) backwashing strategies as discussed below.

The work of Ersahin et al. [36] suggested that the type of support material used affects the DM layer formation in an AnDMBR. In the latter study, it was shown that mono-monofilament filter cloth, which had a smooth surface, favored the formation of a homogenous DM layer which retained the solid particles in this layer. In contrast, the severe accumulation of particles in the pores of staple yarn support material was observed, making it unsuitable for DM filtration. This blocking of pores was due to the twisted structure and uneven surface of the staple yarn. A similar study was conducted by Isik et al. [37] to compare DM formation using two different materials. The reported results showed that a homogenous DM was formed with polyester as support material. In contrast, the DM layer with glass fiber as support material had fine sludge particles that were deposited in between the filaments, which led to filter clogging. This difference in the characteristics of DM formed was attributed to the difference in structure of the support materials, in which the glass fiber was observed to have more filaments than the polyester material. The mesh size of the support material also affects the time of DM formation as shown by Hu et al. [35]. The latter study showed that nylon mesh with the lowest pore size (25 μm compared to 38, 48, and 75 μm) had the shortest DM formation time and lowest effluent turbidity [35]. Salerno et al. [18] also found that smaller mesh size (20 μm compared to 50 μm) of a nylon mesh as support material resulted in faster DM formation. However, Cai et al. [38] noted that support materials with mesh size of 10 μm or lower were not suitable for SFDMBRs due to low permeate flux obtained in such systems.

The study conducted by Liang et al. [25] demonstrated that the properties of the bulk sludge influence the DM's formation, filtration resistance, and fouling propensity. Their results demonstrated that the presence of sludge with more numerous large diameter particles with relatively high hydrophobicity tends to reduce the DM formation time. During the initial stage of SFDMBR operation, larger particles tended to be intercepted more than the smaller particles by the support material. Hydrophobic particles would also be easily deposited to hydrophobic support materials. The higher proportion of large particles in the dynamic layer led to the formation of a more porous DM, and consequently resulted in lower filtration resistance. It was also shown that among the bulk sludge properties, the EPS content strongly influenced the DM fouling propensity. Sludge with high EPS concentration tended to be strongly attached to fresh DMs, which led to fouling. Sabaghian et al. [22] also found that a 5,000–9,000 mg/L Mixed Liquor Suspended Solids (MLSS) concentration could result in higher non-Newtonian activity of activated sludge, resulting in fouling.

Continuous air scouring resulted in less prominent increase in TMP in an SFDMBR [18]. However, large air scouring flow rates were observed to increase turbidity in the effluent. This finding is similar to that obtained by Sabaghian et al. [22], which showed that higher aeration rates tend to destroy the DM due to large shear stress. Aerobic SFDMBRs have utilized aeration to maintain dissolved oxygen (DO) and to keep solids suspended in the reactor. Rezvani et al. [21] used both a mechanical axial-flow stainless-steel (SS) agitator and aeration to keep the bulk liquid mixed and supply the DO in an aerobic submerged SFDMBR. The agitator was used to keep the sludge flocs in the mixed liquor suspended during the DM formation stage. This was important to the operation since the DM formation stage involved the accumulation of the suspended particles on the surface of the support material. After the initial DM formation, the agitator was turned off to switch to the aeration stage. This study suggested that the flow-pattern due to the agitation provided a more uniform DM structure and shortened the DM formation time

[21]. However, this effect of the agitator on the DM structure and formation time must be further validated in future studies.

In submerged downflow AnDMBRs, the gases produced in the anaerobic process are used for gas sparging, keeping the bulk liquid mixed. Application of intermittent biogas recycle to the reactor was found to improve the DM formation compared to that obtained during use of continuous biogas recycle [39].

A recent study by Siddiqui et al. [40] examined the effects of time-based and TMP-based backwashing strategies on the accumulation of EPS in the DM of an AnDMBR. The reported results demonstrated that less frequent backwashing (TMP-based) led to less EPSc accumulation in the DM compared to that obtained from more frequent backwashing (time-based). However, this behavior must be further studied using long-term operations and using aerobic SFDMBRs.

The results of the studies discussed in this section (Sect. 2.1.1) demonstrate that achieving a detailed understanding of the mechanism of DM formation and the factors affecting is highly important for an efficient long-term operation of the SFDMBR.

2.1.2 Aerobic, Anaerobic, and Anammox SFDMBRs

While SFDMBRs that use aerobic processes have been widely studied, their applicability for anaerobic process has been addressed only recently. Siddiqui et al. [12] examined the treatment of low-strength synthetic wastewater using an upflow anaerobic sludge blanket reactor with a side-stream anaerobic SFDMBR. In another study, Alibardi et al. [26] investigated the treatment of high-strength wastewater using an anaerobic SFDMBR, which made use of an anaerobic tank with an external crossflow filter. In the latter study, the DM was found to contribute about 20% to the total COD removal.

In addition to aerobic and anaerobic applications, the SFDMBR approach has been studied in the context of applications of the anaerobic ammonium oxidation (Anammox) process. The Anammox SFDMBR has been shown to be suitable for the treatment of ammonium-rich and low Carbon to Nitrogen (C/N) ratio wastewater. The DM formed on the mesh support materials used in the recent studies provided enhanced biomass retention and favorable condition for the growth of anammox bacteria [29–31].

Results from the study by Zhu et al. [29] showed that the mean value of total nitrogen removal rate (TNRR) in the anammox SFDMBR (0.85 ± 0.1 kg N m^{-3} day^{-1}) was higher than in the conventional MBR with polyvinylidene fluoride (PVDF) ultra-filters (0.62 ± 0.2 kg N m^{-3} day^{-1}). This was attributed to the improved stability of activity of anammox bacteria retained in the DM. Meng et al. [31] reported in an earlier study that the DM formed on a nonwoven fabric module contributed 11–26% to the total TNRR from a synthetic ammonia-rich wastewater.

Anammox bacteria have a slow growth rate, with a 30 days doubling time in a fluidized bed reactor [41] and 11 days in a sequencing batch reactor [42]. The study by Saleem et al. [30] showed that the doubling time of Anammox bacteria was shortened to 6.9 days in an Anammox SFDMBR. The retention of the biomass in the SFDMBR prevented the loss of the slow-growing Anammox bacteria. Zhu et al. [29] also showed that the Anammox bacteria retention in the SFDMBR is comparable to that observed in an MBR with PVDF module.

Membrane fouling mitigation was also observed in the anammox SFDMBR, as shown by the low TMP values. Meng et al. [31] reported <0.5 kPa during the 380 days of operation of Anammox SFDMBR. Zhu et al. [29] observed a TMP value of 10 kPa for 50 days of operation. In the latter work, the EPS content of the DM deposited on the nylon mesh was found to be much lower than the EPS deposited on the PVDF membrane. The thickness of the DM was 95% lower than thickness of foulant layer deposited on the PVDF membrane. Low concentration of EPS was observed in the Anammox bulk sludge, which led to improved sludge filterability and reduced membrane fouling. Meng et al. [31] suggested that the porous structure of the biofilm with Anammox and the release of nitrogen gas (N_2 gas) contributed to the decrease in membrane fouling rate.

2.1.3 Configurations

Most studies on SFDMBRs utilize the submerged configuration and a few have employed the external crossflow filter configuration (see Table 1 and Fig. 1).

Aerobic SFDMBRs (Fig. 1a–e) commonly have an aeration tank equipped with a submerged membrane module [14, 18, 25]. Fan & Huang [13] and Y.-K. Wang et al. [20] utilized aeration tanks with baffles for internal loop circulation. Modifications of this configuration have been developed to improve membrane fouling mitigation or pollutant removal. An example is the system employed by C. Hou et al. [43], where a continuous air lift reactor (CFAR) preceded an aerobic SFDMBR. In this system, the CFAR is an aeration tank with baffles that allowed retention of aerobic granular sludge. This led to the process in which only flocculant sludge instead of granular ones entered the subsequent submerged SFDMBR. Vergine et al. [17] examined the performance of an integrated fixed-film activated sludge SFDMBR (IFAS-SFDMBR), which consisted of one aerated tank with a submerged membrane module and polyethylene carriers. The polyethylene carriers were added to provide surface for attached growth of biomass. However, the presence of the carriers led to reduction of size of sludge flocs due to mechanical action, and consequently to an increased frequency of mesh clogging. On the other hand, the presence of Powdered Activated Carbon (PAC) in a submerged SFDMBR reduced the concentration of EPS and SMP in the DM [44]. Potential foulants' concentrations were decreased by adsorption to or biodegradation by the PAC particles in the reactor. In addition, the presence of PAC produced a more porous and less dense DM layer.

Most of the AnDMBRs in previous studies have utilized the submerged membrane configuration (Fig. 1f, g). In downflow submerged AnDMBRs, agitators or gas sparging is employed to mix the sludge and regulate the deposition of sludge to the DM [15, 39]. Another type of submerged AnDMBR consists of an Upflow Anaerobic Sludge Blanket (UASB) reactor and a dynamic membrane module. This

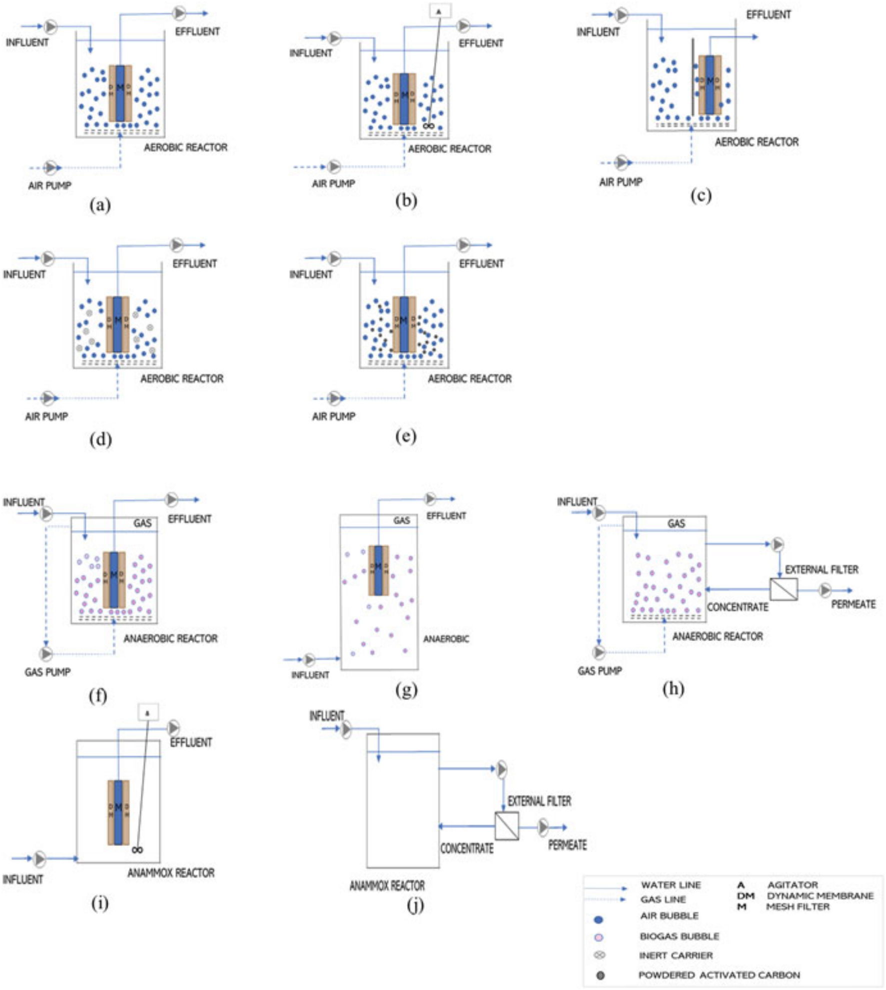

Fig. 1 Alternative configurations of SFDMBRs presented in previous studies. (**a**) Submerged Aerobic SFDMBR, (**b**) Submerged Aerobic SFDMBR with Agitator, (**c**) Submerged Aerobic SFDMBR with Baffle, (**d**) Submerged Aerobic SFDMBR with Inert Carriers, (**e**) Submerged Aerobic SFDMBR with Powdered Activated Carbon, (**f**) Submerged AnDMBR, (**g**) Submerged Upflow AnDMBR, (**h**) External AnDMBR, (**i**) Submerged Anammox SFDMBR, and (**j**) External Anammox SFDMBR

AnDMBR consists of a sludge zone (bottom portion) and a settling zone (upper portion) where the dynamic membrane module is submerged [45, 46].

Aside from submerged configuration, some studies have used AnDMBR system where an external filtration module is coupled to another anaerobic reactor (Fig. 1h) [12, 26, 47]. Ersahin et al. [28] compared the performance of external and submerged AnDMBRs. Longer DM formation time was observed using the external AnDMBR compared to the submerged AnDMBR. In addition, lower filtration resistance was observed in the external AnDMBR. However, the results in this study by Ersahin et al. [28] suggested that the external circulation of the sludge may have led to decreased diversity of microbial community in the external AnDMBR. As a result, the external AnDMBR had lower COD removal and lower biogas production.

Anammox SFDMBRs have also utilized both the submerged and external membrane configurations, as shown in Fig. 1i, j) [29–31].

Aside from the addition of fixed media carriers and powdered activated carbon, SFDMBRs have not yet been widely integrated with other wastewater treatment technologies such as electrochemical processes and advanced oxidation processes.

2.2 Electro Membrane Bioreactors (eMBRs)

Electro membrane bioreactors (eMBRs) are advanced MBRs that make use of the integration of biological process, electrochemical process, and membrane filtration to treat wastewater [48–51]. The integration of MBRs with electrochemical processes is aimed to enhance the MBR performance in terms of pollutant removal and membrane fouling mitigation.

2.2.1 Configurations, Electrode Materials, and Operating Conditions

In early designs, the integration of electrochemical processes with MBR for wastewater treatment utilized electrode plates or meshes that were bound with the membrane modules (Fig. 2a, d). J.-P. Chen et al. [52] first studied effects of the application of electric field to the membrane flux in a submerged MBR. The reactor was composed of two compartments: a tank with anoxic and oxic zones and another aerated pool with the membrane module. The electric field was applied through perforated stainless-steel electrodes connected to an external power supply. The electrodes were placed on the membrane surface. In another study, Akamatsu et al. [2] used platinum mesh as electrodes, which were attached to sides of an external membrane.

As the eMBR was continually studied, new configurations were developed (Fig. 2b–d). Bani-Melhem and Elektorowicz [53] developed a submerged eMBR where the biodegradation, filtration, and electrochemical processes occur in a single tank. In this reactor, the electrodes were located at a certain distance from the membrane module instead of being bound to the membrane. This was to prevent possible oxidation of the polymeric membrane. Perforated circular anode was located near the wall of the tank. The perforated circular cathode was placed at the inner part of the tank at a distance from the anode. The membrane module was at the center of the reactor. In this way, two zones of wastewater treatment were created. The first zone from the wall of the tank to the cathode was the zone for simultaneous biodegradation and electrochemical processes. The second zone from the cathode to

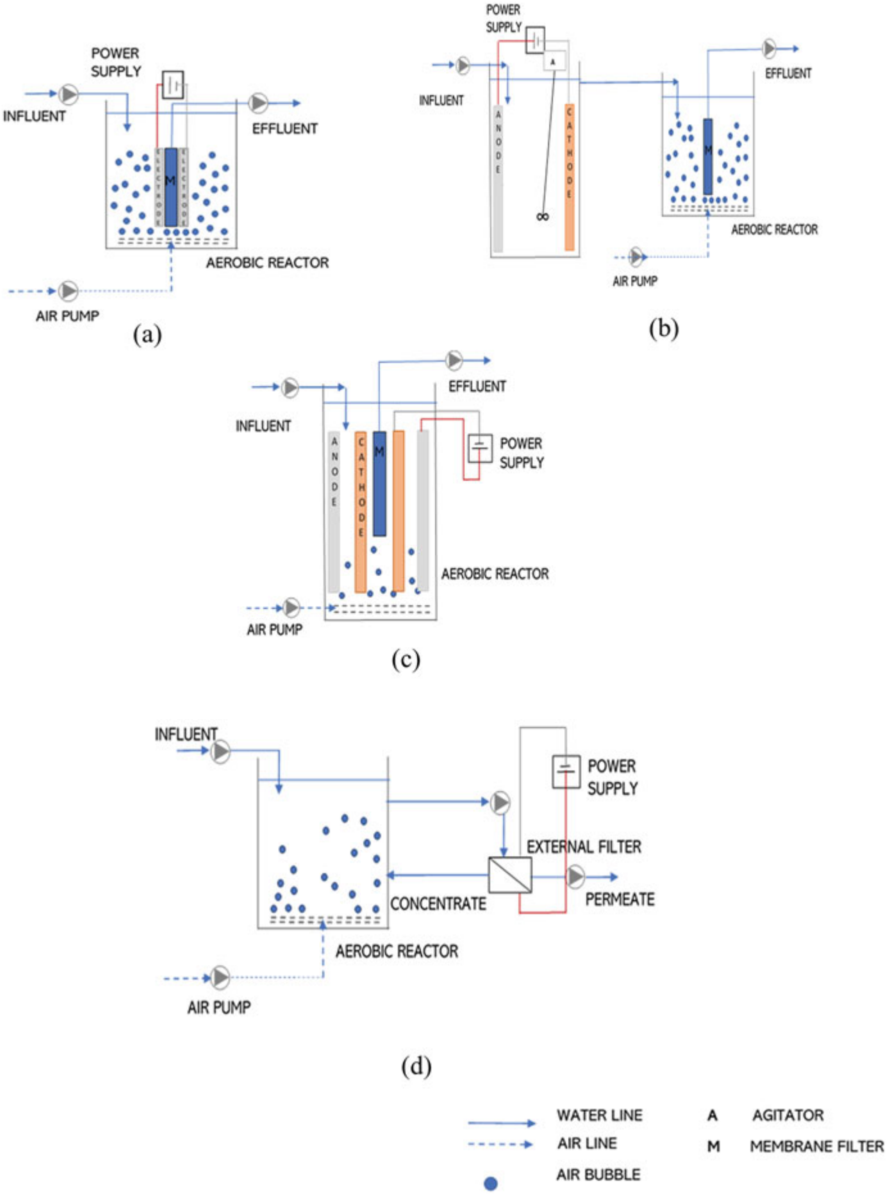

Fig. 2 Alternative configurations of eMBRs (**a**) Submerged eMBR with electrodes bound with membrane module, (**b**) External coagulation unit and submerged MBR, (**c**) Submerged eMBR with circular electrodes, (**d**) External eMBR

the membrane was for biodegradation and filtration. L. Liu et al. [54] also used a submerged eMBR in one vessel, where the stainless-steel anode is located at a distance from the membrane and copper wire cathode sealed in the membrane module.

Another configuration of eMBR used is one where the wastewater goes through an electrocoagulation unit before a submerged MBR unit. Bani-Melhem and Smith [55] investigated the performance of this configuration to treat grey water. The electrocoagulation unit served as a pre-treatment step that enhanced fouling alleviation and pollutant removal.

Applied voltages in eMBRs range from 0.1 to 20 V/cm [2, 52, 53, 56]. The study of Bani-Melhem and Elektorowicz [48] showed that even a low electric field gradient at 1 V/cm could lead to better anti-fouling performance of the eMBR. It was also shown that intermittent application of low voltage in an eMBR could lead to efficient fouling mitigation and pollutant removal, without an adverse effect to the microbial community in an eMBR [2, 51, 57].

2.2.2 Conventional Pollutant Removal in eMBRs

In enhancing permeate quality, the electrochemical processes contribute through different mechanisms. One of such processes is electrocoagulation. In eMBRs, the metal anode is oxidized to release metal ions (e.g., Al^{3+}, Fe^{3+}) that act as in situ generated coagulants [50, 58]. The coagulants allow the formation of larger particles, increasing retention of pollutants inside the reactor. Pollutants tend to be adsorbed to or entrapped in the flocs formed [48]. This results in their further degradation as the microorganisms in the eMBR have longer contact time with the pollutants.

In a study by Yang et al. [59], electrochemically assisted aerobic MBRs with conductive carbon nanotubes hollow-fiber membranes (CNTs-HFMs) obtained COD removal of >92%, which was higher than the removal by the conventional MBRs used in the study. The eMBRs achieved >88% NH_4^+-N removal, which was also higher than NH_4^+-N removal in the MBRs without electrochemical assistance. The application of voltage notably favored the growth of microorganisms *Gemmatimonas*, *Cloacibacterium*, and *Delftia,* and as a result it enhanced organic matter breakdown. In an eMBR examined by Jiang et al. [56], phenol and COD degradation reached up to 100% during a long-term operation. The study revealed that the application of electric field resulted in an increase in the activity of key enzymes related to phenol degradation, namely phenol hydroxylase (PH) and catechol 2,3-dioxygenase (C230).

A submerged eMBR was used to successfully treat landfill leachate [60]. Higher COD and NH_4^+-N removals were observed in the submerged eMBR compared to those in a conventional MBR. Metal removals (Chromium, Magnesium, Zinc, and Iron) were also generally higher in the eMBR compared to those obtained in the conventional MBR. The efficiency in metal removal of the eMBR was attributed to the following mechanisms: (a) surface complexation, (b) electrostatic attraction,

(c) adsorption, and (d) precipitation due to interaction between metal pollutant and coagulant floc.

2.2.3 Membrane Fouling Mitigation in eMBRs

The presence of electric field in eMBRs has been shown to enhance the mitigation of membrane fouling. Akamatsu et al. [2] reported that an eMBR with platinum electrodes had a permeate flux that was 3.5 times higher than that produced from an MBR without applied electric field. In this study, the alleviation of membrane fouling was attributed to the enhanced repulsion between the negatively charged sludge particles and the membrane. This agrees with the result of the study made by Zhang et al. [61] where SS anodes and membrane module with titanium cathodes were used. In this eMBR, the TMPs obtained were 25.3–40.4% lower than those obtained in MBR without applied voltage. In the latter study, fouling rate reduction was also explained by the repulsion between the foulants and the membrane surface. Another reason for the lowering of fouling rate in eMBR treatment was the reaction of iron ions from the SS anode with the organic matter in the mixed liquor. This reaction led to reduction of TOC and the membrane fouling pre-cursors soluble microbial products (SMP) polysaccharides.

A new approach to mitigate membrane fouling in eMBRs is the regulation of quorum sensing (QS). QS is a system used by bacteria to communicate and coordinate their activities by producing and secreting signal molecules [62–64]. Studies have shown correlations between biofilm formation and quorum sensing. Quorum Quenching (QQ) or the disruption of QS resulted in decrease of concentration and in degradation of the signal molecules, commonly N-Acyl Homoserine Lactones (AHLs) [62, 65–67]. Reduction of the levels of the signal molecules was found to inhibit the formation of biofilm, and consequently led to reduced membrane fouling. Most of the studies of QQ as a membrane fouling prevention strategy have been focused on the action of QQ bacteria [62, 64, 67], or QQ enzymes [66, 68]. On the other hand, recent studies have investigated the role of electric field application as QQ strategy in eMBRs. Borea et al. [65] confirmed in their study that the application of electric field affected microorganisms in the eMBR and disrupted their production of N-octanoyl-L-homoserine lactone (C8-HSL) signal molecules. The reduction in C8-HSL content led to lower concentrations of the protein fraction of extracellular polymeric substances (EPSp) and transparent exopolymeric particles (TEP), which resulted in reduced membrane fouling.

Jiang et al. [56] also examined the role of electric field in QS regulation as a membrane fouling reduction strategy in an eMBR. In this work, the degradation of N-acyl homoserine lactone (AHL) molecules was caused by two mechanisms. One of them was the oxidation of carbon chains in AHL molecules by the hydrogen peroxide (H_2O_2) generated at the cathode of the eMBR. Another mechanism was the effect of electric field, resulting in an increase of QQ bacteria and decrease of QS bacteria. This led to lower production of AHLs, which caused lower EPS production and reduced membrane fouling.

2.3 Anaerobic Membrane Bioreactors

AnMBRs combine anaerobic degradation and membrane filtration to remove pollutants from wastewater [69, 70]. One important advantage of the anaerobic process is the high rate of pollutant biodegradation by anaerobic microorganisms. However, anaerobic microorganisms are slow-growing and therefore require high biomass retention in the reactor. This biomass retention is increased when the anaerobic reactor is integrated with a membrane [71]. The increased biomass retention inside AnMBRs results in lower suspended solids concentrations in the effluent [72].

Applications of AnMBRs to treat various types of wastewater have been examined in previous studies. AnMBRs have been applied to treat high-strength [73–77] and low-strength wastewaters [78–80]. Different configurations applied in AnMBRS are shown in Fig. 3. Most AnMBR studies have utilized the submerged AnMBR configuration [76, 77, 81–83], where the membrane module is immersed in the anaerobic reactor, thus anaerobic degradation and filtration occurs in a single vessel. Another examined configuration includes an anaerobic bioreactor coupled with a submerged AnMBR tank [74, 84–86] and involves recirculation of a portion of the sludge from the membrane tank to the other anaerobic reactor. A few studies have also utilized the external side-stream AnMBR configuration [87, 88]. Common membrane materials used in AnMBRs are polymeric (PVDF, polyethylene, polyethersulfone) or ceramic membranes with pore sizes ranging from 0.05 to 1.0 μm [74, 78, 88–90].

2.3.1 Conventional Pollutant Removal in AnMBRs

The different configurations of AnMBRs have been reported to achieve 86% to >99% COD removal from low and high-strength wastewaters [74–78, 81, 84]. C. Chen et al. [91] compared the performance of two AnMBR configurations for treating municipal wastewater. The latter study showed that both configurations, (a) a submerged AnMBR (membrane immersed in an Upflow Anaerobic Granular Bioreactor (UAGB) and (b) a UAGB coupled with an external submerged AnMBR tank, obtained similar COD removal efficiencies >91%.

A limitation in the use of AnMBRs to treat wastewater is their performance in the removal of nutrients. Free ammonia (NH_4^+ and NH_3) and orthophosphate (PO_4^{3-}) are released during the degradations of amino acids and organic phosphorus compounds through anaerobic processes. This leads to high levels of nutrients in the effluent of AnMBRs [92–96]. Hence, post-treatment processes are needed to remove nutrients from the permeate of AnMBRs. The effluent of a pilot-scale gas-sparged AnMBR was subjected to coagulation to remove and recover phosphorus [93]. In the same study, an ion exchanger was used to remove ammonia. Ion exchange using natural zeolite was successfully applied by Deng et al. [97] to remove ammonium-nitrogen from AnMBR permeates. Vu et al. [96] proposed a system of coupled AnMBR and membrane algae photobioreactor (MPBR) for simultaneous

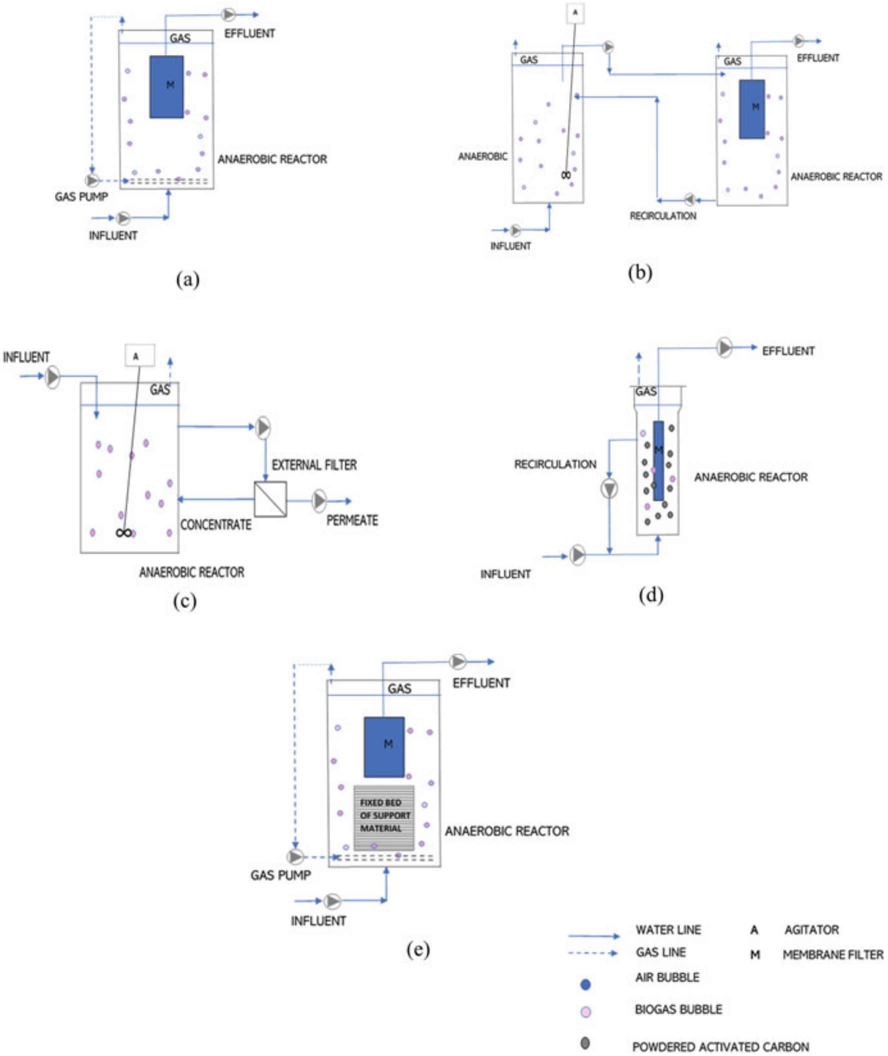

Fig. 3 Alternative AnMBR configurations. (**a**) Submerged AnMBR, (**b**) Two-stage Anaerobic CSTR and submerged AnMBR with Sludge Recirculation, (**c**) External AnMBR, (**d**) AnFMBR, and (**e**) AnMBR with Fixed Bed of Inert Material/Support Material

wastewater treatment, and energy and nutrients recovery. In this system, the wastewater was first treated by the AnMBR. The effluent of the AnMBR was fed to the MPBR, which consisted of a membrane module submerged in media composed of microalgae culture and ANMBR effluent. High levels of NH_4^+ and PO_4^{3-} were obtained in the AnMBR effluent (at levels higher than those of the influent by 1.9 and 1.4 times, respectively). These concentration levels made the AnMBR effluent suitable for microalgae cultivation, having the capability to assimilate dissolved nitrogen and phosphorus. The microalgal biomass can potentially be used as feedstock for biofuel production. The integration of an anaerobic forward osmosis membrane bioreactor (AnOMBR) with a microbial electrochemical recovery unit was also studied to recover NH_4^+ and PO_4^{3-} from the bulk wastewater [16]. Both the microbial nutrient recovery cell (MRC) and the AnOMBR were submerged in that study in a single tank. The potential generated across the electrodes in the submerged MRC allowed extraction of charged ions from the bulk liquid in the reactor. Results showed approximately 28–45% and 41–65% recovery of NH_4-N and PO4-P, respectively, from the bulk solution.

2.3.2 Membrane Fouling and Mitigation in AnMBRs

The high solids concentration in the AnMBR leads to membrane fouling. Several factors contribute to membrane fouling, notably (a) operating conditions, (b) configuration and membrane type, and (c) supernatant and sludge properties, as presented below.

Operating conditions in AnMBRs affect membrane fouling rates. One significant operating condition that should be considered is the Solids Retention Time (SRT) in AnMBRs. It has been demonstrated that at low Hydraulic Residence Time (HRT), prolonged SRT (>60 days SRT or infinite SRT meaning no wasting of sludge) in a submerged AnMBR can result in low rate of degradation and uptake of nutrients by microorganisms [78]. This consequently led to high rate of SMP production, which contributed to membrane fouling. Extended SRT also resulted in too low EPS protein and carbohydrates content, which prevented flocculation of particles and increased number of finer particles in the reactor. These processes aggravated membrane fouling in the AnMBR. In contrast, a short SRT in an AnMBR treating phenol wastewater led to higher rate of increase in TMP values [98]. In the latter study, the protein content of EPS increased at shorter SRT. This was attributed to the response of the microorganisms to the increase in phenol loading, by increasing EPS production to degrade the phenol. The results of these studies demonstrated the need to optimize SRT in AnMBRs to minimize membrane fouling, since there are also other contributing factors.

In AnMBRs, the dominant mechanism of membrane fouling is cake formation [99, 100]. One of the operating conditions influencing the cake resistance in AnMBRs is the food-to-microorganism (F/M) ratio. Y. Liu et al. [100] found that higher F/M ratio in a submerged AnMBR increased SMP and the ratio of tightly bound EPS to loosely bound EPS in the cake layer formed on the membrane. The increase in these values improved the cake layer filtration resistance. Lin et al. [101] noted that a high F/M ratio led to higher ratio of protein to polysaccharide content of bound EPS, which promoted cake formation and consequently led to membrane fouling in a submerged AnMBR.

The system configuration (Fig. 3a–e) also influences membrane fouling in ANMBRs. For example, C. Chen et al. [91] observed higher fouling rate in the submerged AnMBR compared to that in the UAGB coupled with an external AnMBR. This was due to higher EPS and SMP in the mixed liquor of UAGB compared to that in the external AnMBR tank. The membrane material also influences membrane fouling as shown in a study on a submerged AnMBR for treating pharmaceutical wastewater [102]. In the latter study, a hollow-fiber membrane was found to be more prone to irreversible fouling due to pore blocking compared to a flat-sheet membrane. A study made by Z. Liu et al. [103] compared irreversible fouling of a polymeric membrane (PVDF) and a ceramic membrane (CM) used in an external submerged AnMBR coupled with an anaerobic CSTR (Continuous Stirred Tank Reactor). Fouling rate was higher for the PVDF membrane. A difference in the structure and composition of the gel layer formed in the two types of membranes was also observed. More organics were adsorbed onto the PVDF membrane because of its hydrophobicity. On the other hand, more inorganics such as Ca and Mg were observed in the gel layer in the CM. Information on the structure and composition of the irreversible fouling layers are important considerations in the choice of fouling mitigation and membrane cleaning approaches.

The sludge floc size was also shown to affect sludge cake formation in an AnMBR [104]. Fine particles corresponded to higher cake formation rates. Lower back transport force of the fine particles promoted their deposition on the membrane surface. Z. Zhou et al. [105] showed that fine particles (of size from 0.45 to 10 μm) were the more dominant fouling substances compared to dissolved organics in a submerged AnMBR. In another study, these fine particles were associated with microorganisms that favored biofilm formation, increased filtration resistance, and caused pore blocking [90].

Membrane fouling is a major limitation in the application of AnMBRs. One of the strategies to control membrane fouling is the use of biogas sparging [106, 107]. Biogas sparging provides scouring action on the layer formed and also reduces the deposition of foulants on the membrane surface [108]. Berkessa et al. [81] developed a submerged AnMBR which consisted of two zones: bottom portion for bulk sludge digestion and upper portion for submerged membrane module in a relatively lower MSS solution. A three-phase separator is located between the two zones to enhance solid stratification, and eventually reduce membrane fouling.

Another approach to reduce fouling in AnMBRs is to integrate it with other processes, leading to development of modified configurations. Modified configurations can be aimed to mitigate membrane fouling and at the same time to enhance pollutant degradation, as discussed below.

2.3.3 Integration of AnMBR with Other Processes

AnMBR Integrated with Fluidized Bed Process

To reduce membrane fouling, AnMBRs have been modified in some studies to integrate it with fluidized bed processes (Fig. 3b). In this configuration, the membrane is in contact with fluidized particles of a solid phase, for instance Granulated Activated Carbon (GAC) or zeolite.

Kim et al. [109] examined the performance of an anaerobic fluidized membrane bioreactor (AnFMBR) as a post-treatment system after an anaerobic reactor. The fluidized GAC particles contributed to the mitigation of fouling because of their scouring action exerted on the surface of the polyvinylidene fluoride (PVDF) hollow-fiber membrane. In the MBR system without fluidized GAC particles, TMP reached 0.32 bar in just 0.5 days. In contrast, the TMP reached only 0.05–0.07 bar during first 20 days of operation in the presence of fluidized GAC particles in the MBR system. The addition of the AnFMBR as a second stage in the treatment system resulted in an 87% removal of COD from the pre-treated wastewater.

Another study [110] showed that in the first 100 days of operation of a single stage anaerobic fluidized bed ceramic membrane bioreactor (AnFCMBR), TMP was <0.1 bar. The scouring action of the fluidized particles on the membrane also resulted in reduction of fouling.

Aside from membrane fouling reduction, the integration of AnMBR with fluidized GAC particles increased its potential to degrade recalcitrant compounds due to the adsorptive capacity of the GAC [111].

In a recent study by M. Kim et al. [109], PVDF media was used instead of GAC as fluidization agent in an AnFMBR. TMP was kept at levels below 0.05 bar with the fluidization with PVDF. COD removal of 90% was also achieved using the reactor.

AnMBR with Additional Inert Support Material for Biomass

An alternative approach to modify AnMBRs makes use of materials supported on a fixed bed (Fig. 3e). The intended function of these materials is to reduce the concentration of suspended solids or biomass that would be deposited on the membrane's surface. Diez et al. [72] examined the performance of an Anaerobic Filter Membrane Bioreactor, which consisted of a biological chamber filled with suspended inert support material (Biofill-C, Bio-fil, Spain) and of a membrane filtration tank. In this modified AnMBR configuration, biomass was retained by the support material. Suspended particles and organic matter were then trapped and degraded by the biomass attached to the support material. This reduced the amount of solids carried into the subsequent membrane filtration tank, thus reducing membrane fouling.

Li et al. [112] used an Anaerobic Biofilm Membrane Bioreactor (ABMBR) which had a mesh filter as support for the dynamic membrane from biomass, and carbon fiber packing. The carbon fiber packing material served as an additional base for microorganism growth and for pollutant adsorption. This configuration was also observed to reduce the rate of membrane fouling in the reactor.

AnMBR Integrated with Electrochemical Processes

AnMBRs have been modified by combining with them with electrochemical systems. As is the case for aerobic eMBRs, electrochemical processes have been found to increase the potential of AnMBRs to degrade pollutants and mitigate membrane fouling.

Yang et al. [113] found that an anaerobic electrochemical membrane bioreactor with CNTs-HFMs obtained a higher COD removal (95%) than that achieved in AnMBRs without electrochemical assistance. The electric field application increased COD rejection through repulsion by the membrane and COD degradation through enhanced microorganism activity. Ding et al. [114] showed in their study that an electrochemically assisted AnMBR (with applied voltage of 0.6 V) could obtain a COD removal rate that is 20% higher than that of an AnMBR without electric field application.

The latter study also showed that electric field application in the AnMBR process resulted in a decreased membrane fouling rate. The application of increasing voltage to the electrochemically enhanced AnMBR increased the zeta potential and decreased the viscosity of sludge particles. The increased zeta potential prevented formation of compact layer on the membrane. Additionally, the decrease in viscosity lowered the tendency for the sludge particles to form agglomerates and less tendency to form a compact layer. These mechanisms led to the mitigation of membrane fouling.

2.4 Removal of Emerging Contaminants Using Advanced Membrane Bioreactors

Emerging contaminants, which tend to be included in the broader group of trace organic contaminants (TrOC), are defined as the pollutants that are not yet regulated or not routinely monitored but may enter the environment and pose ecological and human health risks [115, 116]. Common emerging contaminants are pharmaceutical products, personal care products (PPCPs), plasticizers, endocrine disrupting compounds, flame retardants, pesticides, fluorinated surfactants, and microbiological entities [115–117].

Because of the potential adverse ecological and human health effects, several studies have examined emerging contaminants' removal from water and wastewater. MBR methods are among the wastewater treatment technologies being studied for emerging contaminants' removal. As discussed, MBRs have been shown to efficiently degrade pollutants found in wastewater mainly because of their capacity to retain microorganisms inside the reactor. Advanced MBRs are being widely developed to enhance the capability of MBRs in the degradation of emerging contaminants (ECs), as discussed in the following section.

2.4.1 Emerging Contaminants Removal by SFDMBRs

In general, research on the use of SFDMBR has been primarily focused on the removal of conventional pollutants. Investigation of the performance of SFDMBRs in the removal of emerging contaminants is still very limited but this aspect of SFDMBRs performance can be examined based on the example of pyridine. Pyridine is a recalcitrant and toxic compound usually used in manufacture of herbicides and pharmaceutical products [118]. In a study by Hou et al. [119], pyridine was degraded using an anoxic/oxic dynamic membrane bioreactor (A/O-DMBR). In the reactor, the influent passed through the anoxic zone first, then to the oxic zone with the dynamic membrane. A portion of the effluent of oxic zone was recirculated back to the anoxic zone. Pyridine degradation started in the anoxic zone of the reactor with the cleavage of the pyridine ring, releasing $NH_4{}^+$. The DM in this type of SFDMBR was crucial in retaining the biomass, which converted the NH_4^+ to Nitrate (NO_3^-). The released NO_3^- was recirculated back to the anoxic zone and became an electron acceptor, resulting in further degradation of pyridine. Residual pyridine was observed to be degraded further in the oxic zone of the reactor where the DM was located.

In a study by Monsalvo et al. [120] on the removal of different TrOCs using an AnMBR, the concentration of retained compounds in the fouling layers (external, cake, irreversible and pore-blocking layers) was examined. The results of the study revealed that the retention on these layers provided a significant contribution to the rejection of the TrOCs. Although this study used an ultrafilter, the results suggested that the potential of the DMs in the retention of TrOCs is worth investigating in future studies.

2.4.2 Emerging Contaminants Removal by AnMBRs

AnMBRs have the potential to degrade recalcitrant compounds in wastewater due to the higher rate of degradation by anaerobic microorganisms. AnMBRs have a high biomass retention, allowing more time for the microorganisms to degrade emerging contaminants such as micropollutants. In a study by Wijekoon et al. [121], adsorption of TrOCs onto the sludge in an AnMBR was shown to increase their biodegradation. Adsorption to the sludge increased the TrOCs' retention time inside the reactor, allowing more time for degradation by the anaerobic microorganisms. Adsorption capacity is also enhanced by presence of the membrane, which is another solid–liquid interface for sorption of the pollutants [122].

Several studies have examined the application of AnMBRs in the treatment of wastewaters with antibiotics [43, 82, 123–125]. Other types of wastewater treated using AnMBR were pharmaceutical effluents containing the non-steroidal anti-inflammatory drug etodolac [102], and endocrine disruptor compounds [126]. Caffeine, which can also be qualified as an emerging contaminant, found in coffee processing effluents, was also found to be degraded using an AnMBR [127]. In that study, caffeine removal at 87.5 ± 5.3% was achieved by methanogenesis degradation.

The performance of hybrid AnMBRs in the removal of emerging contaminants from wastewater has been investigated as well. The efficiency of an AnMBR with powdered activated carbon (PAC) in removing pharmaceutical compounds from wastewater was investigated by Xiao et al. [128]. In the latter work, the removal of trimethoprim, sulfamethoxazole (SMX), triclosan (TCS), diclofenac (DFC), and carbamazepine (CZ) was increased by the action of PAC in the modified AnMBR. The mechanisms of removal were adsorption and increased biotransformation of the compounds. Chen et al. [129] utilized a pilot-scale Staged Anaerobic Fluidized Membrane Bioreactor (SAnFMBR) to treat municipal wastewater containing ibuprofen, naproxen, CZ, and DFC. Naproxen was found to be removed more efficiently by the SAnFMBR compared to ibuprofen, CZ, and DC.

Another modified AnMBR with a downstream nano-filtration (NF) module was used to treat wastewater with 15 TrOCs, which included anticonvulsants, antibiotics, antidepressants, antibiotics, analgesic, antihistamine, flame retardants, insect repellents, herbicide, beta-blocker, and stimulant. The NF module improved the removal efficiency of TrOCs due to filtration and enhanced degradation because of increased retention by the concentrate recycle line from NF module to the AnMBR [130].

In these latter studies utilizing AnMBRs, the removal efficiency of the emerging contaminants by the anaerobic system was observed to be significantly influenced by the nature of the pollutants. Molecular structure, size, and charge affect the removal of emerging contaminants from water [120, 131]. In the recent studies, those that were more efficiently degraded by AnMBR were contaminants with strong electron donating groups such as amino functional groups ($-NH_2$, -NHR, $-NR_2$) [129, 130]. In another study [120], highly hydrophobic compounds such as triclosan, testosterone, androsterone, triclocarban, and nonylphenol were the TrOCs efficiently removed by an AnMBR due to sorption to sludge.

2.4.3 Emerging Contaminants Removal by eMBRs

Combined biodegradation, membrane filtration, and electrochemical processes make eMBRs viable for treatment of wastewater with emerging contaminants.

Removal of pharmaceuticals Amoxicillin (AMX), DCF, and CZ from wastewater using an eMBR was investigated by Borea et al. [49]. The application of electric field resulted in the enhanced removal of the pharmaceuticals due to the effects of electrocoagulation. The generation of the positively charged coagulant (Al^{3+}) from the anode resulted in neutralization of the negatively charged pharmaceutical compounds. This resulted in the formation of agglomerates that adsorbed the small molecules of the pharmaceuticals. This led to the increase in the pharmaceutical compounds' rejection by the membrane filter.

Chen et al. [132] studied effects of electric field to a moving-bed membrane bioreactor (MMBR) for the treatment of wastewater with low-concentration SMX. Using the control MMBR (without electric field application), the SMX removal efficiency was at 44%. The use of the electro MMBR favored the growth of the microorganisms *Actinobacteria* and *Gemmatimonadete*, which contributed to the degradation of SMX. This resulted in an increase in removal efficiency of SMX to 89%.

Tetracycline hydrochloride antibiotics removal using a coupled MBR and MFC was examined by Y. Li et al. [133]. In this type of MBR/MFC system, GAC doped with $FeOOH/TiO_2$ was utilized over the cathode membrane. The removal of tetracycline hydrochloride reached in this case up to 90%. This was attributed to the adsorption and bio-electrochemical catalytic reaction, specifically oxidation by ·OH released from oxygen reduction reactions.

3 Technologies for Energy-Harvesting Membrane Bioreactors

MBRs for wastewater treatment have been shown to have a potential to produce energy. This chapter discusses the performance of AnMBR and MBR-BES for simultaneous wastewater treatment and energy-harvesting.

3.1 Anaerobic Membrane Bioreactors

Anaerobic processes in an AnMBR produce gases, notably methane (CH_4) formed upon the degradation of organic matter present in the wastewater by anaerobic microorganisms called methanogens [134]. This production of gas makes the AnMBR a potential source of energy.

To examine the utility of this energy source, multiple studies of AnMBRs have examined the composition and quantity of biogas produced from these reactors. The theoretical amount of methane produced at standard temperature and pressure is 0.34 L CH_4 per 1 g COD removed [134]. Due to the dissolution of methane in the liquid and other losses in the process, actual yields are lower than this theoretical value (see Table 2).

Recovery of methane from AnMBRs is also influenced by the organic loading rate [77, 135], temperature [137, 139, 140], hydraulic retention time [73], sulfate concentration in the influent [141], and configuration of AnMBR.

Methane yields are typically reported as L of CH_4 per 1 g of COD removed [135]. Different configuration of AnMBRs was reported to obtain methane yield at a range of 0.13–0.33 L CH_4 per 1 g COD removed (see Table 2).

Recovery of the methane produced from the AnMBR is one way of reducing its net energy requirement. The biogas produced from AnMBRs has been used within the treatment system for mixing, suspension, and fouling control [73].

Table 2 Methane yields in different configurations of AnMBRs

Reactor type	Wastewater treated	Influent COD, mg/L	Methane yield, L CH_4/g $COD_{removed}$	References
Submerged AnMBR	Meat processing wastewater	2050–6,880	0.13–0.18	[135]
Submerged AnMBR	Municipal wastewater	320–496	0.15–0.20	[136]
Submerged AnMBR with three-phase separator between bulk sludge and membrane module	Synthetic wastewater	–	0.28–0.29	[81]
Submerged AnMBR with mesh filter and carbon fiber	Synthetic wastewater	1,120	0.29	[112]
External AnMBR	Domestic wastewater	–	At 35°C: 0.30 At 20–25°C: 0.24 At 15°C: 0.15	[137]
Single-stage AnFMBR	Low-strength synthetic wastewater	260	0.27[a]	[110]
Submerged AnMBR	Malting wastewater	4,244–5,130	0.14–0.28	[77]
External AnMBR with sludge recirculation ratio of 3	Synthetic wastewater	500	0.44	[84]
Anaerobic forward osmosis membrane bioreactor with MEC	Synthetic wastewater	2000	0.33[b]	[138]

[a] Reported yield in moles CH_4/m^3 wastewater was converted to L CH_4/g $COD_{removed}$, assuming ideal gas at Standard Temperature and Pressure

[b] Reported yield in L CH_4/g $COD_{in\ influent}$ was converted to L CH_4/g $COD_{removed}$, using the value of 86.1% COD removal

Smith et al. [83] reported that 40–50% of total methane produced by an AnMBR (operated at 15°C) was present as dissolved methane in the effluent. An average of 24% of the total methane produced was found to be dissolved in the effluent of a pilot-scale gas-sparged AnMBR operated at a temperature range of 12.7–31.5°C depending on the season. A common post-treatment process to recover the dissolved methane from the effluent is to use degassing membranes [83, 93, 142]. Longer solids retention time (40 days compared to 20 days) in an AnMBR was found to reduce the concentration of dissolved methane in the permeate and to increase the methane yield [143].

3.2 Membrane Bioreactors and Bio-Electrochemical Systems (MBR-BES)

Integration of membrane bioreactors with bio-electrochemical systems not only enhances the performance of MBRs in terms of pollutant removal and of membrane fouling mitigation but it also allows this type of MBR system to become a source of energy or to lower its net energy requirement [144].

There are two common types of bio-electrochemical systems, namely Microbial Fuel Cells (MFCs) and Microbial Electrolysis Cells (MECs). MFCs are designed to produce electricity from the degradation of organic matter by microorganisms through reduction-oxidation reactions [145, 146]. The production of electricity by the MFC is an advantage and may be used to reduce or meet the energy requirements of an MBR integrated with an MFC (MBR-MFC).

On the other hand, MECs use electrical power to enable the electrochemical reactions for hydrogen production. In an MFC, the hydrogen (H_2) gas is produced at the cathode [146, 147]. The production of this gas makes an MBR integrated with MEC (MBR-MEC) a potential source of alternative energy.

3.2.1 MBR Integrated with MFC

In an MFC, microorganisms break down organic matter through oxidation. The released electrons are transmitted to the anode. The electrons then flow to the cathode through an external circuit. This flow of electrons from the anode to the cathode produces electricity [145].

Different configurations are designed for MBRs combined with MFCs (Fig. 4a–c), as discussed below. The configurations influence pollutant removal, membrane fouling mitigation, and even the energy production (Table 3).

In some studies, an external MFC is integrated with MBRs. In a study by D. Hou et al. [152], MFC was coupled with a submerged osmotic membrane bioreactor (OMBR) to simultaneously treat wastewater and produce energy. In this reactor, high salinity wastewater was pumped first to the MFC. The effluent of MFC is then sent to the OMBR. A portion of the solution inside the OMBR is recycled and mixed with the wastewater fed to the MFC. Coupling the MFC with an OMBR increased the power density from 3 W/m^3 to 11.5 W/m^3. This significant increase in power density was attributed to the increased conductivity of the solution fed to the MFC due to the recycle line from the OMBR. The MFC was also shown to reduce membrane fouling because it served as a pre-treatment stage of the wastewater before going to the OMBR.

The electricity produced from an MFC can be used for fouling control for MBRs. This was demonstrated in an integrated external MFC and anoxic-oxic eMBR [153]. In the hybrid reactor, wastewater was fed first into the anoxic reactor. The effluent of anoxic reactor flowed to the oxic reactor, which consisted of a membrane module and graphite electrodes. A separate MFC was fed with a portion of the

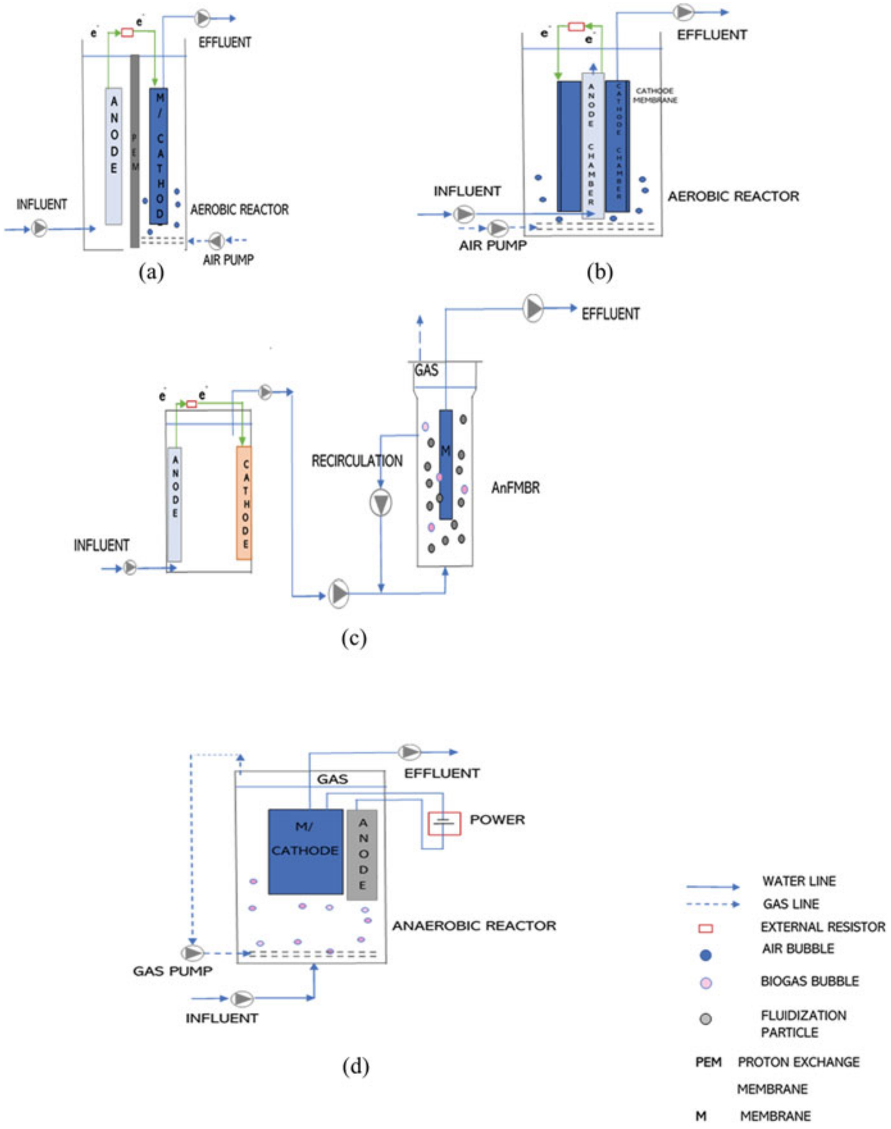

Fig. 4 Alternative configurations of MBR-BES. (**a**) Two-chamber MBR-MFC, membrane as cathode/membrane in cathode chamber (**b**) MBR-MFC with tubular cathode chamber, membrane in cathode chamber, (**c**) Two-stage MFC and AnFMBR, and (**d**) Anaerobic MBR-MEC, membrane as cathode

Table 3 Different configurations of and energy produced from MBR-MFC

Reactor type	Reactor details: MFC electrodes	Wastewater	Energy produced	References
Over-flow type eMBR (MFC)	*Anode*: O ring carbon felt *Cathode*: SS mesh, also served as membrane with 38 μm pore size	Synthetic wastewater	*Power density*: 629 mW/m^3 or 7.18 mW/m^2	[148]
Anaerobic reactor and external AnMBR-MFC	*First set-up*: *Anode*: Filtering anode with SS filter plate *Cathode*: Platinum mesh *Second set-up*: *Anode*: Hybrid anode (PVDF membrane + SS mesh as support) *Cathode*: Platinum mesh	Synthetic brewery wastewater	*Current density*: (1) Filtering anode: <1 A/m^2 (2) Hybrid anode: 2.48 A/m^2	[144]
Combined submerged MBR and MFC	*Anode*: Iron *Cathode*: Conductive membrane modified by polypyrrole (base is polyester cloth)	Synthetic wastewater with conductivity of 0.41 mS/cm	*Power density*: 0.86–2.6 mW/m^2 *Cell potential*: 0.2 V with 100 Ω resistor	[149]
Combined submerged MBR and MFC	*Anode*: Granular graphite *Cathode*: Stainless-steel mesh which also served as the membrane with 40 μm pore size	Synthetic wastewater	*Power density*: 4.35 W/m^3 *Current density*: 18.32 A/m^3 *Coulombic efficiency*: 8.2%	[150]
Submerged MBR and MFC	*Anode*: Activated carbon fiber *Cathode*: Carbon felt	Synthetic wastewater with COD of 400 mg/L	*Power density*: 6.0 W/m^3	[151]
External MFC and submerged OMBR	*Anode*: Carbon brush *Cathode*: Air-cathode	Synthetic high salinity wastewater	*Power density*: 11.5 W/m^3	[152]
External MFC and anoxic-oxic eMBR	*Anode*: Carbon felt *Cathode*: Carbon cloth	Synthetic wastewater	*Cell potential*: 0.52 ± 0.02 V with 1,000 Ω resistor *Electric field density*: 0.114 V/cm	[153]

supernatant of the anoxic reactor. The electricity produced from this MFC was used to supplement the DC power for the electrodes in the oxic reactor. Although only a small portion of the wastewater COD (0.5%) was converted to electricity, it was used to mitigate fouling in the eMBR and reduce energy consumption of the system. In an MFC integrated with an AnFMBR, the energy consumption of the AnFMBR was

0.0186 kWh/m^3 of effluent [154]. The energy demand was mostly for the fluidization of the GAC particles in the system (52.5% of the total energy requirement). In the latter study, the energy produced by the external MFC could supply 100% of the system's electrical energy requirement.

Other studies have utilized the configuration where the MFC and MBR are submerged in one vessel, as discussed in the following subsections.

MBR-MFC with Cathode as Membrane/Cathode in Membrane Chamber

MBR-MFC configurations can utilize the cathode serving either the membrane itself or it is located in the same chamber as the membrane (Fig. 4a, b). For example, Tian et al. [155] used an integrated AnMBR and MFC, in which the hollow-fiber membrane installed inside an SS frame served as the cathodic chamber, to treat wastewater and produce electricity. In another MBR integrated with MFC, a polypyrrole-modified filter functioned as the cathodic membrane [149].

Wang et al. [150] showed that both a conductive SS filter and the formed biofilm on it served as cathode for an MBR-MFC. The growth of biofilm on the SS mesh was shown to be significant in the context of electricity generation in the MBR-MFC. Microorganisms in the biofilm catalyzed the reduction of oxygen at the cathode membrane. This process resulted in a higher output voltage as the biofilm formed on the membrane in the reactor. However, the thickness of the biofilm also restricted oxygen transfer at the cathode, which resulted in a drop in the output voltage after some time of operation of the system.

MBR-MFC with Anode as Membrane/Anode in Membrane Chamber

A recently investigated MBR-MFCs configuration is one in which the anode is either the same material as the membrane or it is combined with the membrane. In the study of Kocatürk-Schumacher et al. [144], AnMBR was integrated with two designs of the microbial anode. The first one is a filter anode made of SS plate. The second one is a hybrid anode, in which an SS anode is combined with a PVDF membrane. Use of the SS anode obtained current density of <1 A/m^2, while the hybrid anode obtained up to 2.48 A/m^2.

3.2.2 MBR Integrated with MEC

As discussed in Sect. 3.2, H_2 gas is produced in the cathode side of MECs. One way of harnessing this source of energy is to integrate AnMBRs with MECs to increase CH_4 production. A common configuration used for integrated AnMBRs with MECs is that in which the membrane is also used as the cathode material (Fig. 4d) [113, 114, 156].

The study by Katuri et al. [156] developed an AnMBR combined with an MEC (AnMBR-MEC), in which a porous nickel-based hollow-fiber membrane served as both the cathode and the membrane filter. The latter work examined simultaneous wastewater treatment and energy harvesting. In addition to a 95% COD reduction, a higher amount of CH_4, which was 71% of the energy based on substrate, was recovered from the AnMBR-MEC. This increase in gas yield was due to the conversion of H_2, which was produced in the cathode, into CH_4.

In another AnMBR-MEC study [113], novel carbon nanotube hollow-fiber membranes (CNTs-HFMs) were used as both the cathode and membrane. The CH_4 yield obtained was higher in this AnMBR-MEC compared to the AnMBRs without electrochemical assistance. The H_2 produced from the cathode was converted to CH_4, contributing to the higher yield. The electric field was observed to increase the growth rate of *Methanomicrobia* and hydrogenotrophic methanogens. These microorganisms aided in the breakdown of Volatile Fatty Acids (VFAs), resulting in more CH_4 produced.

A combined AnOMBR and MEC was used to treat wastewater and recover CH_4 [138]. The application of electric field to the AnOMBR increased the CH_4 yield by 11.04%. The electric field also enhanced the growth rate of H_2-utilizing methanogens, and consequently increased CH_4 yield.

However, the study of Ding et al. [114] has also shown that excessively high voltage applied to an AnMBR could lead to lower COD removal and lower methane production. High voltage could result in destruction of cells of microorganisms, slowing down the processes of COD degradation and methane generation. The results of the study demonstrated the need for optimization of applied voltage in AnMBR-MECs. In this study by Ding et al. [114], the optimum voltage was found to be at 0.6 V.

4 Economic Feasibility of Currently Developed Membrane Bioreactors

The use of the advanced MBRs discussed in this review for enhanced pollutant removal and membrane fouling mitigation is promising. However, to obtain optimal performance and operational utility of such reactors, costs related to acquisition of new materials, energy consumption during operation, cleaning and maintenance of the system need to be accounted for. This section gives particular attention to the specific energy demand of the different advanced MBRs.

In AnMBRs, energy requirement is typically defined by the need to operate the pumps, and blowers for biogas sparging. In modified AnMBRs, additional requirements are associated with fluidization (such as in AnFMBRs), electricity to drive electrochemical reactions, or dissolved methane recovery [93, 110, 157]. In one pilot-scale gas-sparged AnMBR, the total energy demand per volume of treated wastewater was 0.349 kWh/m^3, 48.7% of which was attributed to biogas sparging.

Table 4 Energy requirements and energy produced by different AnMBRs

Reactor type	Energy requirement per volume of treated wastewater, kWh/m^3	Equivalent electrical energy generated from CH_4 produced, kWh/m^{3a}	Scale	Reference
AnFMBR with GAC	0.058	0.19	Laboratory-scale	[157]
AnFMBR with PVDF media	0.019	0.246	Laboratory-scale	[109]
AnFCMBR with GAC	0.0387	0.226	Laboratory-scale	[110]
Anaerobic fluidized reactor coupled with AnFMBR	0.047	0.082	Laboratory-scale	[158]
Downflow floating media filter (DFF) with AnMBR	0.05–0.13	0.22^b	Laboratory-scale	[88]
Gas-sparged AnMBR	0.349	0.254	Pilot-scale	[93]
Submerged AnMBR	At 35°C: 0.31–0.33 At 25°C: 0.19–0.58 At 15°C: 0.97	At 35°C: 0.42 At 25°C: 0.34 At 15°C: 0.17	Laboratory-scale	[137]

[a] This accounts for the efficiency of the conversion of CH_4 into electrical energy
[b] This value reported by the researchers was assumed based on another prior study

In an AnFMBR studied by Kim et al. [157], the energy demand per volume of permeate was 0.058 kWh/m^3. In the AnFCMBR investigated by [110], it was 0.039 kWh/m^3. As seen in Table 4, the range of energy consumption of AnMBRs from previous studies is 0.019–0.97 kWh/m^3. In comparison, full-scale conventional MBRs have been reported to consume 0.64–6.6 kWh/m^3 [159–161]. In addition, the specific energy consumption in conventional activated sludge (CAS) treatment systems ranges from 0.1–2.9 kWh/m^3 [161].

As discussed in the section on energy-harvesting MBRs, AnMBRs produce CH_4 gas which may be utilized to reduce the overall energy requirement of AnMBR systems. The electrical energy that can be generated from the CH_4 produced from the anaerobic process can supply 73% to more than 100% of the energy requirement of some previously studied AnMBR systems, as shown in Table 4. However, it can be noted that the current process of conversion of CH_4 to energy results in only a 21% efficiency due to the operational losses from the pumps, electric motors, and inverters [157].

No study has so far reported the specific energy consumption in SFDMBRs. As in conventional MBRs, the aeration of the mesh and activated sludge in an aerobic SFDMBR is a significant contributor to the energy requirement of the system. In an AnDMBR, this may be reduced via the use of the biogas that may be produced in the system. The main economic advantage of the SFDMBR over the conventional

MBRs is the use of low-cost support materials instead of the micro-filters and ultra-filters.

Previous studies of laboratory-scale aerobic eMBRs reported specific energy requirement for operation from 0.038 to 2.1 kWh/m^3 of treated effluent [59, 162]. A pilot-scale aerobic submerged eMBR was also found to have a specific energy demand at a range of 1.1–1.6 kWh/m^3 treated wastewater [163]. It is noted that in these aerobic eMBRs, the highest energy requirement is for aeration of the system. In an aerobic eMBR, the aeration energy requirement was reported to be more than 50% of the total energy requirement [59]. In the same study, only 4% of the total energy requirement was used to drive the electrochemical reactions.

An AnMBR-MEC, which was used to treat low-strength organic solution and produce methane and hydrogen, was found to have a specific energy demand of 0.23–0.62 kWh/m^3 permeate [156]. However, this energy demand could be reduced by the energy recovered from the production of methane.

5 Challenges and Future Perspectives

Advanced MBRs are still continually being studied, with the objective of being able to apply these technologies on full-scale. The potential of SFDMBRs as a technology to treat wastewater with optimum pollutant removal and minimal costs has been shown in laboratory-scale studies. As of the time of writing of this review, there have been only a limited number of pilot-scale studies made on SFDMBRs [19, 164]. On the other hand, several pilot-scale AnMBRs have already been studied [73, 85, 93, 123, 165, 166]. A few full-scale AnMBR applications have been documented, notably in treatment of industrial wastewater from beverage industry [167] although its full-scale application on treatment of municipal wastewater has not yet been reported. Previous eMBR studies have been mostly on the laboratory scale [50]. Hasan et al. [163] investigated a pilot-scale submerged eMBR to treat raw municipal wastewater. Most integrated MBR-BES applications for wastewater treatment are also on the laboratory-scale [168].

There are current limitations of the advanced MBRs that still need to be addressed for these technologies to be suitable for larger scale applications. The limitations on the following aspects are given attention in this section: (a) pollutant removal, (b) membrane fouling, (c) energy demand and production.

Since the application of SFDMBRs in wastewater treatment is relatively in the nascent stage compared to MBR systems, further studies still must be made to achieve optimum pollutant removal. Areas of research on SFDMBRs that still need more consideration include removal of TrOCs, removal of pathogens, and further application using the anaerobic process.

AnMBRs have been demonstrated to achieve excellent COD removal from high-strength and low-strength wastewaters. Several emerging contaminants were also shown to be potentially removed by AnMBRs. However, as discussed in Sect. 2.3.1, AnMBR effluents tend to have high nutrient concentrations. The limitation of nutrient removal is also the same in AnDMBRs. With the need for a removal of nutrients after treatment with AnMBR or AnDMBR, optimum integration with other processes to obtain efficient pollutant removal and minimized costs need further studies.

Membrane fouling mitigation mechanisms in conventional MBRs include aeration, backwashing, modification of membrane properties, physical and chemical cleaning. In the advanced MBRs, membrane fouling mitigation strategies involve integration with other processes such as fluidization, use of fixed bed of packing material, and electrochemical processes. As previously presented, regulation of QS is a new approach in membrane fouling mitigation and the use of electric field as a QQ strategy has been recently studied. Further research on this new fouling reduction approach is also to be considered.

One significant concern on application of MBRs is the energy consumption. As discussed in Sect. 3, AnMBRs are utilized for simultaneous wastewater treatment and energy harvesting. The produced energy provides a potential to reduce the net energy requirement of the system. However, a concern is on the dissolved methane in the effluent, notably in psychrophilic operations. Post-treatment processes incur additional costs and complexity in system operations. Thus, optimization of parameters to reduce dissolved methane and increase methane yield should be considered in further studies.

One of the largest energy requirements in aerobic MBRs (such as in aerobic SFDMBRs and eMBRs) is the aeration of the bulk liquid and the membrane. With this, reduction of energy demand must be geared towards decreasing energy requirements due to aeration.

6 Conclusions

Advanced MBRS, including SFDMBRs, AnMBRs, eMBRs, and MBR-BES, have been developed to obtain efficient pollutant removal, reduced membrane fouling, and reduced net energy requirement.

Different mechanisms such as aerobic or anaerobic biodegradation, adsorption, electrochemical oxidation and reduction, electrocoagulation, and filtration are utilized by the advanced MBRs to remove pollutants from wastewater. Advanced MBRs have been demonstrated to not only remove conventional pollutants but also a wide range of emerging pollutants. Integration of advanced MBRs with other processes can further enhance the system's performance in pollutant removal and membrane fouling mitigation.

AnMBRs and MBR-BES are systems that can be used for simultaneous wastewater treatment and energy production. The energy produced in these MBRs can be utilized in these systems to reduce net energy requirements.

Use of advanced MBRs in large-scale applications is yet to be realized. The challenges that need to be addressed in future studies include poor nutrient removal in AnMBRs, reduced energy recovery in AnMBRs due to dissolved methane in effluent, and high energy demand due to aeration requirements in aerobic advanced MBRs.

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Membrane Bioreactor for Wastewater Treatment: Current Status, Novel Configurations and Cost Analysis

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Contents

Abstract The membrane bioreactor (MBR) process is a ground-breaking innovation in the field of wastewater treatment, which involves a biological activated sludge process coupled with the membrane separation. The main highlights of the

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MBR are its low footprint, which is due to the elimination of secondary sedimentation process in the conventional activated sludge (CAS). MBR can produce high and consistent effluent quality, which can be a non-potable water source or be readily treated in downstream processes for potable water reuse. With the decrease in the cost of membrane modules over the years, full-scale deployment of MBR plants continues to increase worldwide with scale up to 800 MGD to date. Nevertheless, membrane fouling and energy consumption in MBRs are two technical challenges. MBR membranes are prone to fouling by organic matter originating from the microbial cells. Energy consumption in MBRs is higher than the CAS due to the aeration requirements, particularly for membrane scouring. Several mitigations strategies to address these challenges have been developed, which showed promising results by reducing the operating cost of the MBR plants. These strategies include the development of new membrane materials with chemical and biological resistant properties, novel configurations for enhanced process performance as well as fouling mitigation and control. This chapter aims to present a succinct overview of the status of MBR technology for municipal and industrial wastewater treatment to cover the recent development of energy reduction and fouling mitigation. It is envisioned that MBR will continue as a domain technology in wastewater treatment sector.

Keywords Cost analysis, Energy consumption, Membrane bioreactors (MBR), Membrane fouling, Novel configurations

1 Introduction

Membrane filtration technologies have emerged as a mainstream technology in many industrial applications including wastewater treatment, water reclamation and bioprocessing. The membrane process offers numerous advantages such as stable performance, high efficiency, compact and modular design, and easy operation. There are four types of pressure-driven membrane processes according to their nominal pore size: (i) microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). MF and UF membranes have been commonly integrated with a biological reactor to form a membrane bioreactor (MBR) system. The MBR technology is a ground-breaking innovation in the field of wastewater treatment, which essentially is an upgrade of the conventional activated sludge process by addition of a membrane-based separation process. With the decrease in the cost of membrane modules over the years, the development in membrane configurations, membrane materials, and process optimization experience to alleviate the two bottlenecks (i.e. membrane fouling and energy consumption), MBR has become a preferred wastewater treatment process.

This chapter aims to provide a critical summary of the most recent developments of the MBR process to support the ambitious target of cost-efficient wastewater treatment technology. The chapter reviews the MBR capital and operating expenditures as well as cost analysis of the MBR technology in comparison with the conventional activated sludge process. Process configurations and optimization are discussed along with some successful achievements on the energy reduction. Life cycle assessment of the MBR is also reviewed to delineate the benefit of water reuse and cost reduction of large-scale MBRs. Data corroborated in this chapter are in the favour of supporting the MBR process.

2 Application of Full-Scale MBR

2.1 Overview of the Technology

The MBR technology, as already stated above, is a compact and robust process combining a conventional activated sludge process with a membrane separation to produce a high-quality effluent [1]. This integration can not only ensure effective removal of diverse pollutants (such as bulk organics and nutrients) but can also reduce the footprint due to the absence of the secondary clarifier [2]. MBRs have been widely advanced in municipal and industrial wastewater treatment [3–5]. The application of MBR in wastewater treatment was first reported in 1969, when an ultrafiltration membrane was utilized for the separation of the activated sludge to produce high-quality secondary-treated effluent [1]. In recent years, the MBR technology has also demonstrated its readiness and robustness for the treatment of industrial and high strength wastewater, e.g. textile industries, paper and pulp industries, tanning (leather) industries and landfill leachate [2, 6–12].

Due to the escalating need for high-quality effluent, which can be directed towards water reuse applications, the demand for MBR may eventually exceed than that of conventional activated sludge process (CAS), especially if competitive treatment cost can be realized. Indeed, the number of large-scale (i.e. 80–800 mega gallons per day, MGD) MBR plants continue to increase worldwide (Table 1).

The configuration of the membrane separation in MBR is dependent on the placement of membrane module relative to the bioreactor. Based on the configuration of the membrane module, MBR could be categorized as follows: submerged/internal MBR (iMBR) (Fig. 1a) and side-stream/external MBR (sMBR) (Fig. 1b) [13]. Each configuration has its own advantages and disadvantages in wastewater applications as presented in Table 2. iMBRs can be usually applied to treat municipal and industrial wastewater, while sMBRs are mainly used for the treatment of industrial and high strength wastewater [13, 14]. The geometric configuration of MBR refers to the geometry of the membrane and the direction of water transmission. This configuration involves three categories (i.e. flat sheet, hollow fibre and tubular) [1]. The flat-sheet and hollow fibre membrane modules are usually applied in iMBR, while the tubular configuration is used in sMBR [1].

The membranes for MBRs can be manufactured using a range of materials (i.e. polymers, ceramics, and metals) with different advantages and disadvantages [15–18] (Table 3). Ceramic and polymeric materials are most commonly used for

Table 1 List of the 10 largest MBR plants in the world

Installation	Location	Technology supplier	Peak daily flow (MLD)	Average daily flow (MLD)	(Expected) commissioning date
Beihu WWTP	Hubei, China	Beijing Origin Water Technology Co., Ltd. (BOW)	1,040.0	800.0	2019
Henriksdal WWTP	Stockholm, Sweden	SUEZ – Water Technologies & Solutions	864.0	536.0	2026
Tuas water reclamation plant	Singapore	CH2M	800.0	800.0	2025
Seine Aval WWTP	Acheres, France	SUEZ – Water Technologies & Solutions	357.0	224.0	2016
Canton WWTP	Ohio, USA	Ovivo (GLV Group)	333.0	159.0	2017
9th and 10th WWTP	Kunming Yunnan, China	Beijing Origin Water Technology Co., Ltd. (BOW)	325.0	250.0	2013
Wuhan Sanjintan WWTP	Hubei, China	Beijing Origin Water Technology Co., Ltd. (BOW)	260.0	200.0	2015
Jilin WWTP	Jilin Province, China	Beijing Origin Water Technology Co., Ltd. (BOW)	260.0	200.0	-
Euclid WWTP	Ohio, USA	SUEZ – Water Technologies & Solutions	250.0	83.0	2018
Shunyi WWTP	Beijing, China	SUEZ – Water Technologies & Solutions	234.0	180.0	2016

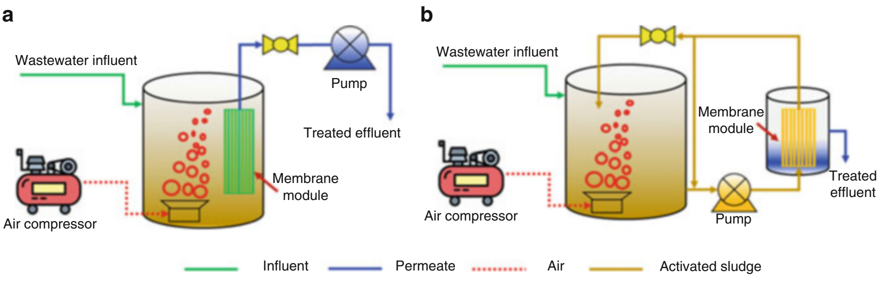


Fig. 1 Two configurations of MBR including (**a**) internal/submerged MBR (iMBR) and (**b**) external/side-stream MBR (sMBR)

manufacturing UF/MF membranes [15, 16]. Polymeric membranes are made of a polymer monolith such as polyvinylidene difluoride (PVDF), polyethylene (PE), polypropylene, polyethersulfone, and polytetrafluoroethylene [19]. Among these

Table 2 Typical characteristics of iMBRs and sMBRs [15, 16]

Factors for consideration	iMBR	sMBR
Operational complexity	Flexible	Complicated
Footprint	Small	Large
Cost per m^2 membrane area	Low	High
Water flux	Low	High
Cleaning mode	Less frequent	Frequent
Energy consumption	Low	High

Table 3 List of membrane materials and their characteristics [15–18]

Membrane materials	Advantages	Disadvantages
Ceramic materials	• Resistance against chemicals • Resistance against abrasion • Better concentration polarization control via backwashing • High fouling reversibility	• Expensive • Fragile • Need supporting materials in hollow fibre or flat-sheet configuration
Metallic materials	• Mechanical strength • High hydraulic performance • High fouling reversibility • Resistance to temperature • Resistance to chemicals	• Expensive
Polymeric materials	• Cost effective • High self-supporting ability	• Vulnerable to chemicals • Susceptible to temperature variations • Moderate hydraulic performance • Susceptible to fouling

polymeric materials, PE is broadly applied [19]. Ceramic membranes are suitable for high strength wastewater treatment due to high resistance against chemical agents [15].

2.2 *Effluent Water Quality*

The MBRs can guarantee high-quality effluent. A combination of biodegradation and sorption of pollutants on sludge and membrane separation are removal mechanisms in the MBR process. High biomass concentration and prolonged solids retention time (SRT) in MBR could result in high COD and Trace organic compounds TrOC removal. It was reported that 79–97% COD removal could be achieved by MBR during the treatment of municipal wastewater [3–5, 20–22]. MBR has also been reported to achieve excellent removal of hydrophobic TrOCs (80–95%) [23–26]. The addition of membrane unit in MBR can improve suspended solid removal efficiency up to 100% [27–29]. An MBR is capable of removing a wide range of microorganisms because the pore size of the membranes (e.g. MF, UF, and NF) employed in MBRs is much smaller than most of the microorganisms. It was demonstrated that an MF membrane can remove total coliform (*E.coli*), faecal streptococci, and salmonella to levels below the detection limit (<1 CFU/100 ml) in the MBR effluent [30].

3 Cost Analysis of MBR Process

3.1 Capital Expenditure (CAPEX)

Total CAPEX to install an MBR can be estimated by considering both the engineering and non-engineering costs. According to the available literature [31, 32], construction of tanks/reactors and equipment procurement account for approximately 70% of the total construction costs, while the layout of the piping network and the membrane module could be around 10 and 20% of those, respectively. In terms of treatment type or level, Xiao et al. [33] reported that the cost of construction can grossly range from 10 to 20% for primary treatment units, 55–85% for the MBR unit (i.e. biological and membrane units), 0–30% for tertiary treatment units, and 5–10% for sludge treatment units.

In the last two decades, CAPEX of an MBR project has been reported in several published articles. For instance, Côté et al. [34] estimated that the CAPEX of an MBR with a capacity of 38,000 m^3/day was approximately 900 USD/m^3. In another study by Verrecht et al. [32], CAPEX of an MBR project with an average capacity of 20,851 m^3/day was estimated to be approximately 376 EUR/m^3 (~425 USD/m^3). Based on the assessment of five full-scale MBR plants (1,100–2,000 m^3/day) in Spain, Iglesias et al. [35] estimated that CAPEX of MBR plants ranged between 625 EUR/m^3 (~706 USD/m^3) and 3,277 EUR/m^3 (~3,703 USD/m^3). In a recent study, a total of 175 full-scale MBR plants ($\geq$10,000 m^3/day) for municipal wastewater treatment in China were surveyed by Xiao et al. [33]. The CAPEX of the surveyed MBRs was between 2,500 and 5,500 CNY/m^3 (~380 and 800 USD/m^3) with an average capital cost of approximately 4,000 CNY/m^3 (~600 USD/m^3). It is important to note that average CAPEX of MBRs in China is higher than that of all municipal wastewater treatment plants. According to the 'China Environment Yearbook 2016', average CAPEX of municipal wastewater treatment plants was 2,500 CNY/m^3 (~400 USD/m^3). The CAPEX of MBRs has been reported to range between 308 and 5,993 USD/m^3 (Fig. 2). It is inappropriate to compare the CAPEX values reported in different studies. This is because the design capacity and unit operations of MBR plants, as well as difference in the costs associated with different components and labour costs, are highly location specific [36].

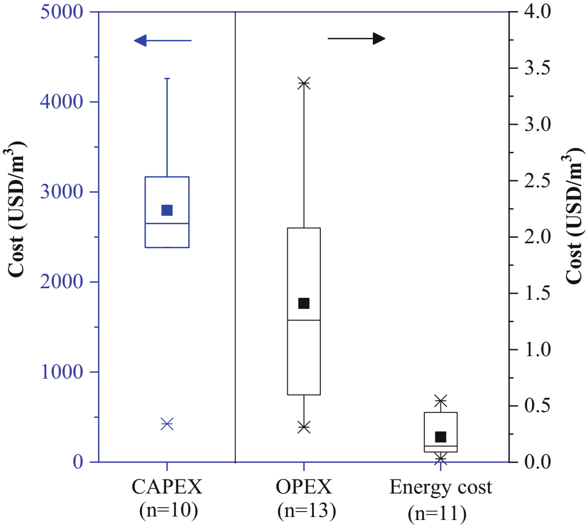


Fig. 2 Box plot of the CAPEX, OPEX and energy cost of full-scale MBR plant for municipal wastewater treatment. Box-and-whisker plot is showing information about the interquartile range; median (horizontal line in the box); min and max (whiskers); and average (block square in the box). Data extracted from [32, 34, 35] and [37]

3.2 Operating Expenditures (OPEX) and Specific Energy Consumption

Operating expenditures (OPEX) of full-scale MBR plants can be mainly divided into energy consumption, sludge disposal and chemical consumption costs. In addition, Labour costs, equipment replacement and maintenance as well as water quality testing and membrane depreciation costs can contribute to the OPEX of MBR plants. Based on the comprehensive survey of 175 full-scale MBR plants ($\geq$10,000 m^3/day) in China, energy consumption, chemical consumption, sludge disposal and other costs account for 40–60%, 10–30%, 5–15% and 5–20% of OPEX, respectively [33]. Depending on their capacity, OPEX of MBR plants has been reported to range between 1.12–2.54 USD/m^3 in Netherlands [37], 0.27–2.64 USD/m^3 in Spain [35] and 0.015–0.045 USD/m^3 in China [33]. Owing to considerable improvement in this technology (e.g. reduction in membrane cost and energy efficiency) over the last two decade, a succinct overview of the existing literature suggests a slight reduction in overall operating costs of full-scale MBR plants [36]. For instance, the OPEX of MBRs installed during 2006–2014 in China was reported to range between 0.12 and 0.2 USD/m^3. On the other hand, MBR plants commissioned after 2014 had an overall OPEX of 0.11–0.18 USD/m^3 [33].

During the operation of an MBR, energy is mainly required for aeration (for bacterial metabolism and membrane scouring), sludge mixing, sludge recirculation, and membrane filtration [31, 32, 38]. Brepols et al. [37] surveyed an MBR plant to identify the main energy consumers and found that aeration required for membrane scouring accounts for approximately 49% of the total energy consumption. The other major energy consumers were aeration for bacterial metabolism (12%), sludge mixing (11.5%), sludge recirculation (1.3%), and membrane filtration (2.7%). In the last 20 years, the development in MBR technology has made it energy efficient, and consequently, specific energy consumption (SEC) by MBR has reduced from approximately 5 kWh/m^3 (in 2001–2005) to less than 1 kWh/m^3 [38–40].

SEC by the full-scale tabular side-stream MBRs was very high (6–8 kWh/m^3) and was mainly associated with the energy required for crossflow pumping [41]. Notably, the submerged MBR, which was invented in 1988 [42], can effectively reduce the specific energy required for mixed liquor pumping from more than 3 kWh/m^3 to less than 0.01 kWh/m^3 [29, 43]. According to a study conducted by Cornel et al. [44], SEC could be reduced by submerging the membrane directly in the aeration tank. The SECs of the MBRs without and with separate membrane tank were around 1 and 2.5 kWh/m^3, respectively [44]. Owing to process optimization as well as advances in membrane module development, more than twofold reduction was observed in the SEC of the full-scale MBRs commissioned in Europe during 2001–2006 [45]. Similarly, the SEC of full-scale MBRs ($\geq$10,000 m^3/day) commissioned during the period 2006–2014 in China was 0.5–0.7 kWh/m^3, while the full-scale MBRs ($\geq$10,000 m^3/day) commissioned after 2014 had an overall SEC of 0.35–0.65 kWh/m^3 [33]. This considerable reduction in SEC could be attributed to improved design and operation of membrane modules as well as efficient aeration equipment. In addition, different operational strategies such as aeration modes, filtration and relaxation cycles, and process automation have all been reported to be favourable for reducing SEC [46–50]. The SECs of the full-scale MBR in different regions of the world have been reported to range from 0.9 to 2.25 kWh/m^3 in Netherlands [37, 38]; 0.8–2.4 kWh/m^3 in France [51]; 0.35–0.9 kWh/m^3 in China [31, 33, 40]; 0.8–3 kWh/m^3 in Japan [52] and 0.4–2.1 kWh/m^3 in Spain [46].

It is important to note that the capital, operating, and energy consumption costs appear to reduce with the increase in MBR capacity. The CAPEX and energy consumption costs would largely reduce exponentially with the increase in the capacity of full-scale MBRs, and the data collected from literature can be fitted using exponential decay model (Fig. 3a). Similarly, despite the difference in unit operations and designs, the OPEX would decrease with the increase in the capacity of MBRs (Fig. 3b).

3.3 Cost Comparison MBR vs. CAS

The MBR has become an established technology with installation in more than 200 countries [53, 54]. However, it is still considered to be expensive, particularly for implementation in developing countries. Comparison of the costs associated with the construction and operation of MBR and CAS has been reported in several studies. Based on the cost analysis over the useful life of the plants, MBR technology was reported to demonstrate overall cost benefits as compared to the CAS technology. However, OPEX of the MBR technology is higher than the CAS technology [55, 56]. This is mainly due to the difference in the extent of energy consumption by the MBR and CAS. The SEC of MBR could be 10–100% higher than that of the

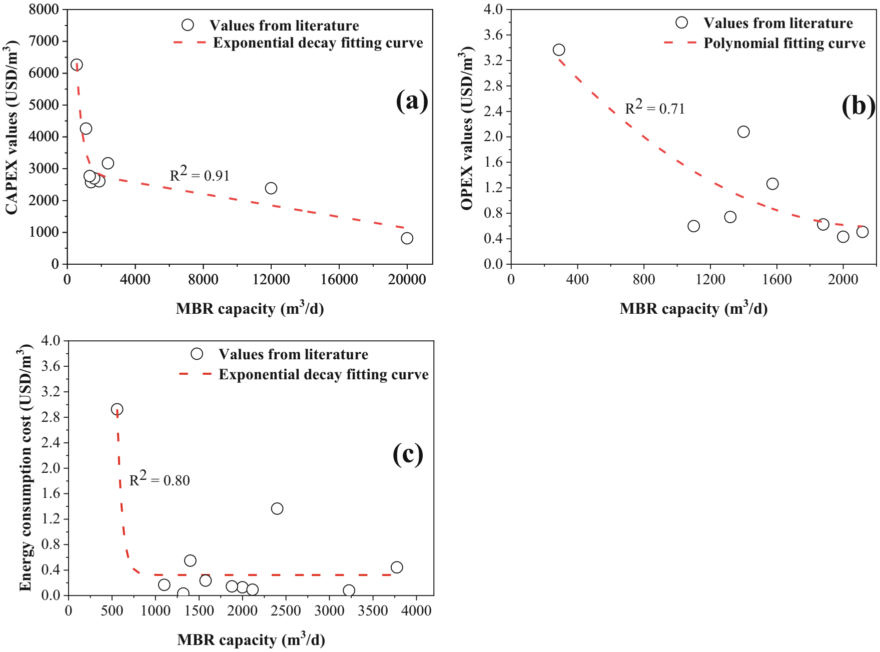


Fig. 3 CAPEX (**a**), OPEX (**b**) and energy consumption costs (**c**) of full-scale MBR plants as a function of MBR capacity. Data extracted from [34, 37]; and [35]

CAS technology [38, 47, 57]. Based on the survey of 985 municipal wastewater treatment plants, Mizuta and Shimada [58] reported that the SEC by CAS ranged from 0.3 to 1.9 kWh/m^3. An SEC of 0.1–0.6 kWh/m^3 has also been reported for the CAS technology [44, 59, 60]. As noted in Sect. 4, MBR has become an energy-efficient technology as evident from reduction in SEC, i.e. from approximate 5 kWh/m^3 (2001–2005) to less than 1 kWh/m^3 (2010 to date). This indicates that the advances in MBR technology have made the gap between the MBR and CAS technology narrower.

Cost analysis of the MBR and CAS technologies should be carried out at equivalent effluent quality for a fair comparison. In a study by Iglesias et al. [35], CAPEX and OPEX values of MBR plants in Spain were estimated for comparison with the CAS using conventional (i.e. physicochemical, sand filtration and disinfection) and advanced (i.e. membrane filtration) tertiary treatment processes. For comparable treatment capacity, the CAPEX values were estimated to be 700–960 EUR/m^3 (~910 and 1,248 USD/m^3) for MBRs, 730–850 EUR/m^3 (~949 and 1,105 USD/m^3) for CAS with conventional tertiary treatment processes and 1,050–1,250 EUR/m^3 (~1,365 and 1,625 USD/m^3) for CAS with advanced tertiary treatment processes. On the other hand, the OPEX values of MBRs were comparable to those of the CAS with extended aeration or conventional tertiary treatment processes. Importantly, they found that MBR becomes a cost-competitive technology when effluent quality suitable for water reuse applications is required [35]. This is consistent with the findings of other studies on the cost comparison of CAS and MBR technologies [37, 56]. Based on the discussion presented above, the CAPEX and OPEX values of MBR technology are higher than those of the stand-alone CAS technology but are comparable to CAS with tertiary treatment processes. The MBR technology becomes cost-competitive as excellent quality effluent is required for water reuse applications.

4 Energy Reduction in MBR

One of the critical drawbacks of MBR systems is energy-intensive consumption for the treatment process, which accounts for 40–60% of total operating expenditure [33]. As explained above in Sect. 3, an MBR consumes a significant amount of energy for its processes such as aeration for bacterial metabolism and membrane scouring, sludge mixing, water transportation and sludge recirculation. Among these, aeration required for membrane scouring to mitigate membrane fouling has a significant contribution to overall energy consumption. It has been reported that membrane scouring, biological aeration and sludge recirculation are three major activities consuming a large amount of energy in MBR systems [51]. Apart from them, pumping for water transportation also partially contributes to energy consumption in MBR [47]. Establishing measures against the major causes of energy consumption is vital for the reduction of SEC of MBRs and for the widespread applications of this technology. This section aims to systematically discuss a wide range of measures for energy-saving in MBRs.

4.1 Novel Configurations

Novel MBR configurations have been recently explored to mitigate membrane-fouling propensity, thus, consequently reducing the cleaning frequency and intensity. As a result, the aeration energy required for membrane scouring can be significantly reduced or even eliminated. These configurations consist of rotation MBR (RMBR), vibration MBR (VMBR), reciprocation MBR (rMBR) and electrochemical MBR (EMBR) [61–65]. Three configurations (i.e. RMBR, VMBR and rMBR) use dynamic shear-enhanced filtration through rotation, vibration and reciprocation movement to mitigate membrane fouling and concentration polarization [62–64]. These fouling preventing measures can be low-energy alternatives to intensive aeration for membrane scouring. In addition, the application of an electric field to mitigate membrane fouling in the EMBR configuration is also an alternative to energy-intensive air scouring [65]. In such case, the decreased fouling tendency is ascribed to the charge neutralization of colloids or particles in wastewater via electro-coagulation, electrophoresis, electroosmotic and electrostatic repulsion/rejection effects created by intermittent electric field [61, 65].

Derived from direct energy-saving perspectives, two new MBR configurations including bioelectrochemical membrane reactor (BEMR) and membrane photobioreactor (MPBR) have been introduced to offset or reduce the total energy consumption by an MBR. An BEMR is a hybrid process, which combines conventional MBR and microbial fuel cells (MFC) [66, 67]. In this concept, microorganisms in MFC are responsible for oxidizing organic matter and generating electricity, which compensates for the energy required for membrane scouring by an MBR [66, 67]. However, the complexity in the operation of this hybrid system and power generation remains a hurdle for the maturity of this technology [47]. The second configuration is the combination of an MBR and microalgae bioreactor for organic and nutrient removal and biomass production. Organic removal is accomplished by the MBR, while nutrients are removed during microalgae cultivation in the photobioreactor, thus reducing energy requirements for nutrient removal in the MBR system [68, 69].

4.2 Process Optimization

Optimization of operating conditions such as aeration rate, hydraulic utilization of membrane, water and sludge transportation has been demonstrated to significantly reduce SEC of the MBR. Briefly, energy-saving in the MBR can be implemented by reducing aeration for membrane scouring, optimizing aeration for biological process, decreasing pumping energy for water transportation and minimizing energy for sludge recirculation (Fig. 4). Furthermore, apart from reducing the total energy consumption, increasing permeate production capacity is beneficial for the decrease in SEC as presented in Fig. 4.

Reduction in aeration required for membrane scouring by directly adjusting air supply modes or by indirectly decreasing the membrane fouling severity is an efficient way to reduce SEC of the MBR (Fig. 5). The direct adjustment of aeration

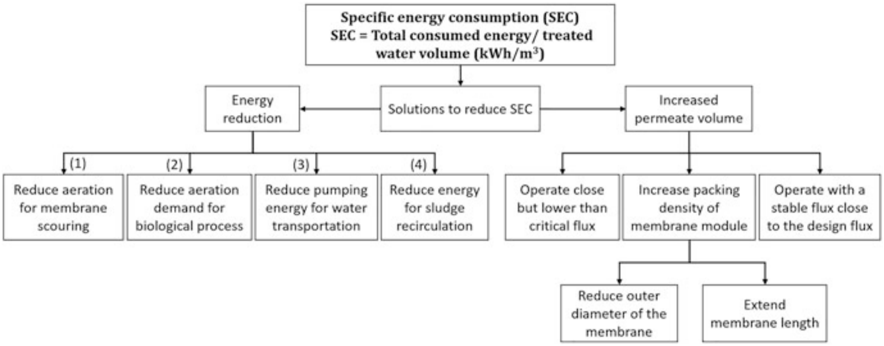
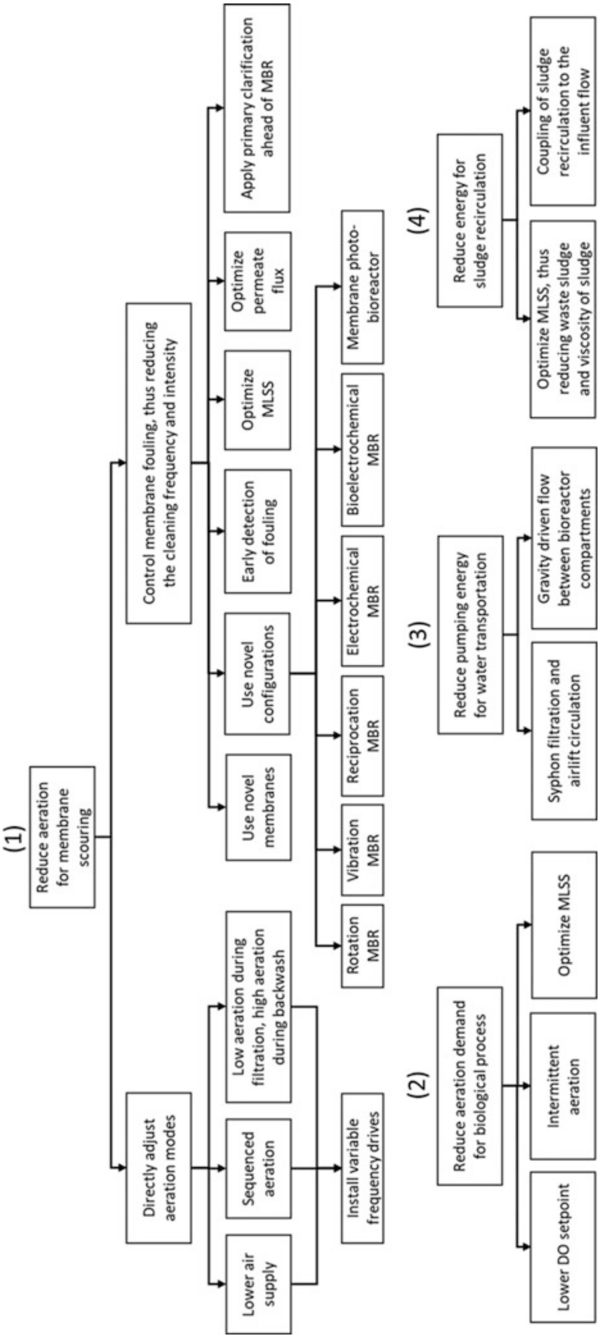


Fig. 4 Overview of measures adopted to reduce the specific energy consumption (SEC) of an MBR system

Fig. 5 Detailed measures to reduce the energy consumption (SEC) of an MBR system



intensity can be carried out by installing variable frequency drivers (VFDs) to lower air supply and generate an intermittent aeration mode for the air blowers. Moreover, aeration intensity during operation can be adjusted to be low during filtration and high during backwash by the installation of the aeration control system [47]. Several measures to prevent or control membrane fouling can be applied to reduce the aeration demand for membrane scouring, which would lead to the reduction in SEC.

Besides the novel configurations presented in Sect. 4.1, the application of novel membranes and membrane modules, early detection of fouling, optimization of MLSS and permeate flux and the employment of primary clarification ahead of MBR is effective to reduce membrane fouling and subsequent energy consumption in MBR. New generation membranes with fouling resistance properties and high water productivity can significantly mitigate fouling and save energy [47]. For example, a General Electric company in 2011 reported that the introduction of a new MBR system called LEAP MBR using novel membranes could reduce the energy consumption by 30% and increase productivity by 15% with a 20% smaller footprint as compared to their previous products.

On-line fouling detection via monitoring permeate flux at given trans-membrane pressure is an effective tool for early identification of fouling tendency, which would facilitate in timely adjustment of air-scouring rate. It is reported that applying this automatic control system can reduce membrane scouring rate by 22% without negative impacts on filtration performance [70]. Optimization of MLSS concentration can reduce the membrane fouling potential and severity, thus, lowering the aeration requirement for membrane scouring. According to the data reported by Tao et al., the average SEC of 0.549 kWh/m^3 could be achieved by reducing MLSS concentration in MBR from 10,000 to 6,000 mg/L [71]. This could be attributed to lower sludge density and better aeration efficiency [72].

Selection of an appropriate flux value plays a key role in preventing the occurrence of severe fouling during operation, thus, lowering the aeration energy for membrane scouring. Operation with water flux higher than the critical flux can cause severe fouling and clogging of the membrane, which is linked with the energy penalty for subsequent fouling mitigation measures. In this regard, reducing the permeate flux to the level lower than the critical flux can result in SEC reduction. It is demonstrated that when permeate flux reduces from 27 to 23 LMH, the SEC in a hollow fibre MBR system can be reduced by 14% on average [46].

Use of primary clarification ahead of the MBR can be capable of decreasing an average via reducing the power requirements associated with aeration and the biological tank volume. Reduction of organic loading by using primary clarification allows the MBRs to operate at low MLSS. Low MLSS concentration decreases membrane-fouling tendency. Thus, cleaning intervals and membrane life can be prolonged, and oxygen transfer efficiency can be improved, leading to lower power consumption by the air blowers [47].

Measures to optimize aeration demand for the biological process are necessary to save energy during MBR operation (Fig. 4). Reduction of the total aeration demand in MBR can be accomplished by lowering aerobic dissolved oxygen (DO) set point required to achieve complete treatment. This step can avoid over aeration in the aerobic tank. It has been reported that when DO set point decreased from 1.5 to 0.5 mg O_2/L, up to 81% reduction in biological aeration consumption could be achieved [73]. In addition, implementation of intermittent aeration for biological purposes and reduction in MLSS concentration have demonstrated to be effective to decrease SEC. Gabarron et al. [46] pointed out that by applying sequenced aeration and reducing MLSS content, SEC of a flat-sheet stand-alone MBR could be reduced from 1.12 to 0.71 kWh/m^3.

Permeate withdrawal and sludge recirculation pumping contributes to SEC of MBR systems. There are opportunities to adapt new methods to reduce the energy consumption at during permeate withdrawal and sludge recirculation (Fig. 5). Syphon filtration and airlift circulation can be adopted to save energy in the total system [74]. Syphon filtration takes advantage of the syphon effect caused by the difference in water head as suction filtration power, whilst airlift circulation uses the driving force of air bubbles for scouring or biological aeration as circulation power. It is noted that the utilization of syphon filtration and airlift circulation leads to the reduction of motor power, enabling energy-saving [74]. In addition, the reduction of pumping energy for sludge recirculation can be implemented through MLSS optimization and the coupling of sludge recirculation to the influent flow [47]. According to the results reported by Yamashita et al. [74], an SEC of 0.29 kWh/m^3 could be achieved by decreasing the scouring aeration rate and decreasing the pump power.

In addition to minimizing the aeration rate for membrane scouring and biological process as well as facilitating water and sludge transportation, increasing effluent production capacity can lead to the reduction of SEC (Fig. 4). This purpose can be implemented through the operation at appropriate flux, which is close, but lower than critical flux or close to the design flux recommended from manufacturers, and increasing packing density of the membrane modules [46, 47, 74]. The former is to maximize the membrane hydraulic utilization without causing severe fouling. The latter aims at increasing the effective surface area of the membrane, thus obtaining more permeate volume at a constant aeration rate. Reduction of the outer diameter of the membrane fibres and extension of the membrane fibre length can be applied to enhance the packing density of the membrane module [47, 74].

4.3 Success Stories

Reduction of SEC to the range of 0.4–0.5 kWh/m^3 has been reported in the literature. Tao et al demonstrated that the adoption of comprehensive and systematic optimization measures (i.e. increasing membrane flux and reducing aeration), the SEC of pilot-scale MBR plants decreased from 1.3 kWh/m^3 to less than 0.8 kWh/m^3 [71]. A further reduction to 0.37 kWh/m^3 was achieved, when energy audit and other optimization strategies, namely decreasing aeration flow-rate by setting up VFDs, applying gravity-driven flow between reaction tanks, reducing MLSS concentration to 6 g/L, controlling biological aeration and introducing 10/30 s on/off cyclic membrane aeration mode were adopted in a municipal full-scale MBR

[71]. Krzeminski et al. reported that the minimum SEC of a large pilot-plant MBR could be only 0.37 kWh/m^3, which was derived from 40% total energy reduction due to the successful implementation of energy-saving solutions including using higher packing density membrane modules [47]. In another study, Yamashita et al. (2019) evaluated four energy-saving MBR systems and indicated that the SEC of the systems could be reduced to 0.26–0.39 kWh/m^3, depending on the specific energy-saving measures applied [74]. These measures consist of increasing packing density by using a stack of modules, decreasing pump power by using syphon filtration and airlift circulation and reducing aeration rate for membrane scouring [74].

5 Life Cycle Assessment of MBR

Environmental impacts of different processes or products or services at each stage of their life could be effectively assessed by performing life cycle assessment (LCA). This tool has been widely implemented in wastewater treatment processes to gain a deep understanding of their environmental impacts [47], which would be helpful for policymaking. An overview of studies on LCA of MBRs is presented in this section as follows.

Ortiz et al. [75] attempted to analyse and compare the environmental impacts of different wastewater treatment processes using an LCA analysis tool (SimaPro 5.1). They selected four treatment processes including a stand-alone CAS, a CAS with tertiary treatment, a submerged MBR and a side-stream MBR. According to the LCA analysis, the stand-alone CAS would be an environmentally friendly option, while the environmental impacts of the CAS with tertiary treatment and both MBR configurations would be comparable. Importantly, as compared to the stand-alone CAS, the LCA analysis showed that environmental impacts of MBRs would not significantly increase, and MBR would make it possible to reuse water for different applications [75].

In a study by Memon et al. [76], LCA analysis was performed to assess the impacts of four processes (MBR, membrane chemical reactor, reed rocks and green roof water recycling system) for greywater treatment. Impacts of the selected treatment processes were assessed based on environmental performance as well as impacts on natural resources, ecosystem and human health. The LCA analysis showed that the impacts of natural treatment processes (e.g. reed rocks) are significantly lower than those of the MBR and membrane chemical reactors [76]. In a recent study on greywater reclamation, Jeong et al. [77] investigated the impacts of combining a submerged MBR with conventional wastewater treatment process on on-site greywater treatment and compared its LCA scores with the stand-alone conventional wastewater treatment process. The LCA scores of the stand-alone conventional wastewater treatment process were 20–41% lower than those of the combined treatment process, and energy consumption by MBR appeared to play a key role in the LCA scores of the combined process. Similar concerns were reported in several other studies [78, 79], meaning that extensive energy consumption by MBR contributes significantly to its environmental impacts. The sensitivity analysis showed that the life cycle impacts of the combined process could be reduced by increasing the population density [77]. Kobayashi et al. [80] performed LCA analysis for decentralized treatment of greywater using constructed wetlands and MBR. According to the LCA analysis, the constructed wetlands outperformed the MBR for decentralized greywater treatment. However, MBR may become an environmentally friendly technology in the case of greywater reuse scenario [80]. In a study by Cashman et al. [81], LCA analysis was performed to assess the suitability of aerobic and anaerobic MBRs for decentralized wastewater treatment. The results showed that the psychrophilic anaerobic MBR was superior to aerobic MBR in terms of net energy benefits at all scales. In the case of drinking water displacement, aerobic MBRs started to show net energy benefits at the treatment capacity of one million gallons per day [81]. Therefore, the benefits of MBR technology could be realized by increasing the treatment capacity as well as by using the large amounts of MBR effluent for water reuse applications.

6 Future Research Outlook

Application of MBR for wastewater treatment should be an informed decision. MBR technology has been demonstrated to be a feasible treatment option for obtaining excellent effluent water [31, 33]. In addition, MBR technology could be easily combined with other processes for potable and non-potable production. These advantages of MBR technology should be kept in mind to maximize its practical value.

MBR technology has been extensively applied as an alternative to the CAS technology for municipal wastewater treatment. However, there is still some scope of reduction in the CAPEX and OPEX of MBRs, which would make them even more attractive for implementation in developing countries. Although membrane modules have been significantly improved, research efforts are required to further: (1) increase the lifetime of membrane for reducing its depreciation cost; (2) improve the resistance of membrane against fouling and chemicals oxidants; and (3) improve the hydraulic performance (i.e. permeate flux) of membranes. As for the OPEX, focus on the reduction in SEC is critical. This could be achieved by improving the design of membrane modules; optimizing the aeration and scouring intensities and refining the process automation and control.

LCA studies on MBR exclusively emphasize the environmental dimensions and may not always consider the socioeconomic and technical aspects to evaluate the sustainability of MBR technology [47, 79]. This could result in an incomplete LCA analysis, which may affect the decision-making process. For example, if the main goal of MBR is to produce high-quality effluent for water reuse applications and to reduce nutrients load on surface water, advantages of MBR could overweigh its disadvantages (e.g. energy consumption). Therefore, all the internal and external factors, as well as benefits associated with water reuse and environmental protection, should be considered for an all-inclusive LCA.

7 Conclusions

MBR has gained its commercial competitiveness as alternative to the CAS to meet stringent effluent discharge regulation and to support non-potable and potable water reuse applications. The number of large-scale MBR plants increase worldwide. It results from combined factors including high effluent quality, stable performance, and reduction in membrane cost, enhancement in operation experience (i.e. new way of operation and new configuration to reduce energy). Indeed, specific energy consumption in the MBR has reduced significantly from 5 kWh/m^3 to below 1 kWh/m^3. Energy consumption continuously reduces to 0.35 kWh/m^3 at MBR plant with the capacity of >10,000 m^3/day. Processes to reduce aeration energy consumption for membrane scouring and biological metabolisms as well as new pumping design for water transportation and sludge recirculation are the four main developments to reduce energy consumption in the MBR technology. Another significant reduction in OPEX is membrane replacement due to the development techniques in increasing permeate (effluent) volume. Information corroborated in this chapter demonstrates the robustness of MBR technology and suggests its future progression to be the dominant technology in wastewater treatment sector.

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Anaerobic Treatment System: A Sustainable Clean Environment and Future Hope of Renewable Energy Production

Abimbola Motunrayo Enitan-Folami and Feroz Mahomed Swalaha

Contents

Abstract Anaerobic digestion (AD) of organic wastes is a popular biological treatment method. It is a useful technology in waste management and environmental health especially for mitigating greenhouse gases (GHSs). It is an economic process that treats a wide range of low- to high-strength organic materials for the production of value-added products such as feed biobased products and bioenergy through a diverse group of microorganisms. Several anaerobic digestion systems have been widely employed to treat both domestic and industrial wastes before they are discharged into the environment. The application of anaerobic technologies is considered a significantly viable economically sustainable system for treatment of both solid and liquid wastes. Its benefits include removal of organic matter, high

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treatment efficiency, pathogens removal, production of renewable energy, capable of power generation at a low cost, and less biomass production. Nonetheless, this chapter is a review of the following: different anaerobic digestion systems in the treatment of waste products; the bioeconomic and social importance of using anaerobic reactor for biofuel production and methods of identification and quantification of microbial consortia in an anaerobic reactor. The review further highlights the role of different methanogens as the major group of archaea for biogas production. Other ways to increase biofuel generation are also explored. The chapter concludes that environmental and economic challenges in waste management and energy resource scarcity could be alleviated sufficiently using an anaerobic digestion system.

Keywords Anaerobic reactor, Bioeconomic, Biogas, Methanogens, Wastes management

1 Introduction

Increase in energy demand, persistent interruption in power supply, and emission of greenhouse gases (GHGs) have led to quest for alternative energy sources in recent years. The use of traditional fossils fuels for energy production is non-renewable and the causes of many environmental issues, like GHGs emissions, global warming, and oil spillage [1, 2]. These environmental issues have led to the need for alternative energy production strategies with less adverse environmental and health effects. Therefore, anaerobic production of bioenergy is a sustainable process for converting organic waste into energy and value-added chemicals through various conversion pathways and treatment methods. For many years, biotechnological production of biofuels such as biomethane, biohydrogen, biodiesel, and bioethanol has been under examination [3]. To this end, the production of bioenergy has been identified as an alternate energy source to substitute fossil fuel with little negative effects on the environment and health [1].

2 Overview of Anaerobic Technologies for Waste-to-Energy Management

Anaerobic digestion technology has proven to be an established oldest biotechnological tool for bioconversion of complex organic wastes produced by human societies. This process takes place in a warm and airtight container (the reactor) where, thorough mixing during treatment creates the ideal conditions for microorganisms to ferment the organic matter into biofuel and useful slurry that can be used as fertilizers [4, 5]. Anaerobic systems' benefits make this method a better alternative

Table 1 Comparison of aerobic and anaerobic digestion [6]

Parameter	Aerobic digestion	Anaerobic digestion
Start-up	Short start-up period	Long start-up period
Space requirement	Large space required for the reactor.	Compact reactor with small area requirements
State of development	Established technology	Still under development for specific applications
Process	Integrated nitrogen and phosphorus removal possible High sludge formation Large reactor volume necessary High nutrient requirement	No significant nitrogen or phosphorus removal. Post-treatment is required for nutrients removal Less sludge formation (5–20%) Small reactor volume and simple configuration Low nutrient requirement
Carbon balance	50–60% conversion of organic materials degradation into CO_2 40–50% conversion of organic materials degradation into biomass	95% conversion to biogas 5% into microbial biomass
Energy balance	Requires a large amount of process energy 60% of available energy is used in new biomass; 40% lost as process heat	Requires less energy instead produces bioenergy 90% retained as CH_4, 3–5% is lost as heat, and 5–7% is used in new biomass formation
Residuals	Excess sludge production No need for post-treatment	Biogas, nitrogen mineralized to ammonia Post-treatment required for removal of remaining organic matter and malodorous compounds
Costs	High operating costs for aeration, additional nutrient, and sludge removal, and maintenance	Often moderate investment costs Low operating costs due to low power consumption and additional nutrients hardly required

for waste treatment and generation of bioeconomic by-products when compared with the aerobic treatment of waste materials (Table 1) [7, 8].

2.1 Anaerobic Reactor Types

In the last three decades, different reactor technologies have been developed and installed to stabilize the sludge and degrade organic matter present in wastewater and solid wastes [9]. Among these technologies are up-flow anaerobic sludge bed (UASB) reactor [10–12], up-flow anaerobic solid-state reactor (UASS), anaerobic plug-flow reactor (APFR), expanded granular sludge bed (EGSB) [13], membrane bioreactor (MBR) [14], and hybrid upflow anaerobic sludge-filter bed (UASFB) [15]. Among other reactors that have been widely used for wastes treatment are anaerobic contact reactor (ACR), anaerobic baffled reactor (ABR), anaerobic sequencing batch reactor (ASBR) [16], continuous stirred tank reactors (CSTR) [2, 17, 18], anaerobic fixed-bed reactors (AFBR), and membrane technology [19, 20]. These reactors have been reported to treat different types of low- and high-strength wastewater such as brewery, cheese whey, palm oil mill, pharmaceutical compounds, and hospital wastewaters among other industrial wastes [2, 13, 21, 22]. However, the EGSB, CSTRs, and UASB reactors are the most widely used to treat high-rate anaerobic reactor and biogas production [23].

2.1.1 Continuous Stirred Tank Reactors (CSTRs)

Lagoons and continuous stirred tank reactors (CSTRs) are the simplest anaerobic systems [18]. The CSTR is also known as a vat- or back mix reactor, [24, 25] and its runs at the steady-state condition with a continuous and uniform feed of substrates and products' removal. Lagoon system that has no unique sludge retention because hydraulic retention time (HRT) is equal to the sludge retention time (SRT); thus, reducing the suspended biomass concentration and limiting the biological treatment capacity [26]. Unlike lagoon system, when sludge is introduced into a CSTR, an impeller or biogas blowers stir the liquor to ensure proper mixing while the outflow from the CSTR is moved into the settler. In the settler, the treated liquid separates from the biomass then returns the biomass to the CSTR (Fig. 1). This reactor is very efficient in treating different organic-rich wastewater [27]. However, it has limitations such as high operational costs, labor-intensive, and operates at relatively low volumetric loading rates due to the flocculent. It also dilutes the nature of the

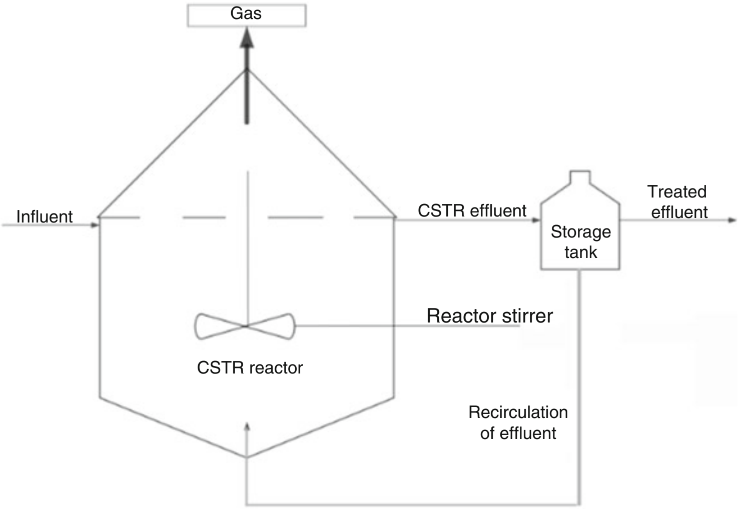

Fig. 1 Schematic diagram of a continuous stirred tank reactor (CSTR)

anaerobic sludge [18, 28]. Although, the CSTR is simple to operate, but less efficient in effluent quality than other reactor technologies [7].

2.1.2 Expanded Granular Sludge Bed (EGSB) Reactor

The use of effluent recirculation combined with a high height/diameter ratio reactors resulted in expanded granular sludge bed (EGSB) reactor [29, 30]. EGSB combines both characteristics of upflow sludge blanket (USB) and biofilm fluidized bed (BFB) processes [31]. It is considered to be a completely mixed tank digester in which both the EGSB and UASB processes use granular anaerobic biomass. They have the same operational principles but differ in terms of geometry and process parameters. A high superficial liquid velocity is applied in this type of reactor for wastewater to pass through the sludge bed while the biomass is present in a granular form. The upflow liquid velocity (10 m/h) causes the granular sludge bed to expand, which enabled the elimination of dead zones resulting in better sludge wastewater contact with the granules for better gas production (7 m/h) [10]. An increase in upflow velocity rate is accomplished by either tall reactor dimension or recirculation of effluent or both (Fig. 2) [32] while hydraulic condition determines the structure of biofilm in the

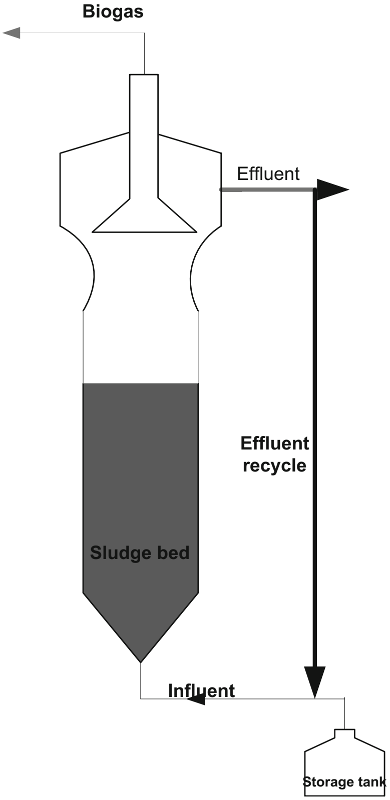

Fig. 2 Schematic diagram of an expanded granular sludge bed (EGSB) reactor

reactor. The high load and mass transfer also affect the microbial proliferation and matrix of the reactor granules [30]. The EGBS reactor is highly efficient for treating low strength wastewater (WW) (0.7–0.9 g COD/L) with good granular composition for biogas production [33, 34]. Likewise, EGSB can be operated as an ultra-high load anaerobic reactor (up to 30 kg COD/m^3/day) to treat effluents from chemical, biochemical, and biotechnological industries [13, 30].

Besides, there is a problem of instability of the granular conglomerates during continuous operation, washout, and granule disintegration due to high upflow velocities application in the EGSB reactor. Due to these facts, so much research had reported the application of EGSB combined with other reactors like anoxic and aerobic bioreactors [13, 33, 35]. Others have recommended the attachment of an extra dissolved air flotation (DAF) system which is often used before secondary biological processes to reduce sludge washout and treat difficult toxic streams [33, 36, 37]. Based on studies conducted by Wenta and Hartman [38], about 95% reduction in TSS concentration during the treatment of pulp and paper mill wastewater was observed when DAF method was used.

2.1.3 Upflow Anaerobic Sludge Blanket (UASB) Reactors

The UASB reactor designed by Lettinga et al. [39] has made anaerobic digestion the most competitive and favorable treatment technology for high-strength organic wastewaters [40, 41]. It has been widely employed to treat industrial and domestic wastes around the world due to its features such as simple design, easy construction, maintenance, low operating cost, high removal efficiency, short retention time, stability, temperature, and low energy demand [11, 42, 43]. Like EGSB, a UASB reactor is highly dependent on granular sludge as the core component during wastewater treatment for effective conversion of organic matter to biogas (Fig. 3) [44, 45]. Several laboratories, pilot, and full-scale reactors have been optimized to treat different types of domestic and industrial wastewaters [46–48]. Some of the industrial effluents treated by UASB reactor include slaughterhouse [49], pulp and paper, textile [50], pharmaceutical [51], sugar factories [52, 53], and brewery wastewater among others [40, 54, 55]. Despite the benefits and simplicity of the UASB reactor, maintaining a steady-state condition is still one of the difficulties faced by UASB reactor operators [6]. Descriptions and further information about other types of reactors have been reviewed in the literature [14, 16, 41].

2.2 Bioeconomy and Ecological Benefits of Energy Recovery from Wastes Using AD Technologies

Over the years, mankind have relied on various energy sources especially coal as the primary energy generator. However, in the twentieth century, waste management strategies and reduction of environmental impacts caused by waste disposal have gained more attention due to its effects on climate change and environmental health

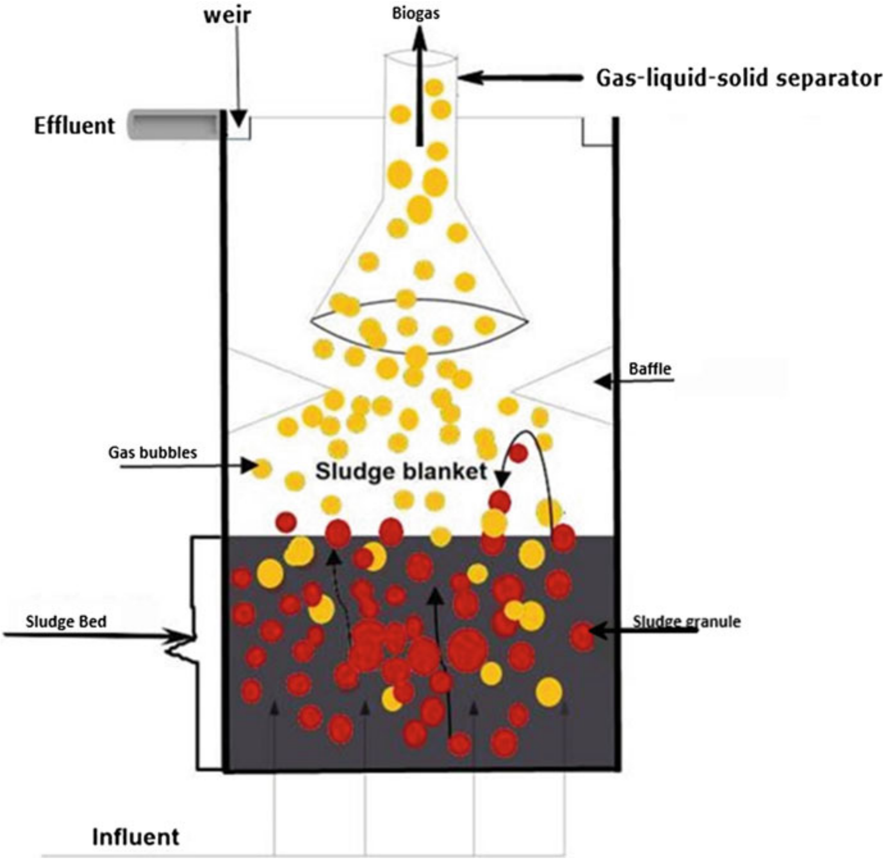

Fig. 3 Schematic diagram of an upflow anaerobic sludge bed (UASB) reactor with red balls indicating granules and yellow balls indicating evolved biogas

concerns. For instance, in 2016 only, the reported data for GHGs produced worldwide from various industrial sectors and processes was about 50 billion tonnes (Fig. 4) [56]. Hence, high measures are being put in place to comply and reduce the biodegradable liquid and solid wastes flowing into water bodies and landfills in order to reduce the amount of GHGs emissions into the environment.

Since methane and carbon dioxide are considered potent GHGs, approximately 18% of global warming is thought to be caused by anthropogenic derived methane emissions. The carbon dioxide released through natural mineralization is considered neutral in terms of GHGs. For example, the uptake of carbon from the atmosphere by plants and its return to the atmosphere as part of the carbon cycle is considered a green approach to mitigate environmental pollution [5]. Therefore, environmental and economic aspects of waste management should be maintained as a circular relationship for facing existing environmental problems and resource scarcity [57]. Treatment of wastes through AD technology is an economic process that

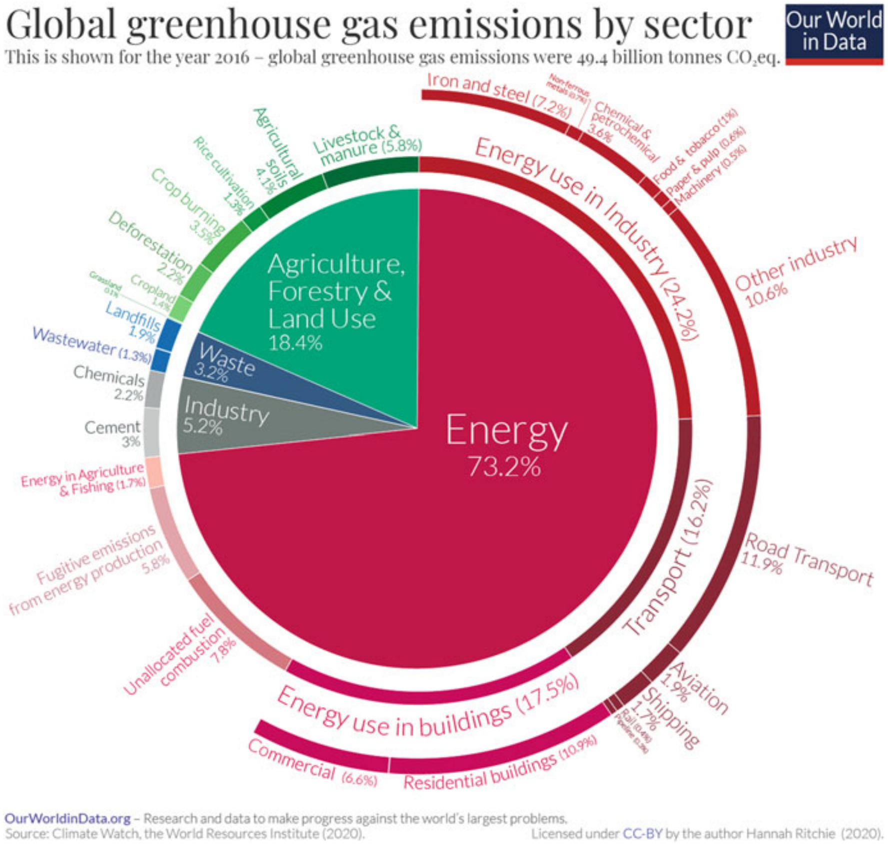

Fig. 4 Global greenhouse gas emission data with 49.4 billion tonnes CO_2 eq. produced from industrial sectors in 2016. Source: Our World in Data, (2020) licensed permission to reuse under the Creative Commons Attribution License – By the author Hannah Ritchie [56]

involves converting waste streams into value-added products, such as feed, biobased products, and bioenergy [3, 57]. Hence, anaerobic treatment of wastes or biomass before being discharged into the environment or municipal sewers is considered an essential aspect of waste management. Such process not only reduces topsoil and freshwater pollution, but also helps in cleaning the atmospheric air, thus prevents the emission of greenhouse gases into an open environment and reduces the coal usage for energy generation [21, 58].

2.2.1 Anaerobic Reactor for Value-Added Products Recovery

Bioenergy (biogas, bioethanol, etc.) production through anaerobic digestion of wastes is a worldwide promising energy source which offers many environmental and socio-economic advantages. The benefits are multifaceted and the process of using anaerobic digestion for the treatment of both solid and liquid wastes are without side effects (Fig. 5). These significant benefits include:

(a) Fermentation of animal/human wastes: Fermentation of wastes produced by animal and humans helps to mitigate environmental issues that could arise due to improper discharge or runoff into the water bodies. This ultimately prevents the spread of pathogens.

(b) Provision of alternative material to unsustainable deforestation: Anaerobic treatment of wastes and biogas production with high CH_4 content is an excellent alternative to fossil fuel because human and industrial activities produce sufficient amounts of wastes [59]. It is interesting to note that if biogas produced during wastes treatment contains more than 50% of CH_4, it could be used as fuel energy; for heating, cooking, lighting, or to generate electricity for domestic and broader industrial activities [60], hence mitigate the act of deforestation [14, 61].

(c) Improves air quality: As earlier mentioned, AD technology combines the treatment of industrial wastes and energy production to reduce environmental pollution. It prevents methane, a GHGs, from entering into the atmosphere by confining the degradation processes in a closed environment. It also helps to control gas flaring leading to production of carbon neutral carbon dioxide back into the carbon cycle. It lowers carbon dioxide production that is not part of the recent carbon cycle [5]. It also cuts down the impacts of emissions during energy generation from coal.

(d) Alternative energy source: Biofuel is a veritable alternative energy source to fossil fuel. Its produce can be used to generate electricity through internal engine combustion and instead of flaring the gas, the resulting biogas is combusted for boiler heating and energy to operate distillation column (see Fig. 6) [2, 62, 63]. Thus, the problems of residual stillage treatment are solved by conversion into biofuel gas and thus mitigate the problems with energy supply and spending [64]. Similarly, biodiesel from fermented animal fats and crops, bioethanol from starch crops, and sugar have shown that AD system, when used properly, could be an efficient and sustainable biofuel generator [65, 66].

(e) Production of by-products: Furthermore, an anaerobic reactor is also beneficial for producing treated sludge that farmers can use as fertilizer. Due to inconsistency in price and environmental pollutions, there are more reasons for more clean and sustainable by-products like biofertilizers. With these, global demands for fertilizers can be met because the effluent from bioreactor has proven to be very rich in nitrogen, phosphorus, and potassium. This suggests that they are useful for agricultural application. Therefore, AD system is effective for waste recycling, production of high-quality manure, and biofuel generation with zero discharge into the environment.

2.2.2 Social-Economic Benefits of AD Technology and Human Empowerment

Bioenergy is an emerging industry. Its development provides several opportunities both economically and socially. For economic and social benefits example, the use

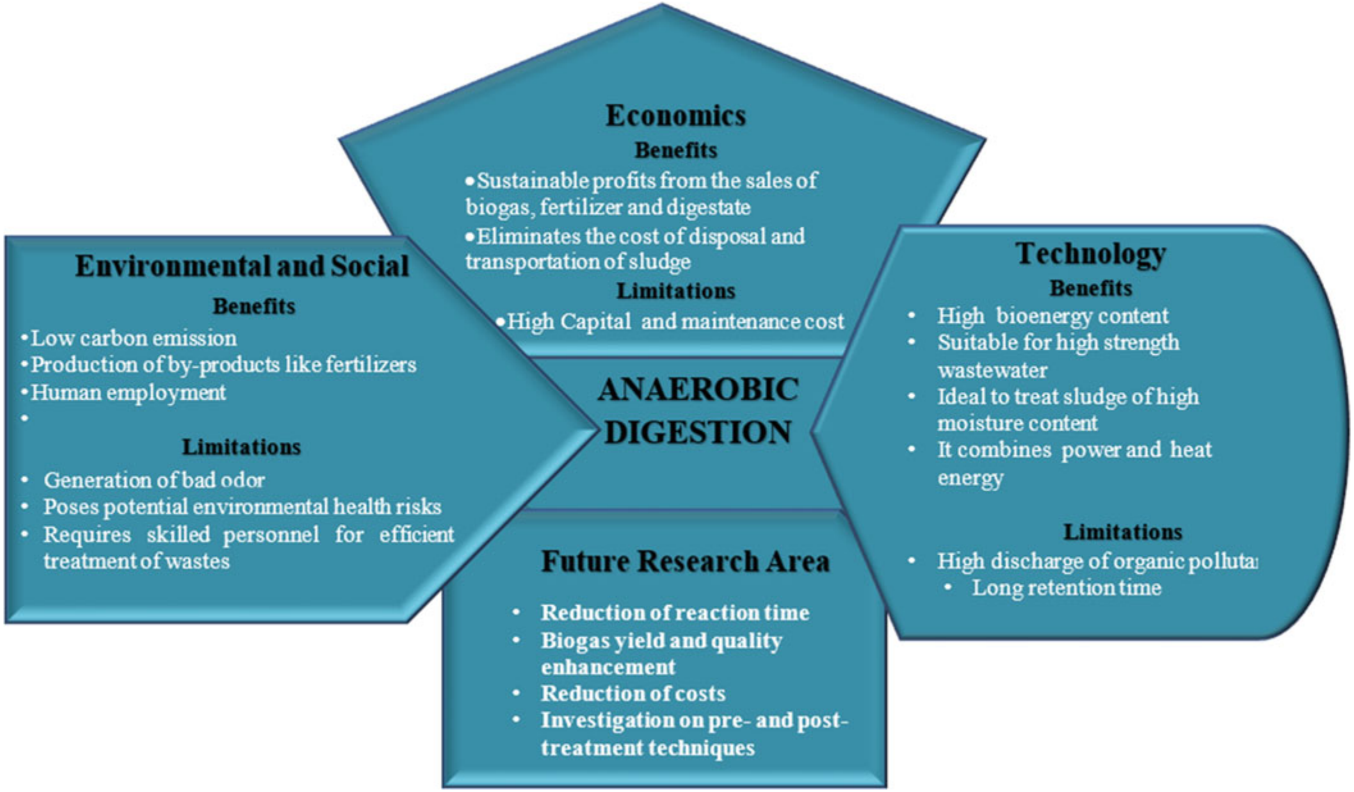

Fig. 5 Environmental, socio-economic, and technological evaluation of anaerobic digestion for wastes treatment

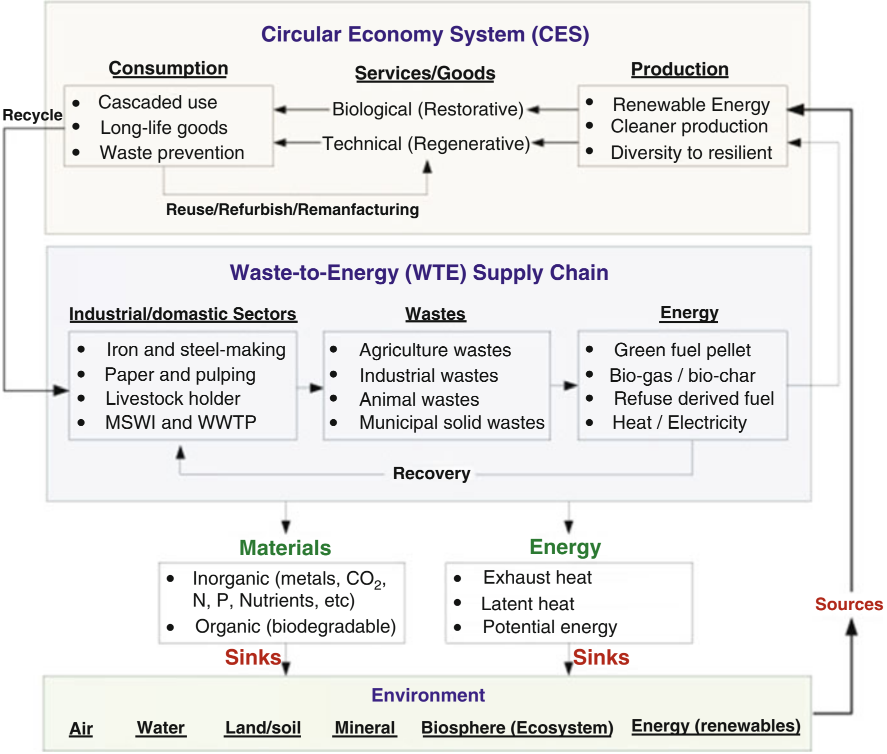

Fig. 6 Conceptual framework of the relationship between environment, circular economy system (CES), waste-to-energy (WTE), and supply chains [56]

of AD system for wastes treatment engenders human empowerment, integrated agriculture through fertilizer production, carbon emissions reduction, and national policy incentives (Fig. 5) [67]. It enhances job creation through the manufacturing of small-scale biogas digesters. More importantly, the use of biogas could assist the female folks to concentrate less on the utilization of wood and charcoal in their cooking activities. In 2016, about 41.6 million rural households in China used biogas [67, 68], which shows that the biogas industry is empowering people, creating jobs, and reducing air pollutants like particulate matters that could be inhaled by people. This is aiding the prevention of health-related issues and thus mitigates the effects of GHGs on the environment and its impact on climate change [69].

3 Development of Biorefinery for Bioenergy Production

From a Clean Development Mechanism (CDM) point of view, mitigating CH_4 emissions is fascinating since the Global Warming Potential (GWP) of Methane is 21 times higher than that of CO_2 [70]. Under anaerobic conditions, CH_4, CO_2, nitrogen (N_2), hydrogen (H_2), hydrogen sulfide (H_2S), and oxygen (O_2) called "biogas" are produced [71] with calorific values of 21–24 Mj/m^3, an equivalent value of 6 KWh/m^3 of CH_4 [9, 72]. Energy generation from biomass is classified as a "carbon neutral" process because CO_2 released during this process is balanced by the CO_2 absorbed by plants during their growth [70]. Electricity production from renewable energy is increasing through the fermentation of sludge produced from sewerage treatment plants into liquid fuels [73]. Tons of biosolids are converted into crude oil that can be used to replace oil extraction from beneath the earth's surface. Based on the US Department of Energy, bioenergy technologies treating municipal wastewater have been described as promising bioenergy production sources [74]. Methane gas from AD as a renewable energy source has been adopted as one of the CDM to obtain a certified emission reduction (CER) credit under the Kyoto Protocol. The ignition of biogas burns cleanly without soot or foul smell as compressed natural gas (CNG) and liquefied petroleum gas (LPG). It, therefore, facilitates biogas promotion for the reduction of greenhouse effect by cutting down methane emissions into the atmosphere.

Biogas generation has been widely adopted in Asia, particularly in places like Bangladesh, China, India, and Nepal for energy production [75, 76]. This offers such developing countries the advantage of foreign investments in sustainable renewable energy projects [76, 77]. Between 2007 and 2015, for instance, implementing national biomass energy from industrial wastes was passed in China with over 118 biomass CDM projects approved by the National and Local Development and Reform Commissions (NDRC and LDRC) [70, 76, 78]. In 2009, the Danish Carbon Fund (DCF) signed six emission reduction purchase agreements (ERPA) (1) with the Thailand Sapthip Wastewater Management project, (2) two China Baotou Energy Efficiency projects, and (3) one Mexico Monterrey II LFG. The worth of these projects was valued at €53.8 million ($77 million) with total emission reductions of 6.6 million tons of CO_2. The Sapthip Wastewater Management Project in Thailand aimed at reducing the emissions at the Sapthip Company's bioethanol plant as part of a clean development mechanism to generate and capture methane-containing biogas produced during the treatment of wastewater in anaerobic reactors. The biogas produced can be used as fuel to operate two 20-ton-per-hour-capacity boilers that supply steam to the ethanol plant's backup capacity [79].

Excluding household biogas plants, approximately 113,000 biodigesters were built throughout China [80], among which 6, 737 are large scale and 34 are super large scale. About 306 reactors treat industrial wastes, 458 plants utilize a straw, and approximately 99.6% of these plants use animal manure as feedstock [67]. In 2015, upgrade of biogas to bio-natural gas (BNG) projects was for the first time carried out at the central government level in China with a total of 65 BNG projects between 2015 and 2017. Meanwhile, 197 projects are estimated to be functioning by the end of 2020 [69]. Yet, it was estimated that fossil energy would gradually be replaced by hydroelectric power and nuclear energy. By 2035, more than half of China's demands will be filled by renewable energy [67]. The Indian waste-to-energy market is presently 750 MW, which is expected to reach a whopping 3 GW by 2050 [81]. In

Brazil, on the other hand, renewable energy was converted to electricity with the capacity of 30 kW microturbine [67].

3.1 Utilization of Anaerobic Reactor for Conversion of Wastes to Bioenergy in South Africa

In Africa, bioenergy generation from wastes is still at the infant stage. Most developing countries like South Africa have paid little attention to implementing national biomass energy from wastewater than the world's implementation of AD technology [82]. The first anaerobic digester in the countries was installed by John Fry to treat wastes produced by a pig farm in 1957. By 1958, the first bioelectricity was generated from the same plant to power pumps [83]. Many digesters have since been installed in the country, although at a slow rate compared to market penetration in the aforementioned countries. South Africa, among other African countries, have been using anaerobic reactors to treat industrial wastes [6, 84]. There was a report on four full-scale reactors treating abattoir, brewery, egg processing, and petrochemical wastes to generate biogas that can be converted to electricity. In another survey, four leading international companies (ADI, Biothane, Paques, and Enviroasia) installed anaerobic treatment plants with typical application of UASB reactors to wastewater from different industries [85]. About 700 installed reactors are currently being employed to treat various South African wastes as shown in Table 2 [83, 87].

For energy sustainability, more development in renewable and sustainable energy was developed by different sectors. For instance, Talbot & Talbot installed four on-site anaerobic digesters to treat food and beverage wastes to produce biogas that can be harvested to power boilers for fuel production which could replace fossil fuel usage [82, 88]. Based on a literature survey, most industries are still flaring or venting the biogas produced from the on-site anaerobic reactor into the atmosphere [86]. It has been shown that biogas produced during the anaerobic treatment process is 10% to 11% of the total energy required to safeguard the power supply for many industries [88]. This demonstrates that the usage of bioenergy from AD system has poorly been integrated into the energy sector, and the opportunity to mitigate greenhouse gas (GHG) emissions has not been fully embraced in many countries.

However, few on-site digesters use biogas to power their reactor, heat boiler, and building spaces [86]. For example, Cape Flats wastewater treatment plant in Cape Town, PetroSA's gas-to-liquids refinery in Mossel Bay, SA breweries Prospecton, Durban, and some isolated communities, households, and small-scale industrial anaerobic digesters are a few exceptions where biogas plants have been adopted for energy generation [82, 86, 89]. Cape Flats wastewater treatment plant in Cape Town installed a reactor to treat dry and pellets wastewater sludge for biogas production while reducing environmental contamination and sludge disposal costs. This plant serves as an energy source while the pellets were reported to have ~16.6 MJ/kg helping a local cement factory as an additional energy source to

Table 2 Energy potentials of wastewaters from various South Africa sectors [86]

Wastewater type	Volume produced	Approach to calculation	Energy potential: thermal power (MWt)	Area
Brewery		Distributed. Seven breweries	17	
Distillery	–	Distributed. Grain, grape, and sugar-cane (molasses) are considered. Compared to grain and grape, molasses have the most significant energy potential; they are not seasonal and less distributed (three significant plants, all in KwaZulu-Natal)	70	KwaZulu-Natal
Winery	0.7 and 3.8 m3/ton of grapes processed (0.8–4.4 L/L of wine produced) COD = 6 g/L; 1,000 ML/year of wastewater	Distributed and seasonal	3	
Fruit processing	20% of 2,100,000 ton citrus fruit (2005) was used For juice, wastewater COD = 15 g/L; 205,000 ton deciduous in 1999/2000 for which the wastewater COD averages 5 g/L	Distributed and seasonal. Only the wastewaters from canning and juicing in Western cape are considered (pulp and pomace excluded). Operates 4 months of the year	68	Western cape
Petrochemical waste	PetroSA electricity plant produces 12 MW electricity using biogas as the raw material	Sasol is assumed to produce 3× more based on plant size. PetroSA and Sasol. Four refineries and one gas to liquid fuel refinery	48	
Textile industry	–	Distributed	22	
Pulp and paper		17 mills	45–100	
Olive production	100 g/L; 89ML/year	Distributed and seasonal	4	
Animal husbandry		Cattle in feedlots. Mixed solid and liquid wastes slurries. They represent point sources that can be accessed through on-site energy recovery. Nine	79–215	

(continued)

Table 2 (continued)

Wastewater type	Volume produced	Approach to calculation	Energy potential: thermal power (MWt)	Area
		feedlots represent more than half the total cattle in feedlots		
		Red meat and poultry abattoirs consider liquid wastes only	1–55	
		Piggeries mixed solid and liquid waste slurries	18–715	
		Poultry farms considers solid waste only	940–2,976	
		Rural cattle considers solid waste only that are collected at night in kraals. Only a small percentage of this energy is realistically recoverable	1,271–3,445	
		Dairies mixed solid and liquid waste slurries collected including washing and milk spills	117–121	
Domestic Blackwater (human feces)	200 L/day wastewater per person. Population of SA = 48.5 million, hence 9,70 × 10^9 L/day is generated. COD estimated at 0.860 g/L, Energy content = 15 MJ	Municipal treatment plants serve only 60% of the population, therefore only 60% of human feces are currently captured. These plants are distributed, approximately 968 WWT plants exist in SA. The majority of these plants are small at <0.5 ML/day, with larger plants of 2.5 ML/day. Treatment plants also receive domestic urine, greywater, and industrial load, not considered here	509–842	
Abattoir	4 t of wastes/day	–	100 kW	Bredasdorp
Abattoir	20 t of wastes/day	–	500 kW	Cavatter

power their kilns [86]. In 2018, a waste-to-energy generator was launched in Cape Town as a sustainable power production with a capacity of 220 kw using a combined heat and power unit (CHP) system for the treatment of abattoir waste with the capacity to produce electrical power and thermal energy.

South Africa's first independent State-owned power plant, PetroSA's gas-to-liquids refinery near Mossel Bay in South Africa was commissioned in 2007 and funded by carbon credits generated under the CDM of the Kyoto Protocol [90]. It is a combined heat and power plant to utilize the biogas production from wastewater treatment plant (WWTP). The electrical output replaces 4.2 MW of grid-based electricity and the plant was expected to produce approximately 33, 000 t per year of certified emissions' reductions (CERs). Along with receiving debt financing from the Development Bank of South Africa, the sale of emissions credits has contributed to the PetroSA project's economic viability [86, 90]. Stafford et al. [86] and Mutungwazi et al. [87] reviewed the treatment of different types of wastewater using an anaerobic reactor (industries and domestic blackwater) (Table 2). Anaerobic reactor was reported to have the potential to recover 3,200–9,000 MWth of energy equating about 7% of current electrical power supply in South Africa with approximately 140,000 MWth or 42,000 MWe energy demand [86].

Anaerobic treatment technology has helped in multifaceted areas by providing solutions to social, economic, and environmental issues with robust commercial viability in biofuel production that can generate heat, electricity, transportation fuel, and mitigation of GHGs [81]. However, implementation of the full potential of bioenergy at the commercial level is facing challenges in South Africa due to limitations such as insufficient skills by anaerobic reactor operators, lack of awareness about AD biogas technology, and non-implementation of research findings among many other factors (Fig. 7) [86].

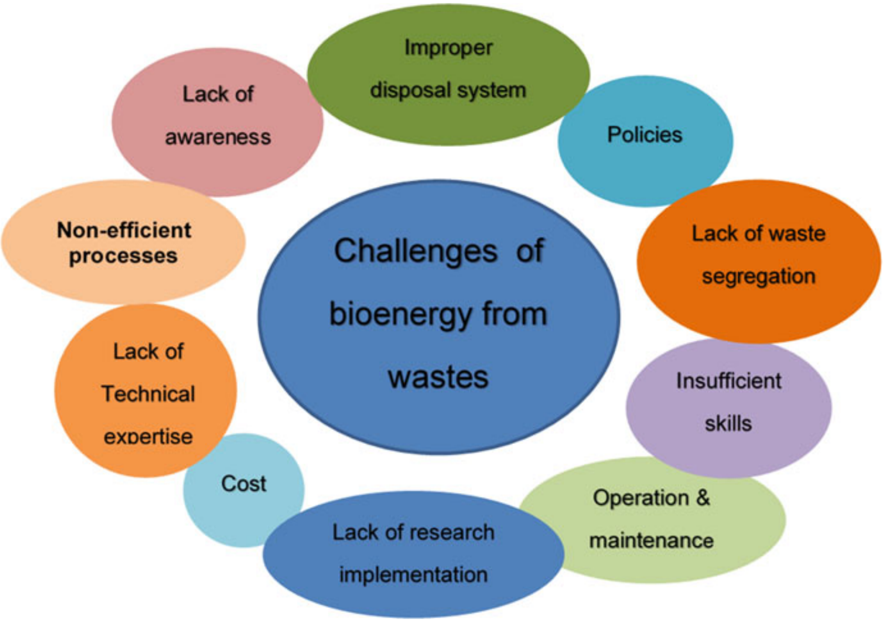

Fig. 7 Various challenges facing the future of wastes-to-bioenergy production

4 Biochemistry and Microbiology of Anaerobic Digestion Process

Understanding the overall biochemistry and microbial composition of technology is necessary to improve bioenergy recovery during the anaerobic digestion process. During this process, there are four key sequential stages, namely; hydrolysis, acidogenesis, acetogenesis, and methanogenesis. At each stage, the breakdown of feedstock in the substrates is facilitated by a group of facultative, obligate, and strictly anaerobic bacteria [91, 92]. These organisms are divided into four groups based on the biochemical processes and the metabolites they produce (Fig. 8, Table 3). Under ideal conditions, these microorganisms breakdown the complex organic compounds through a variety of intermediates into the components of biogas. Example of elements are CH_4 and CO_2 with small levels of H_2S, H_2, and N_2 based on the overall reaction shown in Eq. (1) [6, 92, 96, 97].

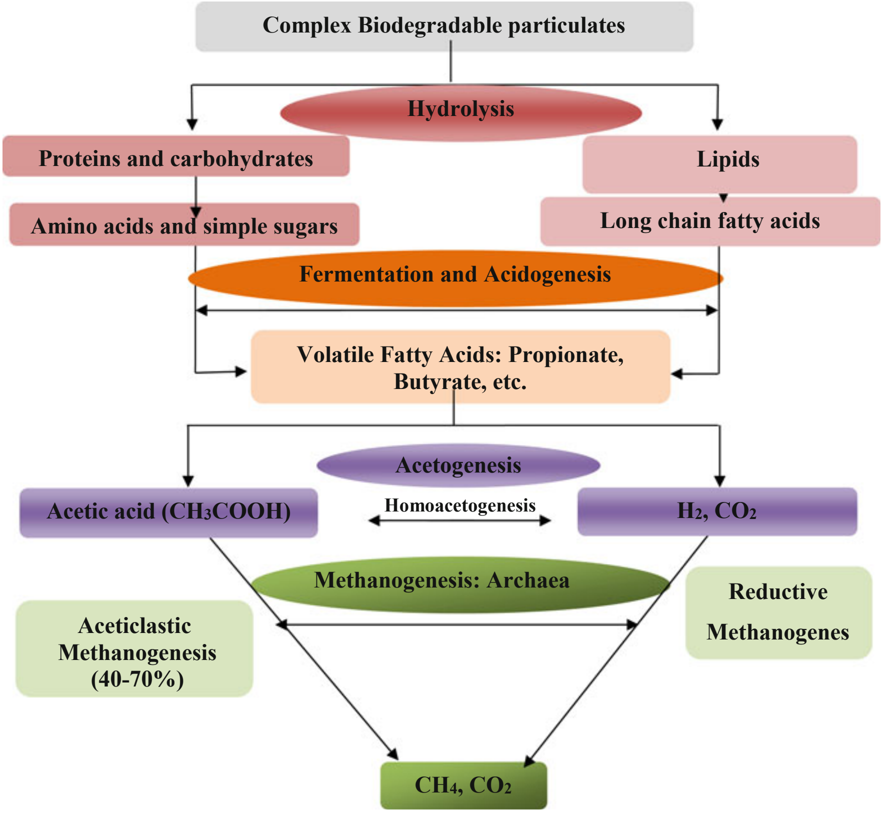

Fig. 8 The key stages of anaerobic digestion process during the treatment of wastes products [6]

Table 3 Fermentation reactions associated with the anaerobic conversion process in a successful operating bioreactor [93–95]

Reaction	ΔG (kJ mol^{-1})
Acidogenesis:	
$C_6H_{12}O_6 + 2H_2O \rightarrow 2$ ethanol $+ 2HCO_3^- + 2H^+$	−225.4
$C_6H_{12}O_6 + 2H_2O \rightarrow$ butyrate $+ 2HCO_3^- + 3H^+ + 2H_2$	−254.4
$C_6H_{12}O_6 \rightarrow 2$ lactate $+ 2H^+$	−198.1
$C_6H_{12}O_6 \rightarrow 3$ acetate $+ 3H^+$	−310.6
$C_6H_{12}O_6 + HCO_3^- \rightarrow$ succinate^{2-} + acetate$^-$ + formate$^-$ $+ 3H^+ + H_2O$	−144.0
3 lactate$^-$ $\rightarrow$ 2 propionate$^-$ + acetate$^-$ $+ HCO_3^- + H^+$	−164.8
2 lactate$^-$ $+ 2H_2O \rightarrow$ butyrate$^-$ $+ 2HCO_3^- + H^+ + 2H_2$	−56.2
Acetogenesis:	
Ethanol $+ 2HCO_3 \rightarrow$ acetate + 2 formate$^-$ $+ H_2O + H^+$	+7.0
Ethanol $+ H_2O \rightarrow$ acetate $+ 2H_2 + H^+$	+9.6
Lactate$^-$ $+ 2H_2O \rightarrow$ acetate$^-$ $+ 2H_2^+ + H^+$	−3.9
Butyrate$^-$ $+ 2H_2O \rightarrow 2$ acetate$^-$ $+ 2H_2^+ + H^+$	+48.1
Benzoate$^-$ $+ 6H_2 \rightarrow 3$ acetate$^-$ $+ 3H_2^+ + CO_2 + 2H^+$	+53.0
succinate^{2-} $+ 4H_2O \rightarrow$ acetate$^-$ $+ 2HCO_3^- + 3H_2^+ + H^+$	+56.1
Propionate$^-$ $+ 3H_2O \rightarrow$ acetate$^-$ $+ HCO_3^- + 3H_2 + H^+$	+76.1
Homoacetogenesis:	
$4H_2^+ + 2HCO_3^- + H^+ \rightarrow$ acetate$^-$ $+ 4H_2O$	−104.5
Methanogenesis:	
Acetate$^-$ $+ H_2O \rightarrow$ methane $+ HCO_3^-$	−31.0
$4H_2^+ + HCO_3^- + H^+ \rightarrow$ methane $+ 3H_2O$	−135.6
$4HCO_2^- + H^+ + H_2O \rightarrow$ methane $+ 3HCO_3^-$	−130.4
4 methanol $\rightarrow 3$ methane $+ HCO_3^- + H^+ + H_2O$	−312.8

$$\text{Organic matter} \rightarrow CH_4 + CO_2 + H_2 + NH_3 + H_2S \tag{1}$$

On the one hand, about 70% of the total CH_4 production by methanogenic archaea during AD is from acetic acid. On the other hand, the remaining 30% comes from H_2 and CO_2 conversion [98]. It has been reported that about 80–90% CH_4 composition can be produced in reactors treating wastewater and more from biosolid wastes. The origin of the AD process and the biodegradable materials determine the composition of biogas produced. The percentage composition of methane is based on biodegradable feedback used in the digestion process and running conditions of the anaerobic reactor (Table 4). The stability of the microbial ecosystem in the AD process has been shown to depend on the methanogenic activity, which is characterized by slow growth rates of microorganisms. They are very sensitive to operational and environmental variations such as salinity, sludge properties, temperature, pH, mineral composition, loading rate, HRT, carbon-to-nitrogen ratio, and volatile fatty acids (VFAs). These factors influence organic matter and biogas production [12, 99].

Table 4 Percentage of methane composition from different anaerobic fermented feedstocks

Feedstock	Composition of methane (%)
Barley straw	77
Beet leaves	84.8
Cattle manure	50.60
Corn silage	54.5
Grass	84
Dried leaves	58
Poultry waste	68
Pig manure	60
Sheep dung	65
Horse dung	84
Wheat straw	77

4.1 Functions of Methanogenic Archaea in Biogas Production

Unlike bacteria, methanogens are archeons. They have no typical peptidoglycan (mureinic) skeleton. Instead, several genera in archaea domain have pseudomurein. Others have walls consisting of lipids composed of isoprenoid hydrocarbons glycerol lipids with different metabolism [100, 101]. They are slow-growing archeons with a generation time between 3 days at 35 °C and 50 days at 10 °C [102]. Generally, methanogens are largely differentiated morphologically. They exhibit almost all shapes occurring in bacteria including cocci (*Methanococcus*), rods (*Methanobacterium*), short rods (*Methanobrevibacter*), spirillaceae (*Methanospirillum*), sarcina (*Methanosarcina*), and filiforms (*Methanothrix*) [6]. They are strict anaerobes and contain neither catalase nor superoxide dismutase with size ranges from 0.3 to 7.4 μm [103].

Studies have shown that three different major pathways exist for CH_4 formation depending on the source of the reducing potential and the carbon compound used as substrate (Fig. 9); which include hydrogenotrophic, aceticlastic, and the methylotrophic [100, 104]. Hydrogenotrophic methanogens are H_2 using organism. They use H_2 as an electron donor to reduce CO_2 to CH_4 (Fig. 9; Eq. (2)). This group helps in maintaining very low levels of partial pressure needed by the aceticlastic methanogens for the conversion of VFA and alcohols to acetate [93].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{2}$$

Abundance of *Methanobacterium*, *Methanobrevibacter,* and *Methanococcus* of orders *Methanobacteriales, Methanomicrobiales, and Methanococcales* in different types of anaerobic bioreactor wastewaters treatment has been reported [18, 54, 105, 106]. The second group is the acetotrophic or aceticlastic methanogens which convert acetate to CH_4 and CO_2 [105, 107]. The overall reaction is shown in Eq. (3);

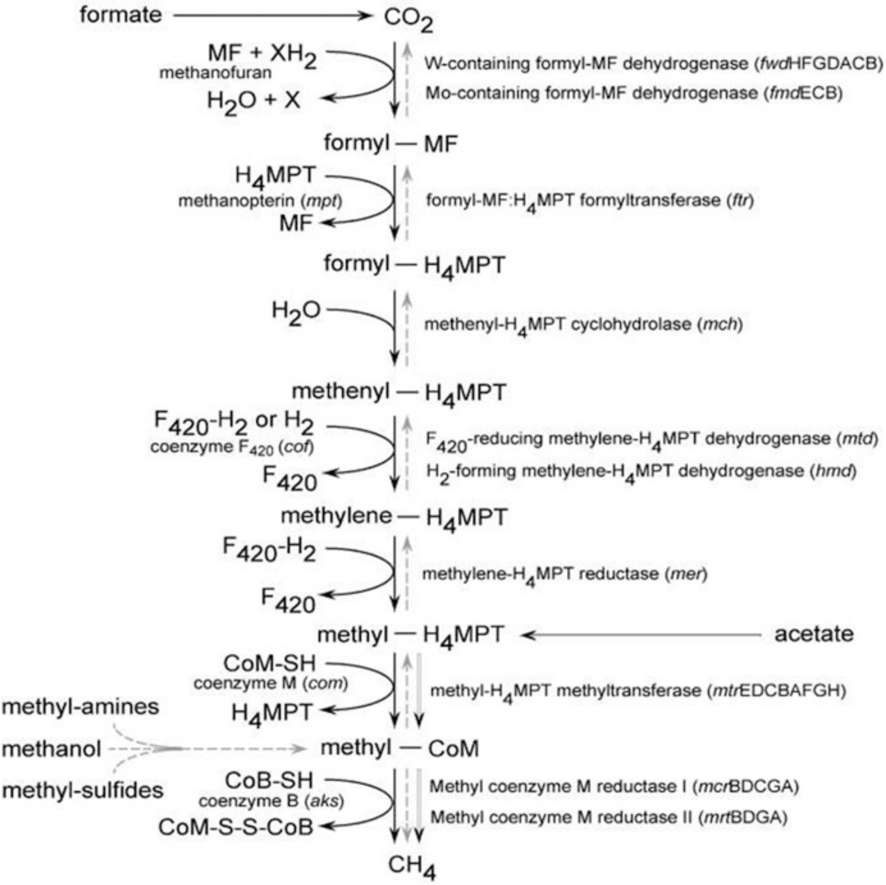

Fig. 9 Biochemical pathways of methanogenesis: hydrogenotrophic (double-lined arrows), aceticlastic (solid arrows), and methylotrophic (broken gray arrows) during anaerobic treatment. Licensed permission to reuse under the Creative Commons Attribution License (https://creativecommons.org/licenses/by/4.0/) [104]

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (3)$$

The most commonly reported aceticlastic methanogens from bioreactors belong to the genera *Methanosaeta* (coccoid bacteria) and *Methanosarcina*-sheathed rods or long filaments bacteria [106, 108]. This group of methanogens helps in the production of about 70% of the total CH_4 generated during the AD of wastewater [98]. *Methanosaeta* sp. such as *M. thermophila* and *M. concilii* belonging to genus *Methanosaeta* utilize acetate, while *Methanosarcina* strains like *M. barkeri, M. mazei,* and *M. thermophila* utilize acetate, methanol, methylamines, H_2, and CO_2 as [108]. The abundance of *Methanosarcina* sp. at high acetate levels and *Methanosaeta* sp. at low acetate concentrations was also reported [108]. An abundance of *Methanosarcina* and *Methanosaeta* sp. in granules treating different wastewaters at steady-state conditions has been reported in the literature [109, 110]. The third group is the methylotrophic methanogens belonging to order *Methanosarcinales* and *Methanobacteriales* which are directly responsible for producing CH_4 from assimilation of methyl groups ($-CH_3$), methylamines $[(CH_3)^3\text{-N}]$, and methanol (CH_3OH) as substrate [93]. Methanol is usually found as organic pollutant in several wastewaters and is a substrate for both methanogens and acetogens [104]. Ziemiński and Frąc [100] reviewed the sensitivity of biochemistry, physiology, and ecology of methanogens to oxygen. Some of their characteristics include their sensitivity to changes in pH and temperature, inhibiting their growth by a high level of H_2, sulfur, NH_3, VFAs, and other compounds in the environment or in the anaerobic bioreactor [100, 111]. For sustainable and economic development using renewable energy and maximization of biofuel yield during anaerobic digestion, operational parameters must be properly optimized to encourage the growth of microorganisms required to produce biofuel of interest [112]. These, therefore influence biogas production during anaerobic digestion of solids and liquid wastes. For more details on this, see Sawyerr et al. [113] and Tabatabaei et al. [112].

5 Determination of Microbial Fingerprint in an Anaerobic Reactor Using Molecular Techniques

The main aims of studying microbial ecology include identifying, classifying, and determining microbial activity in an anaerobic reactor [100]. In the past, traditional methods of identification used to determine the morphology and phenotypic characteristics [114] were time-consuming and limited. Many microorganisms, especially the methanogens, are difficult to culture using such traditional methods because they are slow-growing organisms with restricted environmental conditions and particular nutritional requirements [115]. The development of advanced molecular techniques (Fig. 10) to study the complex microbial populations in environmental samples by targeting the 16S rRNA gene has eliminated the use of more elaborate traditional methods of culturing microorganisms. It has increased our understanding of the microbial communities present in anaerobic bioreactors and contributed to development of an improved process that encourages the growth of desirable microorganisms and enhances bioenergy yield.

Molecular techniques are grouped into two main groups; quantitative and qualitative. Qualitative methods include polymerase chain reaction (PCR), PCR-based denaturing gradient gel electrophoresis (PCR-DGGE) [116, 117], temperature gradient gel electrophoresis (TGGE), and terminal restriction fragment length polymorphism (TRFLP). The most recent technique is next-generation sequencing such as Illumina platform, Pyrosequencing, and Ion Torrent platforms [105, 116, 118]. Microbial profiling techniques involve the amplification of isolated nucleic acids, sequencing and identification by comparing the generated sequences with

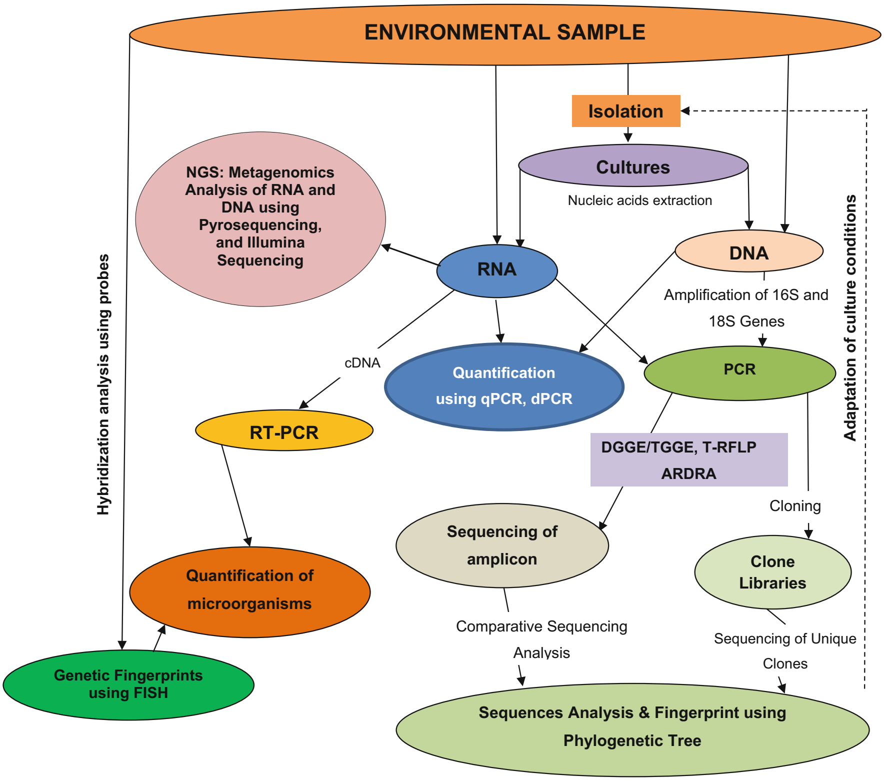

Fig. 10 Flow diagram of different steps used in studying microbial communities' structure and functions in an environmental sample

known sequences in the database. Next-generation sequencing (NGS) has emerged as a powerful tool for studying microbial communities because it is less costly and time-consuming and produces a greater yield of sequence data [119]. These methods have successfully been used to determine the shift and microbial populations in the laboratory- and industrial-scale bioreactors [105, 119, 120]. Due to the high cost of reagents and the need for technical skills to interpret the data generated, NGS's application remains at infant stage to determine the anaerobic organisms. A number of reports are however available on applying next-generation sequencing to understand microbial composition of full-scale bioreactors treating solid and liquid wastes [105, 116, 118, 121].

On the other hand, fluorescence in-situ hybridization (FISH) and quantitative real-time PCR (QPCR) are quantitative techniques that have been adopted for surveying microbial ecologies [52, 106, 122–124]. Fluorescence in-situ hybridization technique is based on the hybridization of whole cells with specific probes and microscopic analysis of dyed hybridized cells using epifluorescence microscopy, flow cytometry, or scanning electron microscopy [106, 122, 125, 126]. Fluorescence in-situ hybridization has been used to analyze and understand microorganisms' spatial distribution [106, 115]. Quantitative real-time PCR, on the other hand, can be used to amplify and simultaneously quantify targeted DNA sequences by employing a PCR-based technique that enables one to quantify the number of gene copies or the relative number of gene copies in a given sample. The reliability and amplified gene copy number of QPCR results strongly depend on the extracted genomic DNA and reflect the relative abundance of the sample's microbial population [123]. The amplification principle of QPCR is similar to that of PCR. It monitors the amplified target's concentration after each PCR cycle using a fluorescent dye or probe change in fluorescence intensity that reflects the amplified gene's concentration in the real-time assay [123]. Either absolute or relative quantification can be used to determine the concentration of DNA or RNA in an extracted sample. The technique has been widely used to quantify the microbial population and dynamics in anaerobic reactors in their natural environments [124, 127].

However, it is challenging to monitor specific groups or a domain using only one technique as each technique has its own merits and demerits. Therefore, a combination of qualitative and quantitative methods, including PCR-DGGE, QPCR, and microarrays could be used to overcome the limitations of using one technique [128]. A combination of different molecular methods such as electron microscopy, PCR-based DGGE, cloning, and FISH to gain insight into the physical appearance, function, and structure of microbial diversity of methanogenic granules in a bioreactor treating wastewater has been explored in the past [18, 129]. The PCR-based DGGE and FISH analysis identify the microbial populations in a full-scale UASB reactor treating brewery wastewater. *Delta* and *Gammaproteobacteria, Methanosaeta concilii,* and *Methanobacterium formicicum* were reported as some of the dominant bacterial and Archaea bands detected in the full-scale UASB reactor [129]. Likewise, PCR-DGGE was used to fingerprint and identify the microbial consortium present in different types of granules collected from the UASB reactor treating brewery wastewater [108] and wastewater polluted with organic solvents [129]. Methanogens such as *Methanosarcina, Methanosaeta, Methanobacterium,* and uncultured bacteria in the Archaea domain were identified and fingerprinted using PCR-DGGE [108]. FISH and PCR also detected the microbial community present in a full-scale reactor treating industrial wastewater [106]. Similarly, microbial fingerprints in a full-scale reactor treating agricultural and industrial wastes were compared using TRFLP and Illumina platforms [130]. Further reviews of the molecular detection of anaerobes that enhances biogas-rich reactors performance are found in the literature [65, 66].

6 Conclusions

As discussed, anaerobic digestion technology is an economic process that uses a biological treatment method to treat a wide range of low- to high-strength organic materials to produce value-added products, such as feed, biobased products, and bioenergy through a diverse group of microorganisms. Due to these benefits, the AD process is considered a significantly viable competent and economically sustainable system in treating organic wastes at a low cost with less biomass production and high treatment efficiency. It has also been shown that the technology is efficient in the removal of suspended solids, chemical and biological oxygen demand notwithstanding the digester temperature with the recovery of bio-nutrients and renewable energy in an enclosed system. Such processes will also reduce topsoil and freshwater pollution; help to clean the atmospheric air; prevent greenhouse gas emissions into an open environment; and reduce coal usage for energy generation. In essence, environmental and economic problems facing waste management and resource scarcity could be tackled using an anaerobic digestion system.

7 Recommendation and Future Perspectives

The principal aims of the anaerobic reactors are to reduce greenhouse gas and improve methane-biogas content for energy generation by treating different types of wastes to produce millions of megawatt-hours of electricity per year. However, there is a need to optimize the digesters for proper functioning and increase the methane content for energy generation by operating the reactors in optimum conditions to avoid formidable technological and dissemination challenges. In addition to the future research focus mentioned in Fig. 5, more research on the mechanisms of action by different microbial groups in the AD reactor for biogas production needs to be investigated. Collaboration and information-sharing between research groups, government agencies, and municipal practitioners on bioenergy production should be encouraged. Furthermore, there should be more emphasis on generating clean and renewable energy by giving incentives such as feed-in tariffs, green energy tariffs, or peak tariffs at the local level. Offer on the certified emission reductions and the production of other secondary products such as fertilizer that could tip the balance of economic feasibility when implementing energy from a wastewater project should be available.

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Prospects and Potential Role of Biological Treatment of Textile Effluent to Restore Water Reservoir

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Contents

Abstract Standing at a second place after agriculture, the textile industries are a source of income to almost 45 million Indian population. Indian textile industries contribute to around 2% of India's GDP, 15% share in export earning, and 7% of industrial output. However, the alluring benefits delivered by the textile industries are intertwined with severe aquatic pollution, which if remains unchecked would soon prove to be catastrophic for humankind and aquatic life. Textile industries are one of the large consumers of harmful dyes, water, and chemicals. The industrial revolution that has first claimed to be a boon is now standing at the edge of turning

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into a bane for the marine ecosystem. The unchecked release of textile dyes into the water bodies has resulted in hazardous aftermath primarily for the vital human commodity (water). Synthetic dyes are broadly classified into azo, anthraquinone, and triphenylmethane dyes. The release of colored dyes and its harmful intermediates into the water streams blocks the sunlight, hampering its light penetration and causing disturbance to the ecosystem. Since safe drinking water is one of the most crucial commodities in the developing countries, the water pollution arising from tons of untreated-textile dye discharges needs a spearheaded, efficient, feasible, and eco-friendly approach. In recent decades, several chemical and biological mediated remediation strategies have been reported by several research groups that focused on evading textile dye menace by degrading the harmful chemical dyes into less-harmful forms. This objective has been attained by controlling the physical parameters of effluent such as Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Dissolved Oxygen (DO), Total Dissolved Solids (TDS) content, etc. This chapter discusses the current perspectives and future prospects of textile dyes remediation scenarios in India, and the associated challenges and reasons for its sustainable implementations for the revival of the existing parched marine environment.

Keywords Biodegradation, Dye, Textile waste, Wastewater management

1 Introduction

Globally, textile industries are considered as the second largest pollution generators. These industries release large amounts of dyes, chemicals, and effluent that pose serious concerns to flora and fauna of the environment. To meet the increasing global demands, most of the industries are situated in developing countries like India, Pakistan, China, and Bangladesh as these sectors create enormous job opportunities playing a significant role in the country's economic growth. India's textile export stood at 11.8% during 2019–2020 [1]. Moreover, the Indian textile industries are the major consumer (80%) of dyestuffs [2]. Annual dye production is estimated to cross 7×10^5 tons, where 3,600 different dyes are identified and 8,000 dyeing chemicals are consumed under various textile processes such as dyeing, bleaching, and finishing [3]. It should be noted that the low utilization efficacy enables 2–50% dye to enter into the effluent streams [4]. Additionally, the untreated industrial discharge loads the end sink (water reservoir) with harmful chemicals, resulting in compromised biodiversity and generation of unfit water (Fig. 1).

Chromophore group and structural characteristics determine the major classes of dyes such as azo, anthraquinone, nitroso, phthalein, nitro, indigoid, and triphenylamine. All of them are able to absorb the visible wavelengths of 400–600 nm producing visible color. The intensity of the color is so strong that

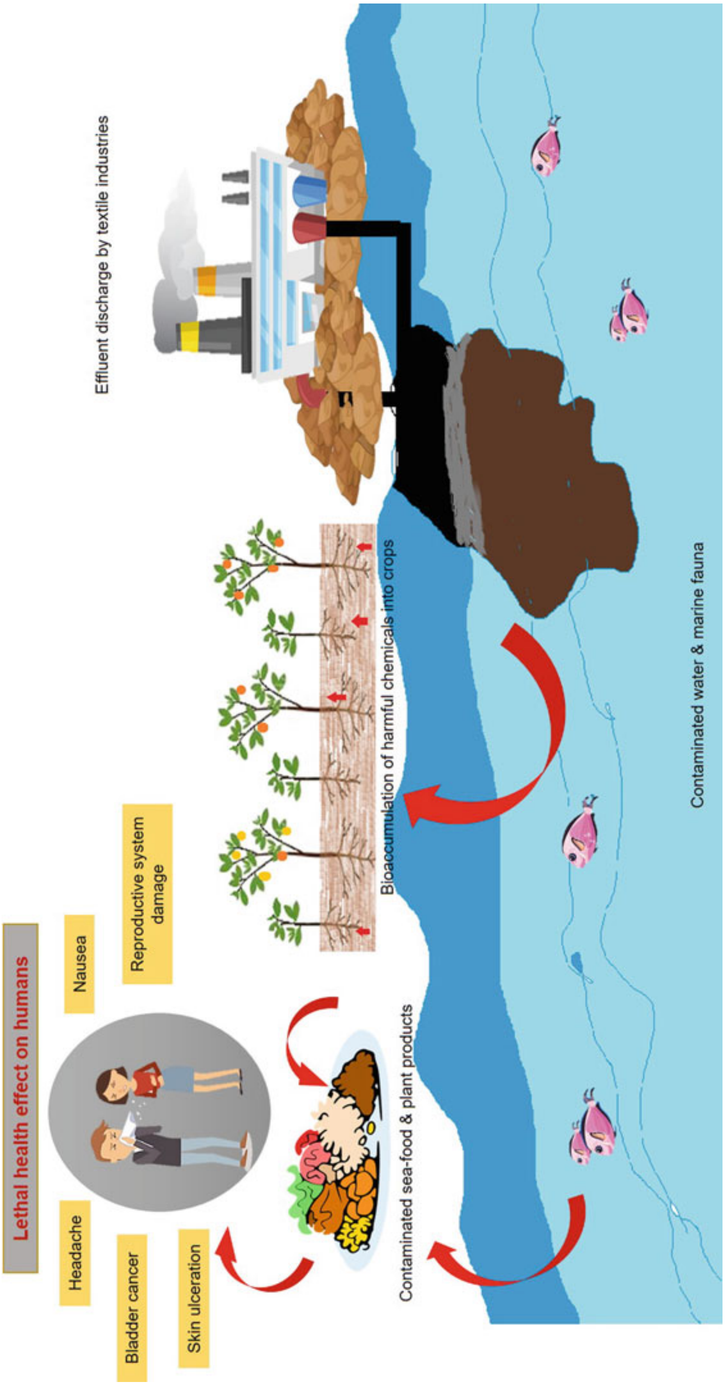

Fig. 1 Schematic diagram depicting the deleterious effect of textile dye effluent on the environment

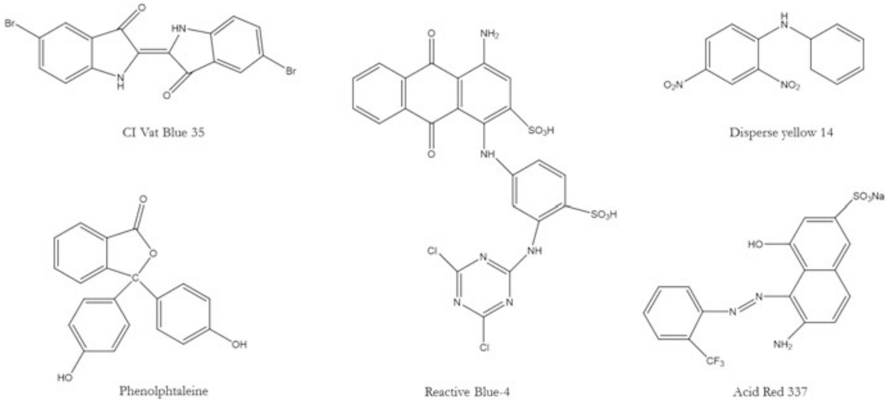

Fig. 2 Chemical structure of popular dyes used in the textile industries

even at lower concentrations, i.e., 1 ppm, water gets pigmented rendering it aesthetically unacceptable. The color decreases its transparency, light penetration, and gas solubility and hence, critically affecting photosynthesis, oxygen deprivation leading to intoxication of fish and adverse health effect on mammals. Some of the popular dyes used in textile industries are shown in Fig. 2.

A maximum azo dye percentage of 70–80% is used in textile industries under different operations [5]. This dye is the most diversified group of dye having its characteristic -N=N- bond linked with benzene or naphthalene compound. The presence of such compound confers toxicity to the dye molecule [6]. The second most pursued dye after azo belongs to anthraquinone group, which is bestowed with relatively higher stability. Hence, these dyes are more toxic toward humans and microorganisms due to their complex molecular structure [7].

Additionally, to meet the growing global needs, every day a new molecular structure is articulated in such a way, offering superior dyeing performance, persistent fabric color, resisting sweat, sunlight, soap, and oxidizing agents. Such measures greatly challenge their ability to degrade in the marine ecosystem, rendering them as recalcitrant and less responsive toward classical mitigation technologies [8].

Thus, the production and effluent management systems in textile industries are in dire need for an effective abatement reform to pave the way for a sustainable, economical, and eco-friendly strategy that can ensure fewer carbon footprints. Taking this into account, this chapter intends to throw light in the textile effluent generation, its sources, entry pathway into the environment and gradually into the food chain, potential health threat to aquatic life and humans, present effluent management techniques and challenges and future perspective.

2 Sources and Discharges of Textile Wastes

Generation and dispersion of enormous volume of untreated effluent wastes (e.g., chemicals and dyes) into the nearby water reservoirs leave behind an intense color blended with organic pollutant, chlorine salts, finishing agents, inorganic agents, total phosphates [9], high biological oxygen demand (BOD) and chemical oxygen demand (COD) [10]. Textile effluent not only pollutes the water bodies through untreated effluent discharge but also percolates groundwater and soil through leaching, causing considerable environmental pollution (Fig. 1). The discharge of textile effluent into the water streams is taken up by marine life through ingestion and accumulates inside their organs causing serious problems. Fish, crabs, mussels, crustaceans, turtles, bivalves, and mammals feeding on dye contaminated water also take up these compounds and suffer through various lethal effects. Contaminated sea-food acts as a vector for bioaccumulation inside the human body, showing its deleterious health effect.

3 Impact on Health and Lifestyle

In the present circumstances, it is well to state beyond doubt that dispense of dyes into water unfolds many associated health hazards not only to the marine ecosystem but also back toward humans. The lethal components of the effluent have been associated to cause detrimental effects on humans such as bleeding, skin and mucous membrane ulceration, dermatitis, irritation, and adverse effects on immune system and nausea [11]. Intensified research for evaluating the toxic effect of azo dye triggered soon after 1895, when workers exposed to azo dye were identified with bladder cancer [12].

4 Microbe Assisted Dye Degradation

Preliminary effluent treatment focuses on the discolouration of textile dyes, followed by the removal of salts, heavy metal contaminants, and other chemical and organic ingredients [13]. The removal strategies aim at reducing BOD and COD of the effluent to a lower limit of 10 ppm (for BOD) and 20 ppm (for COD) as per the latest National Green Tribunal (NGT) norms for treated water in India [14]. Physical and chemical remediation strategies include adsorption, filtration, fenton oxidation [15], photocatalytic oxidation [16], ozone oxidation [17], ultrasonic catalytic oxidation [18], and microwave catalysis [19]. The physical remediation strategies suffer from drawbacks like time consumption, secondary pollution generation, concentrated sludge production requiring additional remediation strategy, high costs, installation of specialized facilities, effective on narrow range of dyes, and being chemical and

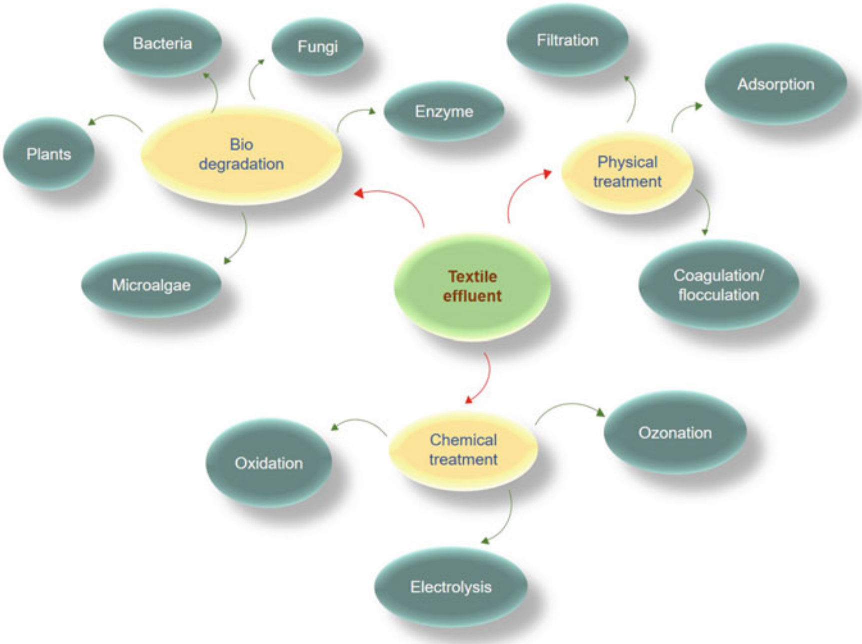

Fig. 3 Various approaches employed for textile wastewater remediation

energy intensives. The chemical-based remediation processes yield potent carcinogenic substances, such as aromatic amines [20]. Moreover, these methods are impractical due to narrow dye susceptibility and associated higher costs.

Greener alternatives such as seeds of *Moringa oleifera* and orange peel have been reported to show superior coagulating properties which are further intensified through the addition of bivalent cations (Ca^{2+} and Mg^{2+}), enabling the formation of clear solution rapidly [21, 22]. However, the disposal of such a concentrated dye adsorbed material again becomes an environmental concern. In such a case, microbial assisted degradation offers a more logical and holistic approach by completely mineralizing the pollutants into non-toxic forms (CO_2 and H_2O) and without causing any secondary pollutants. Thus, the microbial remediation technique is considered highly effective, broad-range, and eco-friendly strategy. Nevertheless, employing a single strategy for the remediation process can be time-consuming, thus, demanding an integrative abatement strategy for efficient remediation and eco-friendly disposal [23, 24]. The overview of textile pollution remediation is presented in Fig. 3.

Anaerobic conditions facilitate the breakdown of azo bond; however, these anaerobic processes are incapable of subsequently degrading the potential carcinogens (aromatic amines) formed during the process under prevailing anaerobic conditions [25]. Also, anaerobic bacteria profusely secrete decolorizing enzymes under oxygen deprivation conditions, since oxygen of carbonyl group itself acts as a

Table 1 Advantages and disadvantages associated with various remediation techniques

Technique	Method	Advantage	Disadvantage
Physico-chemical processes	Coagulation and precipitation	Less time and low cost. Better removal ability	High cost of coagulants and chemicals for pH adjustment; dewatering needed
	Adsorption	Act on broad-range dyes	Concentrated sludge formation
	Ion exchange	Recycling of used resins	Ineffective on neutral dyes
	Membrane filtration	Works on broad-range of dye	Concentrated sludge formation, need additional remediation strategy
	Electrochemical	Non-toxic by products	High cost of electrical supply
Oxidative processes	Fenton's reagent	Works on soluble and non-soluble dye	Concentrated sludge generation
	Ozonation	Effective on most azo dyes, improves biodegradability	Safety concern, high cost, influence of pH and temperature on effectiveness
	Reactive oxidizing radicals (OCl^{-1})	Sludge free	Production of carcinogenic substances (aromatic amines)
Biological processes	Microbes	Green process, cost-effective, and environmental friendly, complete mineralization	Complex dyes are tough to decompose, time-consuming, need for integrative approach
	Enzymes	High specificity	Expensive process due to maintenance of enzyme stability, purity, and immobilization

desirable terminal electron acceptor [26]. Therefore, the utilization of sequential integration of anaerobic/aerobic technique offers higher diversity and metabolic co-operation among species facilitating improved biodegradation efficiencies, hence, making the approach cost-effective and environmentally friendly, yielding complete mineralization of textile wastewater. The advantages and disadvantages of various degradation strategies are listed in Table 1.

The use of microbes for bioremediation has seen an escalated interest among researchers as a potential zero waste strategy. Many microbes such as microalgae, actinomycetes, fungi, and bacteria [13, 27, 28] were found to be proficient dye degraders. Bacterial counterparts offer superior alternatives than other microbes due to their less time consumption, ability to grow at extreme conditions, less nutrient requirement, and complete mineralization of pollutants. Important microbes capable of dye degradation are listed in Table 2.

Table 2 List of microbial assisted degradation of various dyes

Dye	ppm	% Degradation	Microbes	References
Reactive blue 2	100	24	*Pseudomonas strain GM3*	[29]
Acid green 27	100	84	*Pseudomonas strain GM3*	[29]
Direct red-81	200	81	*Shewanella*	[30]
Reactive blue 19	50	90	*Enterobacter* sp. F NCIM 5,545	[31]
Bromaminic acid	100	>96	*Sphingomonas xenophaga* QYY	[32]
Acid blue 277	300	>60	*Escherichia coli* DH5α	[33]
Remazol brilliant blue R	125	60	*Serratia liquefaciens* PT01	[34]
Methyl red	100	*100*	*Klebsiella strain Y3*	[35]
Remazol brilliant blue R	100	100	*Staphylococcus* sp. K2204	[36]
Reactive blue 4	50	97	*Staphylococcus hominis* subsp. *hominis* DSM 20,328	[13]
Reactive red BS C.I. 111		91	*P. aeruginosa*	[37]
Synozol red 6HBN		88	*Aspergillus niger*	[38]
Synozol red 6HBN		96	*Nigrospora sp*	[38]
Red 3B		93	*A. faecalis* E5.Cd	[39]

4.1 Mode of Action

The first step in the microbial degradation of dye occurs when the dye molecule is adsorbed onto the cellular surface via covalent, molecular, and electrostatic forces. Dye adherence on a bacterial cell is dependent on its cellular composition and presence of functional groups that act as a critical binding agent. It is reported that Gram-positive bacterial membrane having 40–80% peptidoglycan is more effective (5–10 times) for dye adsorption than Gram-negative cell wall having 10% peptidoglycan composition [40]. Further, the presence of NH_2 group on the bacterial surface impacts dye adherence significantly, in comparison with CH_2OH, C-O, $CONR_2$, CO-O-C, NH_2, C-N, COO-, and PO_2 groups [41]. Walker and Weatherley [42] reported that autoclaving at 110°C for 15 min increased the cell membrane permeability that improved its biosorption rates up to 13%, 19%, and 18% for Acid Blue 277 dye in inactivated cultures of *Bacilllus godonae*, *Bacillus benzeovorans,* and *Pseudomonas putida*, respectively [42]. However, decolorization activity is attributed to living cells than dead cell.

The surface adhered dye initially undergoes catalytic reduction by the bacterial reductase, resulting into the cleavage of chromophore groups into intermediates of single rings or simple polycyclic aromatic compounds (like naphthalene and anthracene) which are finally and completely degraded into non-toxic forms after further degradation. However, the difference in the exertion of degradation capability is mainly attributed to the difference in the structural and functional moiety. For example, the degradation pathway of Brilliant Blue K2RL determined that parent compound breaks from the attachment site of the reactive group into difluorochlorotrizine ring and anthraquinone complex [43].

4.2 Factors Affecting Microbial Mediated Bioremediation

Many researchers have reported that the variation in physicochemical parameters greatly influences the degradation efficacy. The degradation of dye hinges on the prevailing physical parameters like pH, media components, temperature, dye concentration, aerobic and anaerobic conditions [44]. Simple dye structures are easily dissimilated whereas the complex and branched molecular structures are utilized with difficulty. The presence of a functional group also affects the degradation potential. Hitz et al. [45] have provided sequential degradation trend under different substituents:
$-SO_3 > -NO_2 > -Br > -Cl > -H > -NH_2 > -OCH_3 > CH_3 > -COOH > -OH$ [45].

4.2.1 Carbon and Nitrogen Sources

Wastewater sludge is not sufficient for the growth promotion of indigenous microbes. So, for spiking the microbial activity, the supplementation of carbon and nitrogen sources has been shown to enhance the degradation efficiencies and the maintenance of microbial diversity. Most commonly used carbon and nitrogen source in lab-scale is glucose, glycerol, L-rhamnose, beef extract, sucrose, yeast extract, tryptone, creatinine, and ammonium salts. However, for successful implementation, cheap sources are required which could be obtained using a by-product of agricultural or industrial production, wastewater having biofertilizer potential, and microbial biomass as a carbon or nitrogen source. A higher concentration of external glucose supplementation has been reported to diminish degradation by delimiting tricarboxylic acid cycle [31, 46]. For efficient degradation, the statistical optimization of operational parameters is needed for determining the most significant process.

4.2.2 pH

The solution pH dictates osmotic potential of the microbe and directly influences the growth and metabolism of the microbe. Thus, altering the pH influences the culture conditions and either suppresses or improves the degradation process. Depending on the culture conditions, the microbes which are suitable for a specific pH range are supported for their growth promotion and enhanced metabolism. It helps in playing crucial role in the degradation of various dyes. *Corynebacterium glutamicum* was a potent biosorbent and found to be dependent on pH of dye solution as maximum decolorization was observed under a range of pH 2–5 [47].

4.2.3 Temperature

High temperature is beneficial for dye degradation since high temperature affects the kinetic energy of the solute and increases its surface activity. Increasing the temperature further enhances the uptake of ions and dye molecules by microorganisms. On the other hand, low temperature reduces bacterial metabolism and activities greatly retarding its degradation abilities. Exploration of extremophiles would be beneficial in future remediation technologies, as they can tolerate extreme conditions.

4.2.4 Aeration Condition

Oxygen acts as the terminal electron acceptor in the electron transport chain. For aerobic bacteria, oxygen is vital for growth and metabolism. Whereas, the presence of oxygen inhibits anaerobes, thus, hindering their sustenance and growth. In one study, it was found that *Bacillus cereus* DC11 was able to degrade 55% of Acid Blue 25 (100 μmol/L) under anaerobic conditions, however, presence of oxygen reduced the rate of degradation tremendously till 5%. This implies that the carbonyl group oxygen was utilized as the preferred terminal electron acceptor under anaerobic conditions [26].

4.2.5 Dye Concentration

Initial dye concentration has a great impact on the efficiency of dye degradation. A higher dye concentration (substrate) requires large volume of inoculum sizes for its efficient uptake and remediation. If dye concentration is too low, the available enzyme forms the enzyme-substrate complex [48], which is swiftly degraded by the inoculum. These findings are in accordance with Liu et al. [49], who reported that 70% decolorization of Remazol Brilliant Blue R as observed 10–30 ppm profoundly decreased to 15% when the dye concentration increased to 200 ppm. However, under high dye conditions, the higher substrate is present in the media overpopulates the available enzymes by blocking its active sites and lowering the overall degradation efficiency of the system consuming more time.

4.2.6 Enzyme

The presence of peroxidase in *Vibrio cholera* (VcDyP) is identified to degrade Reactive Blue 19 at arginine (Arg) 230 and aspartic acid (Asp) 144 radical site [50]. Laccase from *Klebsiella pneumoniae* is reported to be effective for degrading anthraquinone dyes. However, the use of enzyme for biodegradation is challenged with the associated expense, stability, and product inhibition. White rot fungi has been extensively reported in degradation studies, their wide applicability is attributed to its competent oxidoreductases enzymatic system capable of degrading aromatic compounds [3].

5 Present Challenges and Future Prospects

Development of robust strains using molecular engineering techniques that are able to utilize broad classes of dye and can work well under high dye concentrations. Bioreactors like microbial fuel cell (MFC) provide novel and eco-friendly dye remediation techniques and it can be coupled with a simultaneous electricity generation [51, 52]. It is essential to elucidate the dye degradation pathway to unravel mechanism and mode of action associated during degradation. Enzymes are a suitable alternative for degradation due to their higher specificity, sensitivity, and recyclability; therefore, further studies on novel enzymes with potential degradation ability need to be explored. Identification of effective and inexpensive agro-waste as carbon and nitrogen source can further cut down the associated cost. Lab-scale degradation studies revolve around classic dyes ignoring the present and more persistent dyes developed on a daily basis, therefore, the lab-cultivated strains fail to deliver convincing results when exposed in field conditions. So, more emphasis is needed to screen the degradation of modern dye structures evolving daily in the textile industry. For the containment of the present dismal conditions because of waste generated from textile industries, we need a two-sword technology, first to combat the present wastes and second to restart eco-friendly productions as bio pigments. Certain natural pigments such as carotenoids (with red, orange and yellow colors) obtained from plants, algae, fungi, yeast, and some bacteria may be exploited. Utilizing these organisms to generate pigments having proficient prophylactic activities would not only uproot the present environmental crisis but also reinstate healthy living.

6 Conclusion

The deleterious impact of textile effluent to the environment needs to be addressed by developing a highly efficient wastewater remediation approach using combinatorial techniques. Reinforcement of stringent laws on textile industries needs to be strictly established for discharging effluent with little or no effect on the environment. Further, in order to achieve an economically viable and effective textile treatment process, it is essential to integrate microbial consortium offering dynamic metabolic intermediates and myriad potential enzyme machineries that are effective against complex dye structures.

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Degradation of Selected Xenobiotics from Wastewater by Wood-Decay Fungi

Adéla Žižlavská and Petr Hlavínek

Contents

Abstract The occurrence of xenobiotics in the aquatic environment is a consequence of the development of the chemical and pharmaceutical industries and the massive use of synthetic substances in various manufacturing sectors. It has a completely different effect on the environment than "normal" organic pollution. It does not primarily affect water quality but acts directly on organisms. It can damage immunity, growth, metabolic processes, reproduction, and the natural behavior of biota. The main source of xenobiotics in the water cycle is an outflow of wastewater treatment plants. Xenobiotics are a diverse group of micropollutants with high persistence and resistance to the normal process of biological treatment in WWTP. For this reason, it is necessary to look for and test new methods and possibilities of

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their elimination in the water management sector. Promising technology is the bioremediation system's effective use of wood-destroying "white root fungi," whose enzymatic apparatus is able to metabolize more complex substances.

This chapter deals with the influence of wood-destroying fungi on the degradation of selected xenobiotics from wastewater and the development of bioremediation technology with a biofilter inoculated with *Trametes Versicolor* mycelium, which could be practically applied in the tertiary stage of wastewater treatment.

Keywords 3D print, Biofiltration, Bioremediation, Environment, Micropollutants, Wastewater, Wastewater treatment technology, Wood-decay fungi, Xenobiotics

1 Introduction

Thanks to advances in the development of water chemical analysis technology, an increased occurrence of substances in natural waters that are not specific to the natural aquatic environment has been observed in the last 30 years. Due to their unnatural origin compared to common organic pollution, they are often referred to as "Xenobiotics." This situation is the result of the development of the chemical and pharmaceutical industry and the massive use of chemicals in various manufacturing or processing industries, which has become indispensable for our society. Xenobiotics represent a large group of substances including pharmaceuticals, pesticides, detergents, paints, varnishes, plastic packaging, food additives, cosmetics, and many others [1].

The name is derived from the Latin terms for xenos – foreign and bios – biological. These are often substances with completely different chemical–physical properties. Their concentration in water is in range of ng L^{-1}–μg L^{-1}. However, even in these low concentrations, the effects of xenobiotics on living organisms are much more dangerous than conventional organic pollutants. Conventional organic pollution usually degrades the state of water, such as turbidity, oxygen conditions, etc. In contrast, xenobiotics directly affect the organism, for example, at gene levels or through the endocrine system. It may evoke carcinogenic growth, mutagenic or teratogenic reproductive changes, or suppress the animal instinct of self-preservation. These effects may also occur in the next few subpopulations that have not been exposed to the harmful substance [2].

Xenobiotics are mostly completely persistent to common biological and chemical degradation processes, which take place in nature or during conventional wastewater treatment. Most of these substances practically go through the treatment cycle and freely spread to surface waters. Xenobiotics also may infiltrate groundwater and contaminate drinking water sources (xenobiotics such as pesticides was also found in drinking water resources) [3–6].

In addition, they enter the water not only in the original parent form, but also in the form of metabolites, which during transport from the source to the recipient (or in the process of water purification at the WWTP) may deconjugate back to the parent form or create new conjugates with other substances [7].

Xenobiotics pose a dangerous threat to all living organisms, including humans, in natural waters and water sources. At present, the issue of these substances is finally beginning to be addressed somewhat more intensively, and the elimination of these substances is in the interests of both the European Union and, for example, the EU (WFD, CIRCAB, EU Watch List [8–11], WHO (The International Program on Chemical Safety [12]), USEPA, and many others.

The terminology on these "new pollutants" is not entirely uniform. It is possible to find names other than "xenobiotics" within the scientific literature, for example, PTS – persistent toxic substances, PBT – persistent, bioaccumulative, and toxic substances, micropollutants (with regard to the range of low concentrations), EC – emerging pollutants, CEC – contaminants of emerging concern, etc. It will be primarily called "Xenobiotics" for the purposes of this chapter. The above names may appear in the text in the case of literary references or citations.

Wood-destroying fungi belong to the parasitic fungi of the Basidiomycetes division, which obtain energy from living or dead tree bodies. The ability of basidiomycetes (mainly white-rot fungi species) to degrade a wide range of substances is based on their non-specific ligninolytic extracellular and intracellular enzymatic system [13–16].

The chapter summarizes the current state of use of white-rot fungi in the field of wastewater treatment and focuses in more detail on the development and testing of bioremediation technology using a 3D printed biofilter inoculated by *Trametes Versicolor* mycelium to degradation of selected pharmaceuticals from water.

2 State of the Art: Application of Wood-Decay Fungi in Wastewater Treatment

Bioremediation methods include use of fungal, bacterial, algae, or plant (phytoremediation) species for the treatment of wastewater. Technological constructions of bioremediation are bioreactors, biofiltration, membrane reactors, root treatment plant, and constructed wetlands.

In general, this method of treatment is suitable either directly for a clean source of pollution (hospital, effluent of industry) or as a tertiary stage of WWTP after biological treatment. At the tertiary stage, organic pollution is already sufficiently degraded, which could cause inhibition of the growth of the bioremediation medium (algae, fungi) due to the excessive growth of activated sludge bacteria [17–19].

Fungi and fungus-like organisms are a relatively complex biological group. For example, they do not have plastids and their corresponding structures compared to the common representatives of the plant kingdom. Fungi do not have an assimilation pigment (except lichen), which leads to a heterotrophic diet. A large number of fungal representatives are parasites, as they obtain nutrients directly from living plant cells (or from more or less dead tissues). Currently, 65,000–70,000 species of fungi are described, with an estimated 1.5 million as yet undetected species [20]. In 2017, there were 2,189 new species of fungi discovered [21]. Wood-decay fungi belong to parasitic fungi from the species division of basidiomycetes (stem-spore fungi) and obtain their energy from living or dead bodies of woody plants. Based on the type of color decomposition of wood, we divide wood-decay fungi into:

- white-rot,
- soft rot,
- brown rot (a specific group is red root fungi, which includes wood-destroying fungi producing the metabolite Fomannoxin [22, 23]).

Wider use of basidiomycetes occurs in the 1980 with the development of enzymology, when enzymes, especially peroxidase, began to be used in the paper industry to remove paint in wastewater from bleaching plants [24]. Gradually, this trend spread to other industries to remove dyes from water, as most synthetic dyes resist common biodegradation processes, which causing a significant esthetic problem in the discharged waters. Since 1990, there has been begun intensive surveys of white-rot fungus ligninolytic enzymatic system utilization for the degradation of organic pollutants such as polychlorinated biphenyls, polyaromatic hydrocarbons, chlorophenols, and various types of synthetic dyes [13–16, 25]. During the test was used the whole fungal culture or the enzyme preparations containing most or all of the extracellular enzymes. Several species of fungi have been verified in studies, such as *Phanerochaete chrysosporium* [26], *Pycnoporus cinnabarinus* [27], *Pleurotus sp.* [28], *Trametes versicolor* [29], and *Bjerkandera adusta* [30].

It was later found that enzymes of the intracellular system (i.e. Cytochrome P450) also play an important role in degradation processes.

The ability of basidiomycetes and predominantly white-rot fungi to degrade a wide range of substances lies in their non-specific ligninolytic extracellular enzyme system, which includes enzymes:

- manganese peroxidase (MnP),
- lignin peroxidase (LiP),
- pyranose 2-oxidase (P2O),
- Lacasse,

as well as intracellular enzyme complexes (cytochrome P450).

Based on comparative studies [31] performed on various representatives of the white-rot fungi, it is known that one of the most effective wood-destroying fungi in removing micropollutants from water is demonstrably the species *Trametes Versicolor*.

Currently, there are three methods of application of wood-decay fungi in the cleaning of water matrices:

- enzymatic methods [32–35] – use of only individual enzymes, or their combinations.

Enzymatic methods – enzymatic preparations are used in which the individual components of enzymes are already predefined. These are subsequently subjected to biocatalytic degradation and enzymes being immobilized on a mediator (often natural compounds such as coumaric acid (PCA), syringaldehyde (SYR), and acetosyringone (ACE)) the biocatalytic reaction is realized in reactors. Most of these methods allow re-use, but they are not living organisms, but only individual enzymes.

- mycelial pellets and suspensions [36, 37] – production of activated pellets or solutions.

Mycelial pellets and suspensions are a very commonly used method, which was discovered in 1978 and is used, for example, in the paper or textile industry in the treatment of water containing synthetic dyes. The production of mycelial pellets consists of inoculating malt agar plugs (2%), which are placed in 500 ml Erlenmeyer flasks containing 150 ml of malt extract medium (2%). The flasks are then placed in an orbital shaker (135 rpm, $r = 25$ mm) at 25°C. After 4–5 days, a dense mycelial mass is formed, which is ground with a homogenizer. The resulting mycelial suspension is stored in sterilized saline (0.85% NaCl) at 4°C.

This suspension is then used directly to obtain pellets by inoculating 1 ml of the suspension with 250 ml of malt extract medium (2%) (adjusted to pH 4.5) in a 1 l Erlenmeyer flask. The flask is further incubated on an orbital shaker (135 rpm, $r = 25$ mm) at 25°C for 5–6 days. This produces pellets that can be stored in sterilized saline (0.85% NaCl) at 4°C, where they remain active without loss of morphology for a maximum of 2 months [37]. In laboratory tests, pellets are used in smaller tests directly in Erlenmeyer flasks, or in larger volume tests at aerated bioreactor.

- cultivation on bio carriers – inoculation and fructification of carrier media.

Immobilization on solid supports – Another possibility is to cultivate the mycelial form immobilized on solid supports. So far, loofah skeletons, zeolites, wood chips, crushed nut shells, corn leaves, and chopped pallet wood have been tested as culture carriers [38, 39].

The design and build of a reactor with suitable conditions for mycelial growth is a crucial problem of the technology application of white-rot fungi in wastewater treatment. There are various prototype configurations successfully applied in the degradation of xenobiotics in wastewater:

- stirred tank reactor [40] – operating with continuous air supply or periodic pulsation of oxygen,
- aerated reactor [41]
- bubble column reactor [42]
- fluidized bed reactor [17–19]
- aerated full bed bioreactor [43]
- counter current leakage bioreactor [39]
- in combination with MBR [44].

Current foreign research focuses mainly on testing a fluidized bed bioreactor with pulsed air and a counter current leakage bioreactor. However, over time, both of these technologies began to show a significant decrease in efficiency during continuous operation under non-sterile conditions, especially when testing with real matrices of wastewater samples without pre-treatment at the WWTP. This deterioration in performance is usually caused by the overgrowth of bacteria that inhibit fungal growth and enzyme production [38, 39]. This phenomenon was observed more markedly in technologies working with the mycelial form of basidiomycetes, on the contrary, the technology using lignocellulosic carriers is able to at least partially resist this bacterial inhibition. Furthermore, it has been shown that in reactors operating in the submerged mode, after 14 days, the efficiency decreases by up to 20%, on the contrary, in leakage reactors and MBR it does not occur [44].

3 Biocarriers Produced by 3D Printing

The method of biocarriers is clearly the best choice in terms of practical operation, economy, and long-term sustainability at real WWTP [44]. The basic condition for the functioning of white-rot fungi as a bioremediator is to use a biocarrier containing a sufficient amount of lignin and cellulose for inoculation. Dried loofah fruits, zeolites, wood chips, crushed nutshells, corn leaves, and chopped pallet wood have so far been tested as culture carriers [39]. Within the AdMaS research centre, we have developed a completely unique type of biocarrier made by 3D printing from PLA material with an admixture of wood up to 30% with the working name “3D cubes” (Fig. 1). The biocarriers are designed in the shape of perforated cubes with side ribbing so that they can be joined into compact sheets. The internal structure and perforation of the cubes were designed on the basis of the internal hierarchical arrangement of the dried fruit of the *Luffa cylindrica* plant.

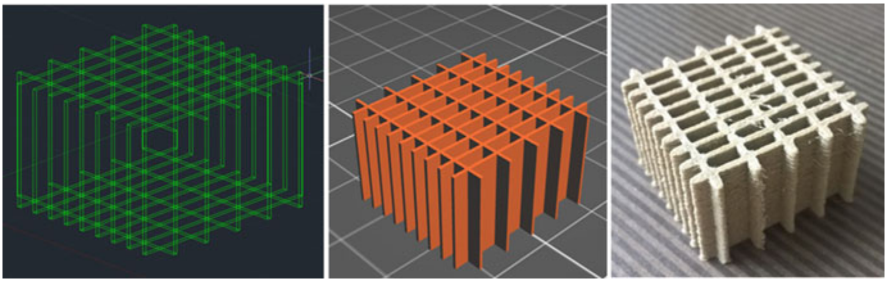

Fig. 1 Biocarrier model 25 × 25 × 15 mm (left: AutoCAD model, model viewed in PrusaControl 09.4_415 beta program, real biocarrier after print)

4 Testing of Biocarriers Produced by 3D Print

4.1 Tested Substances: Sulfonamides Antibiotics

Sulfonamides are broad-spectrum bacteriostatic antibiotics that have found wide applications in human and veterinary medicine. Currently, there are limitations to the use of sulfonamides antibiotics in human medicine due to increasing bacterial resistance and the availability of more active antibiotics. However, their use in veterinary medicine persists and they are very often used in pigs and cattle to treat bacterial diseases [45]. They are metabolized in the liver and excreted in the urine and excrement. A significant amount of these substances enters the wastewater either in the form of metabolites or even unchanged due to poor adsorption and degradability in the intestines of humans and animals [46]. Sulfonamides do not completely removed by wastewater treatment plants. Even during the removal, it was often found a higher concentration of sulfamethoxazole in the WWTP outflows than in input which was a result of the reverse conversion of the metabolite N^4-acetyl sulphonamide [47]. Sulfapyridine, sulfamethoxazole, and its acetylated metabolite N^4-acetylsulfamethoxazol are most often detected in wastewater [48] wherein 20% of the urinary sulfamethoxazole is unchanged drug, 15–20% is the N-glucuronide conjugate and 50–70% is the acetylated metabolite.

The mixed solution of the monitored sulfonamides antibiotics contained Sulfapyridin – SPY (Sigma Aldrich, assay ≥99%), Sulfamethaxazole – SMX (Sigma Aldrich, assay ≥99%), Sulfamethoxazol-d4 SMX d4 (Neochema GmbH, 100 μg/ml v MeOH), Sulfamethazine – SMZ (Sigma Aldrich, assay ≥99%), Sulfathiazole – STZ (Sigma Aldrich, assay ≥99%), Sulfathiazole-d4-STZ-d4 (Toronto Research Chemicals), Sulfamerazine – SMR (Sigma Aldrich, assay ≥99%), Sulfadiazine – SDZ (Sigma Aldrich, assay ≥99%).

The distilled water was used as model water in the Printscreen test and spiked drinking water and wastewater taken from the Modřice Brno WWTP drain was used in the Setup test.

4.2 Inoculation and Fructification Process

The inoculation of the 3D print cubes took place in sterilized 500 mL jars fitted with a perforated aluminum screw cap and cellulose wadding filter. The jars were sterilized in water at 100°C for 30 min. The cubes were printed at least 24 h before inoculation.

The fully grown *Trametes Versicolor* maternal fruiting bodies were used as inoculum, which was cut into approximately 2 × 2 cm pieces and placed in a seed glass along with the cubes. Increased growth was supported by the agar-glucose solution that was added to each sample. The agar-glucose solution was made from 10 g of glucose, 15 g of agar, and 1 L of distilled water. All samples were stored in the dark at about 20°C. Mycelium growth was controlled each 3–4 days after the inoculation process. At the same time was again added 5 mL of agar-glucose solution. The biocarriers were fully fructified 10–12 days after inoculation. The excess AG solution was pipetted from the jars before testing.

4.3 Testing

The testing of biocarriers took place in two tests. The first so-called Printscreen test was performed in order to verify the efficiency of degradation of sulfonamides antibiotics from model water containing a concentration of 1 mg$\cdot$ L^{-1} sulfonamides antibiotics where distilled water used as a model medium. Such a high concentration was approached due to concerns about the possible negative effect of the matrix effect on the evaluation of the tests.

The second test, called the Setup test, aimed to obtain basic key data to verify the effectiveness of degradability depending on the different variations in sulfonamides antibiotic concentration levels and residence time. As part of the tests, there were also used real samples of wastewater from the Modřice WWTP outflow in Brno.

Basic test parameters:

- Printscreen test – The concentration of monitored substances was 1 mg L^{-1} for each analyte in distilled water. The duration of the test was 7 days. Mycelial age 12 days. Cubes measuring 25 × 25 × 25 mm were used as inoculation carrier. A total of three samples were evaluated. The sample was marked as Test I, Test II, and Test III.
- Setup test – Concentration of monitored substances was 20 μg L^{-1}, 100 μg L^{-1}, for each analyte in drink water and 20 μg L^{-1} of each analyte in the wastewater. Test durations for concentration levels 20 μg L^{-1}, 100 μg L^{-1} were set at 3.5 and 7 days. Mycelial age 10 days. Cubes measuring 25 × 25 × 15 mm were used as inoculation carrier.

Testing was performed after completion of the fructification of the biocarriers after removal of any excess agar-glucose solution directly in the inoculation jars, to which was added 250 mL of model water contaminated with the mixed solution. The inlet pH of each sample was measured, and the glasses were provided with an aluminum perforated overlay and placed in a thermoset in the absence of light at 25°C.

4.4 Analysis and Evaluation

4.4.1 Materials and Analysis Methods

Liquid Chromatography-Mass Spectrometry (HPLC/MS) analysis of sulfonamide concentration in aqueous samples was carried out by these instruments and materials: Agilent 1,100 Series liquid chromatography, Kinetex C18 column length 150 mm, internal diameter 3 mm, particle size 2.6 μm, Ascentis Express C18 column length 150 mm, internal diameter 2.1 mm, particle size 2.7 μm, Ascentis Express HILIC column length 150 mm, internal diameter 2.1 mm, particle size 2.7 μm, and Agilent Ion Trap 6,320 LC/MS mass spectrometer.

4.4.2 Evaluation of Printscreen Test

The highest degradation efficiency was achieved with sulfamethoxazole, where the values reached <99.99 removals in all samples (Table 1). On the other hand, the lowest degradability rate was shown by the sulfonamides sulfamerazine, for which the average elimination value was 3.97%, while in sample Test 3 the elimination efficiency was evaluated as zero. In terms of the total content of degraded sulfonamides, the most successful sample was Test 2, where the average value of degradation per sample reaches 31%. The average removal amount was 1.86 mg L^{-1} from all analytes monitored (Fig. 2).

4.4.3 Evaluation of the Setup Test

The Table 2 shows that sulfamethoxazole was best degraded, even within the mean values, as the only one above the limit of 90%, the lowest removal rate was shown by sulfamethazine. For sulfapyridine, sulfamethoxazole, we can observe that the average values after 5 days decrease compared to the values after 3 days, while after 7 days the values increase again compared to the results from the third day. The data also clearly show that during the first 3 days in the test with a concentration of 20 ug L^{-1} achieves the greatest progress in terms of effectiveness. On the contrary, the test with a concentration of 100 ug·L^{-1} increases in aging efficiency after 5 days. The comparing of efficiencies of the test with drink water and wastewater with concentration 20 ug L^{-1} shows the total amount of degraded substances was higher in the wastewater samples (Table 2). A comparison of individual analytes shows that the only exception is sulfapyridine, whose elimination rate at 7 days is higher in the case of drink water but the difference is only 3%. The ability of *Trametes Versicolor* to degrade sulfonamides better in wastewater is probably due to richer stores of organic matter, especially polysaccharides, which provide the mycelium with the energy needed for metabolic processes to allow faster decomposition of more complex macromolecular substances [19, 38].

Table 1 Summary of the Printscreen test results

	Sample						Efficiency of elimination *E*		
	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3	Σ		
Sulfonamides	Efficiency of degradation (%)			Residual concentration μg L^{-1}			*E* (%)	*S* (%)	μg
Sulfapyridine	26,15	22,01	16,85	738,55	779,93	831,49	21,67	4,66	216,68
Sulfadiazine	10,12	10,25	5,77	898,75	897,52	942,28	8,71	2,55	87,15
Sulfamethoxazole	<99.99	<99.99	<99.99	0,00	0,00	0,00	<99.99	0,00	1,000,00
Sulfathiazole	14,60	14,39	3,53	853,97	856,12	964,74	10,84	6,33	108,39
Sulfamerazine	6,64	5,28	0,00	933,59	947,21	1,000,00	3,97	3,51	39,73
Sulfamethazine	39,40	50,19	32,83	605,99	498,09	671,75	40,81	8,77	408,06

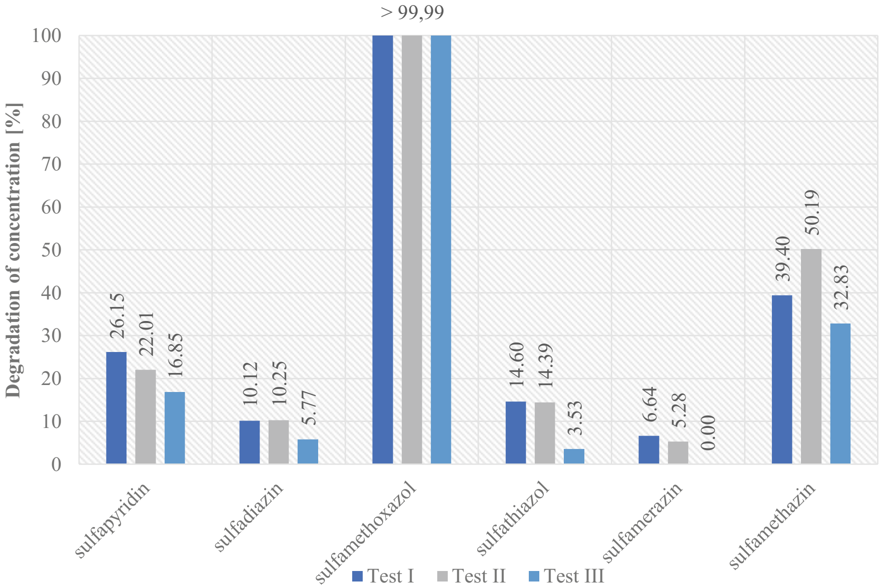

Fig. 2 Graphical comparison of Printscreen test results at degradation efficiency

The degradation efficiency range of sulfonamides in wastewater at a concentration of up to 20 μg L^{-1} after retention time 3–7 days for: Sulfapyridine – 67–80%, Sulfadiazine – 54–81%, Sulfamethoxazole – 78–99%, Sulfathiazole – 51–86%, Sulfamerazine – 49–72%, Sulfamethazine – 46–70%.

Based on the results of the test, it was also possible to compare the degradation efficiency in different water matrix samples at the sulfonamides concentration of 20 ug L^{-1} (Fig. 3). Figure 4 shows that of the total amount of degraded substances, the effluent wastewater matrix samples were clearly more effective. Exception is Sulfapyridine, whose elimination rate at 7 days is higher in the case of tap water, however the difference is about 3%. This effect is conditioned by richer reserves of organic substances in wastewater. Especially polysaccharides provide energy needed for the metabolic processes of the ligninolytic intracellular system enabling the decomposition of more complex macromolecular substances. For example, the degradation of 4-nitrophenol by the white-rot fungi Trametes Versicolor was tested with dilute tomato puree (or tomato juice) as a polysaccharide source [49]. When comparing the data, it is evident that the presence of organic substances in the water sample results in a higher production of mycelia, which is also reflected in an increase of the degradation efficiency. The increase is best observed when comparing the results of tests completed after 3 and 5 days.

Table 2 The Setup test summary results of the sulfonamides antibiotics removed by Trametes Versicolor in the different concentrations

	3 days			5 days			7 days		
	20	100	20WW	20	100	20WW	20	100	20WW
	ug·L^{-1}								
Sulfonamides	Degradation [%]								
Sulfapyridine	72,25	25,20	75,10	67,31	32,22	73,58	80,88	86,31	78,33
Sulfadiazine	54,74	12,69	75,68	58,93	21,37	79,86	73,34	32,48	81,30
Sulfamethoxazole	78,17	7,42	77,38	70,21	25,92	96,73	94,58	99,84	99,80
Sulfathiazole	53,53	0,00	81,42	65,77	5,13	87,86	81,66	50,38	86,01
Sulfamerazine	49,86	0,00	69,72	51,42	0,00	69,06	66,33	20,52	72,05
Sulfamethazine	46,41	1,92	68,96	53,56	12,38	62,34	54,72	7,40	70,23

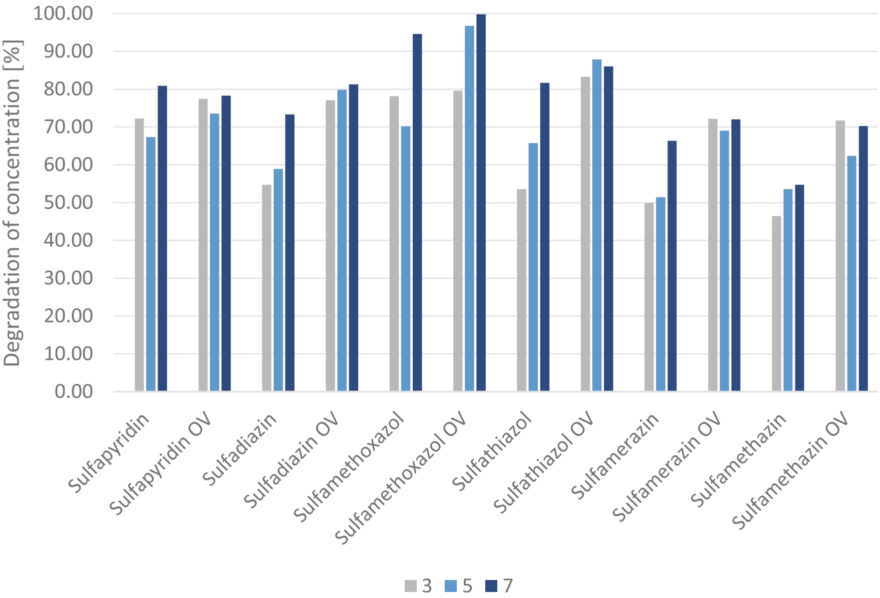

Fig. 3 Comparison of the degradation efficiency of sulfonamides antibiotics in spiked drink water and wastewater at an initial concentration of 20 μg L^{-1}

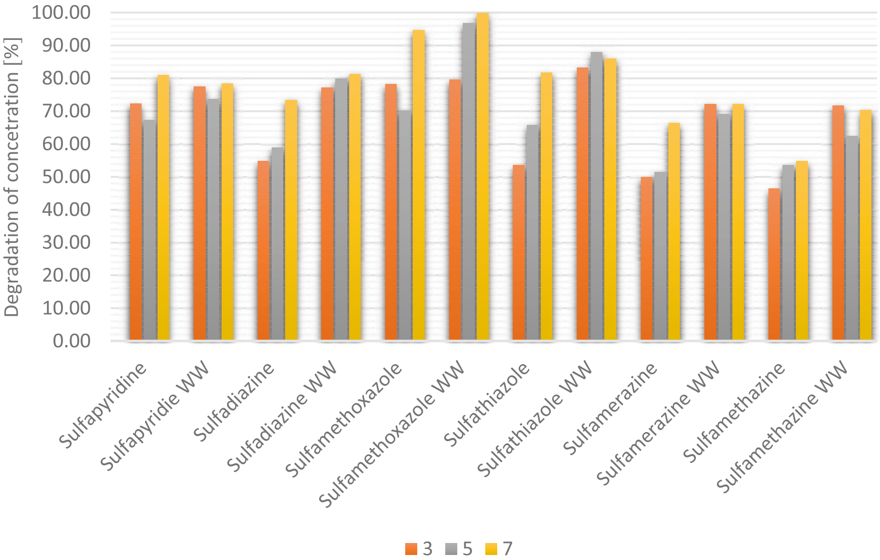

Fig. 4 Degradation efficiency comparison of sulfonamides antibiotics in tap and wastewater at an initial concentration of μg L^{-1}

5 Conclusions

The xenobiotics represent a very wide group of substances with non-uniform physicochemical properties and different degrees of biodegradability. Their presence in wastewater is highly variable and depends on many other factors. These are very persistent and resistant to conventional methods of wastewater treatment, and in some cases during treatment can even form toxic conjugates, which are often more dangerous than the parent substances. In addition, in the case of the presence of antibiotics in the process of biological treatment is the rising risk of bacterial resistance to antibiotics.

Therefore, it can be expected that the legislation in this direction will put increased pressure on WWTPs operators to ensure their sufficient removal in the future. The assumption is that the elimination of xenobiotics will be solved mainly by building a tertiary stage of wastewater treatment which becomes a common part of WWTP.

The bioremediation methods seem to be very promising in the terms of the degree of degradation efficiency, economical aspect, and the current social trend of green technologies inspired by nature.

Wood-decay fungi as a bioremediator have demonstrated the high elimination efficiency of a wide range of xenobiotics from different environmental matrices in various studies. Laboratory testing of *Trametes Versicolor* mycelium immobilized on carriers produced by 3D printing carried out at the AdMaS center (Brno University of Technology) brought very good results. Two different tests have shown an apparent effect on the reduction of sulfonamide antibiotics in model and real wastewater. If these results will be proven by pilot testing, mycelium immobilized on 3D-printed media may be a cost-effective option to reduce xenobiotic contamination at the tertiary level of WTTP.

6 Recommendations

Although fungi, especially wild ones, are still a very unexplored area, their successful testing for medical, biotechnological, or decontamination purposes reveals their great potential, which will certainly bring new and unexpected discoveries in the future. Currently, the application of wood-decay fungi (white-rot fungi) is carried out only on a pilot scale, but the next step should be the transfer of technology to the operational facility, which would better assess their potential from a practical point of view. However, it will be necessary to perform another extensive validation testing for operational facilities, including the effect of hydrodynamic conditions, retention time, pollutants interactions, inoculation and fructification process directly in bioreactors, and especially to verify elimination efficiencies in larger volumes of water.

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Part IV
Advanced and Tertiary Wastewater Treatment Systems

Nanotechnology Enabled Multifunctional Materials for Removal of Toxicants from Wastewater

Rachna Bhateria and Rimmy Singh

Contents

Abstract Providing clean and potable water for human use is a great challenge of the twenty-first century. Globally, water supply wrestles to keep flow with the rapidly increasing demand which is aggravated by global climate change, increasing population and drop-down in water quality. Hence, to enable integrated water management, the need for technological innovation cannot be exaggerated.

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Nanotechnology shows high potential in improving water and wastewater treatment efficiencies as well as enhancement of water supply by safeguarding unconventional water sources. Therefore, next generation water supply systems can be the result of leapfrogging opportunities provided by advancement in nanotechnology. The sustainability of our current water treatment, their distribution and discharge system are no longer viable due to their dependency on conveyance and centralized systems. The provided review accounts for nanotechnology enabled water treatment solutions through various multifunctional nanomaterials capable of transforming the current water treatment systems. High surface area, tunable pore size, optical, catalytic and magnetic properties, antimicrobial activity and surface chemistry are some of the magnificent properties of nanomaterials which make them a potential candidate for multiple applications. These properties of nanomaterials are applicable in water treatment as adsorbents, sensors for water quality monitoring, disinfection and for preparation of high quality nanomembranes. More importantly, the highly efficient, flexible and multifunctional materials enabled by nanotechnology provide a promising route both to retrofit aging infrastructure and to develop high performance, low maintenance decentralized treatment systems including point-of-use devices.

Keywords Adsorbent, Disinfection, Membrane, Nanomaterials, Sensors

1 Introduction

For the sustenance of human civilization and all other forms of the life, water is regarded as the most precious and essential resource. In the twenty-first century, access to clean and potable water is the most important humanitarian goal, but has become a major global challenge for the society [1]. In the early ages from 1900s to 1970s, the objectives of water treatment focussed on (a) the elimination of floating, colloidal and suspended substances (b) treatment of biodegradable organic compounds and (c) decontamination from pathogenic microbes. Unfortunately, these objectives have not been achieved properly. From the 1970s to 1980, environment and aesthetic concerns were the primary objectives for wastewater treatment [2]. Meanwhile, the objectives of pathogen, biological oxygen demand (BOD) and total suspended solid (TSS) reductions were in continuation phase but parallelly nutrients such as phosphorus and nitrogen were also started adding with contaminated substances. Therefore, the intensity of water treatment has increased significantly [3].

In current municipal treatment technologies, water disinfection is achieved by chemical disinfectants such as chlorine and chloramine and by germicidal UV radiations [4]. Processes using multi-barrier approach have no significant effect against all groups of pathogenic microorganisms such as bacteria, viruses and protozoa which are of the emerging global concerns. Extensive infrastructure is required by current large-scale centralized water treatment plants for disinfection [5]. However, there are certain complicated halogenated compounds released during the disinfection processes which require sophisticated optimization and high-profile infrastructure facilities. These techniques can be proved fruitful to developed countries due to the availability of infrastructure and facilities but are not well suited to developing countries and in areas with low population [6]. Hence, there is need to shift on the advanced yet affordable technologies which are capable of decontaminating water and less dependent on chemical and energy. It should be modularly designed but simple to maintain and implement for treating pollutants [7].

Since nanotechnology has shown its potential into various applications of wastewater treatment and environmental remediation, simple and efficient nanomaterials have come up to the way which have high abilities of water treatment. Engineered nanomaterials have large surface area and specific reactivity [8] which can function efficiently in designing a well-defined centralized water system. Engineered nanomaterials (ENM) enabled nanoscale materials have cell wall disruption abilities [9–12], electrostatic interactions based on surface active processes [13], photochemical generation of reactive oxygen species [14–16] and targeted delivery of disinfecting agents [17]. Pathogens can be trapped through nanomaterial-based biofilm inhibition as they have unique surface properties as well as reactivity [9].

For wastewater treatment, engineered nanomaterials show wide applications as they exhibit newer properties which have the capability to develop highly reactive and improved membranes, photocatalytic substances and absorbents [18]. Various organic (phenols, azo dyes, pesticides, etc.), inorganic (Pb, Cr, Hg, Cd, etc.) and biological materials (algae, viruses, bacteria, etc.) can be detected and eliminated by engineered nanoparticles, nanotubes and nanomembranes [19]. Nanomaterials have the potential to offer solutions to disinfection, adsorption, catalysis and water cleaning [20, 21]. For the removal of some specific contaminants, nano traps have been designed. Likewise, researchers in Rice University fabricated iron oxide ceramic membranes (ferroxane membrane) for organic waste decontamination in water [22].

In the present review, we have discussed and highlighted various kinds of nanomaterials that are used in wastewater treatment. Moreover, a brief discussion is addressed on how nanotechnology overcomes the limitations of conventional technologies for water treatment. Nanotechnological applications in water disinfection, media filtration, membrane filtration and in monitoring and sensing are also described in the trailing sections of the review.

2 Treatment Methods

2.1 Conventional Technologies

To meet the complicated wastewater treatment problems, various technologies such as reverse osmosis for inorganic contaminants removal, aeration for odour and taste control, adsorption and ion exchange for ions removal have been developed time to time. But the concern has driven to framework the strategies regarding the

Table 1 Conventional disinfection technologies [36, 37]

Conventional technologies	Advantages	Disadvantages	Application
Chlorine	Easy to handle and economical; residual concentration; technologies consolidated	High contact time; by-product formation; residual toxicity of the effluent; very corrosive	Drinking water; wastewater
Chlorine dioxide	More effective than chlorine over short contact; long residual	Residual toxicity of the effluent; by-product formation; generation onsite; medium-high management costs; increase the concentration of solids in the effluent	Drinking water; wastewater
Ozone	Short contact time	No residues of disinfectant; by-product formation; generation onsite; high energy demand; high management costs	Wastewater
Peracetic acid	Simple solution; residual concentration	Increase BOD and COD concentration in the effluent; by-product formation	Wastewater
UV radiation	No by-products formation; short contact time; inactivation of virus	No residues; high energy demand; high cost; unsuitable for water with high levels of suspended solids, turbidity, colour or soluble organic matter	Wastewater

availability and deliverance of clean and potable water to the growing demands [23–26]. To aggravate the situation, wastewater effluent already emerges toxic and lethal pollutants which include but not limited to endocrine disrupting compounds (EDCs), textile dyes, plasticizers and pharmaceutical products which have potential health effects [23, 27–30]. Conventional wastewater treatment technologies primarily focus on the removal of solid materials while reducing chemical oxygen demand (COD) and biological oxygen demand (BOD) in secondary treatment. Parallelly high levels of nitrogen and phosphorus were added to the water bodies released during conventional treatment practices, which leads to eutrophication. The increase in turbidity results in addition of high levels of disinfectants such as chlorine which can form the carcinogenic by-products (Table 1). In conventional treatment, technoeconomic challenges are also associated with the removal of microbes from the treatment plant. Conventional treatments have not yet applied to the large scale due to high capital investment, complexity of process, high cost of operation and other environmental impacts [31]. Therefore, to develop accessible wastewater treatment technologies, researchers have explored low-cost, sustainable and/or renewable alternatives (such as adsorbents and enzymes) [32–35].

2.2 *Nanotechnology*

Nano is derived from a Greek word which means “dwarf.” Nanotechnology (“nanotech”) is the handling of matter at an atomic, molecular and supra-molecular level.

Table 2 Nanomaterials for water treatment

Nanomaterial	Treatment process	Action	Reference
Silver (Ag)	Disinfection	Release of Ag+ ions, cell membrane disruption	[43, 44]
Gold (Au)	Disinfection	Enhanced antimicrobial activity	[45]
Magnetic nanoadsorbent	Adsorbent	Expulsion of Pb (II)	[46]
Zerovalent nanocopper	Dye degradation	Methyl orange	[47]
ZnO/Zn	Photocatalysis	Methylene blue	[48]
TiO_2/trititanate	Photocatalysis	Rhodamine B	[49]
AgBr/ZnO	Photocatalysis	Methylene blue degradation	[50]
ZnS nanocrystals	Adsorbent	Removal of Hg (II)	[51]

Simply, "nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling the shape and size at the nanometre scale". Nanotechnology is capable of significantly improving the environmental quality and sustainability by pollution prevention, treatment and remediation. Large infrastructure-based wastewater treatment solutions can be replaced by highly efficient nanomaterials which will provide affordable and clean water [38]. For the expulsion of toxic heavy metals and organic wastes, nanomaterials play a significant role in water decontamination (Table 2) [39]. The application of nanotechnology in drinking water treatment and pollution clean-up is promising as demonstrated by a number of field-based (pilot and full scale) and bench-scale studies [40–42].

3 Nanotechnology Enhanced Nanomaterials

3.1 Metal Based Nanomaterials

For heavy metal and radionuclide expulsion, oxides of iron, titanium and alumina act as economical and effective adsorbents. Adsorption is mainly facilitated by the complexation reaction between heavy metals and oxygen of metal oxides [52]. Activated carbon has been replaced with nanomaterials as they have immense potential of eliminating heavy metals such as lead, chromium, arsenic, copper and zinc [53]. Among various heavy metals, arsenic is of major concern and attracted researchers. Activated carbon has limited absorption capacity for arsenic, especially for As(V) but can be good adsorbent for other organic and inorganic contaminants [54]. Magnetite and TiO_2 nanoparticles have shown superior adsorption capacity for arsenic and other metal oxides than activated carbon [55, 56]. The properties of various nanocomposites are illustrated in Fig. 2. There are certain other mechanisms such as co-precipitation, surface complexation and electrostatic attractions that are often used for the extraction of contaminants by metallic nanoparticles [57]. Furthermore, preconcentration and diffusion of contaminants can be facilitated by charged support in order to trap them in the pores of nanomaterials [58]. Various types of bacteria were reported to be killed by metallic NPs (Ag, Au and Cu) by simply disrupting their cell membranes [59].

3.2 Polymer Based Nanomaterials

Polymer nanosorbents have functional groups with large surface area, hence they have efficient and fast adsorption rate. Dendrimers are another class of polymer-based nanomaterials and they are the tailored adsorbents which are efficient in the adsorption of heavy metals and organic compounds. Dendrimers have a unique structure which includes interior hydrophobic shells for the adsorption of organic compounds while exterior branches can be tailored for heavy metal adsorption. Adsorption is based on the hydrogen bonding, complexation reactions, hydrophobic effect and electrostatic interactions between adsorbent and heavy metal [60]. For the recovery of metal ions, a dendrimer-based ultrafiltration system was designed [61]. A highly branched nanoscale dendrimers can act as “cages” for metal ions and trap them to solubilize in apt medium for binding onto specific surface. Polyamidoamine (PAMAM) dendrimers were explored for the removal of copper from water by Diallo et al. [62]. Diaminobutane poly(propylene imine) dendrimers functionalized with long aliphatic chains can remove organic impurities like polycyclic aromatic hydrocarbons from water.

3.3 Membrane Based Nanomaterials

Nanomaterial based membranes show potential in fouling reduction, increment in antimicrobial activity, separation performance and upgrading of other novel functionalities [63–68]. Generally, the membrane material decides the performance of membrane systems. Functional nanomaterials doped into membrane improve the thermal and mechanical stability, membrane permeability and fouling resistance as well as develop new functionalities for contaminant degradation and self-cleaning. The addition of zeolite NPs in TFN (thin film nanomembrane) reverse osmosis membranes helps in controlling the transport process to reach the percolation threshold in the dense selective layer with an individual particle [65, 68]. Zeolite nanoparticle-based TFN membranes show higher permeability, greater negative surface charge and are thick membranes irrespective of the nanoparticle size. Similarly, a thin coating of bundled single-walled CNTs was overlaid on the surface of a poly vinylidene fluoride (PVDF) microporous membrane, which possesses high potentiality in the removal of viral and bacterial pathogens from water at low-pressure inputs [69].

3.4 Carbon Nanotubes

Carbon nanotubes (CNTs) are the allotropes of carbon with a cylindrical nanostructure. CNTs can be single-walled or multi-walled nanotubes depending on the synthesis process, respectively. CNTs are known for their adjustable surface chemistry, high surface area and they possess great accessible adsorption sites. Carbon nanotubes are prone to high aggregation due to hydrophobic nature of surface and therefore have to be stabilized in aqueous suspension. They can be used for the detection as well as adsorption of contaminants [70]. Chemical bonding and electrostatic attractions make metal ions to adsorb on CNTs [71]. Adsorption of different organic chemicals is highly efficient in CNTs than activated carbon [72]. Large external surface area provides high adsorption capacity for contaminants and CNTs interactions [73]. CNTs have interstitial space and grooves which provide high energy sites for organic molecules [70].

3.5 Anti-Microbial Nanomaterials

Metal nanoparticles such as copper, gold and silver found effective to kill certain bacteria. Engineered nanometals have specific mechanism of action and properties. Disruption of cell membrane metabolism is the main antimicrobial mechanism possessed by nanometals [74] (Fig. 1). The antimicrobial ability of nanometals demonstrates different functions which are effective in infrastructure deficient regions. Several ENMs have been explored for water disinfection, including semiconductor photocatalysts such as titanium dioxide [75], nano-silver [17], molybdenum disulphide [47], nano-zinc oxide [76], carbon nanotubes [12] and their functional derivatives [77, 78] as well as carbon-based materials such as fullerenes

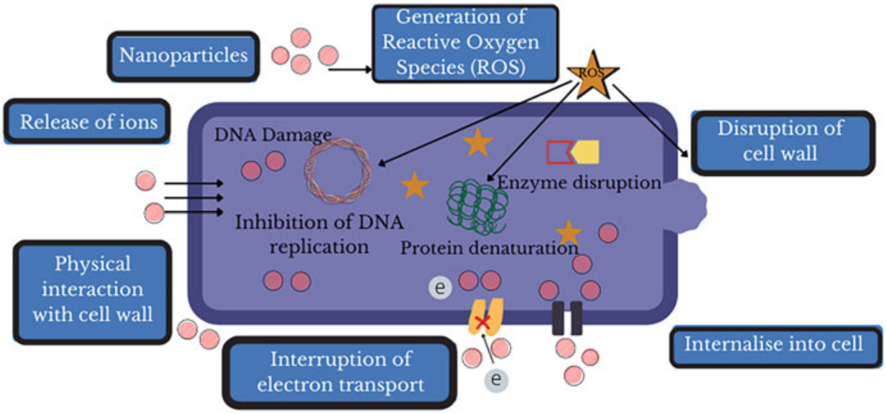

Fig. 1 Cell membrane disruption by antimicrobial mechanism of metallic nanoparticles (modified and adapted from Ref. [83])

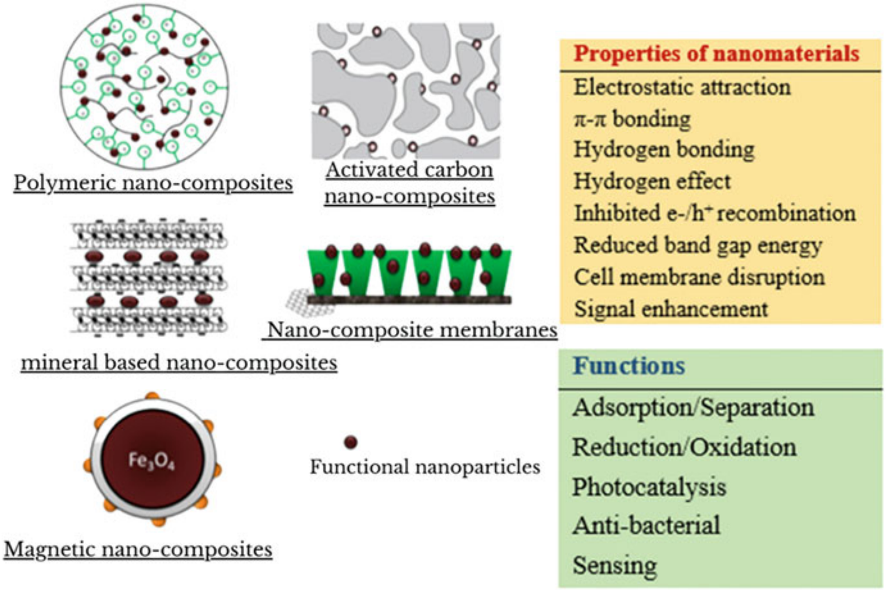

Fig. 2 Illustration of typical environmental nanocomposites and nano-enabled properties (adapted from Ref. [84])

[77, 78]. Recently, silver nanoparticles (nAg) [79], aqueous fullerene nanoparticles (nC60) [80], photocatalytic TiO_2 [14, 81], fullerol [82] and carbon nanotubes (CNT) [12] are some of the nanomaterials which show strong antimicrobial activities. Antimicrobial nanomaterials are not strong oxidants and they are inert in water compared to conventional chemical disinfectants. Therefore, harmful DBPs are not expected to be produced and have the capability to replace or enhance conventional disinfection methods (Fig. 2).

4 Application of Nanomaterials in Wastewater Treatment

4.1 Disinfection

Pathogens in potable water are mainly responsible for acute waterborne diseases around the world, especially in developing countries. Biologically unsafe water attributes to over two million deaths, mainly of children, in a year [85]. Engineered nanomaterials provide unique functionalities for pathogen inactivation, such as large surface area and specific reactivity through mechanisms that have not been well exploited by conventional disinfectants [8]. Various nanomaterials kill microbes by specific methods such as chitosan nanoparticles kill by degrading microbial cell membrane [86], nano silver (nAg) by releasing certain toxins [87] and photocatalytic nanoparticles (TiO_2) by generation of reactive oxygen species (RoS) [88, 89]. Nano disinfectants are capable of continuous operation with high efficiency and low energy consumption which attracts decentralized water and wastewater treatment systems.

4.1.1 Photocatalytic Processes

For the removal of trace contaminants and pathogens from water, photocatalysis is an advanced process. Photocatalysis is a better pre-treatment process for the biodegradation of hazardous and non-biodegradable pollutants [90]. Photocatalysis can be efficient in remediating recalcitrant organic compounds [38]. Semiconductors mainly, cadmium sulphide titanium oxide, tungsten oxide, cerium oxide, zinc sulphide, iron (III) oxide, tin oxide and zinc oxide can be used as photocatalysts [39, 91–93]. Organic contaminants can be oxidized by photocatalysts to safe and nontoxic substances. Groundwater pollutants such as toluene, cis-1, 3 chloromethanes, 1-dichloroethane, xylenes, 2-dichloroethane can be degraded by nano photocatalysts [92]. Among many semiconductors, titanium dioxide is a promising photocatalyst [94] because of its facile synthesis, high photoactivity, semi conductivity, stability and optimum band gap (3.6 eV).

A number of nanomaterials have been used for the photocatalytic degradation of contaminants (Fig. 3). Dyes like rhodamine B and methylene blue can be degraded by photocatalytic TiO_2 nanoparticles. Two per cent Cu doped TiO_2 nanocomposite is effective in catalysing the *Escherichia coli infection* [95]. For the reduction of heavy metal ions (HMIs), hollow structured nanomaterials could be the promising photocatalyst. Similarly, photocatalytic degradation of Cr(VI) into Cr(III) can be

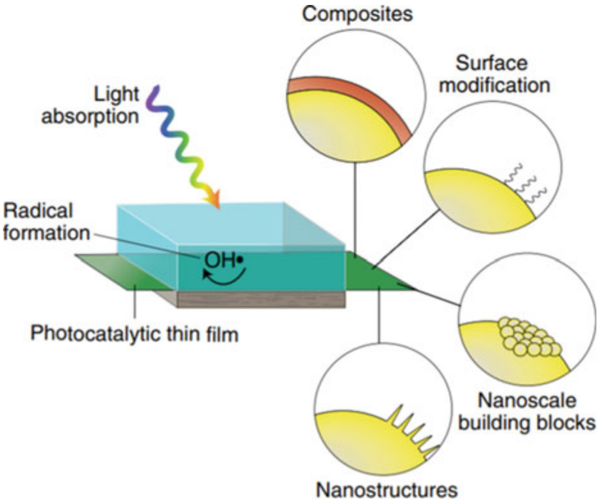

Fig. 3 Possible nanomaterial components for the synthesis of an efficient photocatalyst (adapted from Ref. [6])

achieved using TiO_2 hollow spheres [96]. Oxides and hydroxides were formed in solution by TiO_2 hollow spheres during photocatalytic reduction [97]. Kim et al. doped TiO_2 with another photocatalyst, developing a TiO_2/SiO_2 hollow sphere catalyst using a poly (styrene-methyl acrylic acid) matrix. This catalyst provided a photodegradation rate for methylene blue that was 2.5 times greater than that of pure TiO_2 hollow spheres [98].

4.1.2 Nano-Silver (Ag)

From over 100 years, silver has medical applications. Historically recognized and applied antimicrobial properties of silver and its components have been used in disinfection of medical devices, home appliances and water treatment [99–101]. Nano-silver (Ag nanoparticles) is capable of destroying infectious microbes making it the strongest antimicrobial agent. Quang et al. investigated the antibacterial water disinfection potential of silver nanoparticles supported silica beads (Ag-NPBs) [102]. Silver being less toxic and broad-spectrum antimicrobial agent has been used in the modification of surface membranes. Various researches revealed that nano-silver and nanozeolite surfaces have long-lasting antimicrobial activity at the membrane surface (based on polyvinyl alcohol and polydopamine). Nano-silver can be controlled and released rapidly, stably and efficiently because of the synergetic effect of two components (polyvinyl alcohol and polydopamine) [103]. Zarpelon et al. clarified that silver or polyelectrolyte nanomaterials with self-assembled thin films can remove 93% of total coliform, especially *E. coli*, within 6 h for reuse and 90% for first use of untreated industrial water. This process is influenced by pH, temperature and coliform concentration [104].

4.2 Media Filtration

4.2.1 Adsorbents

Nanomaterials have come up as excellent adsorbents due to their smaller size and high surface area [105] which is responsible for increased adsorption capacity and high chemical activity [105, 106]. Under equilibrium conditions, Langmuir adsorption coefficient K_d determines the process of adsorption and recitation partitioning of heavy metals or organic pollutants [107, 108]. Moreover, for persistent inorganic pollutants redox reaction is favoured to start the ionic structure transformation [109]. Toxicity of pollutants alters with redox conditions [110, 111]. The nanoparticles used for the adsorption of heavy metals are ferric oxides, manganese oxide, graphene, titanium oxide, magnesium oxide, zinc oxide and carbon nanotubes [109]. Nano-adsorbents have innate surface and external functionalization properties. The extrinsic surface structure, intrinsic composite and apparent size of nanoadsorbents relate to their material, physical and chemical properties [112]. In the aqueous environment, the additional factors (other than agitation time, dosage, temperature and ion concentration) affecting the adsorption process are high surface area, adsorption activity, chemical activity, location of atoms on surface, lack of internal diffusion resistance and high surface binding energy [113]. Nanozero-valent ions have been used as adsorbents for contaminant removal and separation by catalysing the chemical and photochemical oxidation process for expulsion of toxic substances. They can be used as beads, powder or porous granules [39]. The adsorption mechanism primarily depends on the chemical and physico-chemical properties of water and the adsorbent [114].

4.3 Membrane Systems

Wastewater treatment has emerged with the introduction of membrane separation technology. Membrane is a selective material with porous structure and allows only water to pass through and inhibits the bacteria, metal salts, etc. [115]. Membranes can be classified as synthetic, nuclear and biological. The nanomaterial-based membranes are the most effective membrane wastewater filtration technique [116–118]. Nanomembranes possess fouling resistance, new and advance functions, high permeability and catalytic reactivity [119]. Low space requirement, quality of water treatment and effective disinfection make this nanomaterial-based membrane technology highly adaptable [120]. Nanomembranes comprise one-dimensional nanomaterials including nanofibers, nanotubes and nanoribbons [121]. Carbonaceous nanofibers (CNFs) assembled with beta cyclodextrin have shown high potential of phenolphthalein and fuchsin acid removal [122]. Zeolite based nanomembranes can be used for the osmotic separation in aqueous solution. Linde type A, sodalite and MFI- type are some of the common zeolite materials used in membranes while the mostly used zeolite in nanomembranes is Zeolite ZSM-5 (MFI) [119]. In addition, the capturing potential of nanoparticles and other small molecules can be positively enhanced by the interconnection of nanoparticles and negatively charged bodies on macroscopic disk-like titanate-nanoribbon membrane [121, 123].

4.3.1 High Performance Membranes

Recent advancement in membrane technology has taken it up to the next level of high-performance membranes. The efficiency of membranes can be enhanced by impregnation of nanomaterials, for example, doping of silver nanoparticles (AgNPs) into membranes improves antibacterial properties of the membrane. Silver nanoparticles were coated on the surface on the membrane which inhibits dissolution of AgNPs and Ag^+. Therefore, enhanced water flux and antibacterial performance can be achieved by the nanocomposite [124]. Nano-Ag, CNTs, nano-TiO_2 and nano-zeolites have been used in thin film composites. Amount, type and size of nanoparticles decide the selectivity and permeability of the membrane. Similarly, nano-zeolites have been used as dopants in TFN to enhance permeability. The addition of nano-zeolites leads to more permeable, negatively charged and thicker polyamide active layer [66]. Modified nanotube membranes have also been synthesized. Carboxyl multi-walled carbon nanotubes/calcium alginate (CMWCNT/CA) composite was synthesized by Jie et al. [125] using a pore forming agent polyethylene glycol with hydrogel nanofiltration membrane. Electrospun nanofiber membranes (ENMs) have been recognized as efficient membrane to treat wastewater [38, 126, 127]. The ENM is a leapfrogging technique which is less expensive, low energy consumption and facile process compared to conventional technologies. This technique is advantageous due to high surface to volume ratio and porosity [128, 129]. Electrospinning is another technique being capable of producing thinner fibres as the diameter of the fibre affects the porosity. Nanofiber membranes have been widely applied in wastewater treatment containing heavy metals, particulate microbes and salts (desalination). In a study by Xu et al. [130] electrospun polysulfone fibre membrane was used to remove the particles from biotreated wastewater.

4.3.2 Antifouling Membranes

Integrated water treatment has an important component, i.e. membrane technology. Hydrophobic membrane when interacts with organic compounds in water results in membrane fouling. Deposition of particles and molecules in the pore or surface causes fouling [131–133]. As a result of fouling, the quality of treated water degrades. Moreover, reduction in the reliability of membrane filtration can be observed [134]. Nanofiltration membranes show lower flux at low pressures [135]. Membrane fouling caused by reduction in flux needs to be cleaned either chemically or mechanically and sometimes should be replaced [133]. Therefore, to minimize the fouling problem, certain techniques such as membrane modification, feed solution properties and optical conditions have been developed [136]. Modification of membrane can be achieved by hydrophilic polymer coating with polyvinyl alcohol and chitosan; however, it has certain constraints of high cost, complexity and pollutant production [125]. Mixed matrix membranes (MMMs) with carbon nanotubes (CNTs) have been synthesized which act as membrane and found to have potential to accelerate flux [137, 138].

4.4 Monitoring and Sensing

Water quality monitoring system faces certain challenges in efficient detection of pathogens and high complexity of the water/wastewater matrices. Current system lacks innovative sensors with high sensitivity and selectivity and reckless response. Therefore, nanosensor can be the alternative solution for water pollutant detection and sensing.

4.4.1 Sensors

A basic nanosensor consists of a nanomaterial and a recognition element for signal transduction. Recognition element interacts with analyte to be detected and produces a detectable signal. When an analyte interacts with nanosensor, the sensitivity arises due to the magnetic, optical and electrical properties of the nanomaterial as well as by transduction method used to induce a signal. Effective integration of nanomaterials and recognition agents (e.g. antibodies, aptamers, carbohydrates and antimicrobial peptides) could yield fast, sensitive and selective sensors for microbial detection [139]. Improved sensor sensitivity speed and multiplex target detection can be achieved by nanomaterial-based sensors as they have unique electrochemical, optical and magnetic properties. The nanosensor research has flourished in CNTs, quantum dots (QDs), noble metal nanoparticles and dye doped NPs. Multiplex target detection can be achieved by single excitation source such as quantum dots that have wide adsorption bands, narrow and stable fluorescent emission spectra [140]. Nanotechnology-enabled sensors are capable of replacing existing water-quality sensors. Till date, a number of nanosensors have been developed for the detection of toxins, pH and pathogens in water [141–144].

4.4.2 High Efficiency Sample Preconcentration

Nanomaterials can be used for the detection of trace organic and inorganic contaminants. CNTs show high adsorption capacity, increased recovery rate and fast kinetics, thus contributes to environmental analysis of trace elements and contaminants. The preconcentration factors of metal ions were found to be between 20 and 300 with fast adsorption kinetics [145]. Preconcentration of organic compounds in real water samples by CNTs has also been studied widely [146]. Changes in conductance affect the adsorption of charged species on CNTs that provides the basis for correlation between analyte concentration and current fluctuation [147]. However, certain other nanomaterials mainly, nano-Au and Quantum dots have also been explored for sample preconcentration. In a colorimetric assay, nano-Au has been shown detection of pesticides at parts per billion level (ppb) [148]; modified nano-Au was shown to detect Hg^{2+} and CH_3Hg^+ rapidly with high sensitivity and selectivity [149]. QD modified TiO_2 nanotubes lowered the detection limits of PAHs to the level of pica-mole per litre based on fluorescence resonance energy transfer [150]. Nano-sensor based on CoTe QDs immobilized on a glassy carbon electrode surface was reported to detect Bisphenol A in water at low concentrations of w10 nM within 5 s [151]. Hence advanced nanomaterials provide a wide range of applications such as elimination of heavy metals and related pollutants, eradication and dormancy of pathogens and conversion of highly toxic substances to least toxic [152]. The major applications of the nanomaterials in wastewater treatment are summarized in Table 3.

Table 3 Potential applications of nanotechnology in water and wastewater treatment (adapted from Qu et al. [38])

Applications	Representative nanomaterials	Desirable nanomaterial properties	Enabled technologies
Adsorption	Carbon nanotubes	High specific surface area, highly assessable adsorption sites, diverse contaminant-CNT interactions, tunable surface chemistry, easy reuse	Contaminant preconcentration/detection, adsorption of recalcitrant contaminants
	Nanoscale metal oxide	High specific surface area, short intraparticle diffusion distance, more adsorption sites, compressible without significant surface area reduction, easy reuse, some are superparamagnetic	Adsorptive media filters, slurry reactors
Membranes and membrane processes	Nano-zeolites	Molecular sieve, hydrophilicity	High permeability thin film nanocomposite membranes
	Nano-Ag	Strong and wide-spectrum antimicrobial activity, low toxicity to humans	Anti-biofouling membranes
	Carbon nanotubes	Antimicrobial activity (unaligned carbon nanotubes) Small diameter, atomic smoothness of inner surface, tunable opening chemistry, high mechanical and chemical stability	Anti-biofouling membranes Aligned carbon nanotube membranes
	Nano-TiO_2	Photocatalytic activity, hydrophilicity, high chemical stability	Reactive membranes, high performance thin film nanocomposite membranes
	Nano-magnetite	Tunable surface chemistry, superparamagnetic	Forward osmosis
Photocatalysis	Nano-TiO_2	Photocatalytic activity in UV and possibly visible light range, low human toxicity, high stability, low cost	Photocatalytic reactors, solar disinfection systems
Disinfection and microbial control	Nano-Ag	Strong and wide-spectrum antimicrobial activity, low toxicity to humans, ease of use	POU water disinfection, anti-biofouling surface
Sensing and monitoring	Quantum dots	Broad absorption spectrum, narrow, bright and stable emission which scales with the particle size and chemical component	Optical detection
	Noble metal nanoparticles	Enhanced localized surface plasmon resonances, high conductivity	Optical and electrochemical detection
	Magnetic nanoparticles	Tunable surface chemistry, superparamagnetism	Sample preconcentration and purification

5 Conclusion

Nanotechnology has enabled the wastewater treatment technologies for improving the centralized water system. It has gained momentum worldwide as nanomaterials possess unique properties to revolutionize water treatment technologies. To meet the global challenge of clean and affordable water, novel water management approaches are required. Hence, nanotechnology plays a critical role in the transformation of water supply systems towards a treatment paradigm. The future prospect of nanotechnology has significant effect on reshaping the water supply systems to make them more sustainable and smarter. Engineered nanomaterials of varied shape, size and composition have been studied for pathogen inactivation, contaminants expulsion and separation with membrane at laboratory scale.

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SnO_2-Mixed Oxide Electrodes for Water Treatment: Role of the Low-Cost Active Anode

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Abstract Recently, electrochemical oxidation water treatment is a promising method to solve environmental pollution issues. During the electrochemical oxidation process, electrode material is a critical factor affecting the treatment efficiency. Sb-doped SnO_2 electrodes are reported as superiors for the decomposition of organic matters from water through the oxidation process. But the weak electrochemical stability is also a drawback of SnO_2 electrodes, which limits their application. This article tries to review SnO_2-based electrodes, which focuses on clarifying their stability and the application in water treatment as well as indicating future research prospects with the aim to highlight the attractive features of this electrode. Specifically, the properties and electrochemical oxidation mechanisms of SnO_2-based electrodes for different pollutants are presented. Furthermore, typical methods for preparation of SnO_2 electrodes along with respective nanostructures synthesized processes are also shown. Moreover, several studies on the application of SnO_2-based electrodes in the treatment of different contaminated-water sources such as textiles, landfills, and phenol wastewaters are reviewed. In addition, recent research trends on development of SnO_2-based electrodes and their recyclability are reported. As a result, this study indicates that the stability and electrochemical performance of SnO_2-based electrodes can be increased by many approaches including doping metal oxide, new fabrication routes, and combining TiO_2 nanotubes with SnO_2. The study also indicates some operational parameters, which need to be considered thoroughly for the practical applicability of SnO_2 electrodes in wastewater treatment.

Keywords Electrochemical oxidation, Nanostructures, Organic matters removal, SnO_2-based anodes, Stability

1 Introduction

Due to the increasingly stringent effluent standards and regulations to approach the “zero-effluent” concept for the goals of sustainable development, more advanced and efficient wastewater treatment technologies need to be developed. On the other hand, depending on the different industrial processes, wastewater is generally contaminated by many organic and inorganic substances, which cause a highly complex wastewater characteristics and lead to a diverse treatment methods. Specifically, traditional biological technology is the most cost-effective and widely used for the organic-rich wastewater treatment. However, toxic and bio-refractory compounds existing originally in the wastewater may inhibit and affect the treatment efficiency, which bases mostly on microbial activities. Therefore, advanced methods such as physicochemical technologies (flocculation, coagulation), chemical oxidation using ozone, chlorine, hydrogen peroxide, and advanced oxidation processes (AOP) using photocatalyst, electron beam, Fenton's are normally employed for treatment of industrial effluents [1, 2]. Nevertheless, many disadvantages are also found with these above methods. For instance, coagulation and flotation produce a huge quantity of sludge while chemical oxidations show low capacity rates and require the use of dangerous reactants, and also high investment costs for chemical and energy [3]. In this study, electrochemical oxidation is introduced as a promising approach for the treatment of organic matters since the reagent used for the electrochemical process is the electron, which is versatile, efficient, cost-effective, and clean [4–7]. Moreover, it is reported that electrochemical processes were effectively used for disinfection and purification of wastewater contaminated with organic matters [1, 2, 4, 8].

Generally, electrode material is the key factor that needs to be considered to develop electrochemical oxidation technique. An efficient electrode used for pollutant removal must be highly stable under anodic polarization conditions and low cost [9]. For the electrochemical oxidation of organic compounds, the electrodes possessing high oxygen evolution over-potential are favored. A variety of electrodes have been investigated by several researchers, including graphite [10, 11], glassy carbon [12], platinum [13], and boron-doped diamond (BDD) [14–17]. Metal-oxide-based electrodes include PbO_2 [18–22], IrO_2 [23, 24], RuO_2 [25], and SnO_2 [26–28]. Among these metal oxide electrodes, Sb-doped SnO_2 electrodes are reported as an ideal material for oxidizing organic matters [27, 29]. However, a major drawback of SnO_2 electrodes is their insufficient electrochemical stability [1]. Sn ion can be dissolved in the solution, which thus limits their application. Therefore, this study is conducted with the aim to highlight the advantages of SnO_2-based electrodes used for the treatment of organic matter-contaminated water. For this, a summary of SnO_2 properties and mechanisms of electrochemical oxidation regarding specific pollutant is presented. Typical methods of preparing SnO_2 electrodes and respective nanostructures synthesis process are also summarized. The applicability of SnO_2-based electrodes to water treatment based on specific cases is clarified. This article also shows recent development and indicates future research with SnO_2-based electrodes, which may help to encourage further studies on electrochemical oxidation for water treatment.

2 Mechanisms for Electrochemically Oxidizing Pollutants

2.1 Indirect Electro-Oxidation Processes

Recently, electrochemical oxidation has been investigated as a new approach for the treatment of different wastewater sources, especially wastewater containing harmful organic pollutants, which can be completely oxidized to CO_2 and water. This technology can be either direct and/or indirect oxidation of organic matter existing in wastewater at the electrode surface. The electrochemical oxidation of industrial wastewater attracts more interest due to many advantages, such as simple equipment, high capacity for medium and small scale deployment, low initial investment, easy for operation, low chemicals requirement, environmental friendly, and high selectivity [1]. Organic matters can be electrochemically oxidized through different mechanisms. One of the most popular methods is the utilization of the chlorine and hypochlorite produced at the anode. At high chlorine concentration (i.e., typically >3 g/L), most of the inorganic and organic compounds can be effectively degraded [30–37]. Since chlorinated organic compounds, intermediates, or final products are possibly generated during the Cl-based oxidation, it is not much feasible to employ this technique for practical application. If the raw wastewater contains a low chloride concentration, the addition of a large salt quantity is needed to improve the treatment efficiency [32, 38–40].

The electrically produced hydrogen peroxide is also reported as a reactant for oxidizing organic pollutants [41–46]. This mechanism is based on the electro-Fenton reaction with an addition of Fe^{2+} salts or the in-situ formation from a dissolving iron anode [43]. Another electrochemically generated product which can be used as a reactant for wastewater treatment is ozone [47, 48]. Another type of electro-oxidation, known as mediated electro-oxidation, was investigated to remove mixed and hazardous wastes [49]. Metal ions including Ag^{2+}, Co^{3+}, Fe^{3+}, Ce^{4+}, and Ni^{2+}, usually called as mediators, are anodically oxidized to be a reactive, high valence state [49–54]. As a result, organic compounds can be degraded by these reactive ions. In addition, hydroxyl free radicals, which may be generated during the process, can also contribute to the removal of the organic matters. However, a highly acidic media is needed for the operation and the addition of the above metal ions results in the secondary waste, which may limit the application of this technique [1].

2.2 Direct Anodic Oxidation

Direct oxidation can be done by producing physically or chemically adsorbed "active oxygen" (i.e., adsorbed hydroxyl radicals, $^{\bullet}OH$ or oxygen in the oxide lattice, MO_{x+1}, respectively) [55]. During this process, organic compounds can be completely degraded by the $\bullet OH$, while selective oxidation products can be generated from the O in MO_{x+1}. Generally, pollutants are oxidized more effectively by $\bullet OH$ than by O in MO_{x+1} [1].

Anodic oxidation is more attractive than other electro-oxidation processes as it does not require a huge amount of chemicals or O_2 to cathodes, which helps to reduce the generation of secondary pollutants and thus fewer accessories are needed [1]. Besides, the anode material is an essential factor, which affects the performance of anodic oxidation process. Several studies examined a variety of anode materials, such as glassy carbon [12], RuO_2 [25], Pt–Ir [56, 57], fiber carbon [35], MnO_2 [58, 59], Pt–carbon black [60, 61], porous carbon felt [62], stainless steel [30], and reticulated vitreous carbon [63, 64]. However, these above materials do not satisfy two important features of anode electrodes, including the activity and the stability. Therefore, further studies have turned to investigate other materials, such as graphite [10, 11], platinum [13, 65], boron-doped diamond (BDD) [14–17], and various metal oxide electrodes including PbO_2 [18–22], IrO_2 [23, 24], and SnO_2 [26–28].

2.3 Typical Designs of Electrochemical Systems

There are a large variety of reactor configurations found in electrochemical oxidation researches, from basic systems like tank cells, filter-press cells, rotating cells, to complex types such as fluidized bed, packed bed cell, and porous carbon packing cells. The tank cell as shown in Fig. 1a is one of the simplest and the most common designs for electrochemical reactor. Determined by a process load, the extent of the tank cells can be easily increased or reduced. The quantity of electrodes in a stack can vary in a range of 10–100 units [1]. Another popular electrochemical oxidation reactor design is the filter-press cell [68]. This design is normally comprised of several consecutive anode and cathode compartments, which are separated from each other by membrane layers.

The design and utilization of the rotating cathode cell (Fig. 1b) resulted from a need to increase mass transfer from the bulk to the electrode surface [69]. This reactor design was demonstrated to induce a decrease of 48.4 ppm in copper

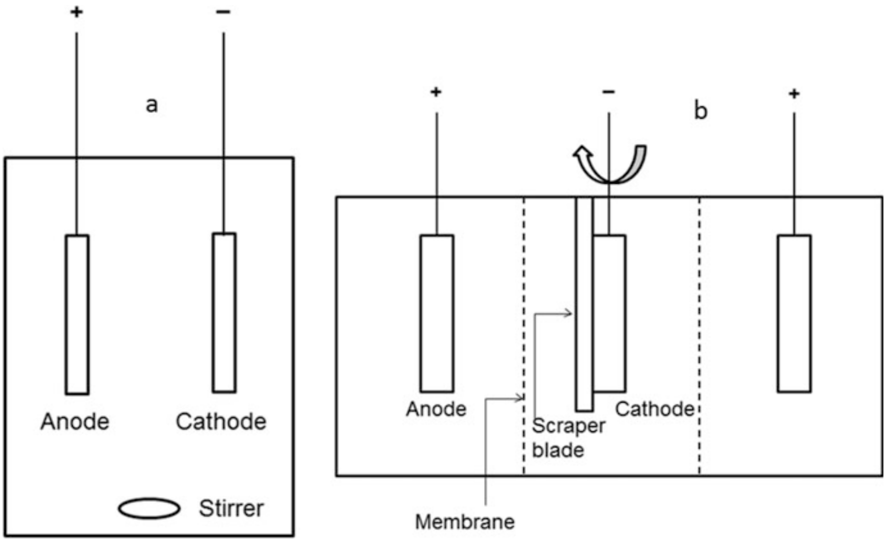


Fig. 1 A simplified model of stirred tank cell (adapted from [66]) (**a**), rotating cylinder electrode (adapted from [1]) (**b**) in one module. Thanks to this module system, the reactor is designed, operated, and maintained fairly simply [67]

concentration when the system in a cascade version was employed [70]. Fluidized bed electrode was designed to improve the specific surface area and hence enhance the space-time yield [71]. Conductive particles were used as the cathode and arranged to contact with a porous feeder electrode. A disadvantage of the fluidized bed type is the sometimes non-contacting problem between the feeder electrode and cathode particles.

In order to control the problem of the fluidized bed electrode, the packed bed cell was produced [72]. It is shown that a packed bed of approximately 1 mm pellets of appropriate materials can be used as the anode [73, 74]. Moreover, the developed packed bed reactor, RenoCell, contains three-dimensional porous carbon cathode, which has a plating area 500 times much more than conventional two-dimensional cells [75].

A further developed electrochemical system has been a bio-electro reactor in which the surface of electrodes has a thin layer of biofilm. It was demonstrated that nitrification and denitrification process could occur simultaneously when there is the presence of respective microorganisms on the anode [76].

3 Methods for Fabrication of SnO_2 Electrodes

Generally, SnO_2 films can be fabricated by different common methods, such as chemical vapor deposition [77–79], thermal decomposition [80], sol-gel dip-coating [81], spray pyrolysis [82], and electrodeposition [83–87]. On the other hand, electrodes with metal oxide nanostructures show excellent chemical and physical properties due to their small size but large surface area. These nanostructure electrode types are different from those composing of bulk materials. In addition, the nanostructure material can enhance the performance and stability of the electrode [88, 89]. Therefore, this section focuses on the electrode fabrication methods using nanostructure materials, which are formed by respective preparation techniques. An overview of SnO_2-based electrodes is also provided. Table 1 shows different methods for fabrication of SnO_2 electrodes and their characteristics.

3.1 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a synthetic process in which the reaction of chemical constituents occurs in the vapor phase to produce a solid deposit [2]. One of the methods of preparing SnO_2 films using CVD was introduced by Aboaf et al. [77] based on the reaction of $SnCl_4$ with water vapor. Briefly, the vapor deposition of SnO_2 films was performed on oxidized Si substrates in a resistance-heated tube furnace. N_2 gas was utilized to carry the high-purity $SnCl_4$ vapor to the furnace where an ambient of either N_2, H_2, or O_2 was preserved. In addition, water-vapor-saturated nitrogen was injected into the furnace approximately 50 mm away from the

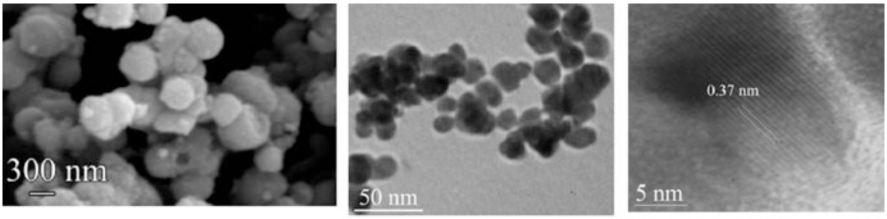
Table 1 Methods for fabrication of SnO_2 electrodes [88, 89]

Method	Principle	Characteristic
Chemical vapor deposition (CVD)	The reaction of chemical constituents occurs in the vapor phase to produce a solid deposit	– Uniform surface – Expensive
Thermal decomposition	Thermal deposition of Sn-precursor at high temperature	– Multilayer coating is necessary – Inexpensive
Sol-gel dip-coating	Thermal deposition of colloid solution at high temperature	– Multilayer coating is necessary – Inexpensive
Spray pyrolysis	The precursor solution is deposited at the electrode surface under carrier gas	– Uniform surface – Expensive
Electrodeposition	Deposition of SnO_2 at the anodic or cathodic electrodes	– Nonuniform coating – Inexpensive

homogeneous hot zone in order to minimize the reaction of $SnCl_4$ with H_2O before coming to the hot zone [77]. CVD method was also utilized by Sundaram and Bhagavat [78] in order to fabricate SnO_2 films. They used anhydrous tin (II) chloride melt by a heater to produce $SnCl_2$ vapor. SnO_2 films deposited on glass substrates were then formed when $SnCl_2$ vapor was driven by an oxygen flow through the furnace. The deposition occurred at different temperatures varying from 350 to 500°C. In conclusion, it is indicated that the films fabricated at a high temperature showed a lower resistivity as compared with the films produced at lower temperatures, with the result that the highest conductivity of 700 Ω^{-1} cm^{-1} was accomplished at 500°C [79]. Applied CVD to fabricate the SnO_2 electronic conduction thin film. Briefly, the vaporization of liquid $SnCl_4$ was carried out with nitrogen gas flow, followed by mixing with oxygen gas flow on the way to a reaction chamber equipped with a quartz plate. SnO_2 was then produced by the reaction between $SnCl_4$ and O_2. The deposition of SnO_2 films happened on the quartz substrates at temperatures between 300 and 550°C with the formation of 5,000 Å thickness. It was demonstrated that the conductivity and carrier concentration of the films were considerably decided by the temperature. In this study, the highest conductivity of 935 Ω^{-1} cm^{-1} was achieved at 450°C. Concerning nanostructures, using CVD at the temperature of 900°C, Ma et al. [90] successfully fabricated SnO_2 nanowires with the diameter of approximately 40–90 nm and the achievable length of above 20 nm. In addition, combustion chemical vapor deposition (CCVD) method, a new CVD technique, was used to synthesize SnO_2 nanotubes with square or rectangular cross-sections on quartz substrates in an opened atmosphere with a temperature range of 850–1150°C [91].

3.2 *Thermal Decomposition*

SnO_2-based mixed oxide electrodes can be prepared based on the following thermal decomposition procedure [80]. Four types of SnO_2-based anodes include



.(a) SEM (b) TEM (c) HRTEM

Fig. 2 SEM images of SnO_2 nanoparticles synthesized by thermal decomposition. Adapted from [92]. (**a**) SEM, (**b**) TEM, (**c**) HRTEM

Ti/SnO_2–Sb_2O_5, Ti/SnO_2–Sb_2O_5–PtO_x, Ti/SnO_2–Sb_2O_5–RuO_2, and Ti/SnO_2–Sb_2O_5–IrO_2 electrodes. A titanium substrate was firstly coated by solutions produced from SnO_2–Sb_2O_5 precursor dissolved in isopropanol, $PtCl_6.6H_2O$ in isopropanol, $RuCl_3.3H_2O$ in isopropanol, $IrCl_3.3H_2O$ in ethanol. Besides, the final coating solutions should have 90 wt.% SnO_2–Sb_2O_5 and 10 wt.% additive metal oxide. After that, a brush technique was utilized to paint the coating solutions onto the Ti substrates. For the next step, an evaporation of the excess solvent was performed with hot air at the temperature of around 80°C. The calcinations were then done at 450°C in 10 min. This process was repeated until a desired oxide coating load was accomplished. The fabrication process was finally finished by annealing at 450°C in 1 h. By using new precursor [$Sn(HAP)_2$] in oleylamine ($C_{18}H_{37}N$) and triphenylphosphine (TPP), [92] synthesized successfully SnO_2 nanoparticles based on the thermal decomposition approach. The fabricated product exhibits tetragonal SnO_2 with no impurities. SnO_2 nanoparticles were demonstrated to have the average diameter of roughly 14–22 nm (Fig. 2). Also, rutile SnO_2 nanowires were successfully synthesized by using a thermal decomposition of precursor $Sn(CO_3)_2$ in the presence of NaCl [93]. The SnO_2 nanowires possess the diameters of 8–25 nm and the lengths of up to 10 μm.

3.3 Sol-Gel Dip-Coating

According to Chatelon et al. [81, 94], the preparation of sol-gel dip-coating technique was done by dissolving $SnCI_2.2H_2O$ in absolute ethanol and $SbCl_3$ in absolute ethanol, followed by stirring and heating separately both mixtures in a closed vessel. After that, two powders were produced by performing the complete evaporation of the solvent. Depending on the doping level, the two powders were mixed together in ethanol. The stirring and heating to 50°C were then carried out for the doped solution in 2 h. Afterwards the dip-coating process was implemented. The substrate was put and taken out of the sol constantly. After completely removed from the solution, the substrate was dried during 6 h, and then drying at 100°C in the air was done for 15 min. In order to heal cracks and defects in the film, the coating procedure was performed twice. Finally, the fabrication process was finished by heating the substrate to 600°C.

SnO_2 nanostructures can be prepared by sol-gel method in which a chemical solution (i.e., sol) and colloidal nanoparticles are initially employed to produce an integrated network (i.e., gel). According to Zhang and Liu [95], different precursors like tin alkoxide and tin tetrachloride can serve as starting materials for the fabrication process. Nevertheless, the disadvantages of tin alkoxides are their high cost and their great sensitivity to moisture, heat, and light, causing the difficulty in process control and cost-ineffectiveness. On the contrary, sol-gel process using tin tetrachloride as precursors is not only cost-effective but also easy to control. In addition to tin tetrachloride, Zhang and Liu [95] used ethylene glycol as precursor to fabricate nanostructured tin oxide powders. Ethylene glycol is demonstrated to serve as a complexion agent to produce a polymeric network and as a spacer to adjust the distance between metal ions, making the aggregation of metal oxides avoided. It was reported that tin oxide began crystallizing at roughly 250°C, and the crystallization increased at higher temperatures. Finally, fine powders (i.e., the average size of particle is 12 nm) were produced by heating at 600°C for 2 h. In another study, Zhu et al. [96] used porous anodic alumina (PAA) membranes as the template to produce polycrystalline SnO_2 nanotubes which had a well-defined composition. Besides, the authors employed the hydrolysis of urea to change the pH value, resulting in the production of colloids. The wall of SnO_2 nanotubes was estimated to be 20-nm-thick.

In conclusion, the preparation of SnO_2 nanoparticles [95, 97] and nanotubes [96, 98] could be conducted successfully by using sol-gel process. However, there are some limitations on the morphologies of the nanostructures as it is hard to fabricate templates with various shapes and sizes.

3.4 Spray Pyrolysis

Correa-Lozano et al. [82] introduced spray pyrolysis process to fabricate the Ti/SnO_2-Sb_2O_5 electrode. Nitrogen gas was used as the carrier substance. The precursor solution included $SnCl_4$ (10%) prepared by $SnCl_4.5H_2O$ in ethanol/hydrochloric acid, $SbCl_3$, HCl (32%), and ethanol. The distance between the nozzle and the substrate was 17 cm and the experimental temperature was fixed between 400 and 700°C. The study reported that when IrO_2 was added into the layer placed between SnO_2-Sb_2O_5 and Ti substrate, the lifetime of the anode could be improved because the electrode became highly stable and an isomorphous structure with TiO_2 and SnO_2 could be formed [27].

Spray pyrolysis has been demonstrated to deposit nanostructured SnO_2 thin films on glass substrate utilizing the $SnCl_4.5H_2O$ precursor [83]. The product exhibits polycrystalline nature with the crystallite size of 29.92 nm and a pure phase formation. It was also indicated that the thin film was composed of pores with nanoparticles. Ong et al. [84] were also successful to synthesize the nanostructured

SnO_2 thin films on glass substrate by using spray pyrolysis process with $SnCl_4.5H_2O$ as a precursor. This study investigated the impact of precursor concentration, substrate temperature, and zinc dopant on the deposited product. Results showed that the grain size of the films could improve when there was an increase in the precursor concentration. Additionally, substrate temperature played an important role in establishing the film crystallinity as the film growth occurred at the temperature above 270°C. On the other hand, the grain size decreased when the dopant was added. It was indicated that the thickness of Zn-doped SnO_2 thin film (deposited at 350 °C and 0.5 M precursor concentration) is roughly 40 µm.

3.5 *Electrodeposition*

3.5.1 Anodic Method

In 1974, the synthesis of SnO_2 films was performed by the anodization of Sn sheets using an ethylene-glycol-based electrolyte in the voltage range of 6–50 V [85]. SnO_2 substrates crystallized at the temperature of under 200 °C with a polycrystalline structure having a thickness varying between 250 and 690 nm [85]. The fabrication of mesoporous SnO2 spheres with tunable particle size from tin foil electrochemically anodized in the electrolyte containing NaOH and NH4F in ethylene glycol was also investigated [86]. As a result, mesoporous SnO_2 spherical particles with a uniform size of 60 nm are formed from agglomeration of SnO_2 nanocrystals with grain size of 5–6 nm, which leads to a high internal surface area. In another study, a tin oxide film based on the electrochemical anodization of a tin film in a fluorine-doped tin oxide (FTO) electrode was fabricated [87]. The obtained nano-size porous tin oxide film possesses columnar-type pore channels with roughly 50 nm diameter and it is optically transparent [88, 89].

3.5.2 Cathodic Method

In 2002, nanostructured SnO_2 films performed on copper substrate were synthesized successfully by Chang et al. [99] by using the electrochemical deposition. Results showed that at 85°C, the films with only a low degree of crystallinity were fabricated. When heat-treatment at 400°C in vacuum condition for 4 h was applied, nanocrystals SnO_2 with tetragonal structure in a grain size of 4–7 nm were found. It is also indicated that a porous surface can be obtained at the current density of 5–15 mA/cm^2. The study was also investigated other conditions with nitric acid solution at 85°C to fabricate nano-crystalline two-layered SnO_2 coatings including an upper porous layer (about 400 nm thick with a surface area of 34.3 m^2/g) and an underlying dense layer (about 12 nm thick) (Fig. 3) [100]. The nano-crystalline particles size in the two above layers were 5 and 10 nm. In this study, the electrolyte needed pre-treatment in order to convert Sn^{2+} ions to Sn^{4+} ions. Other researchers

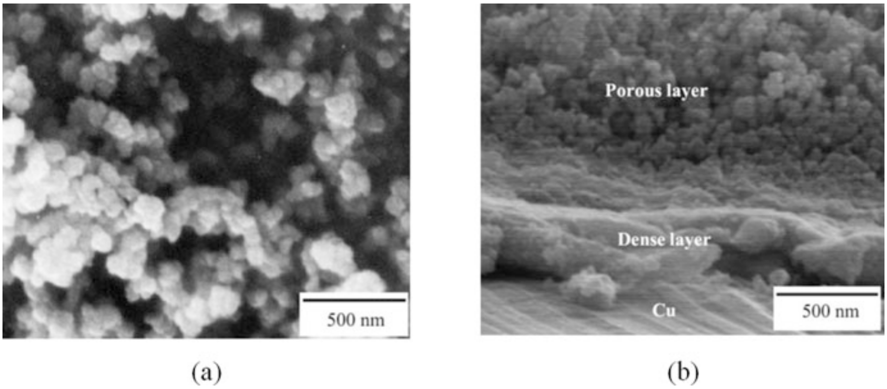


Fig. 3 SEM images of (**a**) the top view and (**b**) the cross-sectional view of the nano-crystalline two-layered SnO_2 coatings. Adapted from [100]

also developed various electrodeposition processes of SnO_2 thin films with several investigated parameters, such as HNO_3 concentration, age of the electrolyte, the electrodeposition temperature, and voltage [101, 102].

Regarding 1D nanostructures, Lai et al. [103] yielded successfully electrodeposited SnO_2 nanotubes by employing a hard template of nanoporous polycarbonate membrane. Before being recovered by centrifugation, the as-deposited nanotubes were dissolved in dichloromethane. Spray and Choi [104] investigated the application of sodium dodecyl sulfate (SDS) as a surfactant. It is shown that interfacial SDS assemblies have been useful for obtaining well-ordered arrangements of Sn^{4+} ions, which are the skeleton of the SnO_2 film producing mesoporous frameworks during the electrodeposition process. Similarly, Ishizaki et al. [105] also fabricated SnO_2 nanowires by using SDS surfactant. This study indicated that the micelles of SDS in the solution resulted in the aggregation of the SnO_2 particles and anisotropic growth of SnO_2 nanowires.

3.6 Stability of SnO_2-Based Electrodes

Although SnO_2–Sb_2O_5 anodes are highly efficient in oxidizing contaminants, their electrochemical stability is insufficient, like PbO_2 [1]. Lipp and Pletcher [106] conducted an experiment using SnO_2–Sb_2O_5 electrode with 0.1 M H_2SO_4 solution and a constant potential of 2.44 V versus NHE. Study found that the current decreased from the initial value of 0.2 A to approximately 0.1 A after a few hours and to 0.06 A after 700 h [106]. The stability of SnO_2–Sb_2O_5 anodes was also tested by using an accelerated life test [27]. Results showed that at a current density of 1,000 A/m^2 in the existence of 1 M H_2SO_4 solution, the lifetime of Ti/SnO_2-Sb_2O_5 lasted only 12 h. When the experimental conditions were adjusted to be 10,000 A/m^2

of current density and 3 M H_2SO_4 solution, the electrode had a lifetime of only a few seconds [107].

The deactivation of dimensionally stable anodes was explained by different reasons including the selective loss of the catalyst to the electrolyte, the resistive layer forming between the substrate and the coating, and the passive layer forming in the external layer of the coating [80]. In addition, the SnO_2–Sb_2O_5 electrodes were reported to be deactivated due to the nonconductive $Sn(OH)_2$ film forming in the external layer of the electrodes [29]. Several researchers suggested that the formation of the external passive layer should be prevented to improve the stability of SnO_2-based electrodes. This can be obtained by using additive metal oxides in the SnO_2–Sb_2O_5 coating, which may extend substantially the lifetime of SnO_2–Sb_2O_5 electrodes [5, 9, 108–111]. For instance, the supplement of IrOx to the raw SnO_2–Sb_2O_5 mixture helped to increase the lifetime of the electrode which lasted 1,600 h under 3 M H_2SO_4 solution and current density of 1 A/cm^2 [108]. Study also indicated that this electrode has a superstable nature, the good conductivity, and the improved bonding with the TiO_2 interlayer. The incorporation of different metal oxides with the Sb-doped SnO_2 coating to increase the electrode lifetime was also demonstrated by Adams et al. [80]. In this study, the thermal decomposition method was employed to fabricate four different types of SnO_2-based electrodes, including Ti/SnO_2–Sb_2O_5, Ti/SnO_2–Sb_2O_5–PtO_x, Ti/SnO_2–Sb_2O_5–RuO_2, and Ti/SnO_2–Sb_2O_5–IrO_2 electrodes. Among these electrodes, Ti/SnO_2–Sb_2O_5–IrO_2 showed to possess the greatest service life (i.e., 155 days) obtained at current density of 160 mA/cm^2 in 0.5 M NaOH solution. On the other hand, Correa-Lozano et al. [27] demonstrated that the presence of IrO_2 film between SnO_2-Sb_2O_5 layer and Ti substrate helped to extend the electrode lifetime. Besides, the impact of solvent on the electrode stability was investigated by Coteiro et al. [112]. The ternary oxide Ru–Ti–Sn electrode was fabricated and investigated by thermal decomposition technique. The precursor solutions were prepared by dissolving the hydrates $RuCl_3.nH_2O$, $TiCl_4$, and $SnCl_2.2H_2O$ with two different solvents including HCl/H_2O (1:1 v/v) and isopropanol. This study pointed out that when isopropanol was served as a solvent, the elimination of tin loss and higher stability could be accomplished.

4 Properties of SnO_2

The oxidation state of Tin (Sn) is either 2^+ in the stannous oxide form as SnO or 4^+ in stannic oxide as SnO_2 due to its dual valence, which facilitates the fluctuation of the surface element as oxygen [113]. SnO_2 possesses a tetragonal rutile structure with space group $D_{4h}{}^{14}$ [$P4_2$/mnm] [114] and one unit cell is composed of six atoms including two tin and four oxygen atoms [113]. The ionic radii for O^{2-} and Sn^{4+} are 1.40 and 0.71 Å, respectively [114, 115]. Also, the SnO_2 is known as Cassiterite mineral [113]. Furthermore, pure SnO_2 is an n-type broadband gap (3.6 eV) semiconductor, which is highly conductive and nearly complete insulator-like transparent. Moreover, the carrier density of un-doped SnO_2 is up to 10^{20} cm^{-3} which is comparable to that of semimetals (i.e., 10^{17} to 10^{20} cm^{-3}) [114, 116]. In addition, SnO2 is a chemically inert substance which also has mechanically strength and high-temperature resistance [117].

Pure SnO2 is very high electrical resistant, which makes it be unsuitable for electrode fabrication [4]. However, the conductivity of SnO_2 considerably improved when mixing it with Ar, B, Bi, F, P, and Sb [29, 77, 114, 118–121]. Among the above doping agents, antimony (Sb) is the most widely used in electrochemical applications [82, 106, 122, 123]. The doped SnO_2 films used as transparent electrodes can be found in different applications, such as high-efficiency solar cells, gas detectors, far IR detectors, and transparent heating elements [124]. The onset potential of O_2 evolution on SnO_2 doped with Sb in 0.5 M H_2SO_4 solution is approximately 1.9 V versus NHE, which is similar to that on PbO_2 [1, 82]. Due to the high oxygen evolution over-potential, which results in a poor catalyst for oxygen evolution reaction, the Sb-doped SnO_2 is considered as a "non-active" anode. This feature, however, promotes the conversion of organic matters to CO_2 [3]. Hence, Sb-doped SnO_2 electrodes are effective in wastewater treatment [3], especially for oxidization of organic compounds [27–29]. Another advantage of SnO_2 is the low-cost feature, as compared to other precious materials (e.g., Pt and boron-doped diamond) [80].

5 Application to Water Treatment

The application of different SnO_2-based anodes in the electrochemical oxidation for removal of diverse contaminants from water is summarized in Table 2**.** A comparison of removal efficiency under different experimental conditions is also presented.

Specifically, the study found that organic contaminants (i.e., phenol) could be oxidized at the anode fabricated by titanium coating with Sb-doped SnO_2 (Ti/SnO_2–Sb_2O_5) [29]. Result showed that the phenol removal efficiency was five times higher than that obtained in the study using Pt electrode [28]. On the other hand, Bonfatti et al. [128] investigated the ability of glucose for mineralization reaction by using the electrochemical incineration in which Pt, SnO_2–Pt composite, and PbO_2 electrodes were used with the addition of H_2SO_4 1 M serving as the supporting electrolyte. However, results showed that the SnO_2-based electrode was not efficient to electrochemically oxide organic compounds. In another study, it was reported that the current efficiency for Ti/SnO_2-Sb_2O_5 of 0.58 was effective to degrade 71% of phenol. In case of PbO_2, IrO_2, RuO_2, and Pt, the current efficiency were 0.18, 0.17, 0.14, and 0.13, respectively, at the same experimental conditions (i.e., the current density of 500 A/m^2, pH 12.5, initial concentration of 10 mM, reaction temperature of 70°C) [129]. Grimm et al. [94] investigated the oxidization of phenol in a cyclic voltammetry using Ebonex/PbO_2 and Ti/SnO_2 electrodes. As a result, the Ti/SnO_2 electrode fabricated by using a sol-gel dip-coating technique showed better performance. Moreover, the study also showed that 10% Sb used for doping the sol-gel solution could help to improve the conductivity of the SnO_2-films and

Table 2 Comparison of the performance of different SnO_2-based electrodes in electrochemical oxidation used for water treatment (see text for further explanation)

Electrode material	Pollutants investigated	Experimental conditions	Initial concentration	Removal efficiency (%)	References
Binary oxide anodes					
Ti/Sb_2O_5-SnO_2	Dye – acid orange 7 (orange II)	200 A/m^2; 6.25 Ah/L; 30°C; in 2 g/L Na_2SO_4	750 mg/L Orange II; 1,120 mg/L COD	27% COD; 98% color; 16% current efficiency	[66, 125, 126]
	Dye – reactive red 120 (reactive red HE-3B)	200 A/m^2; 6.25 Ah/L; 30°C; in 2 g/L Na_2SO_4	1,500 mg/L reactive red HE-3B; 920 mg/L COD	22% COD; 95% color; 11% current efficiency	[66, 125, 126]
	2-chlorophenol	160 A/m^2; electrolysis time 500 min; 1 cm^3/s flow rate; 25°C; in phosphoric solutions	400-600 mg/L 2-chlorophenol; 1,000 mg/L COD	70% COD; 50% faradaic yield	[127]
	Glucose	375-900 A/m^2; 1 M H_2SO_4; electrolysis time 24 h; 25°C	1 g/L glucose	30%	[128]
	Phenol	300 A/m^2; pH 12, in 0.25 M Na_2SO_4	1,000 mg/L	100%	[29]
	Phenol	500 A/m^2; pH 12.5; 70°C	10 mM	71%	[129]
	Cyanide	pH 12, in 1 mol/L K_2SO_4; 4 mmol/L KCl added; 16 mA/cm^2; 25°C	1 mmol/L KCN	Half-life for the degradation was 8.8 min^{-1}; apparent decay rate was 0.079 min^{-1}	[130]
Ternary oxide anodes					
Ti/$Ti_{0.5}Ru_{0.45}Sn_{0.05}O_2$	Landfill leachate	2 A; electrolysis time 8 h; 420 dm^3/h flow rate	780 mg/L COD; 266 mg/L ammonium	35% COD; 52% color; 65% ammonium	[131]
Ti/Sn-Pd-Ru oxide	Landfill leachate	15 A/dm^2; 7,500 mg/L chloride added; electrolysis time 4 h	4,100-5,000 mg/L COD; <1,000 mg/L BOD; 2,100-3,000 mg/L ammonium; 2,500 mg/L chloride	92% COD; 100% ammonium	[39]

Ti/RuO_2-SnO_2-Sb_2O_5	Dye – reactive Black-5	50 mA/cm^2; 2 g/L NaCl added; electrolysis time 1 h	100 mg/L	55% COD; 98% color; 37% TOC (at pH 2-3)	[132]
Ti/IrO_2-SnO_2-Sb_2O_5	Dye – Indigo	0.2 L/min flow rate; 7 mA/cm^2 current density; in 0.05 M NaCl	1 mM	100% indigo degraded; 80% current efficiency; 1.78 KWh/m^3 energy consumption	[133]
Ti/RuO_2–TiO_2–SnO_2	Petroleum hydrocarbons	89 mA/cm^2; 0.25 L/h; electrolysis time 2.3 h	25-30 mg/L of benzene, toluene, ethyl benzene, xylene; 5 mg/L phenol; 15,000 mg/L NaCl	98% organic contaminant degraded	[134]
Ti/SnO_2–Sb_2O_3–PtO	Aniline	15 mA/cm^2; Electrolysis time 1 h; pH 11.0, in 10 g/L Na_2SO_4	80 mg/L aniline; 225 mg/L COD	>88.9% of organic removal	[111]
Ti/SnO_2–Sb_2O_5–IrO_2	2-nitrophenol (2-NPh)	100 mA; electrolysis time 3 h; pH 2, in 0.5 M Na_2SO_4	0.05-0.275 mM	7.66×10^{-3}– 8.17×10^{-3} min^{-1} (rate constant)	[80]
	3-nitrophenol (3-NPh)	100 mA; electrolysis time 3 h; pH 2, in 0.5 M Na_2SO_4	0.05-0.175 mM	3.61×10^{-3}– 3.86×10^{-3} min^{-1} (rate constant)	
	4-nitrophenol (4-NPh)	100 mA; electrolysis time 3 h; pH 2, in 0.5 M Na_2SO_4	0.05-0.175 mM	6.25×10^{-3}– 6.53×10^{-3} min^{-1} (rate constant)	
Quaternary metal oxide anodes					
Ti/Ru–Ti–Sb–SnO_2 Pt/Ru–Ti–Sb–SnO_2	p-benzoquinone	Solid-state electrolyte used; 1.0 A (~0.2 A/cm^2); electrolysis time 64 h	100 mg/L	TOC and COD dropped to 1–2 mg/L	[135]

produce higher current density for the oxidation [94]. Another study conducted by Zanta et al. [136] found that 75% of p-chlorophenol could be degraded during the oxidation using SnO_2–Sb_2O_5-based anodes. Similarly, Adams et al. [80] investigated the removal of 2-nitrophenol (2-NPh), 3-nitrophenol (3-NPh), and 4-nitrophenol (4-NPh) by using SnO_2-based mixed oxide electrodes, including Ti/SnO_2– Sb_2O_5, Ti/SnO_2– Sb_2O_5–PtO_x, Ti/SnO_2– Sb_2O_5–RuO_2, and Ti/SnO_2–Sb_2O_5–IrO_2. The study indicated that Ti/SnO_2–Sb_2O_5–IrO_2 would be a promising electrode for practical application of electrochemical technology in wastewater treatment due to its long lifetime and high reactivity for nitrophenols removal. In addition, the study confirmed that the current of 100 mA was the most effective for the electrochemical oxidation in which the reaction rate constants decreased in the order of 2-NPh $>$ 4-NPh $>$ 3-NPh. Besides, Polcaro et al. [127] used PbO_2-based and SnO_2-based anodes to examine the electrochemical oxidation of 2-chlorophenol. The study found that Ti/SnO_2 anode was more effective as it showed a better performance for oxidation of toxic substances with the faradaic yield of approximately 50%. However, the study also reported that the presence of the biodegradable substance as oxalic acid in the effluent, although with a small quantity, could inhibit the electrolysis at SnO_2 electrode.

Houk et al. [135] incinerated electrochemically p-benzoquinone using a Ti or Pt anode coated with a quaternary metal oxide film of Ti, Ru, Sn, and Sb. The film was stable and the anode showed good reactivity for the oxidation of benzoquinone. During the electrochemical experiments, a solid-state electrolyte was used between the anode and the cathode instead of a dissolved supporting electrolyte. It was reported that the solid-state electrolyte was advantageous in producing pure final product, which can be disposed without a further treatment. However, this substitution caused excessively long electrolysis periods. After 64 h, a solution containing 100 mg/L benzoquinone witnessed a drop to 1–2 mg/L in TOC and COD and a decrease from 5.0 to 4.0. Intermediate products including phenolic and carboxylic acid were detected. The study also indicated that the small amount of carbon content (i.e., $<1\%$) in benzoquinone was converted into acetone and acetaldehyde.

That aniline solution was electrochemically oxidized in alkaline medium of pH 11.0 was investigated by Li et al. [111] in the application of Ti/SnO_2–Sb_2O_3–PtO anode and a Ti cathode. At Ti/SnO_2–Sb_2O_3–PtO anode, intermediates including dianiline, 4-anilino phenol, and azobenzol were detected. The decomposition of intermediates produced initially is done by hydroxyl radicals and the final products would be CO_2 and H_2O. The study results indicated that aniline was oxidized significantly faster at the Ti/SnO_2–Sb_2O_3–PtO anode than at the Ti/Pt, graphite, or Ti/SnO_2 anodes. Generally, it is concluded that aniline can be effectively degraded by electro-catalytic oxidation.

Fugivara et al. [130] investigated the electrochemical incineration of cyanide in alkaline media on Ti/SnO_2–SbO_x electrode at 25°C. The electro-oxidation of cyanide complies with a first-order rate law. In K_2SO_4 and KCN electrolyte, pH 12, and under 16 mA/cm^2 current density, a half-life value of 36 min and 69 min was estimated for Ti/SnO_2–SbO_x electrode and Ti/SnO_2–SbO_x–RuO_2 electrode, respectively. It is explained that the incorporation of RuO_2 into SnO_2-SbO_x mixture changed the water discharge potential value from 2.3 V (SnO_2–SbO_x) to 1.7 V (SnO_2–SbO_x–RuO_2), resulting in the fall in the cyanide electro-oxidation rate. Therefore, the current efficiency could drop when the Ti/SnO_2–SbO_x–RuO_2 electrode was used. Better cyanide electro-oxidation at Ti/SnO_2–SbO_x can be owing to greater levels of hydroxyl radicals formed on the surface of this electrode [55]. The study also evaluated the impact of an addition of chloride to the solution and pointed out that the rate law was not changed but the reaction rate increased. Specifically, the apparent decay rate values on Ti/SnO_2–SbO_x electrode were 0.019 min^{-1} (without chloride added) and 0.079 min^{-1} (with chloride added according to the ratio of [Cl-] to [CN-] standing at 4:1) at pH 12 and 16 mA/cm^2. Moreover, in the chloride-containing solution, the apparent decay rate value on Ti/SnO_2–SbO_x was the highest, compared to SnO_2–SbO_x–RuO_2 and platinum electrodes. On the other hand, there was a growth in the reaction rate when the applied current increased and a plateau was likely to be reached when the current density was above 20 mA/cm^2. Regarding pH, in the range of 10–13.5, the reaction rate experienced a decrease when there was a growth in pH. The study indicated that the lifetime of the Ti/SnO_2–SbO_x lasted 44 h at the current density of 16 mA/cm^2 and the SnO_2–SbO_x electrode was superior to platinum electrode due to its higher current efficiency in oxidizing cyanide and lower cost [130].

Regarding the treatment of landfill leachate, the difference in electrochemical reactivity between Ti/SnO_2–Sb_2O_5 and Ti/PbO_2 anodes was not significant [137]. This might be because high levels of chlorides were present in this type of waste. Chiang et al. [39] used the electrochemical oxidation method to investigate the treatment of landfill leachate which has a low BOD/COD ratio. In this study, four types of anode electrode including graphite, PbO_2/Ti, binary Ru–Ti oxide-coated titanium, and ternary Sn–Pd–Ru oxide-coated titanium (SPR), were investigated. The best performance was obtained with the SPR electrode. Specifically, the experimental results indicated that the SPR anode yielded 92% of the COD treatment in the landfill leachate and a complete removal of 2,600 mg/L of ammonium using a current density of 15 A/dm^2, electrolysis time of 4 h, and an addition of 7,500 mg/L chloride concentration. This study showed that contaminants in the landfill leachate could be effectively removed thanks to the electrochemical oxidation method. Moreover, it is claimed that the contaminants could be chiefly removed due to the indirect oxidation impact of chlorine/hypochlorite which are the products of the electrolysis. Besides, the indirect oxidation impact was increased by the rises in current density and chloride concentration. The study also proved that the electrochemical oxidation has been a potential method for treating low BOD/COD landfill leachate ([39]). The treatment of landfill leachate by using electrochemical oxidation method was also carried out by Panizza and Martinez-Huitle [131] in which three types of anode including Ti–Ru–Sn ternary oxide ($TiRuSnO_2$), PbO_2, and boron-doped diamond (BDD) were investigated. A stainless steel cathode installed in an undivided flow cell was used for the experiment. The operating conditions include 2 A constant current and 420 dm^3/h flow rate. The study indicated that the average values of COD and NH_4^+–N which were 780 mg/L and 266 mg/L, respectively, underwent a removal of 35% COD, 52% color, and 65% ammonium using Ti/RuSnO_2 anode at the electrolysis time of 8 h [131].

Chen et al. [107]; Chen et al. [125]; Chen et al. [66] studied the oxidation of 25 mL of solutions of different azo-dyes at a Ti/Sb_2O_5–SnO_2 anode and 2 g/L Na_2SO_4 solution was served as supporting electrolyte. They utilized a stirred undivided cell equipped with a stainless steel cathode. The study showed that 27% COD decay, 98% color removal, and 16% current efficiency were accomplished for 750 mg/L of Orange II at a current density of 200 A/m^2. At the same initial condition for oxidation of 1,500 mg/L of Reactive Red HE-3B, the results were 95% color removal, 22% COD treatment, and 11% current efficiency [66, 125, 126]. It is also indicated a low mineralization of 1 g/L of 15 reactive dyes which were decolorized in 80% with 27-46% COD removal, and 19-48% current efficiency with an oxidation at pH 4.70–6.73 and 100 A/m^2 [107, 126]. Compared to Ti/Sb_2O_5-SnO_2 anode, a non-active Ti/BDD anode was shown to have much better mineralization for dyestuffs [66, 107, 125]. The better properties of Si/BDD anode as compared to that of Ti/SnO_2 electrode in degrading Orange II were also demonstrated by Hastie et al. [138]. Panizza and Cerisola [139, 140] also employed the electrochemical method for oxidation of 2-naphthol which is largely utilized in manufacturing azo-dyes and bio-refractory. The electrode materials including lead dioxide, boron-doped diamond (BDD), and Ti–Ru–Sn ternary oxide anodes were employed. The study indicated that all the electrodes were active in oxidizing naphthol in the potential region of supporting electrolyte stability, yet the formation of polymeric adhesive films giving rise to electrode fouling also occurred in this region [140]. Regarding the Ti–Ru–Sn ternary oxide electrode, the initial activity was not completely restored by an anodic polarization due to its low-oxygen-overvoltage property and the main reaction occurring being oxygen evolution [140]. On the other hand, the authors evaluated the impact of current density, flow-rate, and chloride concentration on the electrochemical oxidation of 2-naphthol [139]. The study showed that at TiRuSnO_2 electrode naphthol is only mineralized when chloride ions performing as redox mediators are present [139]. Moreover, chloride concentration had a significant impact on COD removal, whereas the current density and mass-transfer coefficient with the optimum values of NaCl 7.5 g/dm^3 and pH 12 showed less effects [139]. In another study, the same authors investigated the electrochemical oxidation of methyl red using lead dioxide, boron-doped diamond (BDD), Ti–Ru–Sn ternary oxide, and platinum anodes in a one-compartment electrolytic flow cell equipped with parallel plate electrodes [141]. Experimental conditions were 0.5 M Na_2SO_4 as supporting electrolyte, 500 mA constant current, and 180 dm^3/h recirculation flow rate. The same results with the incomplete reactivation of the TiRuSnO_2 anode resulting from anodic polarization were indicated. The study also pointed out that at the TiRuSnO_2 anode methyl red was only partially oxidized owing to recalcitrant intermediates accumulated during the oxidation process as well as only a small amount of COD was removed and a current efficiency was low [141]. In general, the authors confirmed the superiority of BDD over other electrode materials due to its less pronounced deactivation, faster reactivation, faster mineralization, and higher current efficiency [139–141]. In another aspect, Ruparelia and Soni [132] showed acceptable results in the electrochemical oxidation of Reactive Black-5 (RB-5), another azo type of dye widely utilized in textile dying and paper industries, based on $Ti/RuO_2–SnO_2–Sb_2O_5$ electrode. In this research, all experiments were conducted under a 50 mA/cm^2 current density and a distance of 8 mm between electrodes in a laboratory scale batch reactor with an addition of NaCl (2 g/L) as the electrolyte in solution. The electrode fabricated with thermal decomposition method provided considerably good results. At pH 2-3, initial concentration of 100 mg/L RB-5 experienced a reduction of 55% COD, 98% color, and 37% TOC. At pH 7-8, the figures for the removal of COD, color, and TOC were 47%, 99%, and 35%, respectively. These findings revealed that the removal efficiency of color, COD, and TOC was decided in the first 10 min of treatment when the maximum degradation happened. Also, five-minute mineralization is suggested as the optimum [132]. Similar results were also reported by León et al. [133] in the study of electrochemical treatment of indigo textile dye. In this research, the electrochemical reactor was an undivided filter-press flow cell with a single electrolyte compartment in which dimensionally stable anode (DSA) prepared by Pechini method was a mesh-($Ti/IrO_2–SnO_2–Sb_2O_5$) and platinum coated titanium flat sheet was served as the cathode. The authors proved that complete degradation of indigo by bulk electrolysis is favored at the $Ti/IrO_2–SnO_2–Sb_2O_5$. The study results also confirmed that the formation of hydroxyl radical will gain an advantage at current densities varying from 5 to 7 mA/cm^2, whereas at 10 mA/cm^2 the oxygen evolution reaction is favored. Besides the predominant role of hydroxyl radical, other reactive species such as active chlorine formed during the electrochemical oxidation process can be responsible for removing simultaneously indigo and/or its by-products. The best results showed that at 0.2 L/min flow rate and 7 mA/cm^2 current density indigo (1 mM indigo in 0.05 M NaCl) was completely mineralized, with the current efficiency of 80% and the energy consumption of 1.78 kWh/m^3. Additionally, the electrochemical reactor equipped with mesh-($Ti/IrO_2–SnO_2–Sb_2O_5$) electrode used in this study proclaimed its usefulness for improving space-time yield which caused better interaction between oxidant species and pollutants, resulting in increases in the organic mineralization efficiency [133].

Electrochemical technology with a mesh $Ti/RuO_2–TiO_2–SnO_2$ anode and stainless steel cathode was applied to study treating petroleum hydrocarbons from produced water by petroleum exploration [134]. The produced water samples contain benzene, toluene, ethyl benzene, xylene, and phenol, with the NaCl concentration of 15,000 mg/L. The experiment was conducted in a one-compartment electrolytic flow cell at the current density of 89 mA/cm^2, temperature 25°C, and electrode area 19 cm^2. It was proclaimed that the flow rate had an effect on the electrode performance. Specifically, under the different flow rate of 0.25, 0.5, 0.8, and 1.3 L/h and the electrolysis time of 0.5–2.3 h, the organic contaminant degradation efficiencies were 98%, 97%, 95%, and 84%, respectively. However, it is important to mention that the removal efficiencies of phenol and ethyl benzene were low under the same experimental conditions. The authors proposed that direct oxidation of hydrocarbons was the main mechanism because higher flow rate impacted inconsiderably the oxidation rate [134].

6 Outlook and Future Works with SnO_2-Based Electrodes

Recently, the development of SnO_2-based electrodes focuses mostly on the nanostructure material, such as nanotube, nanorod, honeycomb, which help to increase the surface area and mass transfer.

6.1 *Ordered Stake Micro-Structured SnO_2/TiO_2 Nanotubes (TiO_2 NTs)*

The electrochemical performance and stability of Sb-doped SnO_2 electrode can be increased by the design of its microstructure. Specifically, the ordered stake micro-structured SnO_2/TiO_2 NTs is a representative example [142–144]. The ordered stake micro-structured SnO_2/TiO_2 NTs electrode was fabricated using electrochemical anodic oxidation and modified surfactant-assisted sol-gel method. This preparation process is useful for building a strong linkage between the Ti substrate and Sb-doped SnO_2 and increasing the electrode stability. In addition, because of the large specific surface and microstructure of TiO_2 NTs, there will be a considerable growth in the Sb-doped SnO_2 loading amount which is vital for the increase of electrochemical activity of SnO_2 electrode. Moreover, it is probable that the Sb-doped SnO_2 particles can reach nanoscale and be highly dispersed, leading to a substantial increase in the loading amount and active sites of Sb-doped SnO_2. As a result, the electrochemical performance of the electrode may be improved.

In terms of electrochemical parameters, the apparent rate constant of benzoic acid (BA) removal on the SnO_2/TiO_2 NTs and SnO_2/Ti is $(1.44 \pm 0.04) \times 10^{-4}\ s^{-1}$ and $(1.01 \pm 0.03) \times 10^{-4}\ s^{-1}$, respectively. Moreover, BA was degraded on the SnO_2/TiO_2 NTs electrode with an initial instantaneous current efficiency of 26.8%, while the figure for the SnO_2/Ti electrode was merely 13.3%. It is demonstrated that the SnO_2/TiO_2 NTs electrode has possessed both excellent photocatalytic properties and excellent electro-catalytic properties. After 3.5-h electro-photocatalytic removal of BA, 100% COD is treated [142].

6.2 *Sieve-Like Mp–SnO_2/TiO_2 NTs*

Another electrode type with remarkable oxidation ability and strong stability is sieve-like macro-porous Sb-doped SnO_2 (Mp-SnO_2)/TiO_2 NTs prepared via a block copolymer based soft template method [143–145]. Such method is helpful to form Mp-SnO_2 with the pore size varying between 150 and 400 nm. These macropores are useful for increasing the specific surface area and providing more active sites.

The Mp-SnO_2/TiO_2 NTs exhibits excellent photocatalytic and electro-catalytic performances. It also has a remarkable photo-electro-catalytic synergistic oxidation ability to vanish the toxicity of p-nitrophenol in wastewater. In 4 h, the removal efficiency of the p-nitrophenol and TOC is 98% and 91%, respectively. In comparison with traditional SnO_2/Ti electrodes, the Mp-SnO_2/TiO_2 NTs has shown lower reaction activation energy, smaller electrochemical impedance, and a larger electrochemical surface absorption volume [145].

6.3 HOEP SnO_2/TiO_2 NTs

Due to very high oxidation potentials of aromatic hydrocarbons, traditional electrodes with a low oxygen evolution potential (OEP) are seemly hard to be used for electrochemical oxidation of such pollutants [3, 143]. In this regard, that the OEP of the SnO_2 electrode is enhanced via microstructure designing has received much attention. For instance, Wu et al. [146] used the pulse electrodeposition method to fabricate a high oxygen evolution potential (HOEP) SnO_2/TiO_2 NTs electrode. Anodic oxidation was also applied to produce an intermediate layer with TiO_2 NTs on a Ti substrate. Additionally, in order to increase the linkage between SnO_2 and the Ti substrate to enhance the electrode conductivity, the electrochemical method was used to reduce partially at the bottom of TiO_2 NTs and copper deposition was performed. Besides, the intermediate layer was advantageous to the deposition of SnO_2 with copper particles.

As compared to the common Sb-doped SnO_2 electrode fabricated by the sol-gel method, the HOEP SnO_2/TiO_2 NTs electrode proposed by Wu et al. [146] exhibits a higher crystallinity, a higher order degree of the atomic lattice, and a lower concentration of oxygen vacancies. Furthermore, the study revealed that the surface of the proposed electrode showed a three-dimension structure (i.e., Sb-doped SnO_2 nanoparticles with a certain micro-spherical structure), which increased significantly the specific area and active sites. This HOEP SnO_2/TiO_2 NTs electrode displayed excellent ability to oxidize fluorobenzene, which can be considered as a highly stable substance and cannot be removed on a BDD electrode possessing a strong oxidation capacity. It was indicated that after 1 h, the mineralization current efficiency (MCE) on HOEP SnO_2/TiO_2 NTs, BDD, and traditional SnO_2 are 16.2%, 8.03%, and 4.9%, respectively; while MCE after 4 h are 7.8%, 5.6%, and 4.1%, respectively. On the other hand, the HOEP SnO_2/TiO_2 NTs demonstrates the lowest energy consumption due to its lower cell voltage than traditional SnO_2 and BDD. Specifically, in order to degrade 60% TOC, BDD consumed the energy 3.1 times higher than HOEP SnO_2/TiO_2 NTs.

6.4 $(Ru_{0.3}Ti_{0.34}Sn_{0.3}Sb_{0.06})O_2$–$TiO_2$ NTs Anode

The same approach based on TiO_2 nanotubes is also used by Xiong et al. [147], but the authors further developed the method by preparing a quaternary metal oxide coating of Ti, Ru, Sn, and Sb. Generally, anodization, deposition, and annealing were utilized to fabricate the proposed $(Ru_{0.3}Ti_{0.34}Sn_{0.3}Sb_{0.06})O_2$–$TiO_2$ nanotubes anode. It is indicated that the incorporation of an appropriate quantity of tin and antimony into the coating was helpful in enhancing the electrochemical stability of the electrode due to the firmed adhesion strength between the coating and the TiO_2 nanotubes. Compared with the conventional dimensionally stable anode, the proposed anode exhibited high over-potential for oxygen evolution reaction and improved selectivity toward chlorine evolution reaction. It also displayed a uniform and compact morphology without crack. In general, the resulting anode showed outstanding electro-catalytic performance and superior stability.

7 Concluding Remarks

Electrochemical oxidation has become a promising technology to solve many environmental pollution issues in general and wastewater treatment in particular. When SnO_2-based electrodes are employed in wastewater treatment to remove organic substances, the operational parameters such as pH, current density, chloride addition are essential factors affecting the removal efficiency. Sb-doped SnO_2 is suggested to be appropriate for oxidizing organic matters due to its high oxygen evolution over-potential and low-cost feature as compared to other metal oxides.

However, some limitations for the practical application of SnO_2 electrodes are also found, which is due to their insufficient electrochemical stability. In order to tackle this issue and improve electrochemical performance, several studies have been conducted to develop new doping routes. The combination of TiO_2 nanotubes and SnO_2 catalyst is also a promising strategy, which can produce TiO_2 nanotubes based unique micro-structured electrodes with remarkable oxidation ability and strong stability. Therefore, more efforts should be put on optimizing the catalysts and the preparation routes with the aim to develop advanced electrochemical oxidation techniques using SnO_2-based electrodes. In addition, further studies are suggested to be done, which focus on the investigation of advanced SnO_2-based electrodes for the treatment of different types of wastewater to find out the optimal operational parameters.

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RuO_2-Based Electrodes for Chlorine Evolution and Its Application in Water Treatment

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Contents

Abstract Chlorine evolution now becomes important in many applications as chemical industry, polymer, pharmaceutical, and water treatment. In chlorine evolution reaction, the RuO_2-based Dimensional Stable Anode is a technologically good and important electrode because of its unique characteristics such as high thermal and chemical stability, low resistivity, and low overpotential. This chapter reviews the chlorine evolution reaction in the RuO_2-based electrode and its application in water treatment, especially in degradation of organic compounds and disinfection. The physicochemical, electrochemical properties and the mechanism of chlorine evolution at RuO_2-based electrode will be summarized in detail. Chlorine evolution reaction mainly happens at the electrode surface. Increasing the chlorine evolution efficiency, the stability and reducing energy consumption become critical issues for the sustainable development of chlorine evolution. The development of nanostructure material for chlorine evolution reaction is a hot topic for wastewater treatment in the near future.

Keywords Degradation, Electrocatalysis, Electrochemical, Physicochemical

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1 Introduction

Chlorine becomes one of the most important chemical in the industry, which is produced by the electrolysis of brine solution [1]. The annual chlorine production in chlor-alkali process now is about 70 million tons, which is used in a lot of application [2]. Approximately, 50% of the products marketed by the chemical industry, 85% of the pharmaceuticals, and 98% water treatment plant are derivatives of chlorine [3]. In chlor-alkali process, chlorine is produced by using the electrolytic of sodium chloride to convert chloride ions (Cl^-) into molecular chlorine (Cl_2) at the anode, as the following reactions (1) and (2) [4]:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{1}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{2}$$

Simultaneously with chlorine evolution, sodium hydroxide (NaOH) solution and hydrogen (H_2) are produced at the cathode side, inducing the rise in pH values. When the proton and the chloride concentrations are not high enough to maintain the Cl_2 species in its domain of stability, the electrogenerated molecular chlorine might undergo a disproportionation reaction in aqueous solution, forming Cl^- and HClO as Eqs. (3) and (4) [5, 6]:

$$Cl_2 + 2H_2O \rightarrow HClO + H_3O^+ + Cl^- \tag{3}$$

$$HClO + H_2O \rightarrow H_3O^+ + ClO^- \tag{4}$$

Hypochlorite ions are formed as a result of an acid-base equilibrium, and then chlorate is formed in a chemical reaction. The formation of chlorate in weakly alkaline media at a chlorine and oxygen-evolving anode is ascribed to two reactions, namely, the direct oxidation of chloride to chlorate and the conversion of hypochlorite as Eqs. (5) and (6)[1] [7, 8]:

$$2HClO + ClO^- \rightarrow ClO_3{}^- + 2H^+ + 2Cl^- \tag{5}$$

$$ClO_3{}^- + H_2O \rightarrow ClO_4{}^- + 2H^+ + 2e^- \text{ (anode)} \tag{6}$$

For being a well-performing electrode material in the chlorine evolution reaction, four major requirements have to be fulfilled: high catalytic activity, high stability, high selectivity, and high electric conductivity [4, 5]. Ruthenium is a chemical element that can easily adopt various formal oxidation states from −II to +VIII in chemical bonds. RuO_2 reveals a complex and unique redox surface chemistry and acts as a versatile oxidation catalyst and electrocatalysis in many application. RuO_2 exhibits excellent corrosion resistance, electronically conducting, and low

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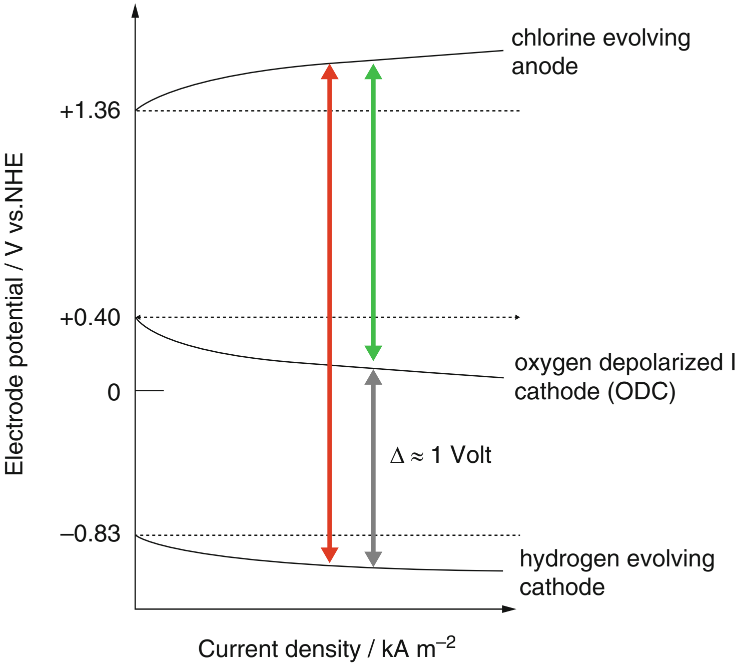


Fig. 1 Electrode potential in chlor-alkali electrolysis from NaCl aqueous solution as a function of current density (adapted from [11])

overpotential for anodic chlorine evolution reaction [6, 9]. Dimensional Stable Anodes (DSA) are such kind of catalytic electrodes for chlorine evolution, which consist of RuO_2, IrO_2, or a mixture of its metal oxides coated on metal substrate, mainly titanium. The use of DSA in chlor-alkali electrolysis industry came in the 1960s when Henri Beer invented this type of electrode, and further P. Hayfield, were then developed and industrialized by De Nora. The performance of RuO_2/Ti was so outstanding that all graphite anodes were replaced by these anodes in a few years of their discovery [10–14].

RuO_2 is a noble and expensive metal oxide, the price of ruthenium is about 10 times lower than that of platinum. Roughly 10–15% of the annual production of ruthenium goes into the production of such DSA (in 2010 about 3 tons) while most of the ruthenium is deployed as buffer layers and thin film resistors in the electronic industry (about 20 tons) [2]. Electricity is essential to produce chlorine in the chlor-alkali industry, and it accounts for about a half of the total production cost [15]. Energy savings arise primarily through using more efficient technologies, such as the replacement of the less energy-efficient mercury, diaphragm processes by the most energy-efficient and environment friendly membrane technology, which is shown in Fig. 1. The energy consumption in modern membrane cells is about 2,600–2,800 kWh per produced ton of Cl_2 [1, 2]. This power consumption can be further reduced to 1,600–1700 kWh per ton Cl_2, if the cathode is replaced by an oxygen-depolarized cathode in which oxygen is reduced to water in a kind of internal fuel cell ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, $E_o = 0.4$ V/SHE), which is shown in Fig. 1 [15, 16]. The combination of these innovative techniques has been put into demonstration practice and becomes the most preferred choice in the design and construction of new chlor-alkali plants. Meanwhile, chlor-alkali industry is also one of the resource-intensive production processes, which depends highly on the use of the rare strategic metal ruthenium as catalysts [9].

High electrical efficiency is closely related with the electrocatalysis performance. High-quality electrodes can improve the electrocatalytic activity of the desired reactions, such as chlorine gas evolution, but depress the electrocatalytic activity of the side reactions, such as oxygen gas evolution [17]. The total consumption of electric power is proportional to the voltage applied to the cell for a given current density (the rate of electrode reaction). The cell voltage consists of several components as Eq. (7) [18]:

$$\Delta V = \Delta E + \Delta \eta + \mathrm{IR} + \Delta \nu \tag{7}$$

where ΔV is the thermodynamic potential difference for a given anode/cathode reaction, $\Delta \eta$ is the sum of the overpotentials for the anodic and cathodic reactions (which are dependent on the electrocatalysts), IR is the ohmic drop of the electrolyte, and $\Delta \nu$ is the additional ohmic drop from the membrane, gas bubble effect, stability of the electrode, etc.

In general, the intrinsic electrocatalytic properties of an electrode material can be simplified to the exchange current density and the Tafel slope. Chlorine evolution is characterized by a low Tafel slope about 40 mV at pure RuO_2 and 30 mV with RuO_2-TiO_2 at the current densities of 200–250 mA/cm^2 in 5 M NaCl solution at 80–90°C (Fig. 2) [17, 19]. High exchange current density, low Tafel slope, and a high density of active sites are beneficial for electrocatalysis [18].

This chapter overviews about the chlorine evolution process at RuO_2-based electrodes and its application in water treatment, especially in degradation of organic compound and disinfection. It is organized as follows: first, discussing about the general physicochemical and electrochemical property of RuO_2. Later is involving of chlorine evolution reaction kinetic and mechanisms. Finally is the summary of recent development and future of chlorine evolution researches in the field of wastewater treatment.

2 Physicochemical Properties of RuO_2

In general, the electrons in d^n oxides of RuO_2 can quite easily be removed from the partially filled d orbitals so that d^n oxides are considered to be much more chemically active than d^o oxides. Its first valence state is Ru^{3+}, occurring as Ru_2O_3 at 0.738 V vs HE. Because this oxidized species is insoluble in the absence of complexing agents, the metal is passive in the higher potential range. The next redox step is Ru^{4+} as

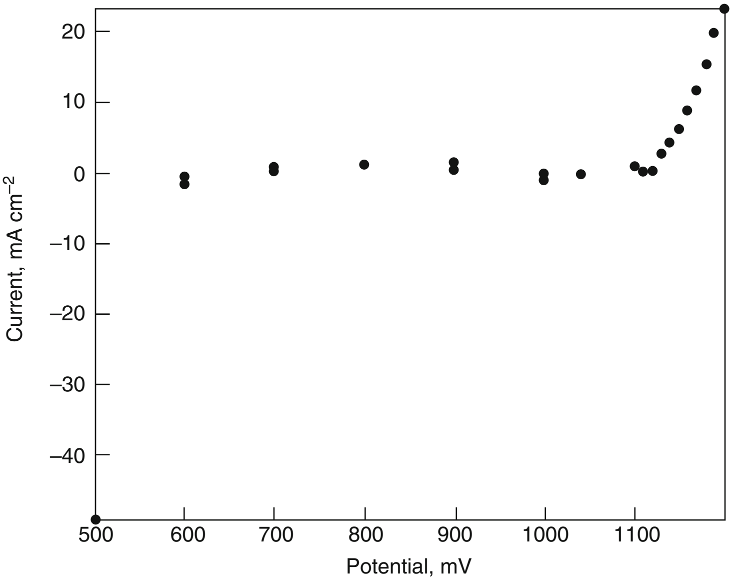


Fig. 2 Electrochemical characteristic of RuO_2-TiO_2 (35–75) electrode in 5 M HCl (adapted from [17])

RuO_2 at 0.937 vs HE, volatile yellow ruthenium tetroxide (melting point 25.51°C, decomposition at 1081°C), RuO_4, or soluble H_2RuO_5 (Ru^{8+}, yellow hyperruthenate), depending on the solution pH [20–23]. RuO_2 belongs to the class of metallic conducting transition metal oxides whose electrical resistivity is 35.2 ± 0.5 μΩ cm at room temperature, higher than that of metallic ruthenium (about 16 μΩ cm). Red balls are ruthenium atoms (this site is shared by other transition metal for the mixed oxide), and green balls are oxygen atoms [24]. The Fermi energy lies in the t_{2g} range of the density of states (DOS), falls in the relative minimum of the DOS between peaks originating from ruthenium−oxygen π and π^* states. Therefore, the π^* states are empty, explaining the stability of RuO_2 [25–27]. The point of zero charge can be seen to shift towards higher pH values as the temperature of preparation is increased [28–37] (Fig. 3).

The electrochemical and interfacial properties of RuO_2 are of utmost importance for a deeper understanding of how RuO_2 catalyses electrochemical reactions. A number of investigations have pushed forward the idea that most of the features of oxide electrodes may be governed by the acid−base properties of the oxide/solution interface. For instance, the state of oxide surfaces depends critically on solution pH, which may point to the formation of surface hydroxyl complexes. The oxygen evolution and chlorine evolution in H^+ or in OH^- has often been found to be fractional [38–41]. Equally important for the state of the electrode surface in solution is the specific adsorption of anions. The acid/base properties of RuO_2 (110) are related to the 1f-cus Ru and bridging O sites which serve as Lewis acid/base and Bronsted base, respectively. The potential of zero charge (PZC) is the potential value

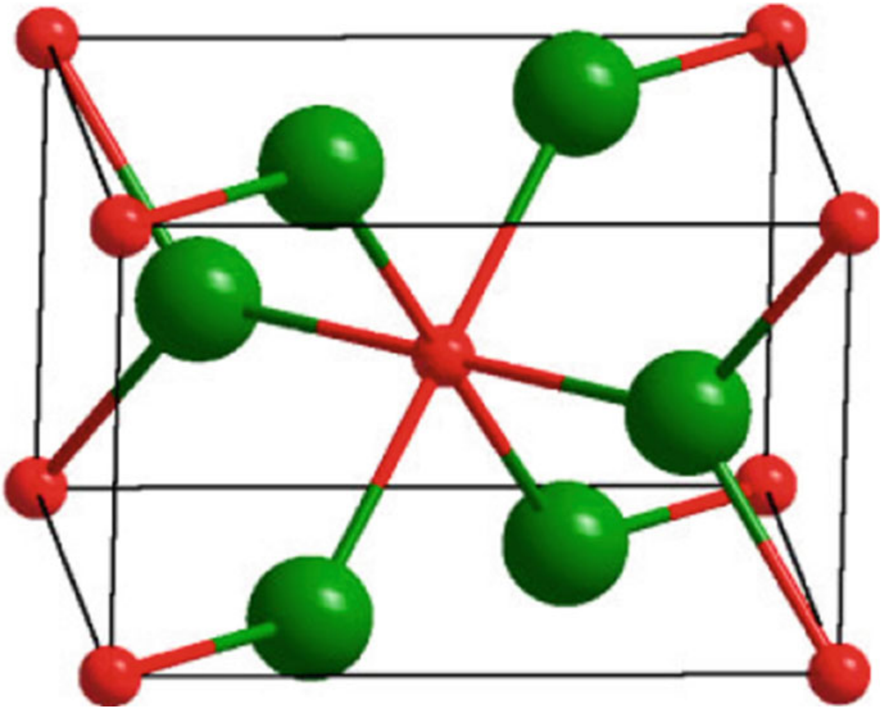


Fig. 3 Tetragonal rutile structure (*P*42/mnm, space group 136) of the active phase (adapted from [18])

at which the surface is uncharged, that is, the surface dipole is compensated. From this one the potential of zero total charge is distinguished, which also includes possible adlayer species. Here the overall dipole of the surface adlayer is compensated. The PZC is governed by the strength of the interaction between the surface Ru atoms and the oxygen of the surface OH groups attached to it. Therefore, electrocatalytic properties and the PZC of oxide surfaces may be intimately interconnected. Using the Gouy−Chapman−Stern model for the double layer, the experimental capacitance is composed of two capacitors in series [42–46] (Fig. 4):

$$1/C = 1/C_d + 1/C_i \tag{8}$$

With C_d is the diffuse layer capacitance and C_i is the inner layer capacitance. The inner capacitance is independent of the electrolyte concentration and can be extracted from concentration-dependent measurements of $1/C$. Assuming a planar geometry of the double layer, values of $C_i = 60–80\ \mu\text{F/cm}^2$ is derived, while C_i is 300–500 $\mu\text{F/cm}^2$ for a spherical double layer. In an aqueous environment the oxide surface is normally covered by OH groups (due to water dissociation) which are stabilized by “co-adsorbed” and coordinated water and which mediate the interaction of the underlying metal ions with chemical species in the solution [43, 44]. RuO_2 in

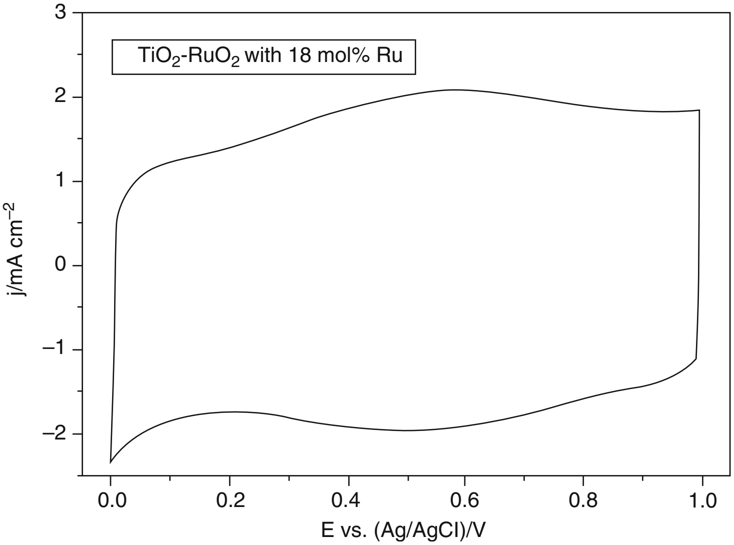
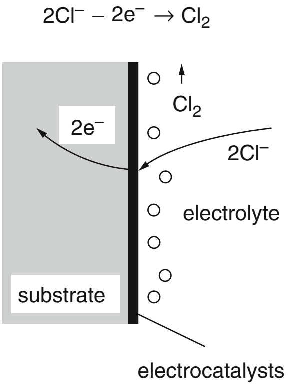


Fig. 4 CV of a TiO_2–RuO_2/Ti coating with 18 mol% Ru, recorded in 0.5 M H_2SO_4, room temperature, 100 mV s^{-1} (adapted from [47])

Fig. 5 Chlorine evolution reactions at the anode side (adapted from [48])



aqueous solution adsorbs water rapidly with a constant H/Ru ratio throughout the thickness of the oxide layer. Active sites on hydroxylated oxide surfaces act preferentially as Bronsted acids and bases. Hydrous RuO_2 is permeable to protons while dry RuO_2 is not. If protons are constituents of both the solid and the aqueous phase, a Nernstian response results as a consequence of the interfacial equilibrium of H^+ ions. Because of the high electronic conductivity, space charge effects can be neglected for RuO_2 [45]. The surface response CV in Fig. 5 is related to redox reactions at the surface active sites which is assisted by proton exchange δH^+ with the solution and electron transfer δe^- according to Eq. (9) [47]:

$$\mathrm{RuO}_x(\mathrm{OH})_y + \mathrm{zH}^+ + \mathrm{ze}^- \rightarrow \mathrm{RuO}_{x-z}(\mathrm{OH})_{y+z} \tag{9}$$

This behaviour plays an important role for hydrous-RuO_2 when applied as supercapacitors. The ionic adsorption strength on RuO_2 electrodes is constant as the electrode potential is varied. This can be understood by oxidation/reduction of the surface sites which are compensated by releasing or addition of protons into or from the electrolyte solution. There are two ways to charge an oxide surface: one is driven by the electrode potential, the other by the pH. Both change the electrochemical potential of the electrons. While the electrode potential acts on the metal sites whose charge variation is compensated by proton exchange, the pH variation acts on the surface hydroxyl complexes whose dissociation with the formation of a surface charge is compensated by adsorption of ions from the solution [48–51].

3 Mechanism of Chlorine Evolution Reaction

Figure 5 shows the kinetic of the chlorine evolution reactions at the anode side. The model mechanism of chlorine evolution at the electrode surface is described as the Volmer–Kristalik–Tafel mechanism (2002). Three different reaction mechanisms are distinguished according to the kinetics and the rate of the separate reaction steps as Eqs. (10) to (14) [52]:

$$-\mathrm{S}^{\mathrm{Z}} + \mathrm{H}^+ \rightarrow \mathrm{SH}^{\mathrm{Z}+1} \tag{10}$$

$$-\mathrm{S}^{\mathrm{Z}} \rightarrow \mathrm{S}^{\mathrm{Z}+1} + \mathrm{e}^- \tag{11}$$

$$-\mathrm{S}^{\mathrm{Z}+1} + \mathrm{Cl}^- \rightarrow -\mathrm{SCl}^{\mathrm{Z}+1} + \mathrm{e}^- \quad \text{Volmer} - \text{step} \tag{12}$$

$$-\mathrm{SCl}^{\mathrm{Z}+1} + \mathrm{Cl}^- \rightarrow -\mathrm{S}^{\mathrm{Z}+} + \mathrm{Cl}_2\ (\mathrm{g}) \quad \text{Kristalik} - \text{step} \tag{13}$$

$$2 - \mathrm{SCl}^{\mathrm{Z}+1} \rightarrow 2 - \mathrm{S}^{\mathrm{Z}+1} + \mathrm{Cl}_2\ (\mathrm{g}) \quad \text{Tafel} - \text{step} \tag{14}$$

Where $–S^{Z}$ and $–S^{Z+1}$ are the non-oxidized and oxidized superficial sites, respectively, and reaction (10) is an equilibrium step independent of the chlorine evolution reaction, being an intrinsic property of the oxide. This step explains the dependence of the electrode behaviour on pH. Reaction (11) is the oxidation of the superficial sites (S^{Z}), which generate the active sites where the adsorbed chlorine intermediate is formed from the chloride ions. In this step, the active sites (S^{Z+1}) are generated as one electron is released. Here, S^{Z} and S^{Z+1} are active sites in different oxidation states. In reaction (12), the chloride ion is electro-adsorbed on the generated active sites since the active site is the metallic cation site to give the atomic chlorine intermediate (SCl^{Z+1}). There are δ and π interactions or construction from t_{2g} orbital of the surface between metal cation and p orbital of the adsorbed Cl atom. The later discharge of chlorine can occur either by the recombination of the adsorbed intermediates or by the reaction of an intermediate with a chloride ion (reactions (13) and (14)). These reactions involve the formation of the Cl-Cl and the cleavage of the bond between the adsorbed Cl atom and the electrode surface accompanying with the electron transfer. The mechanism is based on experimental results from polarization resistance measurements close to the reversible potential. Theoretical potential decay curves were deduced for both the Krishtalik reaction and the Tafel reaction as a rate determining step in the formation of molecular chlorine. To maintain a current it is essential to supply reactants to the electrode surface and also remove the products (the mass-transfer processes, such as diffusion and convection of the reacting species between the electrode surface and bulk of the solution). The electrocatalytic properties of different oxides are correlated with the energy change involved in the lower → higher valency state transition [9, 17, 53]. Electrocatalysis can be expressed, to a first approximation, in terms of bond strength between the electrode surface and reaction intermediates. The concepts applied to the oxygen evolution electrocatalysis can thus be extended to chlorine evolution, including the calculation of the change in the crystal field stabilization energy for the transition from one surface complex to another [54–56].

Another mechanism of chlorine evolution can be proposed by Erenburg and Jansen in 1981 and 1984 [9, 17]. Since metal cations on oxide electrodes are not directly accessible to Cl^- discharge because they are covered with surface OH groups. The oxidation of the anode surface precedes the Cl^- oxidation, and the Cl^- discharge happens over adsorbed oxygen. The last step of removal of chlorine is the lowest step. The reactant Cl^- moves to the interface (mass transport), electron transfer occurs close to the interface (electron transfer reaction), the product Cl_2 moves away from the anode to allow the fresh reactants to the anode surface as Eqs. (15) to (17):

$$\mathrm{S-OH \rightarrow S-O+H++e^-} \tag{15}$$

$$\mathrm{S-O+Cl^- \rightarrow S-OCl+e^-} \tag{16}$$

$$\mathrm{S-OCl+Cl^-+H^+ \rightarrow +S-OH+Cl_2} \tag{17}$$

The reaction pathway of the Cl_2 evolution reaction was investigated by combining electrochemical and Raman spectroscopy to monitor vibrations of the crystal lattice of RuO_2 and changes in the surface concentration of the adsorbed species as a function of the electrode potential, as depicted in Fig. 6. It is shown that oxidation and reconstruction of the catalyst surface during chlorine evolution is a consequence of the interaction between RuO_2 and water. Water (more precisely the OH adlayer) is understood not just as a medium that allows adsorption of intermediates, but also as an integral part of the intermediate formed during the electrochemical reaction. HClO was a crucial intermediate for the catalytic reaction. The vibrational modes of the crystal lattice of RuO_2 were very similar to the vibration of the ClO bond in HClO dissolved in water as Eqs. (18) to (20) [58]:

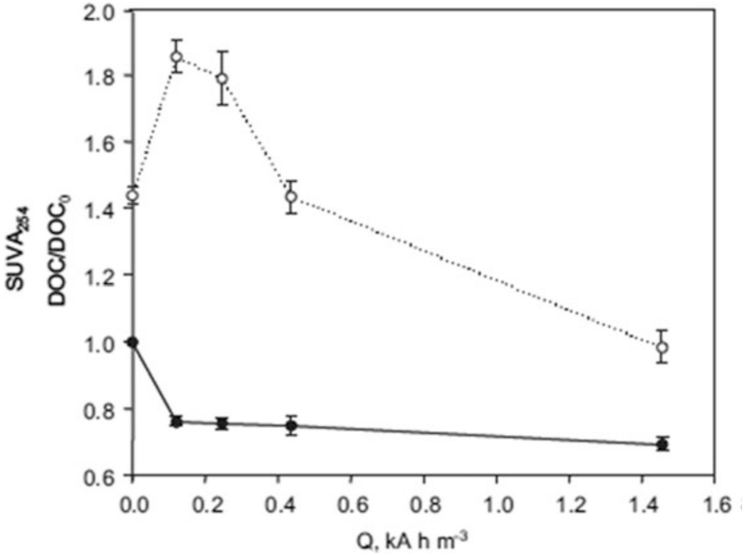


Fig. 6 DOC removal and SUVA254 vs Q in anodic oxidation in batch mode at 574 J = 250 A m^{-2} of ROC-1 spiked with the trace organic contaminants ○ SUVA254, ● DOC/DOC$_o$ [57]

$$H_2O \leftrightarrow OH_{ad} + H + +e^- \tag{18}$$

$$OH_{ad} + Cl^- \leftrightarrow HClO + e^- \tag{19}$$

Rate determining step $b = 40$ mV dec^{-1}

$$HClO + H^+ + Cl^- \leftrightarrow Cl_2 + H_2O \tag{20}$$

Interpretation of the derived "volcano" curve suggests that electrocatalysis is governed by a resonance phenomenon using a dynamic catalytic descriptor. The characteristic vibration of the M-O bond and the maximum of the volcano curve corresponded to the vibration of the Cl-O bond in HClO [58].

4 Application in Water Treatment

Oxidative electrochemical technologies offer an alternative route to many environmental problems in the process industry because electrons are a versatile, efficient, cost-effective, easily automatic, and clean reagent [59]. RuO_2-based electrodes can be applied widely in wastewater treatment to degrade or remove trace amounts of contaminants or microorganism disinfection. Heterogeneous redox catalysis RuO_2 has been demonstrated for the electrooxidation of inorganic, organic molecules as ammonia, H_2S, formaldehyde, acetic acid, phenol pharmaceuticals, pesticides, etc., via indirect electrolysis [59–66]. Owing to the natural abundance of chloride in most polluted water, chlorine-mediated oxidation is the most widely used in situ generated chemical oxidant for wastewater treatment since the generated active chlorine species such as Cl_2, HClO, ClO^-, and ClO_2^- can attack the organics [59, 67]. The additional generation of ClO_3^- and even the total transformation of the chlorinated ions into ClO_4^- have been suggested. The indirect transfer of oxygen to organic molecules can be obtained both on the anode surface through adsorbed oxy-chloro species or in the bulk of the solution through chlorine, hypochlorous acid, or hypochlorite depending on the pH. Nevertheless, the main drawback and concern of the electrochlorination process is the likely formation of chlorinated organic compounds during electrolysis, resulting in increased wastewater toxicity, as is known in common chlorination chemistry which can be considered to be mutagenic and carcinogenic [59, 68–71]. Table 1 shows the summary of the recent wastewater treatment using RuO_2-based electrode.

The predominant species are Cl_2 until pH near 3, HClO in the pH range 3–8, and ClO^- at $pH > 8$. The mediated oxidation with active chlorine species is faster in acid than in alkaline media because of the higher standard potential of Cl_2 ($E^\circ = 1.36$ V vs. SHE) and HClO ($E^\circ = 1.49$ V vs. SHE) compared to ClO^- ($E^\circ = 0.89$ V vs. SHE) [93]. The combination of the generation of oxygen species (ROS) in the water treatment of non-chloride effluents and chlorine active species when using chloride effluents, makes the degradation rate and current efficiency of these processes to be a function of experimental parameters such as pH, temperature, stirring, substrate concentration [94]. Similarly showed a large decay of drug with a Ti/RuO_2-IrO_2 anode. It followed a pseudo first-order reaction and its rate increased with increasing current density. Tetracycline was directly oxidized at the anode via electron transfer without CO_2 production [95]. The same behaviour was described by Rossi et al. for the degradation of oxytetracycline hydrochloride with a Ti/RuO_2 anode, which led to complete loss of its antibacterial activity with respect to *Staphylococcus aureus* [96]. Radjenovic et al. addressed the electrochemical destruction of reverse osmosis concentrates generated by membrane treatment of secondary STW effluent contaminated with 27 pharmaceuticals and pesticides with contents between 8.1 and 33.7 μg L^{-1} using a divided flow reactor with a 24 cm^{-2} $Ti/Ru_{0.7}Ir_{0.3}O_2$ anode [57]. Figure 6 shows that DOC and the specific UV absorbance at 254 nm decreased for current densities 5 mA cm^{-2}, reaching 9% and 27% reductions, respectively, at 25 mA cm^{-2}. In this current density range, free and total chlorine were largely accumulated in the system. The active chlorine species generated for current densities 15 mA cm^{-2} promoted the total destruction of most pharmaceuticals, except ibuprofen and iopromide. Electrocoagulation can combine with electrooxidation as an effective method for treatment of wastewater [97].

Ammonia is effectively removed by chlorine oxidation. The increases in both operating current density and chloride concentration also enhanced the indirect oxidation effect in the electrochemical oxidation treatment efficiency (Fig. 7) [98–100]. Main reactions in the aqueous phase as follows Eqs. (21) to (24) [101]:

Table 1 The recent wastewater treatment using RuO_2-based electrode

Matrix	Criteria	Anode material	Removal efficiency	$[Cl^-]$	Current density	Ref.
Landfill leachate wastewater	COD	SnO_2-PdO_2-RuO_2	92%	7,500 mg L^{-1}	15 A dm^{-2}	[72, 73]
Textile wastewater	Polyvinyl alcohol	Ti/RuO_2	70.18%	17.1 mM	1.34 mA cm^{-2}	[74]
Textile waste water	COD	$RuO_2/IrO_2/TaO_2$	54%	5,069 mg L^{-1}	5.446 mA cm^{-2}	[75]
Biodiesel wastewater	COD	Ti/RuO_2	95%	0.061 M	5.51 mA cm^{-2}	[76]
Glyphosate herbicide	Phosphate	RuO_2	91%	3,500 mg L^{-1}	50 mA cm^{-2}	[77]
Geosmin	Geosmin	RuO_2–Pt	99%	3.0 g L^{-1}	40 mA cm^{-2}	[78]
Petroleum wastewater	Organic pollutants	RuO_2–TiO_2–SnO_2	98%	15,000 mg L^{-1}	89 mA cm^{-2}	[79]
Naphthol	COD	Ti/RuO_2-SnO_2	Almost 100%	7.5 g L^{-1}	33 mA cm^{-2}	[80]
Dye wastewater	Procion Black 5B	RuO_2/Ti	74.05% COD and 100% colour	0.1 M	2.5 A dm^{-2}	[81]
Wastewaters	Ammonia	RuO_2/Ti	61%	10 g L^{-1}	80 mA cm^{-2}	[82]
Reverse osmosis concentrate	DOC	$Ti/Ru_{0.7}Ir_{0.3}\ O_2$	25.1%	1.5 g L^{-1}	250 A m^{-2}	[83]
Textile	TOC	$Ti/Ru_{0.3}Ti_{0.7}O_2$	25%.	0.1 M	60 mA cm^{-2}	[84]
Reverse osmosis concentrate	Colour	RuO_2-TiO_2	90%	0.1 M	100 A m^{-2}	[85]
Domestic wastewater	H_2S	RuO_2-IrO_2	77.1%	0.10 M	10 mA cm^{-2}	[7]
Microcystins	Microcystins	RuO_2-TiO_2	100%	1.85 mM	8.89 mA cm^{-2}	[8]
Wastewater	Ammonia	RuO_2-TiO_2	88.7%	7 g L^{-1}	1,200 A m^{-2}	[86]
Paracetamol	TOC	Ti/RuO_2	80.0%	0.1 M	50 mV s^{-1}	[87]
Active Orange 5R	Colour, COD	RuO_2–PdO–TiO_2/Ti	98.14% colour, 51.43% COD	0.02 M	0.36 mA cm^{-2}	[88]
Phenol	COD	Ti/TiO_2–RuO_2–IrO_2	99.7%	524 mg L^{-1}	5.4 A dm^{-2}	[89]
Ammonia	Nitrogen	RuO_2/Ti	88%	300 mg L^{-1}	15.4 mA cm^{-2}	[90]
Wastewater	Ammonia	RuO_2–IrO_2–TiO_2/Ti	100%	400 mg L^{-1}	10 mA cm^{-2}	[91]
Textile wastewater	COD, TOC	RuO_2–IrO_2–TiO_2/Ti	82.8% COD, 44.7% TOC	1.5 g L^{-1}	36.1 mA cm^{-2}	[92]

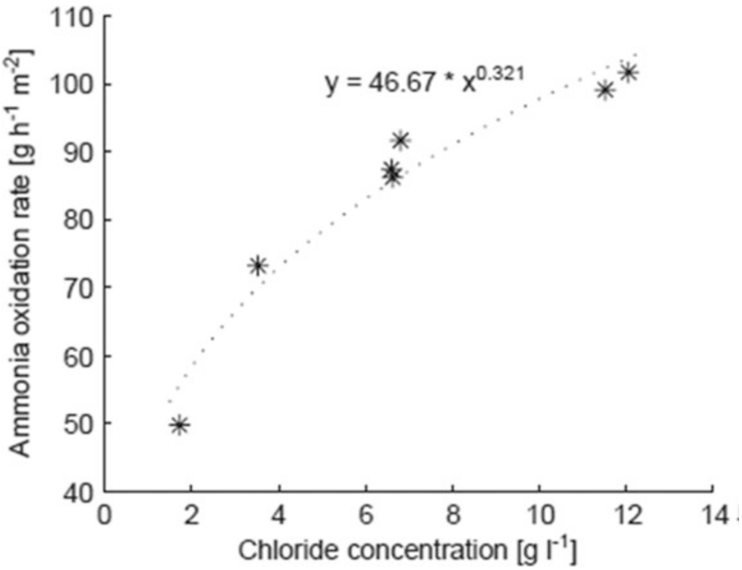


Fig. 7 Influence of chloride concentration on ammonia oxidation rate (current density: 500A m^{-2}, pH of 5.5) (adapted from [98])

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- \tag{21}$$

$$HOCl + 2/3NH_3 \rightarrow 1/3N_2 + H_2O + H^+ + Cl^- \tag{22}$$

$$HOCl + 2/3{NH_4}^+ \rightarrow 1/3N_2 + H_2O + 5/3H^+ + Cl^- \tag{23}$$

$$HOCl + 1/4{NH_4}^+ \rightarrow 1/4{NO_3}^- + 1/4H_2O + 3/2H^+ + Cl^- \tag{24}$$

According to the classical breakpoint chlorination mechanism [102, 103], the addition of active chlorine species (HOCl or OCl^-) to ammonia containing solutions results in stepwise formation of chloramine species (monochloramine, dichloramine, and trichloramine) according to Eqs. (25) to (27):

$${NH_4}^+ + HOCl \rightarrow NH_2Cl + H_2O + H^+ \tag{25}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \tag{26}$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \tag{27}$$

The formation and speciation of chloramine species in a given solution depends mainly on the pH, temperature, and active chlorine to ammonia concentrations ratio [104]. Under operational parameters typical for conventional breakpoint chlorination (which is often used also to describe indirect ammonia electrooxidation), i.e., pH 7–8 and 20°C, a gradual increase in the Cl_2/N ratio should result in monochloramine formation during electrolysis, until a Cl_2/N mole ratio of 1 is attained. Considering this mechanism, translated into the conditions prevailing in electrolytic cells, further electrolytic production of Cl_2 must then lead to decomposition of monochloramine, formation of dichloramine and its subsequent decomposition, and to $N_2(g)$ and NO_3^- release (trichloramine is reported to be the intermediate species of mono- and di-chloramine decomposition) [105].

Electrochlorination can be used as pretreatment methods to reverse osmosis (RO) or can be used after electrocoagulation to remove the suspended solids. Then the wastewater was further treated by electrooxidation for COD removal. The RuO_2 mix metal oxide electrodes are widely used in water treatment [85]. It was found that Ru^{4+} doped into the cell while Pd anchored with enriched concentration on the surface of TiO_2. In the presence of Ru and Pd, the binding energy of Ru increased, while the oxygen vacancies of TiO_2 decreased. This interaction of metals accordingly raised the oxygen evolution potential, decreased the chlorine evolution potential, and enhanced the conductivity of the electrode. Therefore, the electrochemical ability of RuO_2–PdO–TiO_2/Ti anode was improved and Rhodamine B could be destructed effectively yielding a total organic carbon (TOC) removal of 71.70% within 30 min [103, 104].

A procion blue dye effluent was treated by photo and electrochemical oxidation process as well as by combining photocatalytic degradation using TiO_2 suspensions. The maximum COD reduction and colour removal were 96% and 100%, respectively. Photodegradation efficiency of dye was high when photolysis was carried out in the presence of 40 mg/L of TiO_2. The decrease in flow rate and increase in current density significantly increase the reduction of COD [105]. The chloride photoelectrochemical method is effective for mineralizing citric acid [106], humic acid [107], phenol degradation [108]. In this process, 100% of phenol and 75% of total organic carbon were removed within 6 h in the presence of 0.3 g L^{-1} NaCl electrolyte at a current density of 30 mA cm^{-2} and pH 6. However, by assisting electrolysis with UV radiation, the total organic carbon (TOC) reduction rate was greatly improved. For instance, at 20 mA cm^{-2}, electrolysis was responsible for 25% of TOC reduction after 180 min of reaction time. On the other hand, the decrease during the photoelectrolysis reached 65% at the same current density and processing time, at pH 5.5 removed 59% of total organic carbon (TOC) in 4 h (NaCl ¼ 200 mM, current ¼ 5 A). UV irradiation (254 nm) in the reactor induced the photoelectrochemical reaction, increasing the TOC removal from 59% to 99.4%. Normally, UV-driven chlorine produces hydroxyl radicals (^{o}OH) as Eq. (28) [109]:

$$\mathrm{HClO} + \mathrm{UV\ protons} \rightarrow {}^{o}\mathrm{OH} + \mathrm{Cl}^{o} \tag{28}$$

The most common method of electrochemical disinfection is the use of electrogenerated oxidants, such as active chlorine as disinfectants [61]. The characteristics of microbial inactivation as a function of electrode material were effective under the presence of an inert electrolyte using *Escherichia coli* as an indicator microorganism [14]. The electrochemical inactivation of selected bacteria living in paper mill circulating waters was investigated. It was observed that inactivation was mainly due to the electrochemically generated Cl_2/HClO. The good oxidation

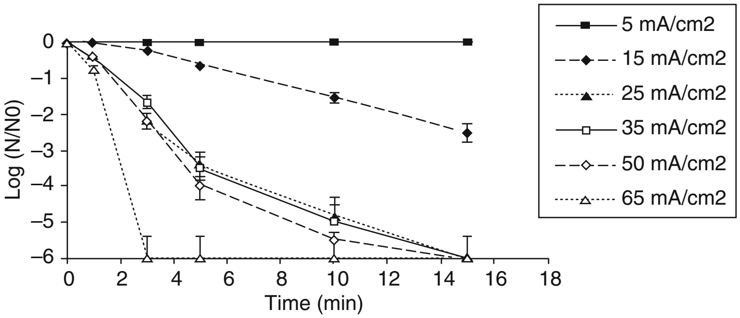


Fig. 8 Inactivation of *Deinococcus geothermalis* in SPW using MMO electrode and different current densities during the galvanostatic electrolysis (pH = 7) (adapted from [110])

performance for inactivation these primary biofilm forming bacteria species with improved current efficiency by higher initial chloride concentrations. In summary, paper mill bacteria (*D. geothermalis*, *P. taiwanensis,* and *M. silvanus*) were inactivated effectively (>2 log) at MMO electrode with current density of 50 mA cm^{-2} and contact time of 3 min. Increasing current density and initial chloride concentration of SPW fastened inactivation. Initial pH value of SPW did not have significant influence on the inactivation rate. Inactivation was mainly due to the indirect electrochemical oxidation (electrochemical formation of chlorine/hypochlorite).

Comparing different bacteria species proved that they have different response to different oxidants. *D. geothermalis* was sensitive against other oxidants than chlorine/hypochlorite, while *P. taiwanensis* and *M. silvanus* were sensitive against chlorine/hypochlorite but not particularly against other oxidants. Current efficiency of the inactivation process was improved by higher initial chloride concentration of SPW because of higher amounts of chlorine/hypochlorite produced at anode during the experiments (Fig. 8) [110]. The electrochemical disinfection of germinated brown rice (GBR) circulating water and cooling tower water containing *Legionella* bacteria was investigated. Results showed the total aerobic plate counts (APC) in the treated GBR circulating water decreased significantly and the turbidity was largely improved at a pulse voltage of 1.0 kV, *Legionella* bacteria were also disinfected effectively at 1.0 kV. The disinfection was attributed to the synergistic effects of the oxide anode, the electric field, and the radicals formed during the electrochemical treatment. This suggests that electrochemical treatment could be applicable to the disinfection of water from other sources [111]. The bioluminescence inhibition test with *Vibrio fischeri* and the combined algae test with *Pseudokirchneriella subcapitata* indicated a substantial increase in non-specific toxicity of the reaction mixture due to the formed halogenated by-products, while the specific toxicity (inhibition of photosynthesis) remained unchanged. However, baseline toxicity as determined by *Vibrio fischeri* bioluminescence inhibition tests (Microtox) was increasing with higher applied charge during batch and continuous oxidation, indicating the formation of toxic oxidation products, possibly chlorinated and brominated organic compounds [112].

5 Conclusion and Future Remark

The industrial sector accounts for about a third of the both global primary energy consumption and energy-related CO_2 emissions. Industrial energy efficiency has a significant impact on the mitigation of the climate change, security of energy supply, and sustainability. In terms of electrocatalysis, the chemical reaction proceeds electrochemically driven by the electrode potential. Overpotential related to the electron transfer reactions at the electrode could be reduced by proper selection of electrode materials. Performance improvement in electrode coatings also plays a critical role in reducing energy consumption (overpotential) in the electrolytic chlorine production. The performance dependence on the electrode material, surface area (especially outer surface area), chemical composition, surface morphology, and phase structure of the oxide coatings has been investigated systematically. Thus, it is a key for chemists to develop and evaluate new catalytic materials and accordingly new preparation routes to meet the continuous expansion of industrial requirements. This is one of the motivations of the present research project to optimize the electrocatalysts and to innovate in the preparation strategy of electrocatalysts. Furthermore, the design in electrode coating morphology (surface and cross-section) was studied regarding the issue of electrode deactivation caused by the substrate passivation. Optimization in the electrode catalytic activity and stability has been accomplished through adopting alternative preparation routes such as sol–gel and electrodeposition. Particular emphasis has been put on nanostructuring of the anode in order to reduce the detrimental effects of gas bubble evolution. It is known that a major part of the overpotential originates from hindered bubble detachment from the electrode surface in particular at higher current density. Other studies relate with mixed metal oxide or lot of attention. The substrate development to increase the stability and conductivity also are received a chlorine indirect oxidation also will be developed. Multi-doping can be easily obtained by controlling the bath composition. The structural and crystal size-controlled preparation of mixed oxide catalyst coatings can be extended to the design of other multicomponent electrocatalyst fabrication routes for chlorine evolution. Further improvements of the electrolysis cell rely on decreasing the cathodic overpotential and membrane ohmic drop, since both contribute largely to the total cell voltage.

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Comparing Tertiary Wastewater Treatment to Seawater Desalination Using Life Cycle Assessment

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Contents

Abstract The Gulf Corporation Council (GCC) countries consume approximately half of their oil production for water and energy cogeneration. This intricate situation of increasing water consumption and freshwater scarcity paradox have made wastewater treatment and reuse indispensable. Reuse of treated wastewater contributes to

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savings fossil fuels and entailed environmental impacts. The objective of this chapter is to demonstrate the application of life cycle assessment (LCA) to evaluate the environmental impact and missed opportunity of treating municipal wastewater to tertiary quality compared to conventional water production. The conventional method compared is the dominant seawater desalination using multistage flash distillation (MSF). The study follows the ISO 14040/44 standards and uses a functional unit of 1 M m^3 of tertiary treated effluent (TTE). The modeling concept adopts the cradle-to-gate consequential modeling paradigm. The life cycle inventory is based on filed data collection, reports, literature, and Ecoinvent database processes. The inventories include: infrastructure, grid, materials, energy requirements, chemical additives, and sludge disposal; for primary, secondary, and tertiary treatment. The life cycle impact assessment is applied on both the characterized and normalized level using the ReCiPe method. The normalized results indicate that MSF has over 70 times the impact on fossil depletion and over 8 times the impact on particulate matter formation, human toxicity, and climate change for water production compared to the effects of TTE. The TTE effluent is best for agricultural use.

Keywords Desalination, GCC countries, Kuwait, Life cycle assessment, Multistage flash distillation (MSF), Wastewater treatment, Water reuse

1 Introduction

The widening gap between the consumption and availability of potable water is now a worldwide problem. Water use has been growing globally at more than twice the rate of population increase in the last century [1]. By the year 2030, the global water demand will increase from 4,500 billion m^3 to 6,900 billion m^3 (53.3% increase) [2, 3]. More regions are reaching the limit at which water services can be sustainably delivered, especially in arid regions. This gap is at its peak in the Gulf Corporation Council (GCC) countries [4–6], as the GCC has the lowest renewable water resource index score worldwide [7–9].

To satisfy their demand for water, GCC countries primarily rely on expensive seawater desalination followed by nonrenewable groundwater resource extraction [10–13]. Over the past decade, water consumption has increased almost 12-fold, and the population has almost tripled during the same period [14]. Half of the oil produced in most of the GCC is consumed by cogeneration to power desalination plants [15–18]. The abundance of fossil fuels at relatively low extraction costs has allowed the predominant desalination technology in the GCC to be a thermal technology, namely, multistage flash distillation (MSF). Although numerous contracts in the GCC have been signed to make the transition to membrane-based desalination [19–22], MSF is still the leading technology due to its robustness with respect to distilling feed water turbidity and salinity [4, 18, 23–25]. Burning fossil fuel entails considerable ecological and health impacts due to emissions of substances including greenhouse gases.

In response, wastewater (WW) reuse is now considered indispensable for meeting the staggering water demand, particularly under conditions of alarming water scarcity [26–29], which are now already affecting every continent [1]. The GCC has already embarked on constructing mega wastewater treatment plants (WWTPs) and projects, most of which treat water to tertiary quality, except that the resultant tertiary treated effluent (TTE) is not utilized to realize sufficient reliance on desalinated water. We believe that the complex water scarcity situation will only be solved with a dual approach of sustainable water consumption and WW recycling and reuse. This chapter evaluates tertiary WW treatment using life cycle assessment (LCA) and compares the environmental impact of such treatment with that of desalination water.

2 Assessing Wastewater Treatment Technologies Using LCA

LCA has been repeatedly applied since the 1990s to assess the environmental impact of different technologies, scenarios, and operation alternatives associated with WW and sludge management [30–38]. To date, more than 100 research papers have been published in this field [39]. Detailed literature reviews comparing different LCA objectives, challenges, methodological choices and results related to WW treatment and sludge management can be found in Corominas et al. [39], Yoshida et al. [40], Pradel et al. [41], and Gallego-Schmid and Tarpani [42]. In addition, LCA has been used to analyze environmental impacts in the field of stormwater management [43]**;** to determine appropriate solutions in the field of the urban water cycle [44]**;** to control emitted greenhouse gases [45]**;** and to identify the environmental impacts of sea water desalination [46].

LCA has also been used to address the environmental impacts as well as the benefits of supplementing, upgrading, and improving treatment processes [47–50]. Liu, et al. [51] and Bai, et al. [48] used LCA as a standardized approach to evaluate the environmental performance of replacing secondary treatment units with green biosorption reactors and constructed wetlands, respectively. These authors used several scenarios to implement their LCA analysis, where the best choice was based on adverse impacts to the environment, reuse of materials or byproducts, and sustainability. Two different sewage treatment plants currently operating in China were selected as case studies. According to the results obtained, these two studies underline the importance of allowing the stakeholders of WWTPs to participate in the analysis of the results of LCA practitioners.

Awad, et al. [47] suggested additional tertiary treatment and sludge processing methods that comprise preliminary, primary, and secondary units to improve the performance of WWTPs in developing countries. To achieve this goal, several different scenarios were analyzed for their economic and environmental impacts: the addition of anaerobic digestion of sludge, the addition of a tertiary treatment stage, and the combination of the two.

Anastasopoulou, et al. [52] discussed the quality of WW discharged from two systems: the Nano Membrane Toilet with a conventional pour flush toilet and a urine-diverting dry toilet. These two sanitation systems have been suggested to be applied in South Africa due to the poor sanitation infrastructure in this country. Samples from WW effluents were taken and then subjected to microbial analysis to reflect the environmental impacts of each sanitation system on human health and the ecosystem. Afterward, LCA was used to compare the environmental impacts of each system. A similar study was conducted by Li, et al. [53] to determine the environmental impacts of organic pollutants at microconcentrations. LCA was used to compare the performance of three treatment technologies toward the removal of micropollutants in China. These technologies included reverse osmosis, adsorption using activated carbon, and ozonation.

Bai, et al. [48] discussed the environmental impacts that result from the implementation of wetlands for WW treatment. In their research, three scenarios were considered: a bioaugmented constructed wetland, a nonbioaugmented constructed wetland, and raw WW without treatment (reference scenario).

Liu, et al. [51] discussed four scenarios for upgrading an oxidation ditch by employing an emerging green biosorption reactor. LCA was used to model the data from four scenarios: an oxidation ditch model (reference scenario); a scenario in which end-of-life alum sludge remained the asset of the water treatment facility; a scenario in which end-of-life alum sludge was considered an input similar to WW and its final disposal process was considered; and the reuse of end-of-life alum sludge for agricultural application instead of landfilling. Tavakol-Davani, et al. [43] focused on several scenarios to control sewer overflows: toilet flushing, a high release rate, a hybrid system.

Pradel and Aissani [54] discussed possible scenarios regarding the environmental impacts of the production of sludge-based phosphate fertilizers, including biological dissolution by acidification to separate phosphorus from organic matter. In this approach, sludge is digested and then dewatered, and eventually, the phosphorus is recovered.

The guidelines of LCA [55] indicate that an LCA study needs to cover:

1. Definition of the goal and scope of the study,
2. Life cycle inventory (LCI),
3. Life cycle impact assessment phase (LCIA),
4. Results interpretation and decision-making.

The literature on how these elements have been addressed in WW LCA is provided in the following sections.

2.1 Goal and Scope in LCA of Wastewater Applications

The goal of an LCA states the intended application, the reasons for carrying out the study, the intended audience, and whether the results are intended to be used in comparative assertions to be disclosed to the public [56]. Table 1 shows the different goal statements for selected WW LCA studies.

2.1.1 The Scope and Functional Units in Wastewater LCA

The scope and systems boundaries indicate which aspects of the system are included to enable better comparative analysis and interpretation. The scope in WW LCA encompasses different boundaries, including the WW treatment itself, additional water purification, electricity production, the sewer system network, and materials production processes. In most WW LCA studies, the system boundaries have excluded end-of-life WWTP demolition due to the lower impact of this stage than other phases of the LCA. A comparison among different WW treatment scopes in LCA is shown in Table 2.

The functional unit (FU) applied in WWTPs is quantified by the specific volume of WW generated or treated as a result of human activities on a daily basis (m^3/day) [47, 48, 50]. It is used as a benchmark in the assessment of sewer systems from the generation point to the targeted treatment units [43, 44].

In Liu, et al. [51], the FU is defined in terms of 1 m^3 of primary pretreated WW per day. All the chemical, physical, and biological constituents other than the treatment efficiency are calculated according to this FU. This FU constitutes the most common FU in WW LCA [47, 49, 58]. Bai, et al. [48] used an FU of 0.1 m^3 of WW to be treated using the constructed wetland method. This unit was used to correspond to the processing capacity of the constructed wetland in one cycle. Guven, et al. [50] used two FUs in his dual WW and food waste treatment system. The first FU was 1 m^3 of influent municipal WW to the Istanbul WWTP, which was used for LCA application for WWTP analysis. The second value is related to solid waste and was set to 2.88 kg of food waste. It was considered equivalent to 1 m^3 of WW influent.

Ma, et al. [57] expressed the FU in terms of electricity produced, i.e. 1 kWh equivalent to replace electricity generated from coal. Along the same lines, Raghuvanshi et al. [45] considered an FU of 1 MJ produced from a biodiesel energy generator that consists of microalgae, which was applied in both WW and freshwater treatment systems.

Some studies in WW LCA have considered the system a multiproduct system, particularly when embracing concepts of a circular economy. Hence, when the boundaries include the municipal water cycle, treated WW will displace an equivalent amount of conventional potable water production in GCC seawater desalination. This invites the consideration of the ISO multiproduct/multifunction hierarchy. A process is multifunctional when it provides more than one function, meaning that

Table 1 The different LCA goal statements for selected WW LCA studies

Literature	Intended audience	Goal	Country
Ma et al. [57]	Decision makers	Examine effective methodologies to reduce freshwater consumption as well as WW discharge.	China
Bai et al. [48]	Stakeholders	Evaluation of different WW treatment processes using multiple weighting methods and conjoint analysis.	China
Liu et al. [51]	Stakeholders	To support the early stage and upgrade of a green biosorption reactor, i.e., an oxidation ditch treatment method; LCA was applied for this purpose.	China
Zhang et al. [46]	–	To identify and eventually reduce the environmental impacts of microbial desalination cells used in WWTP and seawater desalination.	USA
Tavakol-Davani et al. [43]	Stakeholders	To evaluate the environmental sustainability and benefits of rainwater harvesting systems used to control overflows in a combined sewer system.	USA
Anastasopoulou et al. [52]		Presents a comparison using Nano membrane toilets with different systems of lavatories.	South Africa
Petit-Boix et al. [44]	Decision makers	To determine critical variables and LCA stages of the urban water cycle.	Spain
Li et al. [53]	–	To investigate the critical issue of environmental impacts of organic micropollutants in advanced WWTPs for three different WW treatment technologies: Ozonation, granular activated carbon adsorption, and reverse osmosis.	China
Awad et al. [47]	Decision makers	Address the economic and environmental benefits of adding a tertiary treatment/sludge treatment unit to primary and secondary treatment processes by using LCA.	Egypt
Raghuvanshi et al. [45]	–	LCA was used in the assessment of the associated impacts from biodiesel production from microalgae feedstock cultivated in two different media: WW and fresh water.	India
Guven et al. [50]	–	LCA is used to compare two options for upgrading a preliminary WWTP. The first uses a high-rate activated sludge system. The second option adds a food waste process.	Turkey
Lopes et al. [49]	–	To evaluate the technical aspects and the environmental performance of a WWTP consisting of high-rate algal ponds as an alternative method for the activated sludge secondary treatment unit.	Spain

(continued)

Table 1 (continued)

Literature	Intended audience	Goal	Country
Zhao et al. [58]	Decision makers	To investigate the importance of incorporating a regional impact category using LCA in order to reflect the local impact of organic pollution.	China
Pradel and Aissani [54]	–	To investigate the environmental impacts related to phosphorus recovery from WWTPs.	–

Table 2 The different FUs and scopes for selected WW LCA studies

Literature	FU	Scope/system boundary
Ma et al. [57]	1 kWh of electricity With a reference flow of 3.2×10^{-3} m^3/kWh	Coal power supply plant: Coal mining, washing, transportation, and power generation technology
Bai et al. [48]	0.1 m^3	The operational stages of the constructed wetland
Liu et al. [51]	1 m^3	WWTP: Green biosorption reactor/oxidation ditch
Zhang et al. [46]	0.001 m^3	Cradle to grave of microbial desalination cells
Tavakol-Davani et al. [43]	1 m^3	Rainwater harvesting system to control combined sewer overflows
Anastasopoulou et al. [52]	10-adult-occupant household	From cradle to grave: Nano membrane and conventional pour flush lavatories
Petit-Boix et al. [44]	1 m^3	Raw material procurement, pipe production, transport to the construction site, pipe installation and trench preparation, and operation and maintenance
Li et al. [53]	1 m^3	Ozone-sand filter, granular activated carbon-sand filter, microfiltration-reverse osmosis, and disinfection (tertiary effluent)
Awad et al. [47]	1 m^3	Primary, secondary, and tertiary treatment stages and anaerobic digestion of sludge
Raghuvanshi et al. [45]	1 MJ of energy produced from biodiesel from fresh water and WW	Cradle-to-grave: The biodiesel production phases of cultivation, flocculation, centrifugation, extraction, and transesterification
Guven et al. [50]	1 m^3 of influent WW And 2.88 kg of food waste	Cradle-to-grave WW treatment, sludge treatment, and food waste treatment
Lopes et al. [49]	1 m^3	Cradle-to-gate: From the stage of untreated WW input to sludge treatment
Zhao et al. [58]	10,000 m^3	WWTPs
Pradel and Aissani [54]	1 kg	WWTPs

it delivers more than one product output and/or provides more than one service [59]. In our case, WW treatment (treatment of end-of-life waste) and water production are applied. According to the ISO [55], system expansion is recommended over allocation to identify the net impacts of the original system without accounting for interactions due to impacts from the conventional products displaced by the coproducts, such as electricity or heat production (from methane or sludge), fertilizers, etc., that are subtracted from the primary system [49, 50, 54]. On the other hand, some WW LCA studies have applied system allocation or attributional analysis [50, 52]. Zhang, et al. [46] used attributional modeling to assess impacts associated with microbial desalination cell technology, where electricity generation is considered a byproduct of seawater desalination and WW treatment processes.

2.2 Life Cycle Inventories and Databases Used for Wastewater LCA

The life cycle inventory (LCI) lists the comprehensive collection of the required data associated with the input and output of materials, energy, and emissions of the system boundary under consideration, including foreground and background data and elementary flows for the scenarios under consideration [59, 60]. The typical application is to adapt processes found in available LCI databases, which vary according to the applied system boundary. The vast majority of WW LCA studies have used Ecoinvent [43–47, 49, 54]. The USEtox and Ecovalue databases were used in Li, et al. [53] and Zhao, et al. [58], respectively. Ma, et al. [57] created new LCI processes based on a coal-based power generation plant located in China. Liu, et al. [51] used a Chinese LCI Database. For WW LCA, the LCI database is often integrated within commercially available software such as SimaPro [44, 49, 52] or GaBi [43, 46]. Other software programs include Umberto NXT [45], e-Balance, open LCA, and others.

2.3 Life Cycle Impact Assessment for Wastewater LCA

Life cycle impact assessment (LCIA) is where the LCI’s information on elementary flows is translated into environmental impact scores using an LCIA method. An ISO-compliant study mandates the selection of the appropriate impact categories. The LCA practitioner needs to justify this choice and clearly defend the reason for leaving out an impact category. The best way to do this is to look at existing studies or assess the concerns of the relevant stakeholders; after all, a study will only be accepted if the relevant stakeholders can find the desired information or understand why that information cannot be made available [61]. Table 3 shows some of the LCIA methods and impact categories discussed in WW LCA in various studies.

Interpretation typically follows LCIA to answer the questions posed as part of the goal definition. In WW LCA studies, sensitivity analysis and uncertainty analysis

Table 3 LCIA methods and categories used in selected WW LCA studies

Literature	LCIA method	Impact categories
Ma et al. [57]	USEtox™	Carcinogens, noncarcinogens, freshwater ecotoxicity, aquatic eutrophication, and water scarcity.
Bai et al. [48]	CML-AI	Acidification, eutrophication, human toxicity, photochemical oxidation, global warming, and abiotic depletion of fossil fuels.
Liu et al. [51]	CML2002	Fossil depletion potential, acidification potential, eutrophication potential, global warming potential, and the impacts of three emitted gases (CO_2, NO_x, and SO_2).
Tavakol-Davani et al. [43]	TRACI based on US impact data	Global warming potential, ecotoxicity in water, eutrophication potential, and ozone depletion potential
Anastasopoulou et al. [52]	ReCiPe	Damage to human health, damage to resources, and damage to ecosystems.
Li et al. [53]	USEtox	Ecotoxicity, human health related to carcinogenic or noncarcinogenic pharmaceutical compounds, global warming, ozone depletion, acidification, eutrophication, smog air, and fossil fuel depletion.
Awad et al. [47]	CML 2000	Acidification potential, global warming potential, eutrophication potential, photochemical oxidation, depletion of abiotic resources, ozone layer depletion potential, terrestrial ecotoxicity potential, and freshwater aquatic ecotoxicity.
Guven et al. [50]	ReCiPe	Climate change, terrestrial acidification, freshwater acidification, marine eutrophication, human toxicity; terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, and fossil fuel depletion.
Lopes et al. [49]	CML-AI	Abiotic depletion of fossil fuels, global warming, ozone layer depletion, photochemical oxidant formation, acidification, and eutrophication.
Zhao et al. [58]	CML-AI	Eutrophication, acidification, freshwater aquatic ecotoxicity, human toxicity, ozone depletion, photochemical oxidation, global warming, abiotic depletion of fossil fuels, and abiotic depletion of elements.

have been applied as part of the interpretation to guide the development of conclusions [52, 57].

3 Methodology

WW treatment is a method used to eliminate impurities from WW so that it is returned to the water cycle with minimum harmful impacts on the environment or humans. The WW generated from activities of residential, governmental, commercial, and public areas is collected and then directed to the target treatment plant via dedicated sewer systems. In contrast, stormwater is drained by stormwater network lines and then discharged without treatment to the sea. The present LCA evaluates the environmental burden of TTE while adhering to the four stages outlined by ISO 14040 [62], including the goal and scope, a life cycle inventory (LCI), a life cycle impact assessment (LCIA) and interpretation according to the International Reference Life Cycle Data System, ILCD [63], to the best of our understanding [64].

3.1 Goal

The intended application is to assess the environmental impact of treating municipal WW to tertiary quality as opposed to using desalinated water. The final result is planned to be provided to policymakers in local governments, agricultural authorities, and/or farms while providing CE perspectives and maintaining ISO 14040 [65] standards.

3.2 The Functional Unit

The FU used is 1 Mm^3 of TTE meeting (not exceeding) the specifications found in Table 4.

Table 4 Specifications of TTE used in FU [66]

Parameter	Unit	Raw WW	Tertiary treatment
pH	—	6.5–8	6.5–7.5
Conductivity	μs/cm	1,200–3,000	1,100–2,200
T.S.S	mg/L	100–500	< 10
V.S.S	mg/L	70–350	< 7.0
C.O.D	mg/L	250–750	< 40
BOD_5	mg/L	100–400	< 10
Grease & oil	mg/L	10–50	NIL
T.D.S.	mg/L	700–1800	800–1,500
Chloride	mg/L	200–400	200–400
Ammonia	mg/L	15–50	1–5
Nitrite	mg/L	0.04–0.7	0.1–1.5
Total count	Colony/100 mL	2.40E+09	1E+03
T. Coli	Colony/100 mL	3.20E+08	400
F. Coli	Colony/100 mL	4.10E+07	0–10
Salmonella	Colony/100 mL	4.50E+06	NIL
Streptococci	Colony/100 mL	1.40E+07	NIL

3.3 System Scope and Boundary

The system boundaries are from cradle-to-gate, so all processes, materials, energy requirements, and chemical additives through operation are calculated through field visits, report, or the literature. It includes: Water delivery and disposal are excluded. Electricity generation is modeled by LCA to partially supply requisite power to major WWTPs in the GCC. The phases included in the system boundary are provided in the following sections. The system boundary is shown in Fig. 1.

3.3.1 Primary Treatment

Primary treatment is the physical/mechanical process that removes suspended and floating particles from WW entering the WWTP [67]. Primary treatment includes screening to screen grit and other suspended solids. WW primary treatment removes 50–60% of the total solids and 20–30% of the BOD [68]. Four bar screens are used to remove large objects from the WW, such as plastics, papers, packets, and rags. The WW then passes through grit chambers to separate inorganic particles/fine materials such as sand, hence preventing damage to pipes. Oils are removed from the WW using oil screens. The system includes eight oil screens. After this step, the WW undergoes an odor control process.

3.3.2 Secondary Treatment

Secondary treatment uses biological processes to digest and dissolve organic pollutants to produce settleable solids [27]. In this stage, microorganisms consume organic matter and then convert it to water, energy, and CO_2. The process is followed by aeration basins or settling tanks to clarify the influent by removing approximately 85% of its suspended solids and BOD [68, 69]. The biological treatment stage uses a vertical loop reactor (VLR), which is operated on the basis of partial ventilation and depends on a lack of oxygen [70]. The WW is then moved by gravity to secondary WW treatment, which consists of aeration chambers and primary clarifiers. The system includes four aeration tanks. Each aeration tank has two treatment systems: a VLR and return activated sludge (RAS) line. At the VLR, an average denitrification rate of approximately 80% is achieved without the need for internal recycling of sewage water. The oxygen supplying the VLR is supplied by six outside blowers into the aeration tank. The air is blown through diffusers at the upper end perforated with holes to form bubbles on the surface of the aeration tank. The suspended solids are reduced to no more than 15 mg/L using a peripheral feeding process using a hydraulic distribution system and sludge removal pipes at the bottom of the VLR [70]. The liquid from the aeration tanks passes to the clarifier and remains there for 8 h. The type of clarifier used is a "rim flow clarifier," which has a depth of six meters with an internal diameter of 45 m to accommodate maximum flow with a capacity of

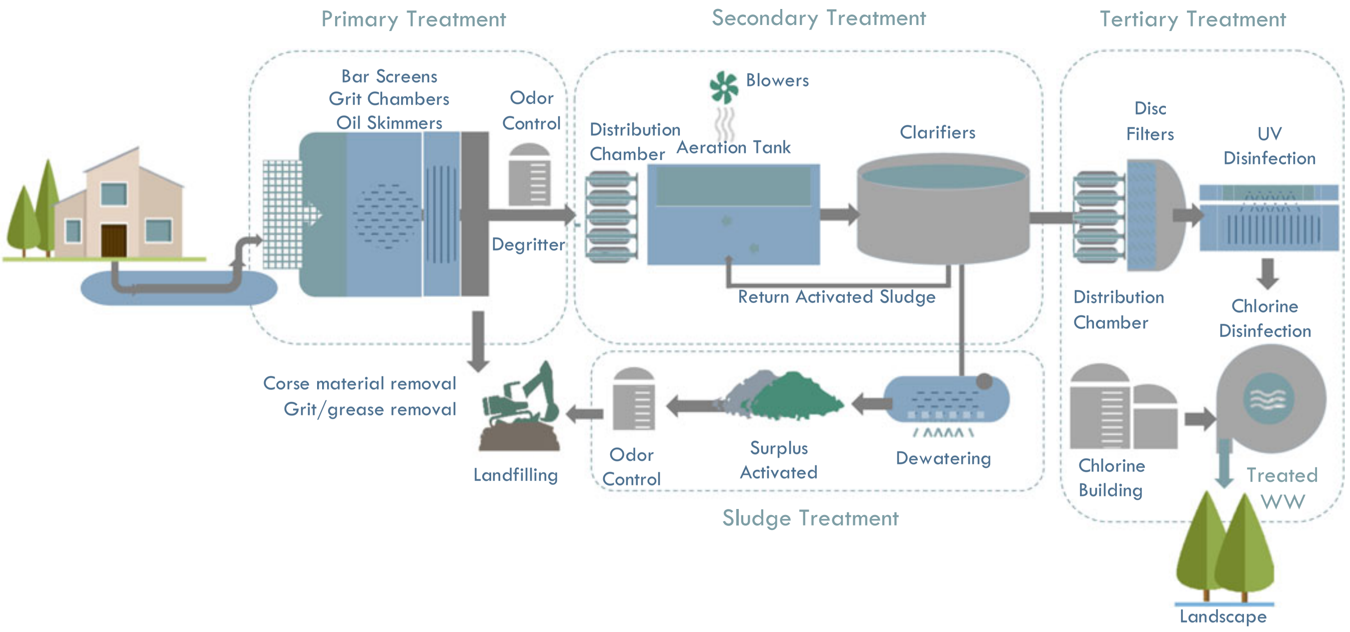

Fig. 1 System boundary for WWTP

270 K m^3/d. The flow inlet is at the center, while the outlet is along the periphery for the center feed clarifier. A concentric baffle spreads and distributes the discharge evenly in the radial direction. The resultant active sludge is continuously recycled to the aeration tank, where it mixes with incoming WW to feed bacteria and maintain the required food to microorganism (F/M) ratio. The surplus activated sludge (SAS) goes to sludge treatment.

3.3.3 Tertiary Treatment

Tertiary treatment eliminates over 95% of all impurities from sewage. Tertiary treatment upgrades conventional secondary treatment by removing additional pollutants, residual suspended solids, phosphorus and nitrogen from secondary treated WW [68]. The effluent discharge is distributed using a special chamber for purification using 24 rotating disc filters with a 100 m^2 effective filtration area per unit. The disc filters have a size of 10 μm (0.000393 in.). The effluent is disinfected using an ultraviolet (UV) system. A four-channel UV system is used. The chlorination step is used for disinfection, color removal, and odor control. The effluent is treated at a concentration to achieve between 0.5 and 1.0 mg/L residual chlorine.

3.3.4 Sludge Treatment

Excess sludge is thickened to reduce its volume. The system under study includes three operating units. A polymer preparation unit (PPU) is used for additional thickening and flocculation [70]. Eight aerobic digesters use gravity belts that carry sludge for dewatering to form a sludge cake. This sludge cake is landfilled.

3.4 Life Cycle Inventory

The LCI is built in accordance with the system boundaries described earlier using processes from Ecoinvent version 3.0. The chemical additives used are found in Table 5.

Table 5 Tertiary chemical additives per cubic meter of TTE

Chemicals	Formula	Amount (g/m^3)	Process [71]
Sodium hydroxide 50%	NaOH	1.096E+00	Sodium hydroxide 50% solution state
Sodium hypochlorite 12.5%	NaOCl	2.740E+00	Sodium hypochlorite 15% solution state
Activated carbon	C	3.044E-02	Carbon black
Cationic polymer	—	1.461E+00	Cationic resin
Chlorine liquid	Cl	3.288E+00	Chlorine liquid

A new process was created for the UV disinfection system based on [72]. The disinfection system with a flow rate of 100 K m^3/day is based on a 20-year lifetime. The LCI of the UV system is provided in Table 6.

The electrical energy required for tertiary treatment is 0.39452 kWh/m^3. The electricity production process adopts the high voltage from Ecoinvent based on data found in Al-Shayji and Aleisa [73] and [14] using an energy mix of heavy fuel oil, diesel, crude oil, and natural gas (see Table 7).

Table 6 LCI of UV disinfection system [72]

Part List	Materials	kg/Mm^3	Materials	Total (kg/Mm^3)	Process (Ecoinvent)
Quartz sleeve	Pure quartz	3.15E-02	Quartz	3.15E+06	Silica sand
Pneumatic cylinder	Coated Aluminum	4.11E-02	Aluminum	4.11E-02	Aluminum removed by drilling, conventional
Ballast	Painted sheet steel	2.74E-01	Steel	9.27E-01	Steel, chromium steel 18/8, hot rolled
Flood gate	STS 304	2.19E-01			
Junction box	STS 304	1.18E-01			
Hoist	SSb400	1.16E-01			
Sensor support bracket	STS 304	6.85E-02			
Module frame	STS 316	3.29E-02			
UV module	STS 316	3.29E-02			
Automatic washing equipment	STS 316	2.19E-02			
Shaft	STS 304	1.64E-02			
Support bracket	STS 304	1.37E-02			
Bevel gear	STS 304	1.10E-02			
Inspection window	STS 304	2.74E-03			
UV lamp	UV glass	1.37E-01	Glass	1.37E-01	Glass tube, borosilicate
Lubricant (mL)		1.64E-01		1.64E-01	Lubricating oil
Inspection window	STS 304	2.74E-03	STS 304	2.74E-03	Ethylene bromide

Table 7 Modifications made in the electricity production process by Al-shayji and Aleisa [73]

Fuel type	Amount (g/kWh)
Heavy fuel	2.98E-02
Gas oil (diesel)	8.02E-03
Natural gas	3.52E-02
Crude oil	1.06E-02

The landfilling facility is designed for biogenic waste from the Ecoinvent database version 3.0. It has a design capacity of 1.8 million m^3 volume with a 30-year lifetime. It is equipped with a leachate and landfill gas collection system.

3.5 Life Cycle Impact Assessment

The LCIA phase is conducted according to ReCiPe 2016 (H) V1.03 on the midpoint [74, 75] to determine the adverse effects on the dominant environmental impact categories: climate change (CH) expressed in kg CO_2-eq to air, fossil fuel depletion (FD) in kg oil-eq, metal depletion (MD) in kg Cu-eq, human toxicity (HT) in kg 1,4-DCB-eq to urban air, and particulate matter formation (PM) in kg PM2.5-eq to air; these categories are considered the most critical in irrigation applications, which are the end use of TTE. The results are discussed in terms of both their characterized and normalized values, as are the process contributions and inventory substances with the most environmental impact.

4 Results

This section presents the LCIA results and their interpretation. The LCIA phase was performed according to ReCiPe 2016 (H) V1.03 to determine the adverse effects on the dominant environmental impact categories. Figure 2 shows the network flow chart with a cutoff value of 15%. The arrows present the flows between the processes. The red bars indicate the environmental load generated by each process and its upstream processes [61]. The chart shows that at the WWTP facility, the grid and energy contribute almost equally to the total impact.

Figure 3 shows the characterization results. The x-axis shows the different processes in tertiary water treatment, the y-axis is the percentile comparison of impact within an impact category. The characterized results shown in Fig. 3 and Fig. 4 are the relative environmental impact for each process with respect to midpoint impact categories. Infrastructure has the most significant impact on HT and MD. Generated electricity impacts CH and PM. Normalization enables an absolute comparison among scenarios on the basis of the average human consumption and footprint within each category. Values are measured with a composite single score index indicated as points (pt) as calculated using the ReCiPe (H) method.

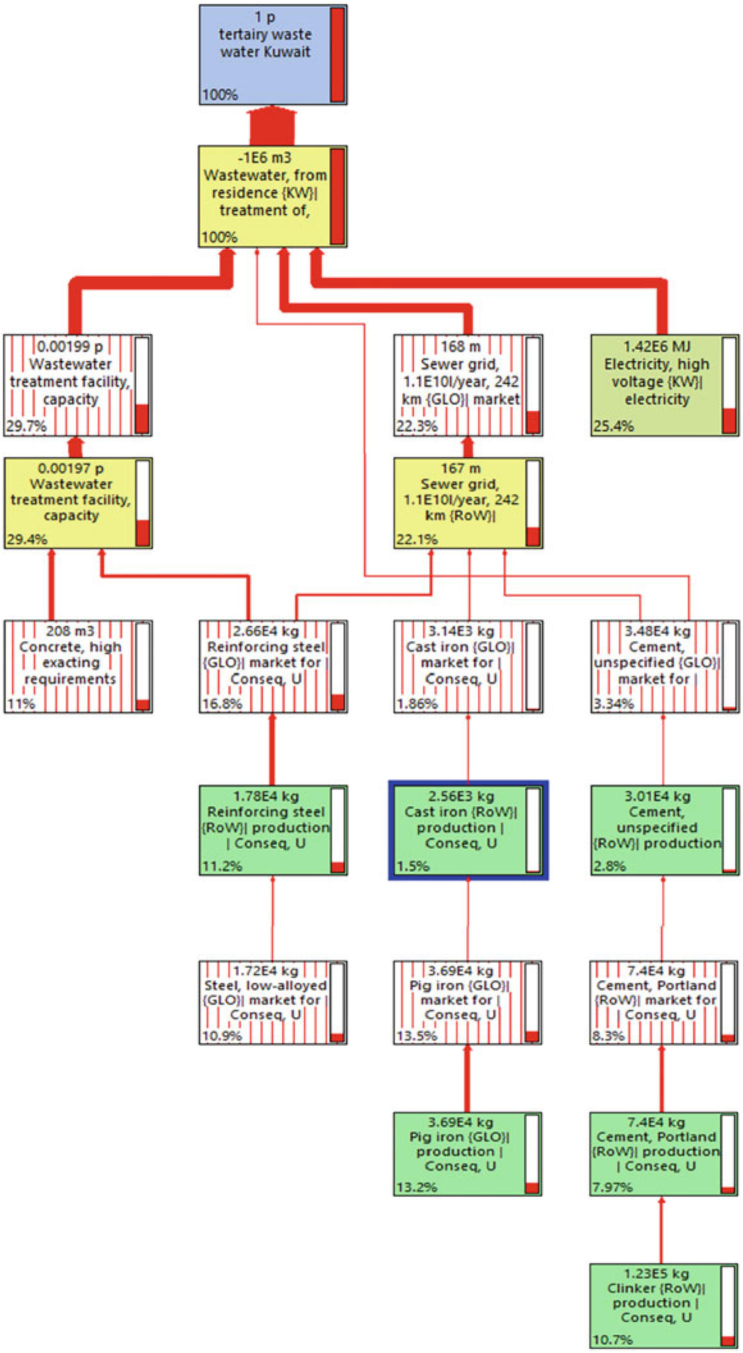

Fig. 2 Process network flow chart with single score results using ReCiPe Midpoint (H) V1.10. The arrow thickness depicts the environmental impact at a 15% cutoff

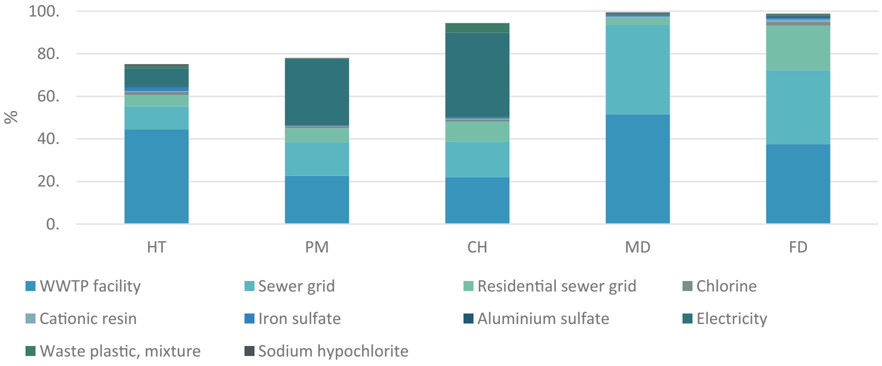

Fig. 3 Characterized results for the production of TTE using ReCiPe Midpoint (H) V1.10

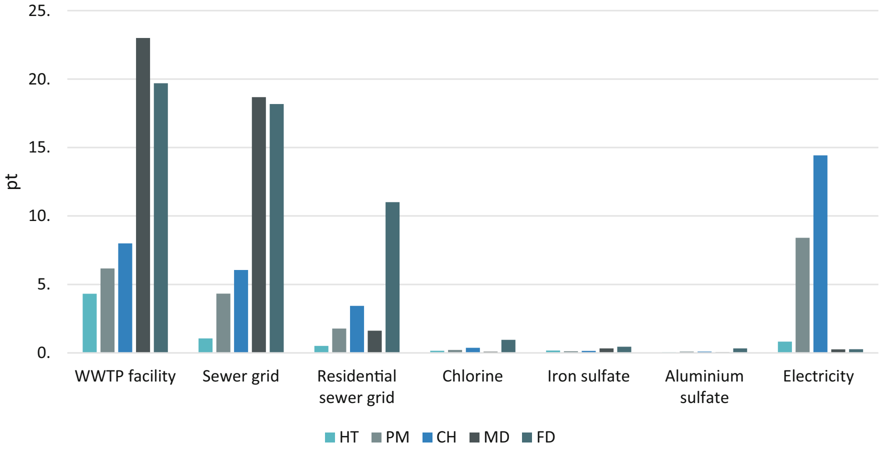

Fig. 4 Normalized results for the production of TTE using ReCiPe Midpoint (H) V1.10

Figure 4 shows the normalized results per impact category. According to ISO 14044 [62], normalization is an optional step that allows the interpretation of the characterized results in terms of relative environmental impacts. Nevertheless, normalization has an important role in providing a relevant representation for decision-making, to support the interpretation of the LCIA results [76]. In Fig. 4, the x-axis represents the different tertiary treatment processes and the y-axis represents the normalized "pt" or point in the Recipe method. As shown in Fig. 4, the categories that are most affected are MD, FD, and CH. The high impact in these categories is due to the high impact of the substances and processes. Substances high in manganese, iron, and nickel affect the MD category, while high coal, oil, and natural gas (NG) substances also affect the FD category. The normalized elementary flows or inventory results represent the significant number of substances that contribute to the impact categories. Using a cutoff of 1%, the five substances with the greatest impact are fossil depletion, carbon dioxide, dinitrogen monoxide fossil, fossil methane, and biogenic methane.

As indicated earlier, MSF remains the dominant water production technology in the GCC [14, 18, 73]. In this study, we applied the thermal energy requirements for MSF from Mezher et al. [6], 80 kWh/m^3. The electrical energy required for MSF was set at 4 kWh/m^3 [77]. The types and amounts of chemical additives per cubic meter of desalinated water were obtained from local desalination plants [78] and are provided in Table 8.

Figure 5 compares the characterized environmental impact of TTE with desalinated water produced using MSF and NG as an energy source using an FU of 1 Mm^3 for irrigation purposes. Comparing the LCIA results of MSF and TTE for the same FU reveals staggering differences in environmental impact in all categories. The

Table 8 MSF chemical additives per cubic meter of desalinated water [18, 78]

Chemical	Formula	Amount g/m^3	LCI materials in Simapro
Sulfuric acid	H_2SO_4	7.33111	Sulfuric acid
Antifoam	$C_3H_8O_2$	4.3124E-01	Propylene glycol, liquid at plant
Anti-corrosion	Na_2SO_3	7.5467	Sulfite, inorganic chemical
Sodium nitrite	$NaNO_2$	1.33E-04	Nitro compounds, regional
Anti-scalant	H_3PO_4	2.52E-04	Phosphoric acid, industrial grade 85% in H_2O
Cleaning	HCl	3.74E-03	Hydrochloric acid (30%) in H_2O
Neutralization: Caustic soda	NaOH	3.01869	Sodium hydroxide 50% in H_2O mix

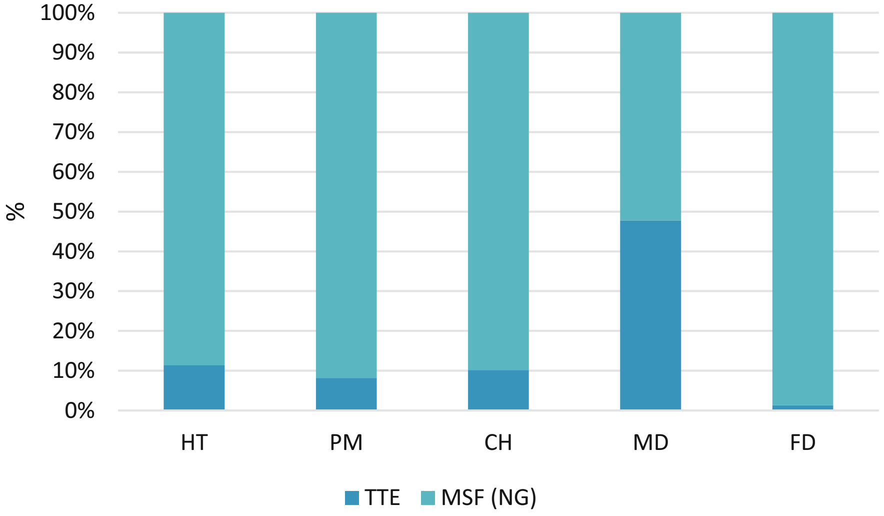

Fig. 5 Characterized results comparing TTE with MSF desalination production using ReCiPe Midpoint (H) V1.10

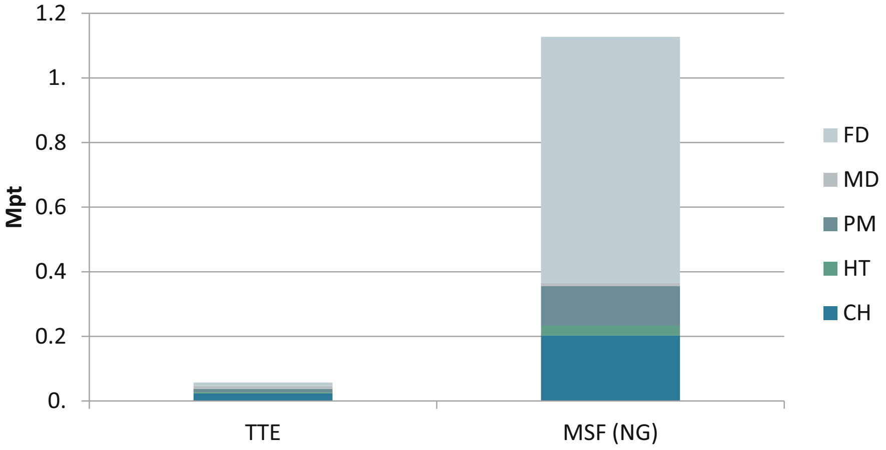

Fig. 6 Normalized results comparing TTE with MSF desalination production using ReCiPe Midpoint (H) V1.10 The y-axis in million normalized points

largest drawback of MSF is its high energy requirement [5, 18, 79], which creates a high environmental burden [4, 80, 81]. Figure 6 shows the normalized LCIA results comparing MSF and TTE water. It is true that the water quality of MSF is generally better than that of TTE; however, MSF is not the best option for landscape or irrigation purposes. The normalized results indicate that MSF has over 70 times the impact on FD, over 10 times the impact on PM, and approximately 8 times the impact on HT and CH compared to the effects of TTE. With respect to MD, the results are similar. Regulations exclude all amenity uses for TTE and restrict agricultural use to safe crops even if its quality exceeds that for potable use [82]. Hence, TTE is utilized for landscaping and fodder irrigation, whereas MSF desalinated water is used for amenities through the municipal network in the GCC. Nonetheless, this approach has led to lost opportunities in the effective utilization of TTE. Research shows that TTE is a better option than MSF for crop irrigation, including irrigation of vegetables and fruits consumed raw. This is because TTE contains essential salts and nutrients that are necessary for plant growth. This saves a proportion of the cost of organic and inorganic fertilizers and chemical compounds that are typically added to maximize crop yield [82].

Despite the severe water scarcity in GCC countries, there is a huge difference between the actual cost of desalinated water production and the imposed tariff. On average, the tariff is no more than 10% of the actual cost [83]. The cost of desalinated water production ranges between 1.1 and 2.0 U.S. $\$/m^3$, except in Bahrain, where the cost is reduced to 0.65 U.S. $\$/m^3$ due to mixing of the less expensive groundwater with desalinated water at a 1:3 ratio [16, 84]. Moreover, the cost of tertiary treated water using filtration and chlorination reaches one-third of that of MSF desalination [22]. Thus, the first step towards meeting the challenge of the water scarcity problem is to reduce governmental water subsidies in the GCC and impose a tariff on WW collection and treatment for all residents. Stepwise cost functions or block rates for the WW volumes generated could encourage consumers to maintain a reasonable water consumption level.

5 Conclusions

The objective of this chapter was to use LCA to evaluate the environmental burden of TTE while adhering to the four stages outlined by ISO 14040/44, including the goal and scope, LCI, and LCIA. The WW generated from residential, governmental, commercial, and public areas is collected and then directed to the target treatment plant via dedicated sewer systems. The scope of the LCA includes assessment of primary, secondary, tertiary treatment and sludge management. The system boundaries are from cradle-to-gate, so all processes, materials, energy requirements, and chemical additives through operation are calculated through field visits, report, or the literature. Electricity generation is modeled by LCA to partially supply requisite power to major WWTPs in the GCC. The FU used is 1 Mm^3 of TTE meeting (not exceeding) the specifications found in local environmental authorities in terms of pH, conductivity, chloride, ammonia, and other specifications. The analyses were contrasted with the conventional MSF seawater desalination. The LCIA phase was conducted according to ReCiPe 2016 (H) V1.03 on the midpoint with respect to CH, FD, MD, HT, and PM. The results were discussed for both characterized and normalized values.

For TTE: Infrastructure has the most significant impact on HT and MD. Generated electricity impacts CH and PM. In normalized values, the categories that were most adversely affected were: MD, FD, and CH. The impact was due to the high manganese, iron, and nickel contribution to the MD category. Oil and NG contributed to FD. The normalized elementary flows indicated that the most significant polluting substances were: carbon dioxide, dinitrogen monoxide fossil, fossil methane, and biogenic methane.

When comparing TTE to MSF, the largest drawback of MSF was its high energy requirements. The normalized results indicated that MSF contributes over 70 times to the FD impact category compared to TTE, over 10 times the impact on PM, and approximately 8 times the impact on HT and CH compared to the effects of TTE. With respect to MD, the results are similar. Regulations exclude all amenity uses for TTE and restrict agricultural use to safe crops even if its quality exceeds that for potable use. Hence, TTE is utilized for landscaping and fodder irrigation, whereas MSF desalinated water is used for amenities through the municipal network in the GCC. Nonetheless, this approach has led to lost opportunities in realizing TTE full potential. The study provides cost and tariff comparison of TTE versus MSF. For MSF, in the GCC, the tariff is no more than 10% of the actual production cost. The cost of desalinated water production ranges between 1.1 and 2.0 U.S. \$/m^3, while the cost of TTE is one-third of MSF. Although WW treatment in the GCC is commendable, the effluent reuse requires additional awareness, supporting legislation and better applied strategies. Policies to promote sustainable water consumption remain by far the most important factor in addressing freshwater scarcity issues in the GCC.

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Cavitation-Based Processes for Water and Wastewater Treatment

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Abstract Cavitation based on advanced oxidation processes (Cav-AOPs) is interesting alternatives for already implemented wastewater treatment technologies. Destructive and strongly undesirable phenomena in the industry, i.e., cavitation, revealed to be useful in a positive manner as a source of energy for chemical reactions. During the implosion of cavitation bubbles, focused energy and resulting high temperature and pressure allows to effectively degrade many chemical compounds present in the cavitated liquid phase. The main reactions taking place in the cavitation zone are the thermal decomposition of chemical moieties as well as oxidation with dissolved oxygen and hydroxyl radicals produced during the implosion of cavitation bubbles. Great interest on this topic is supported by an increased number of publications dedicated to several aspects relating to the formation of cavitation phenomena and its application for water and wastewater treatment as well as hybrid processes based on external oxidants providing effective formation of radical species in cavitation conditions. In this chapter, a state of the art of cavitation-based water treatment technologies, including AOPs, as well as recent trends in this field is discussed. The principles of cavitation combined with AOPs are presented, followed by the evaluation of their effectiveness in the oxidation of organic contaminants. A comparison of hydrodynamic and acoustic cavitation processes for the same type of pollutants has been discussed. For example, the sanitization (disinfection) of water, as well as the degradation of pollutants including sulfide ions and several groups of organic compounds such as sulfur, nitrogen, and oxygen-containing organic compounds, aromatic hydrocarbons, dyes, and pharmaceuticals, has been taken into account while comparing the different cavitation processes.

Keywords Advanced oxidation processes, Cavitation, Ozonation, Persulfates, Radicals, Wastewater treatment

1 Introduction

Cavitation is defined as a phenomenon of formation, growth, and subsequent collapse of microbubbles in extremely short time intervals (milliseconds), which generates large amounts of energy focused in small space. It must also be noted that although energy is released over a very small pocket, cavitation occurs simultaneously in several reactor locations (some indication of the number of cavities in the reactor can be obtained by using theoretical modeling of dynamic bubble equations even if the exact number of cavitation events is difficult to be quantified). Cavitation is generally categorized into four types according to its generation method:

1. Acoustic cavitation: Pressure differences inside the fluid are achieved using sound waves, generally ultrasounds, which relates to a frequency range of 16 kHz to 100 MHz. The chemical modifications resulted from cavitation induced by the passage of sound waves are generally known as sonochemistry [1, 2].
2. Hydrodynamic cavitation: Cavitation is generated by fluctuations in pressure caused by the fluid flow through different system geometry. For example, a restricted aperture, Venturi flow in the pipe, etc., can be used to achieve an interchange of pressure and kinetic energy [3, 4].
3. Optical cavitation: Cavitation is generated by photons of high intensity (laser) light rupturing the fluid [3].
4. Particle cavitation: Cavitation is produced by any other type of beam of elementary particles such as protons, which ruptures a liquid, as in a bubble chamber [3].

Acoustic cavitation and hydrodynamic cavitation are of scientific and industrial interest among the numerous ways of producing cavitation. In the last few years, acoustic cavitation/sonochemistry has been extensively studied. However, despite extensive research, the lack of expertise in various areas such as materials science, acoustics, chemical engineering, and others to scale up the successfully developed in the lab-scale processes, it cannot be said that these solutions are ready for implementation in chemical processing performed at the manufacturing level. Some attempts of the scale upended successfully. Similarly, the cavitation phenomenon can be generated readily and identified in hydraulic machinery involving liquid transportation. The researchers in the field of hydraulics were aware of cavitation and studied the effects of cavitation in hydraulic machinery [5]. There were several attempts made to understand the physiochemical effects of the cavitation phenomenon. Few research groups later explored the distinctive properties, mechanisms, and physical/chemical transformation of materials under the influence of the cavitation phenomenon. Up to now, several studies proved the potential of cavitation technology as an alternative energy-saving tool for various applications like wastewater treatment, process industries, etc. [6, 7].

2 Acoustic Cavitation

Acoustic cavitation is a physical phenomenon in a fluid medium characterized by the growth and collapse of bubbles or cavities under the influence of ultrasounds. Generally, sound waves with frequency ranging from 16 kHz to 100 MHz are used for acoustic cavitation. The ultrasound waves in the liquid medium, causing vibration inside of the liquid, promote the generation of cavities or bubbles. The continuous propagation of ultrasounds leads to the expansion of bubbles, followed by their collapse. The collapse of bubbles under the influence of ultrasound generates several physical effects such as turbulence, shock waves, microjets, etc. Also, the bubble collapse releases extreme energy resulting in a rapid increase in temperature and pressure for a short period named hot spots. It has been observed that under these extreme conditions, highly reactive radicals are generated and used for various applications such as degradation of complex compounds, synthesis of medicines, etc. [1, 2, 8, 9].

2.1 *Optimum Design Parameters for Maximizing the Effects of Acoustic Cavitation*

The important parameters affecting the intensity of collapse and hence the yields from the reactors are:

1. The intensity of irradiation;
2. Frequency of irradiation;
3. Initial radius of the nuclei.

2.1.1 Intensity of Irradiation

The ratio of power introduced to the device and the energy dissipated in the medium is described as the intensity of the ultrasonic equipment. Thus, the intensity of irradiation can be varied by either altering the system power input or by transmission technique where two transducers are placed opposite to each other in the system.

Different types of equipment to induce acoustic cavitation are presented in Fig. 1. In ultrasonic probes (horns), the vibrations are emitted radially in all directions into the solution from the surface of the probe. In ultrasonic bath type systems, the transducers are placed under the bottom of the reactor such that the ultrasound waves are transmitted through the bottom wall of the bath. The equipment with multiple frequency or transducers is supplied to improve the energy dissipation.

The pressure increase created by a collapse of single-cavity reduces with a rise in irradiation intensity. However, certain key points are needed to be considered. Firstly, the positive impacts of cavitation begin to happen at a critical intensity

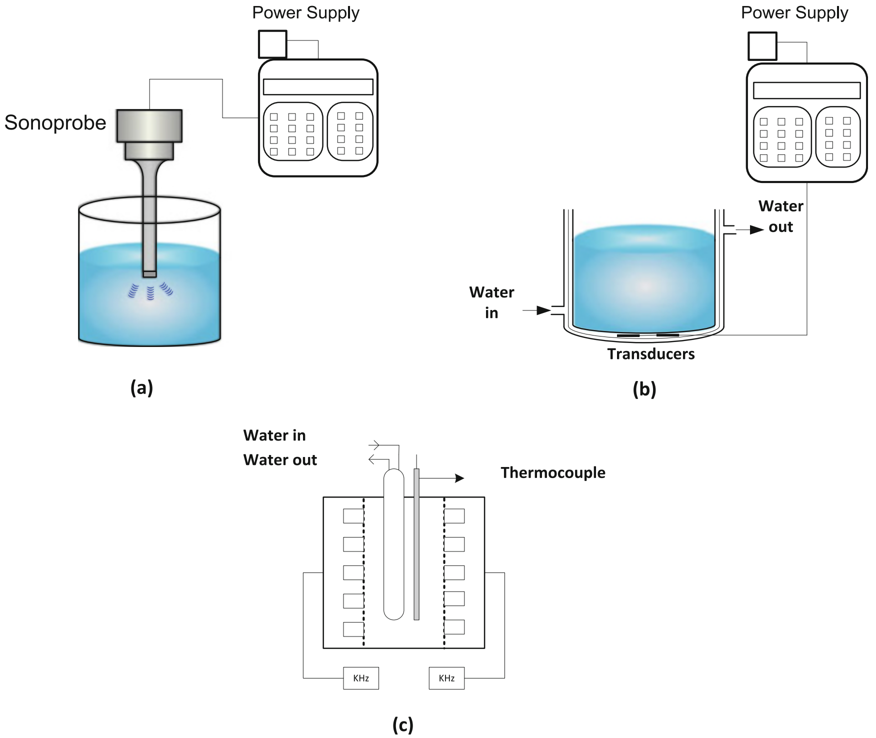

Fig. 1 Various types of sonocavitation reactors (**a**) ultrasound probe, (**b**) ultrasound bath, (**c**) dual-frequency flow cell

(the optimum range of intensity varied from 10 to 300 W/cm^2). It follows the chemical reactions induced by cavitation, which result from the creation of a relatively small amount of free radicals. This amount of free radicals relies on the intensity and amount of cavitation events that, in turn, depend on the intensity of the radiation.

The change in intensity of irradiation plays an essential role in cavitation behavior. This change can be done either by varying the power input to the system or by providing multiple transducers where energy dissipation is increased. If the intensity is increased by raising the system's power input (P/V), there is a rise in the number of cavitation events and an increase in the cumulative pressure pulse (number of produced cavities multiplied by single bubble collapse pressure). In this situation, because of the larger magnitude of the released pressure energy, the degradation rate will be greater. Further increase in energy input enhances the number of cavities causing its coalescence, which results in lowering the degradation rate [10]. At a lower intensity, the change in the transmittance area of ultrasound equipment means that the same energy dissipation happens in a wider area, which results in uniform dispersion, with a greater active region of cavities resulting in increased cavitation output. Thus, the change in transmittance area of ultrasound equipment at lower intensity gives higher cavitational yield. The studies on emulsion characteristics of an oil-water system revealed that, although the power input to the ultrasound bath and horns are virtually identical, bath showed better emulsification effect. In the case of the ultrasound bath, the energy is dispersed over a wider transmission area comparing to the ultrasound horn [11].

It can be inferred that a gain in intensity increases the cavitational effect up to an optimum level. The maximum cavitational yield can be obtained at a lower intensity with a large transmittance area of ultrasound equipment. Campbell and Hoffmann [12] observed that there is a deviation from the increasing trend of cavitational effect when the intensity is increased beyond the optimum value of 250 W/L. At higher intensity, the decreasing effect was attributed to the loss of energy in the form of heat, as well as the increase in bubble coalescence, which ends in a lower intensity of bubble collapse, lowered mass transport, and reaction kinetics.

2.1.2 Frequency of Irradiation

The produced collapse pressure has already been shown to increase with a rise of radiation intensity in the frequency range typically studied (20–200 kHz frequently observed in ultrasonic applications) using theoretical simulations of Rayleigh–Plesset equations governing the bubble dynamics [13, 14]. Higher irradiation frequencies will, therefore, be preferred in the wastewater treatment systems to degrade chemical pollutants [15]. The enhanced sonochemical effects at higher frequencies can be attributed to reduced cavity dimensions (also leading to greater pressure effects during bubble collapse) and the greater region to volume ratio (improved spreading and mass transfer of liquid-phase reactants to vapor phase when pyrolytic degradation occurs). Moreover, at a higher frequency, the generated bubbles go through fewer acoustic cycles before reaching the required resonant dimension for collapse. Therefore, more bubbles at higher frequencies promote diffusion at a faster rate before a transient bubble collapse takes place. The frequency of ultrasound equipment cannot be changed over a variety of ranges since the transducer gives the highest transmission effectiveness at its resonating frequency. The range of frequencies usually used for physical effects is between 20 and 200 kHz, while greater frequencies are still used effectively for some cases.

The liquid inside the reactor is irradiated by immersion type transducer (ultrasound probe/sonotrode/horn) or the transducers placed at the bottom (ultrasound bath). The active regions under the influence of ultrasound waves are localized mostly near the surface of the transducer. To overcome these limitations, two or more transducers with similar or different frequencies are used. Transducers are mostly used in series of few to several pieces localized in a line parallel to the axis of the reaction chamber (often localized vice-versa on both sides of reaction chamber) – but sometimes also other geometries of transducers placing are used. In the case of the immersion type transducer, the irradiation is strongly localized in the place of sonotrode immersion. The irradiation intensity decreases along with the distance of sonotrode.

In the ultrasound reactor, there is a possibility of acoustic standing waves formation with consecutive positive and negative pressure phases from the different medium interface or reflection of waves from the reactor wall [16]. Due to the standing waves, big bubbles tend to coalesce, and thus, the energy is not evenly dissipated, leading to a reduction in reactor efficiency [17]. To overcome these limitations, the use of a dual-frequency processor or a parallel plate ultrasonic processor is a viable alternative. The attenuation of the sound would be decreased when the plates are positioned close together and result in the interference pattern of waves, minimizing standing waves and improving the cavitational process. The use of multiple frequency acoustic cavitation showed a fourfold increase in cavitational yield when compared with the single frequency. These multiple frequency modes (dual-frequency (17 kHz + 33 kHz)) has been employed in the treatment of large volume of wastewater (about 50 L) containing bacteria subtilis (concentration of approximately 10^4 CFU/mL) resulted in 85.25% efficiency (to reduce bacteria contamination) of treatment in 30 min while the single frequency mode (33 kHz) gave only 30.26% [18].

2.1.3 Initial Size of the Nuclei

The growth and collapse of bubbles from small-sized nuclei are more intense. Therefore, the reduction of the initial bubble size promotes a better cavitation effect. The physical properties such as viscosity, surface tension, and vapor pressure of the fluid influence the behavioral characteristics of bubbles produced [19, 20]. The threshold pressure required for bubble collapse increases with the increase in viscosity due to cohesive forces. Thus, the liquid medium with lower viscosity promotes a better cavitation effect. The use of a high vapor pressure medium instantly increases the vapor content inside the bubble, which results in a lesser cavitation effect due to the condensation process. Hence, liquid medium with low vapor pressure is preferred for higher bubble collapse intensity, which will lead to a higher cavitation effect. The surface tension of the liquid medium is directly proportional to the bubble formation and collapse pressure intensity because higher surface tension medium increases bubble contraction. The bubble collapse causes extremely high-pressure increase near the place of collapse; therefore, high surface tension media give higher preference when cavitation is used for treatment applications like disinfection of bacteria, milk process, etc. [21].

3 Hydrodynamic Cavitation

Hydrodynamic cavitation is a rapid transformation in the liquid when the liquid passes through a constriction such as a Venturi tube or orifice. In the place of constriction, the linear velocity of the liquid significantly increases at the cost of pressure drop – often below the vapor pressure of the liquid– leading to the formation of cavitation bubbles [22]. After the constriction, the diameter of the tubing gets back to normal value, the linear velocity of the liquid falls, and the static pressure recovers, which results in the collapse of the cavities. Turbulence intensity in the cavitation and collapse zones has a high impact on the intensity of cavitation. Thus, by varying the geometric and operating conditions of the reactor, the cavitation intensity is optimized concerning the degradation effects of target pollutants present in the treated medium.

To link flow conditions with the strength of cavitation, a dimensionless number, known as cavitation number (C_v), is used (Eq. 1):

$$C_\mathrm{v} = \frac{P_2 - P_\mathrm{v}}{\frac{1}{2}\,\rho v^2} \tag{1}$$

where P_2 is the fully recovered downstream pressure, P_v is the vapor pressure of the liquid/medium, ρ is the liquid density, and v is the velocity of the liquid at the throat of the constriction [8].

Ideally, the initiation of cavitation happens at $C_\mathrm{v} = 1$, and important cavitation impacts occur at C_v values below 1. When C_v reaches zero value, supercavitation takes place. At this condition, a cavitation cloud is formed, which strongly minimizes the effect of the bubbles collapse due to the coalescence of the bubbles.

The major advantages of hydrodynamic cavitation are as follows:

1. Reactions that require moderately rigorous conditions can be carried out under the surrounding conditions, which is the main benefit of the hydrodynamic cavitation.
2. It is the cheapest and most energy-efficient method of a cavitation generation.
3. The construction of cavitational equipment is relatively simple.
4. Such reactors are easy and cheap in maintenance.
5. It is relatively simple to scale up such processes.

It should be noted that, in terms of temperature and pressure, hydrodynamic cavitation provides a significantly lower intensity of collapse than acoustic cavitation. However, the simplicity and potential for implementation of hydrodynamic cavitation in the industry make it of high interest in scientific work as well as real scenario applications.

3.1 Optimum Design Parameters for Hydrodynamic Cavitation

Three aspects are commonly included in the studies for a full understanding of the hydrodynamic phenomenon:

1. Cavitation number.
2. Physicochemical properties of the liquid and initial size of the nuclei.
3. Type of cavitating reactor and its design details.

In terms of bubble collapse, pressure based upon numerical simulation using bubble dynamics equations and studies in separate reactors, the impact of the multiple design parameters listed above is widely examined. It is worth noting that there has been thorough research about the impacts of multiple design parameters on the efficiency of hydrodynamic cavitation-reactors, and only guidance on the selection of a certain parameter has been provided with fundamental discussions.

3.1.1 Cavitation Number

Cavitation number is one of the most important parameters for measuring the efficiency of the cavitation treatment process. This parameter is mutually interrelated with system inlet pressure. The required pressure on the fluid induces velocity via the cavitation system. With the increasing operating pressures, the flow velocity is increased across the throat, and the number of cavitation is decreased. The lower cavitation number generates more cavities as a result of high-pressure input, resulting in more hydroxyl radicals helping in maximum degradation of the pollutant compound. Many research studies found that the cavitation number ranging from 0.14 to 0.29 with operating inlet pressure 3–5 bar gave maximum efficiency in treatment processes [23].

3.1.2 Physicochemical Properties of the Liquid and Initial Size of the Nuclei

Similar to acoustic cavitation, the degradation process of hydrodynamic cavitation can be influenced by physicochemical properties of the aqueous medium such as liquid vapor pressure, density, viscosity, surface tension, dissolved gas in the liquid, etc. Cavitation takes place in a liquid medium when the cohesive forces are overcome. Thus, liquids with high viscosity have a much lower cavitational effect than liquids with low viscosity. As a result, the maximum cavitation effect can be achieved in liquids with low viscosity, such as water. For non-Newtonian fluids, the effect of viscosity on cavitation effectiveness is even more pronounced. The vapor pressure of the liquid medium also affects the efficiency of the cavitation. The production of cavities increases with the increase in the vapor pressure of the liquid medium. The cavities produced from high vapor pressure medium have lower cavitational intensity, which can efficiently degrade only simple organic compounds. While the lower vapor pressure medium generates cavities with a higher cavitational intensity, which is needed to degrade persistent organic compounds efficiently. The liquid medium with high surface tension has the most powerful cavitational effect (relating to the energy of bubble collapse). The nature of the contaminant molecule in the liquid medium also influences the efficiency of degradation with hydrodynamic cavitation. When the pollutant molecules are hydrophobic, they diffuse to the gas–water interface; thus, they are near the collapse of cavities. This results in the direct attack of $^{\bullet}$OH radicals formed during bubble collapse and thus increases the degradation efficiency. If the pollutant molecules are hydrophilic, the molecules remain in the liquid medium and are not affected by the cavities collapse. The radical species need some time to reach these compounds.

3.1.3 Type of Cavitating Reactor

Hydrodynamic cavitation can be generated when the liquid is passed through a constriction. The kinetic energy and velocity of the liquid passing through a constriction increase. At the same time, the static pressure falls to fulfill the Bernoulli equation. Cavitation occurs when the static pressure becomes lower than the vapor pressure of the liquid. Simply, it could be said that under this condition, "the liquid starts to boil." The phenomenon of cavitation generation can take place at an orifice plate, in the throat of the Venturi tube, as well as near the surface of the high-speed rotor or high-speed homogenizer. Orifice and Venturi-based systems are efficient in generating cavitation for chemical reactions. Among orifice and Venturi, the cavitation generation is stable in Venturi-based hydrodynamic cavitation (HC) devices and, therefore, is mostly preferred for water treatment applications. The different types of Venturi-based and orifice-based HC devices are presented in Figs. 2 and 3.

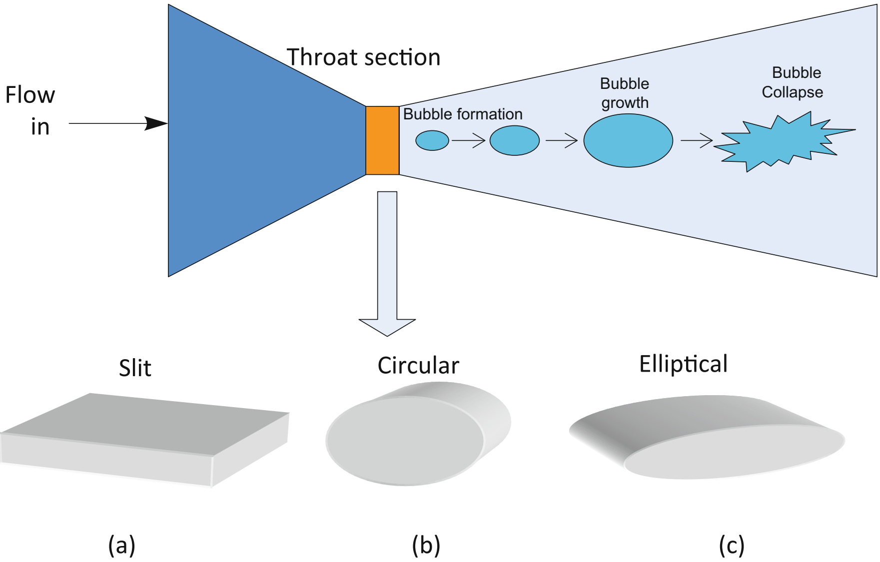

Fig. 2 Venturi-based cavitating device (**a**) slit Venturi, (**b**) circular Venturi, (**c**) elliptical Venturi

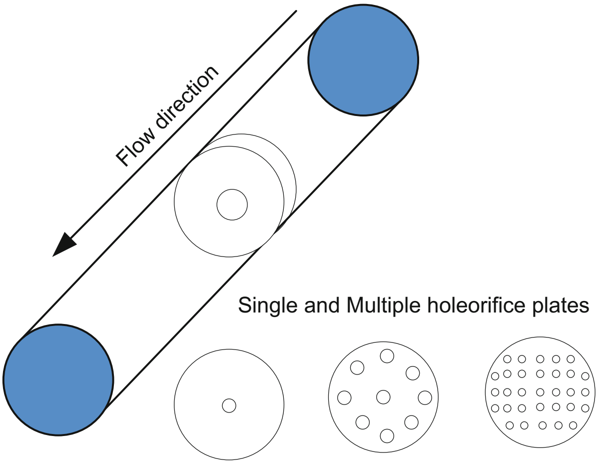

Fig. 3 Different types of orifice-based HC device

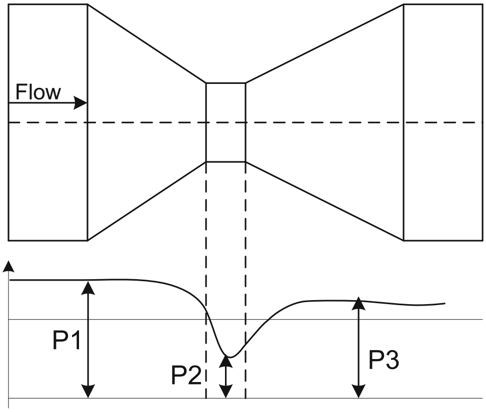

Fig. 4 Scheme of static pressure profile in the Venturi – P1 pressure before, P2 pressure at the throat, P3 – pressure after the throat

The constriction can have a form of a throat (Venturi system, it can have a circular shape or other like elliptical or a slit type), i.e., a short length of Venturi, between the convergence and divergence sections, having much smaller diameter compared to the diameter of the inlet and outlet of the Venturi. In the case of the orifice, a plate placed inside of the orifice has one or mole holes having a small diameter. In each system (throat or orifice), the small internal diameter region is responsible to “speed up” the liquid to a liner velocity allowing to (according to Bernoulli equation) obtain an effective increase of dynamic pressure and a corresponding decrease of static pressure causing the formation of cavitation bubbles (Eq. 1 – cavitation number below 1 and – value P_2) Fig. 4.

A schematic arrangement of the hydrodynamic cavitation reactor is illustrated in Fig. 5 where a Venturi tube is used to generate a cavitation effect. The set-up consists of a closed circuit with a storage tank, a pump, and a cavitating device (Venturi tube). The pump discharge is divided into 2 sections. The primary first line consists

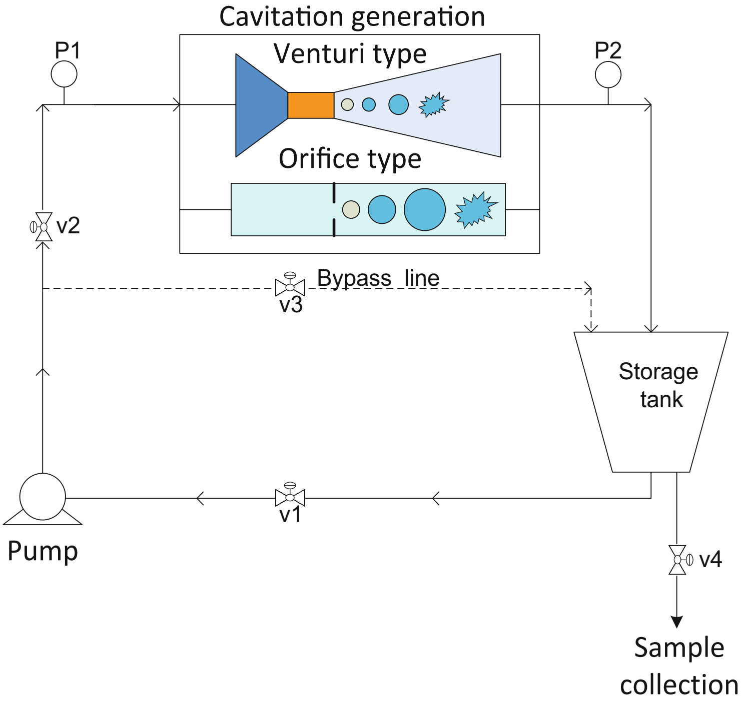

Fig. 5 Schematic representation of hydrodynamic cavitation reactor set-up

of a Venturi or orifice (cavitating device). The pressure gauge (P1) is mounted near the inlet of the Venturi or orifice, another one (P2) is attached to the outlet or discharge line from the Venturi or orifice. The fluid flow rate through the cavitation device is regulated by the pump total flow rate and a bypass line. The bypass line allows the use of optimal rotation speed of the pump and to split the stream to the desired flow rate into the cavitation system, and the remaining volume passed through the bypass. The flow rate through the mainline is regulated at the appropriate places using regulation valves. The application of the bypass is used mainly for research purposes. It allows using one pump with the regulator of the flow rate, which along with the bypass line, allows optimizing the cavitation conditions with respect to cavitation number (affected directly by the volumetric flow rate by the resulting linear velocity through the constriction). The flow rate splitting is not economically feasible; thus, it is not used in industrial practice. Furthermore, this feature should be included in economic analysis performed in research papers for adequate calculation of energy demand for optimized cavitation numbers.

4 Cavitation-Based Advanced Oxidation Processes (Cav-AOPs)

4.1 Formation of Radical Species Under Cavitation Conditions

The energy associated with physical phenomena can be used for intensification of chemical processes, which helps in developing novel solutions in various industries. Thus, the energy released during the cavitation phenomenon can be used to accelerate the formation of reactive radicals used in advanced oxidation processes (AOPs). AOPs have shown significant potential in the removal of organic pollutants over the past few decades. AOPs are defined as a class of techniques involving strong oxidizing species such as hydroxyl radicals ($HO^{\bullet}$) to degrade the pollutants. Having a high capability for destruction of pollutants, $HO^{\bullet}$ are generated and used in a majority of AOPs. Various types of AOPs were explored to decompose or mineralize even the refractory organic molecules which possess recalcitrance to be conventional and biological water treatment technologies. As effective treatment technologies, AOPs can be applied as a single treatment process or incorporated into conventional treatment schemes depending on properties of the pollutant, wastewater origin, water matrix, pH, etc. Despite the high efficiency demonstrated in lab-scale experiments, AOPs found limited use in industrial-scale, mainly due to the high cost of the treatments as well as maintenance [24].

This effect of cavitation is often used in effluent treatment technologies because it ensures the disruption of bacterial cultures, decomposition of persistent organic compounds, and dissociation of water molecules into a variety of radical species, including $H^{\bullet}$, $HO^{\bullet}$, $HO_2^{\bullet -}$, $HOO^{\bullet}$ [3, 25]. The generated radicals are extremely unstable and reactive due to their high redox potential. The reaction between organic contaminants and these reactive radicals is extremely fast and non-selective, mainly controlled by the production yield of radicals and mass transfer processes between radicals and pollutants. According to recent reports, cavitation is effective in the degradation of organic pollutants present in a variety of water matrices such as tap water, groundwater, and industrial effluents. When applied individually, cavitation was often reported to give a low rate of degradation, which ranges from 20 to 50%. Comparably, high degradation rates were obtained when cavitation was combined with hydrogen peroxide, ozone, and/or peroxone, often leading to 100% removal efficiency [3].

4.2 Effect of External Oxidants – Oxygen, Ozone, Hydrogen Peroxide, Persulfates: Hybrid Processes

A combination of cavitation with an AOP is a physicochemical technique, recently adopted for wastewater treatments. As a hybrid water treatment technique, the combination of cavitational methods with various AOPs has been reported in the literature for the degradation of many organic pollutants [25–27]. Obtained results indicated a considerable increase in degradation rates of pollutants, which was attributed to the intensification of the production of radicals and their facilitated diffusion into the liquid. It is widely recognized that the enhancement is a result of synergism between cavitation and AOP due to the similarity in the mechanism of pollutant degradation and jointly overcome drawbacks [28]. To measure the improvement obtained in the hybrid technique, the index of synergy (ε) can be calculated using Eq. 2. Its value indicates the degree of synergism between the combined techniques in the observed experiment or its absence if the calculated value of the synergy index is below 1.

$$\varepsilon = \frac{k_{\mathrm{Cav/AOPs}}}{k_{\mathrm{Cav}} + k_{\mathrm{AOPs}}} \tag{2}$$

Typical hybrid approaches include hydrodynamic and acoustic cavitation at optimum operational conditions coupled with AOPs based on external oxidants, UV irradiation, photocatalysis, electrochemical oxidation, and Fenton's reaction. Most of the typically used external oxidants (oxygen, ozone, hydrogen peroxide, persulfate) were already tested in Cav-AOPs.

4.2.1 Hybrid Processes Based on Ozone and Cavitation Phenomenon

Appreciable insights on the decomposition of methyl tert-butyl ether have been gained by acoustic cavitation in the presence of ozone [29]. In this study, the combination of ozone (0.30 mM) with ultrasonic irradiation (205 kHz, 200 W) compared to sole ultrasonic treatment increased the observed first-order rate constant of methyl tert-butyl ether from 8.5×10^{-4} to $33.2 \times 10^{-4}\ \mathrm{s}^{-1}$. It was concluded that the increase in kinetic rates was caused by enhanced direct reaction of the substrate with ozone at the cavitational bubble interface or due to indirect reactions with ozone decomposition products. Further studies of the ozone effect on the formation rate of hydrogen peroxide provided a more plausible explanation for the observed reactions [29]. Thus, in the coupled process of ozone and ultrasound, ozone molecules were proposed to undergo thermal decomposition in the gas phase of the cavitational bubble to yield molecular and atomic oxygen. A wide variety of radical reactions may occur initiated by an unstable oxygen atom, including the formation of hydroxyl radicals ($HO^{\bullet}$) [3]:

$$\mathrm{O_3} \overset{\text{Cavitation}}{\rightarrow} \mathrm{O_2} + \mathrm{O}\left({}^3\mathrm{P}\right) \tag{3}$$

$$\mathrm{O}\left({}^3\mathrm{P}\right) + \mathrm{H_2O} \rightarrow 2\mathrm{HO}^{\bullet} \tag{4}$$

At the interfacial zone, ozone reacts with hydroxide ion HO^- and the conjugate base of H_2O_2 ($HO_2{}^-$) to generate hydroperoxyl ($HO_2{}^\bullet$) and hydroxyl radical ($HO^\bullet$) in accordance of reactions (5) and (6).

$$O_3 + HO^- \rightarrow HO_2^- + O_2 \tag{5}$$

$$O_3 + HO_2^- \rightarrow HO_2^{\cdot} + O_3^- \tag{6}$$

$HO_2{}^-$ can be formed not only as a product of the reaction between ozone and $HO^\bullet$ but also as a result of H_2O_2 disassociation (reaction (7)):

$$H_2O_2 \overset{pKa=11.8}{\rightarrow} HO_2^- + H^+ \tag{7}$$

Substantial enhancement in the degradation of methyl tert-butyl ether was achieved by the combined process of ozonation plus ultrasound compared to the sole use of ozonation or ultrasound. The enhanced degradation was attributed to the significant contribution of the direct reaction of ozone with the pollutant. This reaction is almost negligible at ambient conditions but accelerated due to zones of high temperature at the interfacial regions of the cavitational bubbles and can be illustrated as follows:

$$\text{Substrate} + O_3 \overset{\Delta}{\rightarrow} \text{Products} + H_2O_2 \tag{8}$$

During the ozonation-ultrasound process, H_2O_2 was reported to play a crucial role. Being readily formed by sonolysis of water, it also reacts with ozone (reaction (9)) contributing to the overall removal of pollutants:

$$O_3 + H_2O_2 \rightarrow HO^\bullet + HO_2^\bullet + O_2 \tag{9}$$

Reaction (9) initiates a chain of radical reactions, which leads to the decomposition of ozone and the formation of reactive radicals ($HO^{\cdot}HO_2^{\cdot}$). On the other hand, the accumulation of H_2O_2 quenches radical species, thus terminating the radical chain reactions. The combination of reactive radicals to form stable products could be considered as chain-termination reactions (e.g., Eqs. 10 and 11):

$$HO_2^\bullet + HO^\bullet \rightarrow H_2O + O_2 \tag{10}$$

$$HO^\bullet + HO^\bullet \rightarrow H_2O_2 \tag{11}$$

Similarly, the higher removal efficiency of organic contaminants has been reported for ozonation, coupled with hydrodynamic cavitation [30]. Enhancement of mass transfer of ozone along with the accelerated formation of $HO^\bullet$ and atomic oxygen induced by cavitation was highlighted as the main advantages of the coupled process. The mineralization degree of reactive orange 4 dye was significantly increased when hydrodynamic cavitation was coupled with ozonation. TOC removal of 14.67% was obtained in the sole hydrodynamic cavitation process, which increased to 76.25% by combining ozone with hydrodynamic cavitation [30]. The synergy index of 3.03 was estimated based on the mineralization rate and indicates that the hybrid process of hydrodynamic cavitation with ozone is better as compared to individual processes [30]. Similar observations were made for the degradation of methyl tert-butyl ether by ultrasound coupled with ozonation and phenol under suction-cavitation in the presence of ozone using orifice as cavitation unit [29, 31]. Studies on the degradation of triazophos revealed the superiority in the effectiveness of ozonation combined with hydrodynamic cavitation over ozonation alone. The Pseudo-first order rate constant of 41.3×10^{-3} min^{-1} observed in ozonation alone was increased to 58.26×10^{-3} min^{-1} for the combined process. TOC removal of 96% was achieved in 60 min when ozone loading of 1.95 g/h was injected directly into the solution tank. The introduction of ozone into the solution tank instead of at orifice improved the degradation rate of triazophos by 8%. This was attributed to the effect of a drop-in inlet pressure of the medium before the orifice plate resulting from the introduction of ozone and thus the limitation of the cavitation phenomenon. At the same time, amounts of oxidants in the system become limited due to decreased solubility of ozone and oxygen caused by the lowered pressure. The introduction of ozone at the orifice plate dropped the flow rate of water from 290 to 120 L/h at 5 bar pressure. A lowered flow rate leads to a decrease in the number of passes of the liquid in the reactor, thus affecting the dissociation of water and ozone-producing reactive radical species [32].

Another example of the application of the ozonation, coupled with hydrodynamic cavitation, is the treatment of organic pollutants present in the effluents from bitumen production. Oxygenated organic compounds such as 1-propanal, 2-pentanone, furfural, 1-hexanol, phenol, m-cresol present in the complex composition of real industrial effluent were almost completely degraded by hydrodynamic cavitation aided with ozone after 180 min of treatment. Studies on COD and BOD profiles of the effluent revealed a 40% and 50% reduction of these parameters describing changes in total pollutants load – which in terms of industrial, highly polluted effluents confirms the applicability of this technology for effective pretreatment of such effluents before biological treatment stage [27]. Ozonation combined with hydrodynamic cavitation was suggested as a potentially effective approach to lower the content of toxic organic compounds, especially phenols, its derivatives, as well as other oxygen-containing compounds that are known to be toxic to activated sludge used in biological treatment of refinery effluents. Furthermore, this process is sufficient to simultaneously decolorize, disinfect, and reduce malodorousness of the effluent.

4.2.2 Hybrid Processes Based on Hydrogen Peroxide and Cavitation Phenomenon

The aqueous solution of hydrogen peroxide is an effective and green oxidizing agent commonly used in various technologies. Having $\mathrm{p}K\mathrm{a} = 11.69$, hydrogen peroxide is considered a weak acid, and its properties strongly depend on the pH value of the reaction medium. At acidic conditions, hydrogen peroxide shows an oxidation potential of 1.80 V, while this value drops to 0.87 V at pH 14. Under alkaline conditions, reactions with hydroxyl ions induce an increasing tendency of decomposition of H_2O_2 resulting in the formation of per hydroxyl anion and water (Eq. 12) [33]:

$$H_2O_2 + HO^- \overset{pH>7}{\rightarrow} HO_2^- + H_2O \tag{12}$$

Low stability of H_2O_2 in alkaline media is the main disadvantage, which limits its practical use as a sole oxidizing agent. As a sole oxidant, H_2O_2 is used in industrial processes involving direct oxidation of carboxylic acids, polycyclic aromatic hydrocarbons, and haloalkenes at acidic conditions. Extreme conditions of collapsing gas bubbles during hydrodynamic and acoustic cavitation, lead to the thermal dissociation of H_2O_2 into $HO^\bullet$, which is capable of decomposing a wide range of organic contaminants in water and wastewater:

$$H_2O_2 \overset{Cavitation}{\rightarrow} 2HO^\bullet \tag{13}$$

Once generated, $HO^\bullet$ initiate radical chain reactions and amplify oxidation of organic contaminants, which are reduced or degraded completely. Despite numerous studies, the detailed mechanism of oxidation reactions has not yet been fully elucidated. Nevertheless, it has been established that the oxidation of halogenated organic compounds involves abstraction of halogen atom followed by the addition of oxygen to the formed organic radical. This step results in the formation of the corresponding intermediates, such as aldehydes, ketones, carboxylic acids, etc., which are subsequently converted to CO_2, H_2O, and halogen anions in the final step.

Both hydrodynamic (HC) and acoustic cavitation (AC), in combination with H_2O_2, showed an enhanced degradation efficiency for a variety of pollutants. The improvement in the degradation efficiency was concluded as a result of the intensification of $HO^\bullet$ production in treated medium [3, 34, 35]. For example, organosulfur compounds (2-ethylthiophene, dibutyl sulfide, di-tert butyl sulfide) were degraded above 80% under HC induced by Venturi tube ($C_v = 0.14$, inlet pressure 8 bar). Phenol and its derivatives (4-ethylphenol, m-cresol, o-cresol) were completely degraded in 360 min [3]. After 180 min of the treatment, the lowest oxidation degree was observed for 2-nitrophenol (66.9% – AC + H_2O_2, 62.9% – HC + H_2O_2). In this case, the lower degradation rate was attributed to the formation of intermediate products, which compete for $HO^\bullet$ due to its non-selective nature. Comparable results in degradation of 2-nitrophenol were obtained by AC + H_2O_2 under acidic conditions (59% in 90 min at pH 3.7, $C_0 = 1\%$, $V = 7$ L, $T = 28°C$, $[H_2O_2] = 5$ g L^{-1}, AC = 25 kHz, 1 W). Complete degradation of imidacloprid was obtained for hydrodynamic cavitation aided with H_2O_2 in 120 min in acidic media (pH 3, $C_0 = 20$ ppm, $V = 4$ L, $T = 34°C$, $[H_2O_2] = 80$ ppm, inlet pressure = 4 bar, $C_v = 0.37$). When comparing two different cavitating devices (hydrodynamic and acoustic) aided with H_2O_2 in terms of the degradation efficiency, an improvement of 5–10% was observed for hydrodynamic cavitation. It was suggested that the reactor of hydrodynamic cavitation with a cavitation number of 0.14 possesses a higher cavitation intensity and provides a longer residence time in the cavitational zone, increasing the probability of the reaction with $HO^{\bullet}$ comparing to an acoustic cavitation system based on 25 kHz frequency ultrasonic transducers. According to these results, both cavitation techniques, in combination with H_2O_2, can effectively be used in the degradation of organic contaminants in a wider pH range.

Decomposition of diclofenac sodium using hybrid processes based on hydrodynamic cavitation and hydrogen peroxide has been reported by [36]. It was combined with the addition of catalyst (TiO_2). Effect of inlet fluid pressure (2–4 bar), initial pH of the solution (2–7.5) as well as TiO_2 and H_2O_2 loadings were studied to optimize the operating conditions. The maximum extent of degradation of diclofenac sodium achieved by sole hydrodynamic cavitation was 26.85 at an optimized inlet pressure of 3 bar and pH of 4. Hybrid processes of hydrodynamic cavitation with UV, UV/TiO_2, and $UV/TiO_2/H_2O_2$ resulted in enhanced degradation as compared to individual processes. 95% degradation and 76% TOC removal have been observed when hydrodynamic cavitation was coupled with $UV/TiO_2/H_2O_2$ at optimal conditions. In this case, the synergy index was estimated to be 2.5.

Studies on the degradation of 2,4-dinitrophenol revealed higher removal efficiency for a homogeneous Fenton process coupled with HC rather than Fenton-like processes coupled with HC. Thus, underestimated optimal conditions, conventional Fenton process ($[H_2O_2] = 0.3$ g/L, $[FeSO_4] = 0.6$ g/L) in combination with hydrodynamic cavitation gave complete degradation of 2,4-dinitrophenol in 60 min, whereas Fenton ($[H_2O_2] = 0.4$ g/L, $[Fe] = 0.6$ g/L) resulted in 54.1% of degradation in 120 min. The Fenton-like process, with a loading ratio of H_2O_2: CuO (1:6), achieved 29.8% in 120 min [37]. These processes have demonstrated greater efficiency than the sum of individual efficiencies that could be achieved with a separate treatment – which proved the synergism of the combined processes.

4.2.3 Hybrid Processes Based on Peroxone and Cavitation Phenomenon

The combination of H_2O_2 with O_3 is a type of AOP with a high oxidation capacity and is named as peroxone. The reaction of H_2O_2 with O_3 gives rise to a large number of $HO^{\bullet}$, responsible species for the degradation of organic contaminants present in wastewaters. The superior activity of the peroxone process over ozonation was demonstrated for the degradation of refractory organic compounds. An increase in $HO^{\bullet}$ concentration in the reaction system was suggested as the main factor of the improvement, which was induced by accelerated decomposition of O_3 in the presence of H_2O_2 [25]. The mechanism of reactive radicals ($HO^{\bullet}$ and $HO_2^{\bullet}$) formation during the peroxone process involves decomposition of O_3 via electron transfer with H_2O_2 or activation of H_2O_2 at alkaline conditions. The resulted $HO^{\bullet}$ and $HO_2^{\bullet}$ are capable of oxidizing practically every contaminant present in the treated medium.

The reactions generating reactive radicals during peroxone process can be summarized as follows [23]:

$$H_2O_2 + O_3 \overset{\text{Cavitation}}{\rightarrow} HO^{\bullet} + HO_2^{\bullet} + O_2 \tag{14}$$

$$HO^{\bullet} + O_3 \overset{\text{Cavitation}}{\rightarrow} HO_2^{\bullet} + O_2 \tag{15}$$

$$HO_2 + O_3 \overset{\text{Cavitation}}{\rightarrow} HO^{\bullet} + 2O_2 \tag{16}$$

It was reported that H_2O_2 transforms into ionized form (HO_2^-, p$Ka = 11.6$), which rapidly reacts with ozone yielding $HO^{\bullet}$ according to the following reaction [38]:

$$O_3 + HO_2^- \rightarrow HO^{\bullet} + O_2 + O_2^- \tag{17}$$

This reaction is significantly intensified at high pH values and increases $HO^{\bullet}$ concentration, thereby increasing the efficacy of the process. Favorable contribution of basic pH on the removal of various pollutants by cavitation/peroxone system has been widely reported. For instance, carbon disulfide (CS_2), dimethyl sulfide (C_2H_6S), and di-*tert*-butyl-disulfide (t-Bu_2S_2) were effectively removed from the effluent of bitumen production by HC and AC combined with peroxone process at strongly alkaline pH [26]. Complete degradation of CS_2, C_2H_6S, t-Bu_2S_2 by the combined operation of hydrodynamic cavitation ($C_v = 0.14$) with peroxone was achieved in 30 min, while the sole use of HC took 120 min to reach the same degradation rate. Similar trends in the degradation of the target organosulfur compounds were observed during acoustic cavitation (173 W/L, 25 kHz) with peroxone. Based on oxidation rates, the system of AC + peroxone was found faster than HC + peroxone in the degradation of t-Bu_2S_2, as the sonic energy is effective in breaking down and oxidation of this contaminant. Both techniques demonstrated the rapid removal of sulfide ions and organosulfur contaminants from the caustic industrial effluent without pH adjustment. COD reduction results of the post-oxidative effluent showed no significant difference between hydrodynamic and acoustic cavitation in combination with peroxone. Thus, 51 and 59% of COD removal were obtained for acoustic (172.9 W/L, 25 kHz) and hydrodynamic cavitation (220 W/L) aided by peroxone in 360 min, respectively. Slightly higher effectiveness of the HC + peroxone system was attributed to the increase of ozone solubility in the bulk of the effluent as the stream of O_3 is injected into the overpressure zone of the Venturi tube.

Further investigations revealed that both methods are highly effective in the degradation of aromatic compounds, alcohols, aldehydes, and ketones [39]. Similarly, the positive impact of the combination of HC ($C_v = 0.11$, pH 7.8) and peroxone was demonstrated in the elimination of natural organic matter from drinking water. In this case, studies on the efficiency of DOC removal showed a decrease of the initial concentration (up to 3 mg/L) by 40% after 60 min [40].

The application of hybrid processes based on cavitation and peroxone proved to have significant advantages. It follows from [3]:

- increased formation of hydroxyl radicals in cavitation conditions,
- increased mass transfer of ozone to the aqueous phase (it must be absorbed by water from injected gas phase), and
- the higher rate constant values of organic pollutant degradation.

4.2.4 Hybrid Processes Based on Persulfate and Cavitation Phenomenon

In recent years, sulfate radical based AOPs (S-AOPs) have been identified as an alternative to classical AOPs (i.e., hydroxyl radical based AOPs) and received a growing interest of researchers. S-AOPs generate and use sulfate radicals ($SO_4^{\bullet-}$), which possess a strong oxidation potential (2.6 V). Sulfate radicals have a longer half-life than $OH^\bullet$ ($SO_4^{\bullet-}$ = 30–40 μs and $^\bullet OH$ = <1 μs) [41]. Therefore, $SO_4^{\bullet-}$ could diffuse efficiently into the reaction mixture with high mass transfer and larger contact time for the reaction with target contaminants [41]. $SO_4^{\bullet-}$ prefer electron transfer reactions, whereas $OH^\bullet$ react through a series of reactions involving electron transfer, electrophilic addition, and hydrogen abstraction [41]. The combination of the high oxidation potential of $SO_4^{\bullet-}$ and slow consumption rate of precursor oxidant (stability), makes S-AOPs very effective for the degradation of recalcitrant organic compounds. Two types of $SO_4^{\bullet-}$ precursors are commonly used in S-AOPs: persulfate (PS) and peroxymonosulfate (PMS). Persulfate ($S_2O_8^{2-}$) can be activated by heat, UV irradiation, and transition metal ions to produce $SO_4^{\bullet-}$. Cavitation bubbles induced by ultrasound irradiation or generated by hydrodynamic cavitation were reported to initiate the activation of PS in aqueous solution at ambient conditions. The mechanism of PS activation in a cavitating bubble system was proposed to occur by two possible mechanisms. First, the $SO_4^{\bullet-}$ can be formed as a result of the thermal dissociation of PS due to localized high temperature and high pressure in the "hot spots" of collapsing bubbles. Second, extreme conditions in the "hot spots" lead to homolytic cleavage of water molecules yielding $HO^\bullet$ and $H^\bullet$. Interaction of the produced radicals with PS results in the formation of $SO_4^{\bullet-}$ [42, 43]:

$$S_2O_8^{2-} \xrightarrow{\Delta} 2SO_4^{\bullet -} \tag{18}$$

$$H_2O \xrightarrow{\text{Cavitation}} HO^\bullet + H^\bullet \tag{19}$$

$$S_2O_8^{2-} + HO^\bullet \rightarrow H^+ + SO_4^{2-} + SO_4^{\bullet -} + \frac{1}{2}O_2 \tag{20}$$

$$S_2O_8^{2-} + H^\bullet \rightarrow H^+ + SO_4^{2-} + SO_4^{\bullet -} \tag{21}$$

Thermal dissociation of water takes place in the gaseous phase of the cavitational bubble, inside of which the temperature can reach 2,000–5,000 K. The released temperature heats the liquid sheath surrounding the bubble core resulting in a higher temperature, pressure and possible supercritical water zone in the interfacial region. It is assumed that the formation of $SO_4^{\bullet -}$ takes place in the interfacial region between the gaseous and liquid phase, inside the supercritical water layer, where the diffusivity and reactivity of PS are enhanced. Formed adducts are released from the interfacial region to bulk aqueous solution, where the activation of PS is negligible due to ambient temperature [43]. In addition, the energy emitted during the cavitational bubble collapse increases the production of $HO^{\bullet}$ by the reaction of $SO_4^{\bullet -}$ with water and HO^-. $HO^{\bullet}$ can destroy oxidizable contaminants or convert SO_4^{2-} to $SO_4^{\bullet -}$ by electron transfer mechanism [43]:

$$SO_4^{\bullet -} + H_2O \rightarrow HO^{\bullet} + SO_4^{2-} \tag{22}$$

$$SO_4^{\bullet -} + HO^- \rightarrow HO^{\bullet} + SO_4^{2-} \tag{23}$$

$$HO^{\bullet} + SO_4^{2-} \rightarrow SO_4^{\bullet -} + HO^- \tag{24}$$

PS activated by cavitation exhibited a considerable potential in water treatment due to low operating cost and simple design of the equipment. PS activation achieved by HC was found effective in the degradation of persistent organic pollutants, endocrine-disrupting chemicals, bio-refractory dyes, etc. The degradation of bisphenol A was investigated under a cost-effective HC-PS system using varying operating conditions [44]. To achieve optimal degradation efficiency, the operating parameters such as HC inlet pressure, PS loading, pH, temperature, and water matrix have been studied. In this study, an orifice plate with a concentric hole of 2 mm diameter was used as a cavitating device. Application of the PS-HC process at the optimum pressure of 0.5 MPa and cavitation number (C_v) of 1.02 showed that the degradation rate constant of bisphenol A was 12.7×10^{-3} min^{-1}.

On the other hand, degradation rate constants of 1×10^{-3} and 4.7×10^{-3} min^{-1} were calculated for sole HC and sole PS treatments, respectively. The synergy index was 2.23. Although the main degradation mechanism of bisphenol A using the PS-HC system corresponded to $SO_4^{\bullet -}$, a minor contribution from $HO^{\bullet}$ (10.32%) was also observed.

Combined treatment strategy based on cavitation and PS was examined to decolorize model wastewaters containing widely used bio-refractory dyes, i.e., Orange Acid-II and Brilliant Green [45]. Comparison of cavitating conditions generated by HC and AC indicated maximum decolorization for HC combined with PS for both dye effluents. At the optimum conditions, HC combined with PS ($C = 535.72$ mg/L) completely decolorized Orange Acid-II after 60 min of the treatment. In the case of the AC-PS system, at an oxidant loading of 1.61 g/L, 70% of decolorization was obtained after 120 min. Enhancement in dye decolorization was related to the active zone, over which cavitational events occur. Thus, HC provides more active sites in the pipe line to form $SO_4^{\bullet -}$, whereas cavitational events in AC occur near the tip of the horn generating US irradiation. Significant enhancement in the degradation of naphthol blue-black dye was achieved by PS activated by AC at low US frequency and power [46]. Sonochemical degradation of naphthol blue-black in the presence of PS investigated at 20 kHz showed enhancement in degradation efficiency of 36% compared to the sole AC process.

On the other hand, the enhancement was only 10% in the US system, with a very high frequency of 585 kHz. These observations coincide with the study on operating acoustic power, where the enhancement of the degradation rate increased significantly at the lower acoustic power. Such a trend of reactions was attributed to the intensification of radical-radical recombination reaction due to excess of radicals production. Generation of $SO_4^{\bullet -}$ was elevated at higher acoustic power as more heat from cavitational bubbles was dissipated. The maximum internal bubble temperature was reported to be 4,140 K at 80 W and 1,147 K at 10 W.

4.2.5 Hybrid Processes Based on Peroxymonosulfate and Cavitation Phenomenon

$SO_4^{\bullet -}$ can also be produced by breaking the two oxygen bonds from peroxymonosulfate (PMS). Activation technologies of PMS are similar to PS and include different methods such as thermal activation [26, 47], UV irradiation [48], transition metal ions (Fe^{2+}, Cu^{2+}, Co^{2+}) [41, 49, 50], carbonaceous materials [51], etc. Extreme conditions generated by the implosive collapse of cavitational bubbles have also been tried as an activation approach of PMS [41, 52]. Activation of PMS, along with the degradation reactions of target compounds, is all assumed to occur near the interfacial region during the cavitation process. In general, activation of PMS has resulted in the formation of $SO_4^{\bullet -}$ and $HO^{\bullet}$ [53]:

$$HSO_5^- \overset{\text{Cavitation}}{\rightarrow} SO_4^{\bullet -} + HO^{\bullet} \tag{25}$$

Application of cavitation was reported to be highly efficient in PMS activation toward the degradation of contaminants present in water [42, 52, 53]. Degradation of Cresol Red dye was drastically intensified by the addition of oxone (PMS) under the US with a working frequency of 300 kHz. 99% of decolorization degree was attained in the presence of PMS in 75 min, while sonolysis alone gave 90% in 120 min [54]. The increase in PMS concentration from 10^{-4} to 10^{-1} M substantially increased the apparent rate constant of the bleaching process from 0.042 to 0.083 min^{-1}, respectively. Simultaneous formation of $SO_4^{\bullet -}$ and $HO^{\bullet}$ was proposed favorable to the rapid degradation of Cresol Red molecule as both radicals have a unique mechanism of the reaction. Synergistic effect of $SO_4^{\bullet -}$ and $HO^{\bullet}$ produced by PMS/acoustic cavitation system (20 kHz, 500 W) resulted in 95% removal of Cresol Red in 60 min, while 83% and 46% of decolorization degree were obtained by using PS/acoustic cavitation and H_2O_2/acoustic cavitation systems, respectively [55]. Simultaneous generation of $SO_4^{\bullet -}$ and $HO^{\bullet}$ during the PMS/US process (20 kHz, 600 W) was demonstrated by quenching experiments and electron paramagnetic resonance spectrometry. The contribution of both radicals increased the efficiency of sulfamethazine antibiotic degradation. Kinetic studies revealed that the degradation rate of sulfamethazine by PMS/US was 6.4 and 86 times higher than that of sole PS and US processes [52]. Reduction of the reaction energy barrier required for the oxidation of amoxicillin was observed during its degradation under Co^{2+}/Oxone/US process (20 kHz, 200 W). Studies on mineralization of amoxicillin showed that COD removal efficiencies were in the order of Oxone $<$ Oxone/Co^{2+-} $<$ Oxone/US $<$ Co^{2+}/Oxone/US [56, 57]. The accelerated formation of free radicals ($SO_4^{\bullet -}$ and $HO^{\bullet}$) provided by an increased number of active cavitation bubbles and fast activation of PMS is considered as the main enhancement routes of PMS/US process assisted by the US irradiation [54, 58].

4.3 Sonocatalytic Advanced Oxidation Process

Recently, the utilization of ultrasound in the presence of an appropriate catalyst is named sonocatalysis and is considered as one of the promising and efficient treatment techniques for the degradation of refractory organic pollutants in aquatic environments. Ultrasound alone cannot directly interact with organic compounds because the ultrasound energy is not sufficient to even change their vibrational energy levels. Moreover, the ultrasound waves are larger than the dimension of the target molecules [59]. Utilization of ultrasound alone leads to the formation of $^{\bullet}OH$ in the bulk solution to degrade organic pollutants due to the cavitation phenomenon; however, the amount of $^{\bullet}OH$ generated via ultrasonication is not enough to effectively destruct and mineralize the organic pollutants. Therefore, the treatment of polluted streams by ultrasounds alone needs higher reaction time and, consequently, higher energy to overcome this issue. To solve this limitation, catalytically enhanced ultrasonic degradation, i.e., sonocatalysis, was developed as an AOP for the decomposition of refractory organic pollutants based on the implementation of an appropriate catalyst with sonocatalytic properties [60, 61]. In this regard, nanostructured catalysts such as ZnO [62–64] and TiO_2 [65, 66] are widely applied for the sonocatalytic processes. An aquatic phase with a sufficient amount of heterogeneous catalyst produces many more interfaces for the enhanced creation of cavitation bubbles [67]. The best results have been obtained when nanostructured sonocatalysts are used for the sonocatalysis due to their higher surface area and remarkable active sites. Therefore, nanostructured sonocatalysts produce more free radical species under ultrasonication. The presence of a suitable sonocatalyst results in the fast decomposition of organic pollutant owing to the formation of extra nuclei for the creation of cavitation bubbles. High pressure ($>$1,800 atm) along with high temperature ($>$5,000 K) is produced via violent collapse of cavitation bubbles named as “hot spot” phenomenon, promoting the pyrolysis of water molecules to $^{\bullet}OH$ and $H^{\bullet}$ as presented in the following equations [61, 68]:

$$H_2O + \text{Ultrasound} \rightarrow {}^{\bullet}OH + H^{\bullet} \tag{26}$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{27}$$

Therefore, hydrogen peroxide can be produced as a result of the interaction of the generated $^{\bullet}OH$ in the bulk solution as well as the liquid-bubble interface (Eq. 27). Hydrogen peroxide molecules further reacted with hydrogen radicals, producing $^{\bullet}OH$ in the solution (Eq. 28):

$$H_2O_2 + H^{\bullet} \rightarrow H_2O + {}^{\bullet}OH \tag{28}$$

When an appropriate heterogeneous sonocatalyst (both undoped and doped sonocatalyst) is used, as-generated hydrogen peroxides react with the sonocatalyst surface, thereby generating a number of free radicals for the improved degradation of organic pollutants. In addition, extra nuclei are provided when heterogeneous sonocatalyst is used, which intensifies the formation rate of cavitation bubbles, promoting the pyrolysis rate of water molecules [68, 69]. The cavitation phenomenon is unsymmetrical close to the solid–liquid interface because the sonocatalyst fine particles act as a wall for the transmission of cavitation bubbles. The inrush of liquid from one side of the cavitation bubbles initiates forceful microjets, resulting in the surface cleaning, the boundary layers extermination, and enhanced mass and heat transfer in the bulk solution [59]. From another point of view, heterogeneous sonocatalyst can act as a photocatalyst that can utilize the energy emitted during the bubble collapse (named as "sonoluminescence" phenomenon). In this regard, the ultrasound leads to the formation of a wide-wavelength light during cavitation phenomenon, which stimulates the sonocatalyst to play photocatalytic role generating electron-hole (e^-/h^+) pairs and subsequently, $^{\bullet}OH$ in the sono-reactor as shown in the following reactions [68, 69]:

$$\text{Sonocatalyst} + \text{Ultrasound} \rightarrow h^+ + e^- \tag{29}$$

$$e^- + O_2 \rightarrow O_2^{\bullet -} \tag{30}$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+ \tag{31}$$

$$\begin{aligned} \text{Organic pollutant} + {}^{\bullet}OH &\rightarrow \text{Intermediate byproducts} \\ &\rightarrow \text{Inorganic species} + H_2O + CO_2 \end{aligned} \tag{32}$$

According to the above reactions, the as-generated e^- interact with dissolved oxygen molecules producing superoxide radical anion ($O_2^{\bullet -}$) as well as the reaction of h^+ with water results in the formation of $^{\bullet}OH$ in the solution. At the same time, h^+ or e^- can react directly with adsorbed pollutants. According to the published reports [61, 70–73], sonocatalytic degradation of various organic compounds by different sonocatalysts (ZnO, TiO_2, MgO, etc.) followed pseudo-first-order kinetic model, described as Eq. 33:

$$\ln C = \ln C_o - k_{app}\, t \tag{33}$$

where C_o and C are the initial and remaining concentration of the target compound at the specified reaction time of zero and t min, respectively. k_{app} refers to the apparent reaction rate constant of the kinetic model (min^{-1}). The application of doped sonocatalysts has also been considered to hinder the recombination of sono-generated e^{-}-h^{+} pairs in order to enhance the production rate of $^{\bullet}$OH. For this purpose, heavy and rare-earth metals have been incorporated into pure sonocatalyst lattice that has successfully improved catalytic activity of the sonocatalyst under ultrasonication [64, 68, 73]. Regarding the economic aspects of the sonocatalytic treatment techniques, immobilization of particulate sonocatalysts on suitable support including clay [62, 69, 71] and carbon [65, 66, 74] based substances is considered to avoid the washout of precious catalyst from the sono-reactor. Also, it has been confirmed that the immobilization of particulate sonocatalysts may lead to the enhanced sonocatalytic decomposition of organic contaminants. This enhancement is associated with the creation of additional nuclei for the formation of more cavitation bubbles, thereby generating more $^{\bullet}$OH in the liquid phase [62]. Besides, the immobilization prevents the aggregation of fine sonocatalyst particles in the solution [61, 71]. In the case of carbon-based substances supported sonocatalysts, the lower recombination rate of sono-generated e^{-}-h^{+} pairs is reported [67]. Overall, the sonocatalysis is an efficient purification method for the decomposition of organic compounds in comparison with the ultrasound alone. However, this process needs to be further examined to verify its ability under real conditions to treat real industrial wastewaters containing both organic and inorganic compounds. Moreover, the release of sonocatalyst particles into various ecosystems must also be considered. It is required to assess the bio-toxicity of the treated effluent before being discharged into the environment.

4.3.1 Applications of Sonocatalysis

Sonocatalysis is considered as a powerful and promising treatment technique for the effective degradation of various persistent pollutants in aquatic environments. In this regard, sonocatalysis has been successfully utilized for the treatment of colored wastewaters containing organic dyes. There are many research results in which the sonocatalysis has been effectively applied for the decolorization of synthetic and real textile wastewaters using various forms of sonocatalysts [66, 75–78]. The efficiency of the sonocatalysis for the treatment of real textile wastewaters is specified in terms of chemical oxygen demand (COD) and total organic carbon (TOC) reduction. However, longer reaction time is required to attain effective decolorization and mineralization in real wastewaters in comparison with synthetic wastewaters. In the case of sonocatalysis for real wastewaters, the issue of the presence of scavenging compounds is of great concern. The hydroxyl radicals formed during sonocatalysis are prone to be deactivated by various inorganic (CO_3^{2-}, Cl^{-},

HCO_3^-, etc.) and organic (alcoholic compounds, phenols, organic acids, etc.) radical scavengers which are abundant in real textile wastewaters [79]. Overall, the sonocatalysis is an economically feasible treatment process with high usability for the reclamation of real textile wastewaters if the careful selection of the sonocatalyst, along with the optimization of operational parameters, is conducted.

The sonocatalytic process is also used as an effective alternative to the photocatalytic process (ultraviolet irradiation together with a suitable photocatalyst) for the treatment of wastewater generated through the pulping process. The turbidity of the pulping process wastewater decreases the efficiency of photocatalytic processes. Overall, the sonocatalysis has been utilized for the degradation of lignin as well as for the pretreatment of the biomass of lignocellulose for the enhanced saccharification via an enzymatic process [80].

In recent years, the sonocatalytic processes are widely utilized for the effective degradation of emerging contaminants such as antibiotics, endocrine-disrupting compounds, personal care products, pesticides, herbicides, veterinary medications, chromate, perchlorate, nitrosamines, fuel oxygenates, etc. [81–83] from polluted water and wastewater. Sulfa drugs as widely used pharmaceutical compounds were effectively degraded by the sonocatalysis over neodymium-doped lead selenide. The removal efficiency of 86% was obtained within the reaction time of 90 min in the presence of 0.5 mmol/L peroxydisulfate as an effective radical enhancer [63]. There are many successful reports regarding the sonocatalytic degradation of various antibiotic compounds such as gemifloxacin [59], tetracycline [60, 84], ampicillin [85], and ciprofloxacin [86]. Catalytically enhanced ultrasounds have been utilized for the decomposition of hormones such as 17α-ethinylestradiol (EE2), Estrone (E1), and 17β-Estradiol (E2) [81]. Among them, 17α-ethinylestradiol and endocrine-disrupting compound, bisphenol A, are efficiently decomposed through sonocatalysis over TiO_2-wire mesh. This type of sonocatalyst can be continuously reused for the catalytic production of hydrogen peroxide and subsequent degradation of such emerging contaminants [87].

Because of its high potential to be reused in repeated experimental runs, magnetically separable TiO_2 is also used for the degradation of ibuprofen as a nonsteroidal anti-inflammatory drug (NSAID). According to the reported results, an average rate constant value of $17 \pm 0.3 \times 10^{-3}\ \text{min}^{-1}$ has been obtained within five repetitive experimental tests [88]. A cost-effective mineral catalyst named sepiolite has also been for the sonocatalytic degradation of methylparaben. This emerging compound is extensively used in a variety of personal care products and cosmetics. Based on the obtained results, the high frequency of ultrasounds favored the sonocatalysis of methylparaben [89]. Overall, sonocatalysis could be considered as an efficient treatment process for the degradation of emerging contaminants, but attempts have been focused on the treatment of emerging contaminants in laboratory scale experiments. The impact of radical scavengers and co-existing inorganic anions on the effectiveness of sonocatalytic processes has been extensively studied. However, the effectiveness of this type of catalytic process for the treatment of real wastewaters containing emerging contaminants should be assessed.

5 Factors Influencing the Efficiencies of Treatment Processes

5.1 *Effect of pH*

The efficiencies of the treatment processes depend on the pH of the solution medium. The initial pH of the solution plays an essential role in the formation of pollutant speciation, active intermediates, and the reactivity for their decomposition [90]. The influence of pH on the oxidation potential of intermediate compounds and $^{\bullet}OH$ produced at the cavitation process is considered for the degradation studies. Many studies reveal that acidic conditions are generally preferable for dye degradation when compared with alkaline conditions. The use of lower pH enhances $^{\bullet}OH$ formation and reduces the recombination rate. Furthermore, the pollutant in a molecular or ionic state depends on its acid dissociation constant value (p*K*a) [91]. For different contaminants, the optimum pH value for higher degradation efficiency is different.

In hydrodynamic cavitation processes combined with oxidants or Fenton's reagent, the oxidation potential of the oxidants or Fe concentration in the solution was strongly influenced by the initial solution pH. Fenton's reagent is more efficient at acidic conditions in the range of pH 3–4. At pH lower than 3, the generation of $(Fe(II)(H_2O))^+$ enhances, which reacts slowly with hydrogen peroxide, thereby reducing the production of reactive hydroxyl radicals [92]. Furthermore, at a very low pH, the scavenging effect of H^+ comes into effect, which could restrict the rate of degradation by consuming hydroxyl radicals. Furthermore, hydrogen peroxide reacts with a proton to give an hydroperoxonium ion ($H_3O_2^+$) and makes hydrogen peroxide electrophilic. Thus, the stability of hydrogen peroxide increases, and their reactivity with ferrous ion decreases, which results in a reduction of degradation kinetics of Fenton's process at very low pH [93].

Wang et al. [90] reported that the hydrodynamic cavitation process combined with TiO_2 photocatalysis gave a high rate constant for degradation of tetracycline at pH 10. As solution pH increases, hydroxide anions increase, which favors the generation of hydroxyl radicals through holes oxidation in the photocatalytic system. This can be the main cause for higher degradation effect at alkaline pH for the combined hydrodynamic cavitation and photocatalysis process.

5.2 *Effect of Temperature*

Temperature is considered one of the most influential parameters on the ultrasound cavitation leading to changes in the reaction rate and degree of degradation. Higher temperature causes a rise in the vapor pressure of the solution leading to the formation of vaporous cavities in the system. At higher temperatures, the solution boils, leading to negative acoustic wave pressure. In the meantime, the cavitation bubble fills with water vapor instantly, which decreases degradation efficiency. Choi et al. [44] investigated the effect of temperature in changing the activation energy and behavior of the bisphenol A. It was reported that the increase in temperature from 10 to 50°C results in the increase of reaction rate constant by 12-folds. Son et al. [94] reported that an increase in bulk temperature reduced the cavitation effect. When the temperature was increased beyond the optimum temperature of 30°C, the degradation efficiency of 1,4-dioxane decreased. This is because, at higher temperatures, the collision of cavities occurs, which lower the implosion effect; thus, a steady decline in the generation of hydroxyl radicals occurs. Therefore, lower operating temperature ranges from 25 to 40°C is generally preferred. In some cases, it could be raised to 50°C, where the radical formation from the pollutant also plays an essential role in the degradation mechanism [95].

5.3 Effect of the Initial Concentration of Pollutant

Another essential parameter influencing the effectiveness of treatment processes is the initial pollutant concentration. Generally, the increase in the initial concentration of pollutants leads to a reduced degradation efficiency of a cavitation process. This negative effect in cavitation treatment may be due to the insufficient amount of hydroxyl radicals generated for the available pollutant molecules. The amount of $^{\bullet}OH$ which attacks the pollutant molecules would be constant while the increase in pollutant concentration gives rise to a greater number of available pollutant molecules. As a result, the level of pollutant degradation percentage would be lowered. In the hydrodynamic cavitation process combined with photocatalytic treatment [96], it has been shown that the degradation of RR 180 dye at an operating pressure of 5 bar was reduced from 67 to 41% (in terms of TOC) as the dye concentration increased from 50 to 150 mg/L.

5.4 Effect of Inorganic Ions

The domestic and industrial wastewater contains inorganic salts in higher proportions. Therefore, many researchers studied the influence of inorganic ions on hydrodynamic cavitation-based wastewater treatment processes. Some studies revealed that the presence of chloride and sulfate salts exerts no significant effect on the treatment process [90]. Khodami and Nezamzadeh-Ejhieh [97] postulated that the increase in chloride ion reduces the degradation efficiency as chloride acts as an electron donor. Thus, the increase in chloride ions reduced the generation of $^{\bullet}OH$. Also, the chloride radicals have much lower oxidation potential than $^{\bullet}OH$. The inhibition effect of sulfate salts is due to their ability to act as electron scavenger.

The effect of CO_3^{2-} and HCO_3^{-} as hydroxyl radical scavengers was investigated by several researchers. Interestingly it has been found that the carbonate radicals, resulted from the reaction of carbonate ions with $^{\bullet}OH$, react very fast with electron-rich organic compounds such as aromatics and anilines. Besides, the recombination rate of these radicals is very slow, and the presence of these compounds increases the pH value, which also contributes to the lower degradation [90, 98, 99].

6 Applications of Cavitation Processes in Environmental Protection

6.1 Application of Cavitation for Wastewater Treatment Containing Volatile Organic Compounds

Volatile organic compounds (VOCs) are organic compounds that can evaporate under normal atmospheric conditions of temperature and pressure. More strictly, according to European Union regulations, it is any organic compound having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101.3 kPa (European Parliament and Council, Directive 2004/42/CE) [100]. Industrial discharges (pharmaceutical, petroleum refinery, paper, dye, and textile industry effluents) are the main sources contributing to the presence of VOCs in municipal wastewater [101–106]. Among other classifications of VOCs, there are three important groups of VOCs, i.e., nitrogen-containing VOCs (N-VOC), sulfur-containing VOCs (S-VOC), and oxygen-containing VOCs (O-VOC). Hydroxyl radicals are very reactive species that effectively degrade pollutant molecules, and a combination of AOPs with cavitation technologies generates more hydroxyl radicals, which will enhance VOC removal from wastewater [107].

High concentrations of VOCs are found in wastewater originated from the refinery industry, i.e., petroleum bitumen effluents containing a high amount of VOCs [27]. These effluents are produced during oxidation of the vacuum distillation of crude oil to produce oxidized bitumen. During vacuum distillation as well as bitumen production (bitumen blowing process), a partial thermal cracking takes place on the heating elements of the installations. Under such conditions, several groups of VOCs are formed – primary aromatic and other unsaturated compounds that undergo further conversion via oxidation reactions. A considerable amount of organosulfur compounds, ketones, aldehydes, pyridine, and its derivatives, as well as polycyclic aromatic hydrocarbons (PAHs), are present in post oxidative effluents which contributes to its odorous character and high toxicity in the environment [108, 109]. Except for biodegradation and adsorption, the AOPs and their combination with cavitation are seen as a good approach in the treatment of refinery effluents. Treatment of bitumen effluents was performed by AOPs, sole and in combination with hydrodynamic cavitation. A combination of hydrodynamic cavitation and ozone was found to be the most effective process compared with other approaches of HC and AOPs in the treatment of effluents from the production of bitumen with 40% COD and 50% BOD_5 reduction [23]. In another study where wastewater from bitumen effluents was performed by sole AOPs, the authors claimed that the most effective AOP was the peroxone process (a combination of O_3 and H_2O_2) with 43 and 34% reduction of COD and BOD_5, respectively [27]. The BOD_5 reduction was 10% higher when ozone was coupled with hydrodynamic cavitation, compared to the peroxone(O_3/H_2O_2) process.

The effectiveness of cavitation in the degradation of VOCs was also proved by Gągol et al. [26]. They studied the degradation of sulfide ions and organic sulfides with combined processes of hydrodynamic cavitation and AOPs. They concluded that in 30 min of reaction, 60% of organosulfur compounds were oxidized by the sole cavitation process; meanwhile, complete oxidation was obtained for the coupled process of cavitation and oxidants O_3, H_2O_2, O_3/H_2O_2. Complete degradation was obtained in 15 min for the coupled process of hydrodynamic cavitation and peroxone.

The combination of AOPs and cavitation have shown promising results in degrading the organic pollutants in terms of both treatment time and cost-effectiveness. Goel et al. [110] performed the treatment of several volatile and non-volatile organic compounds (Benzene, Toluene, Styrene, Ethylbenzene, Trichloroethylene, Eosin B) in two types of sonication reactors, a probe, and ultrasonic bath. Effect of oxidant (H_2O_2) and electrolyte (NaCl solution) coupled with sonocavitation, was also investigated. They found that sonochemical degradation was a suitable alternative, and the reaction rates were higher for ultrasonication with probe compared to ultrasonic bath for both volatile and non-volatile compounds. Operating conditions are important factors in the decomposition of VOCs. Jiang et al. [111] studied the degradation of volatile chlorinated aromatics (chlorobenzene, 1,4-dichlorobenzene, and 1-chloronaphthalene) using an ultrasonic transducer and found that initial substrate concentration and ultrasonic intensity were important features in the sonochemical decomposition of volatiles.

Hydrodynamic cavitation is a large-scale technique, which generates free reactive radicals and high temperature that easily degrade pollutant molecules, being, therefore, an AOP [112]. Chakinala et al. [113] investigated the mineralization of phenol with hydrodynamic cavitation and heterogeneous advanced Fenton process (AFP). They concluded that AFP, in combination with hydrodynamic cavitation, effectively degraded phenol from wastewater. Moreover, zero-valent iron was considered as a promising catalyst for the treatment of phenolic aqueous solutions by the combination of HC/AFP.

6.2 *Removal of Pesticides from Wastewater by Cavitation Technologies*

Pesticides are substances used to prevent or destroy certain insects and various types of parasites [114]. Pesticides can be classified into two major groups based on target organisms (insecticide, herbicides, fungicides, rodenticides, wood preservatives, garden chemicals, and household disinfectants) and based on chemical structure (organochlorine, organophosphate, carbamates, and pyrethroids) [115]. Pesticides are discharged in aqueous systems by agricultural wastewater and non-agricultural wastewater (industrial facilities, public health, forestry activity) [116]. Pesticides acquire a detrimental effect on human health, and they can enter into the body through different routes such as food chain, inhalation, dermal and ocular exposure [114]. Therefore, it was highly important to develop advanced technologies that prevent or destroy pesticides.

Atrazine (1-chloro-3-ethylamino-5-isopropylamine-2,4,6-triazine) is a herbicide widely used in agriculture. Degradation of atrazine was investigated using hydrodynamic cavitation combined with chemical oxidants H_2O_2, UV, SPS (activated sodium persulfate) [117]. Jawale et al. [117] found that the combination of HC + H_2O_2 + SPS resulted in complete degradation and 87% COD reduction. Their results demonstrated that the hybrid treatment approach based on cavitation could be effectively used for the degradation of ATZ. Dicofol, an organochlorine pesticide, was degraded by hydrodynamic cavitation under optimized conditions (inlet pressure 7 bar, $C_v = 0.17$) with 85% total organic carbon (TOC) removal in 60 min treatment time [118].

In another case, the degradation of methyl parathion using hydrodynamic cavitation with different additives (H_2O_2, CCl_4, Fenton's reagent) resulted in 56.4% TOC reduction in 30 min for the process of HC + H_2O_2 [119]. Similarly, Joshi et al. [120] studied the degradation of dichlorvos by hydrodynamic cavitation under optimized parameters and a maximum extent of degradation of 91.5% in 60 min treatment time was obtained for the coupled process of hydrodynamic cavitation and Fenton's process. The same contaminant was degraded in the sonochemical reactor combined with additives (H_2O_2, CCl_4, Fenton's reagent), and the highest degradation was obtained for the combined process of sonocavitation and Fenton's reagent named as a sono-Fenton process [121]. Therefore, it can be understood that in the studies as mentioned above, optimized treatment schemes, based on a combination of sonochemistry or hydrodynamic cavitation with Fenton's chemistry, were effective approaches in the removal of dichlorvos from aqueous systems.

Randhavane et al. [122] studied the effect of geometric parameters in the treatment of chlorpyrifos using hydrodynamic cavitation, and the obtained results confirmed that the highest COD removal (60%) and 98% chlorpyrifos degradation was obtained for orifice plate with a configuration of 17 holes having a 1.5 mm diameter and the cavitational number of 1.54 in 120 min treatment time.

Ultrasonic cavitation, in combination with H_2O_2, Fenton's, and photo-Fenton's process, was used to degrade methomyl, a carbamate group pesticide that is used against many insects and pests. It was proved that the most effective process with maximum mineralization of 78.8% was ultrasound and photo-Fenton's process in only 9 min time of treatment [123].

6.3 Removal of Pharmaceuticals from Wastewaters Induced by Cavitation Technologies

Emerging Compounds (EC) have become a major concern in the pollution of the aquatic environment; therefore, increased attention toward this problem resulted in the development of new technologies for wastewater treatment [124]. Pharmaceuticals and their by-products have been in the scope of researchers as pollutants of emerging concern that need to be kept under control. The pharmaceuticals are discharged into the aquatic environment via healthcare facilities, hospital discharges, agriculture wastewater, and veterinary activities [125]. The concentration of pharmaceuticals in wastewater is found to be in the range of ng/L to ug/L [126]. The resistance of these compounds to treatment is favored by their physicochemical properties and biodegradability. Low removal of organic compounds, high cost of treatment, and low efficiency are some of the drawbacks related to conventional methods that can be easily overcome by the use of AOPs [124, 127]. AOPs include photocatalysis, sonocatalysis, Fenton, electro-Fenton, ozone-based hybrid processes, and cavitation processes [128, 129]. Sonocavitation is already proved to be an effective method in the removal of ubiquitous compounds from wastewater [130, 131]. Hydrodynamic cavitation (HC) is considered as a good opportunity to fade away the disadvantages of ultrasound, such as high energy consumption, and it is seen as a more viable and worthwhile method [124].

Antibiotics from the representative group of fluoroquinolone and β-lactam antibiotics (cephalosporin and penicillin) are the most consumed pharmaceuticals. They are found in municipal waste treatment plants [MWTP] from hospital wastewater discharges [HWW] [126, 132, 133]. Serna-Galvis et al. [131] studied the sonochemical degradation of six antibiotics from three different classes such as fluoroquinolones (ciprofloxacin and norfloxacin), penicillins (oxacillin and cloxacillin), and cephalosporins (cephalexin and cefadroxil). They concluded that the application of ultrasonic waves leads to a satisfactory result in the degradation of antibiotics. Hydroxyl radicals that are generated from ultrasound attacked the penicillin and cephalosporin cores from the β-lactam antibiotics, whereas the fluoroquinolone was decarboxylated. Other researchers [134] evaluated the effect of high-frequency ultrasound to degrade the penicillin antibiotic (oxacillin). They concluded that under the effect of ultrasound treatment, by-products of antibiotics were converted into biodegradable compounds. Furthermore, it was proved that the combination of the sonochemical process with biological systems could be a practical alternative for the treatment of water containing oxacillin and other pharmaceutical additives.

Dicloxacillin (DXC) is another β-lactam antibiotic of the penicillin family. Villegas-Guzman et al. [135] studied the inhibition effect of dissolved salts present in water for the degradation of DXC assisted by ultrasound. They found that antimicrobial activity was eliminated after 360 min under ultrasonic treatment with 30% of COD removal.

Ciprofloxacin (CIP), a fluoroquinolone class pharmaceutical, has an irreversible effect in the ecosystem, resulting in toxicity to microorganisms [130]. CIP removal from aqueous systems by sonochemical, sono-nano-chemical, and sono-nano-chemical/persulfate processes was studied by Igwegbe et al. [129]. They found 99, 70, and 36% removal efficiency of CIP by sono-nano-ZnO/PS process (US/ZnO/PS), sono-nano-chemical (US/ZnO) process, and sonochemical (US) process, respectively, at a frequency of 60 kHz, 10 min treatment time, and neutral pH. The effect of ultrasonic cavitation in the degradation of CIP and ibuprofen in the presence of different organic compositions was investigated by Xiao et al. [136], and a high rate of degradation was reported. Sonochemical degradation of levofloxacin under the effect of rate enhancers (CCl_4) and rate inhibitor (t-butanol) was investigated by Guo et al. [137] and concluded that sonochemical oxidation could be used for pretreatment of effluent containing levofloxacin before biological treatment processes.

Ibuprofen (IBP), a NSAID, is a widely used medicament that helps to reduce fever, headache, toothache, or pains caused by other injuries. It is used for humans and domestic animal healthcare, farming, etc. [138]. Degradation of IBP by sonocavitational treatment was studied by Mendez-Arriaga et al. [139], and they inferred that degradation of IBP under ultrasound treatment was increased from 30 to 98% in 30 min; meanwhile, the same analgesic solution was treated by hydrodynamic cavitation, and over 60% of ibuprofen was degraded in 60 min [124].

Except for uses of ultrasonic cavitation in the degradation of different groups of pharmaceuticals, hydrodynamic cavitation is also considered as a reliable technology to degrade pharmaceutical contaminants. Degradation of six pharmaceuticals such as clofibric acid, ibuprofen, naproxen, ketoprofen, carbamazepine, and diclofenac under the effect of hydrodynamic cavitation (HC), biological processes, and UV was studied by Renita et al. [127]. The studies revealed that under optimal conditions for hydrodynamic cavitation, removal efficiencies were ranging from 72 to 86% in the case of naproxen, carbamazepine, and diclofenac, and from 45 to 52% for clofibric acid, ibuprofen, and ketoprofen. Ibuprofen, naproxen, and ketoprofen were degraded to concentrations below the LOD of the analytical method used for its determination, while the efficiency of >98%, was observed for carbamazepine and diclofenac.

Degradation of diclofenac in the aqueous system based on hydrodynamic cavitation and heterogenous photocatalysis has revealed that combined processes of hydrodynamic cavitation with photocatalysts or AOPs resulted in higher degradation of contaminants than in individual processes [36]. They found that the combination of hydrodynamic cavitation with UV, UV/TiO_2, and UV/TiO_2/H_2O_2 enhances the degradation of target pollutants. The highest degradation was observed for the hydrodynamic cavitation process combined with UV/TiO_2/H_2O_2 with 95% degradation and a 76% reduction in TOC. Another use of the combined process of hydrodynamic cavitation and AOPs was investigated by Thanekar et al. [140]. They found that the degradation of carbamazepine by hydrodynamic cavitation as a sole process reached only 38.7% degradation, while for combined processes of HC + O_3, HC + H_2O_2, HC + UV, HC + O_3 + H_2O_2 obtained degradation rates were, respectively, 91.4%, 58.3%, 52.9%, and 100%. It can be understood the effectiveness of the combined process of HC and AOPs. Degradation of carbamazepine was also studied under the effect of sonoelectrochemical oxidation, sonophotodegradation, and combined hydrodynamic and acoustic cavitation (HAC) [141–143].

Villaroel et al. [144] studied the degradation of acetaminophen (ACE) in water by ultrasound. They found that ultrasound has a great potential in the degradation of ACE because it transforms to biodegradable by-product. The effect of ultrasonic degradation was also studied by other researchers [145, 146]. Mirzaee et al. [128] studied the degradation of paracetamol under ultrasonic irradiation combined with air-dispersion cathode with a sacrificial iron anode, which generates Fe_3O_4 nanostructures that help in the degradation of paracetamol. The hybrid method of US coupled with NADC-ECP (nano-composite air-dispersion cathode) in the presence of Fe_3O_4 nanostructures was proved to be a very effective method with a synergism of 39.8%. The sonocatalysis of ACE over catalysts of nano-sized ZnO incorporated into PSW (powdered stone waste) (ZnO/PSW) was studied by Soltani et al. [61]. They concluded that the highest degradation efficiency of 98.1% was achieved for ZnO/PSW-sonocatalytic process assisted by UVC light.

6.4 Domestic Effluents

The rapid growth of urban communities, along with the development of industrial and agricultural water consumption, raises an increasing demand for water sanitation and protection. The use of water for industrial, agriculture, and domestic purposes is commonly associated with the deterioration of water quality due to the constant accumulation of contaminants. Characterization of wastewater is a part of research activities undertaken to optimize the design of the unit of wastewater treatment plants (WWTPs). Domestic wastewater in municipal WWTPs consists of waste produced by households with various contributions from rainwater, industrial, and agriculture wastewaters. Domestic effluents are produced by individual users and have been less described at habitat scale due to the broad variability of the behavior, lifestyle, and standard of living among different users. Domestic effluent is the water that has been used by a community. It is composed of human body waste, together with the water used for flushing toilets, personal washing, laundry, food preparation, and cleaning of kitchen utensils [147]. Domestic effluents are historically classified into two main categories: blackwater and greywater. Blackwater is collected from toilets and consists of fecal matter, toilet paper, flush water, urine, and spillage. This fraction of domestic effluents contains pathogenic bacteria, which may cause diseases. Greywater includes various emission sources, such as kitchen sink, dishwasher, washing machine, shower, and other personal care activities [147, 148].

The contaminants present in domestic effluents are divided into three categories: suspended solids, organic matter (chemical oxygen demand and biological oxygen demand), and nutrients (nitrogen and phosphorus-containing compounds).

Conventional water treatment processes are used to remove the contaminants for reuse of the treated water [149]. Many studies have been conducted to improve the quality of the treated water by upgrading the existing conventional treatment processes. Thus, suspended and dissolved solids amenable to biological treatment are suggested to be removed by assisting the preliminary treatment with a chemical coagulant [150]. Introduction of AOPs, as well as other physicochemical processes into conventional water treatment practices, is the recent trend in the development of rational use of water resources.

6.5 Treatment of Industrial Wastewater by Cavitation

Industrial activity is a topic of concern in environmental pollution due to the large quantity of wastewater discharge in the aquatic environment, contaminated with pharmaceuticals, dyes, pesticides [140]. Researchers have studied the treatment of industrial wastewater with cavitation, AOPs, and the combination of both [27, 39].

The combined process of HC/O_3 was reported to be a very effective method in the treatment of bitumen effluent with a maximum reduction of 40% in COD and 60% in BOD [39]. Chakinala et al. [151] studied the treatment of industrial wastewater containing phenolic compounds using hydrodynamic cavitation induced by a liquid whistle reactor coupled with the AFP. The combined process of HC/AFP resulted in (60–80%) removal of TOC in 150 min time of treatment.

The treatment of the textile dyeing industry (TDI) effluent was studied using a hybrid combination of HC with air, ozone, oxygen, and Fenton's reagent [152]. The combined process of HC and Fenton's reagent ($FeSO_4.7H_2O$: H_2O_2 as 1:5) was the most effective process with 48% TOC and 38% COD reduction in 15 and 120 min, respectively, with almost complete decolorization 98% of the TDI effluent. Raut Jadhav et al. [153] studied the efficiency of the combination of hydrodynamic cavitation with additives (H_2O_2 and O_3) for the treatment of pesticide industry effluent. They found that the combined process of HC + H_2O_2 was the most cost-effective due to its higher cavitational yield and lower power consumption.

Gore et al. [30] studied the degradation of orange 4 dye using hydrodynamic cavitation-based hybrid techniques. They revealed that the mineralization rate was higher for the combined process of hydrodynamic cavitation and ozone (76.25%), followed by HC + H_2O_2 (31.90%) and (14.67%) for HC alone. The synergetic coefficient of greater than one for the hybrid processes of HC + H_2O_2 and HC + Ozone showed that the combination of HC with other oxidizing agents is better than the individual processes for the degradation of dye effluent containing orange 4 dye.

Ayare et al. [154] investigated the treatment of phosphonate containing industrial wastewater by sonocatalysis combined with oxidation processes. They found that maximum COD reduction was obtained for the combined operation of sonocatalysis (TiO_2) with ozone and H_2O_2 (US+O_3 + H_2O_2 + TiO_2) with 95.8% COD reduction, while the use of sole ultrasound resulted in 37.2% COD reduction. A study regarding the removal of dinitrotoluene and trinitrotoluene from industrial wastewater by sonocavitation combined with titanium dioxide was carried out by Chen et al. [155]. They concluded that ultrasonic irradiation, coupled with TiO_2, is a potential method for the treatment of nitrotoluenes in wastewater, and the mineralization of nitrotoluenes leads to carbon dioxide, nitrate ions, and water.

6.6 Miscellaneous Application of Cavitation Technologies

In addition to the wide use of cavitation in wastewater treatment, such as removal and degradation of different types of pollutants (pharmaceuticals, pesticides, volatile and non-volatile organic compounds, heavy metals, dyes, etc.), it also has miscellaneous applications like biotechnology [156], food and water processing [157], mineral processing [158], biodiesel production [159], upgrading of heavy oil [160], desulfurization/denitrogenation of fuels [161].

Hydrodynamic cavitation was found to be an effective application technique in yeast cell breakage and is considered as the most energy-efficient method compared to blade blender and acoustic cavitation techniques [162]. In the food processing industry, hydrodynamic cavitation is used for food sterilization to prolong the shelf life of easily-spoiled products [157, 163, 164].

Hilares et al. [165] studied bioethanol production from sugarcane bagasse using hydrodynamic cavitation assisted-pretreatment and column reactors. They found that HC-assisted alkaline-hydrogen peroxide ($NaOH\text{-}H_2O_2$) pretreatment strategy might offer an option for sugarcane bagasse based biorefineries. Askarian et al. [166] investigated the role of hydrodynamic cavitation in upgrading the heavy oil in the presence of an appropriate hydrogen donor. They revealed that adding 2 vol% gasoline as hydrogen donor into the heavy oil cavitational upgrading process reduced the viscosity of heavy oil by about 33%. It was observed that diesel cuts and API gravity increased by 6.5 vol% and 2.9%; meanwhile, extra heavy cuts and viscosity decreased 20 vol% and 84%, respectively. Ramos et al. [167] studied oxidative desulfurization of model diesel with the ultrasound-assisted synthesis in the presence of mesostructured catalysts (FeOx/SBA-15 and FeOx/Zr-SBA-15). SBA-15 is mesoporous silica which was impregnated with Zr and desired amount of an aqueous solution of $Fe(NO_3)_2{\cdot}9H_2O$ to obtain FeOx/SBA-15 and FeOx/Zr-SBA-15. They reported that dibenzothiophene (DBT) (30% Fe/Zr-SBA-15, 300 ppm DBT in 100 ml n-hexadecane) was completely removed from model fuel within 30 min of treatment time.

In addition to hydrodynamic cavitation, ultrasound is also an applicable technology in the food industry, mineral processing, nanotechnology, industrial welding, surface cleaning, and environmental protection [168–172].

The literature published so far indicate that cavitation is useful for the major research fields and for economy driving industries such as wastewater treatment plants, food industry, and fuel processing. Currently, ongoing research strongly focuses on improvements of cavitation-based technology concerning environmental protection applications as well as to make it more beneficial from the economic point of view.

7 Conclusions and Future Perspectives

Cavitation-based AOPs already proved its usefulness for several applications. In many cases, the sole use of cavitation allows us to effectively degrade the pollutants present in aqueous phases such as dyes, pharmaceuticals, and VOCs. An important advantageous aspect of hybrid processes based on cavitation is the synergy between this phenomenon and external oxidants, which are effectively converted to reactive radical species.

Future research on this topic should include two essential aspects – first related to the scientific value of published results and second to the applicational character of developed processes.

In the first case, to assure usefulness of obtained results on fundamentals of cavitational phenomena in relation to AOPs, scientists must provide as many details as possible on their system configuration and process conditions. The most important data are often missing, and their importance is explained below.

1. A lack of a clear description (or a scheme) of geometry and dimensions of elements present in the hydrodynamic cavitation system, as well as used flow rates and pressure in the system, makes the published results less useful for other researchers. This information is essential to calculate the cavitation number. All necessary data, along with the calculated cavitation number, should always be provided in the article or supplementary material linked to the article. Cavitation number should be calculated based on Eq. 1 instead of other concepts of defining this parameter.
2. In the case of sonocavitation systems, geometry and type of ultrasonic device must be characterized, including power and frequency of the instrument, as well as all details of ultrasonic transducers or sonotrodes used in the studies. It should also include the placement of the transducers in the system.
3. The aqueous medium treated in the studies must be characterized in terms of all physicochemical parameters that can affect the obtained results. These parameters include pH, color, clarity, the occurrence of emulsions, the presence of inorganic ions, and details of present dissolved organic compounds. In the case of real wastewater, the matrix effects often have a significant influence on the obtained effectiveness. Lack of deep analysis of factors affecting the obtained effectiveness lowers the value of obtained results as well as make them highly uncertain.
4. Studies on model effluents must include all these aspects mentioned in point 3 during process optimization.
5. Catalytic processes must be characterized in terms of catalyst used and its recycling ability concerning comparable performance over several cycles of

treatment. The high energy of cavitation can cause leaching of several elements, including metal ions from catalyst into the aqueous phase. This aspect must be controlled during the process. Examples of such discussion can be found in paper of Fedorov et al. [173].

6. Processes aided by UV light must be characterized concerning power and type of UV lamp. The wavelength at which photooxidation is expected in the spectrum of the lamp should be provided. This allows evaluating what the real power is needed for a specific wavelength to obtain effective degradation of target pollutants is.
7. Turbidity values of the aqueous phase and their changes dependent on heterogenous catalyst concentration must be measured for sonocatalytic and photocatalytic processes. This aspect is very important in the discussion of the effect of catalyst dose since the turbidity of the high load of catalyst solutions often is a limiting factor of the sonocatalytic and photocatalytic processes effectiveness.
8. Evaluation of the changes of a total load of pollutants (controlled by COD or TOC and BOD) and its mineralization should be studied along with monitoring of target pollutants. If total degradation is not obtained, the COD should be used to measure the degradation of organic pollutants rather than TOC. In the case of TOC, the effect will be underestimated (transformation of one organic compound to another one is not changing the organic carbon content in the effluent).
9. Optimization of the process conditions should include the minimization of the addition of external oxidants coupled with the analysis of energy costs of the cavitation process.
10. The monitoring of by-products formation should be included in the studies. Especially oxygen-containing compounds should be monitored as one of the most possible by-products formed during AOPs [174].
11. Compounds present in the matrix of real wastewater should be characterized along with the defined purpose of the treatment. In several cases, the treatment process is focused on the removal of some target compounds, which should be degraded due to its specific toxicity. Often, the final treatment stage is performed via biological treatment using a dedicated to the type of wastewater activated sludge. Overall load of pollutants (and its change at the pretreatment stage by chemical oxidation) is not so important; however, the presence of “critical” pollutants – highly toxic for such a type of microorganisms is the main aspect causing the need of implementation of pretreatment by AOPs. Thus, the context of the research must be pointed out, and the advantages of cavitation-based AOPs highlighted.

The second aspect of future research relates to the applicational value of obtained results. The studies should focus on the evaluation of the effectiveness of cavitation-based AOPs in pilot-scale units. Moreover, the development of protocols allowing to scale up the processes to industrial scale is one of the important niches in this field. Studies on improvements of process economics in the laboratory as well as pilot-scale systems should focus on the energy-efficient generation of cavitation as well as coupling with solar cell units to make the cavitation processes a fully "green chemistry" approach.

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Emerging Organic Compound (EOC) Removal from Water and Wastewater Using Innovative Technologies and Materials

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Contents

Abstract There is a growing concern about the presence of EOCs in the environment, which could be preferably called "the contaminants of emerging concern," including pharmaceuticals, specifically antibiotics, antiseptics, hormones, and pesticides that are available commonly in untreated wastewater. These substances that

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are produced due to various industrial and human activities constitute a significant environmental risk worldwide. Currently, several treatment methods have been investigated for the removal of EOCs that entail different processes (e.g., adsorption, ozonation, and biological) and advanced processes (e.g., advanced oxidation processes and membrane-based technologies). However, these processes often suffer from operational problems and have inadequate treatment capacity when used as stand-alone solutions for all types of EOCs. Due to the fact that EOCs have different physicochemical properties and distinctive toxic concentrations in water, the treatment processes that are combined with innovative technologies and/or materials are required to sustainably remove EOCs at desirable levels. The combined processes are defined as holistic treatment technologies that could synergistically amass several advantages of single processes such as modularity, low cost, and high removal efficiency. Thus, the membrane processes appear as one of the best available technologies to effectively and safely eliminate EOCs due to their improved applicability potential in combined treatments via maximizing the technical performance of overall treatment. This chapter reviews the technological aspects, performances, and economic analysis of EOC removal methods. The innovative or promising combined technologies and membrane processes has been suggested based on the risk groups that rely upon the basic specific properties of EOCs.

Keywords Combined technologies, Emerging organic contaminants, Membrane-based technologies, Removal of priority contaminants, Risk grouping, Water media

Abbreviations

AC	Activated carbon
AeMBR	Aerobic membrane bioreactor
AnMBR	Anaerobic membrane bioreactor
AOP	Advanced oxidation process
AS	Activated sludge
BAT	Best available technology
BOD	Biochemical oxygen demand
CAPEX	Capital expense
CCM	Catalytic ceramic membrane
CNT	Carbon nanotube
COD	Chemical oxygen demand
CTA	Cellulose triacetate
DEfOM	Dissolved effluent organic matter
DO	Dissolved oxygen
EfOM	Effluent organic matter
EOC	Emerging organic compound
ERA	Environmental risk assessment
FO	Forward osmosis

GAC	Granular activated carbon
GC-MS	Gas chromatography-mass spectrophotometer
HRT	Hydraulic retention time
LC-MS/MS	Liquid chromatography-mass spectrophotometer
LMP	Low and medium pressure
MBR	Membrane bioreactor
MC	Mesoporous carbon
MEC	Measured environmental concentration
MF	Microfiltration
MP	Mesoporous phenolic
NF	Nanofiltration
OLR	Organic loading rate
OMBR	Osmotic membrane bioreactor
OPEX	Operational expense
PAC	Powder activated carbon
PEC	Predicted environmental concentration
PhAC	Pharmaceutical active Ingredients
PNEC	Predicted no effect concentration
PP	Polypropylene
pPAC	Pressurized powder activated carbon
PVDF	Polyvinylidene fluoride
RO	Reverse osmosis
ROS	Reactive oxygen species
RQ	Risk quotient
SBR	Sequencing batch reactor
sPAC	Submerged powder active carbon
SRT	Sludge retention time
TOC	Total organic carbon
TSS	Total suspended solid
UASB	Upflow anaerobic sludge blanket
UF	Ultrafiltration
UV	Ultraviolet
UV-Phc	Ultraviolet photocatalysis
VSS	Volatile suspended solid
WoS	Web of science

1 Introduction

Pharmaceutically active compounds (PhACs), personal care products, pesticides, natural hormones, industrial chemicals (flame retardants, plasticizers, and food additives) are widely used globally due to the increase in industrial activities. Most of these products have the risk potential for the ecosystem even when they are at trace levels (ng/L or μg/L) in the environment [1], and these compounds are called Emerging Organic Compounds (EOCs) [2]. EOCs should be removed in wastewater treatment plants and discharged at non-toxic concentrations to receiving water bodies. Since conventional wastewater treatment plants were not designed for EOC removal, the treated wastewater with EOC content could be discharged to receiving water bodies due to limited biodegradability [3–5]. When compared to conventional contaminants and other specific organic pollutants, the diversity and specific properties of EOCs make them difficult to control in water media and eliminate using conventional treatment technologies. For instance, the low biodegradability of EOCs reduces the removal efficiency of biological treatment and their molecular size, weight, and surface charge affect their treatability via physical and chemical processes.

Developed countries have started to develop adaptation plans to upgrade existing wastewater treatment plants [6] to include EOC removal; however, most nations still conduct laboratory or pilot-scale studies. Furthermore, it could be argued that single processes are inadequate in complete EOC removal in water media. The hybrid/combined systems, which have two or more treatment units, improve EOC removal due to the synergistic effects of single processes [7]. Furthermore, the performance of combined systems minimizes the shortcomings of single process systems [8]. Despite the fact that significant research efforts focused on the development of new process configurations for EOCs removal, substantially higher costs of these innovative processes hinder full-scale application. Moreover, the current uncertainties about EOC metabolites and toxicity levels lead to significant treatment problems. It is essential to conduct further studies to (1) determine the toxicity of EOC metabolites after treatment, (2) investigate the effect of operating conditions, and (3) develop further cost-effective applications. The selection of Best Available Technology (BAT) depends on copious factors such as environmental desirability, applicability, technical aspects, social acceptability, and economic viability. Among the BATs, it was determined that the membrane-based treatment processes were promising in alleviation of EOC-oriented problems in water media [9]. The membrane technology represents important and attractive interactions such as electrostatic exclusion/repulsion, steric hindrance, and solution effects between the membrane and the solute [10]. Furthermore, different mechanisms associated with these interactions, namely convection, diffusion, and charge effects, which are extremely interrelated, have been considered during membrane separation. Undoubtedly, the structural properties and limited concentrations of EOCs are other important factors that affect their removal efficiencies with membrane technologies [11].

This chapter aimed to analyze and summarize numerous scientific research papers available in the literature in three main sections: (1) determination of EOC risk groups in water media using a frequency-based approach, (2) the innovative technologies and material applications used in combined treatment systems based on their advantages and drawbacks for EOC risk groups, and (3) economic analysis of combined technologies for EOC removal.

2 Risk Grouping of Emerging Organic Compounds (EOCs) in Water Media

EOCs reach wastewater treatment plants and receiving water bodies after utilization [12]. There are numerous studies that reported relatively high EOC concentrations in wastewater treatment plant effluents in both developed [13–23] and developing countries [24–33]. The upgrade of existing wastewater treatment plants with innovative technologies has been implemented in developed countries such as Switzerland [15, 34, 35], Austria [4], and the USA [36]; however, no treatment plant upgrade strategies have been developed in other developed and developing countries. Furthermore, there are no regulations to control EOCs in wastewater treatment plants and water sources. Despite that, Australia published recommended EOC values in water recycling guidelines for the enhancement of drinking water supply [37]. There are thousands of compounds that could be considered as EOCs in water media; therefore, the contaminants should be prioritized at management levels based on their environmental risks, especially in developing countries due to the technical applicability and economic reasons. The risks induced by chemical compounds depend on their concentrations in the environment and toxicity for organisms. Based on the Environmental Risk Assessment (ERA) approach, the ratio of Predicted Environmental Concentration (PEC) to the Predicted No Effect Concentration (PNEC) equals to the risk quotient (RQ) [38, 39]. Although the risk threshold assumption might vary among different studies, an RQ value between 0.1 and 1 indicates a potential risk. The use of Measured Environmental Concentrations (MEC) rather than PEC could be more reasonable to obtain factual RQ [40]. For two decades, the analytical methods have been developed for EOC measurements, and EOC concentrations have been investigated in various regions in several countries. However, the measurement data are still not complete or limited, especially in developing countries due to the complexity and high cost of measurement methods. Therefore, the use of the existing MEC values when grouping the EOC risks could provide a perspective to determine the focus groups for innovative removal technologies and materials. Due to the fact that there are thousands of EOCs, MEC/PNEC data were combined for EOC groups with quadratic mean in this chapter.

The existing literature demonstrated that MEC and PNEC data were ubiquitous for some PhACs; however, the EOC data for the group of personal care products, pesticides, natural hormones, industrial chemicals (flame retardants, plasticizers, and food additives) were limited to group analysis. For the EOCs, for which MEC and PNEC data are available, PhACs were categorized based on therapeutic groups such as antibiotics, analgesics/anti-inflammatory drugs, psychiatric drugs, β-blockers and lipid regulators and hormones and presented in Table 1. Each group included EOCs with various MEC/PNEC ratios. To indicate the environmental risk by group, quadratic average of the EOCs in the therapeutic group was analyzed and presented in Fig. 1a. Analgesics exhibited the highest MEC/PNEC value since they included several EOCs with a ratio of >1, including the EOC with the highest MEC/PNEC

Table 1 Classification of PhACs based on the therapeutic groups with available data for MEC/PNEC

Groups	Compounds	MEC/PNEC	Frequency I	Frequency II
Antibiotics	Tetracycline	0.02 [41]	0.89 [27]	–
	Norfloxacin	0.22 [42]	0.79 [27]	–
	Chloramphenicol	0.33 [42]	0.65 [43]	–
	Erythromycin	1.89 [42]	0.71 [44]	0.33
	Sulfamethoxazole	1.9 [41]	0.57 [44]	0.65
	Ofloxacin	5.4 [42]	0.63 [27]	0.24
	Trimethoprim	8.93 [41]	0.71 [44]	0.48
	Amoxicillin	16.03 [45]	0 [46]	0.1
Analgesics, Anti-inflammatory drugs	Acetaminophen	0.14 [47]	0.43 [44]	–
	Ketoprofen	0.01 [41]	0.5 [46]	–
	Hydrochlorothiazide	0.01 [41]	–	–
	Salicylic acid	0.076 [48]	1 [46]	–
	Naproxen	0.41 [41]	1 [46]	–
	Acetylsalicylic acid	0.91 [49]	–	–
	Paracetamol	1.03 [42]	0.72 [43]	0.37
	Roxithromycin	1.63 [42]	–	0.19
	Fluoxetine	3.98 [42]	0.14 [44]	0.11
	Ibuprofen	33.71 [42]	1 [46]	0.46
	Diclofenac	246 [42]	1 [44]	0.49
Psychiatric drugs	Diazepam	0.01 [50]	0.65 [43]	–
	Salbutamol	0.38 [49]	0 [46]	–
	Carbamazepine	18.32 [42]	0.86 [44]	0.2
β-Blockers	Sotalol	0.02 [49]	–	–
	Metoprolol	0.29 [51]	–	–
	Propranolol	2.4 [48]	–	0.27
	Atenolol	0.08 [42]	–	0.28
Lipid regulators	Fenofibric acid	0.13 [52]	–	–
	Gemfibrozil	0.21 [42]	0.25 [46]	–
	Clofibric acid	0.92 [53]	1 [12]	–
	Bezafibrate	1.06 [42]	1 [46]	0.27
	Sulfasalazine	64.3 [41]	0 [46]	0.01
Hormones	Estrone	0.32 [42]	0.71 [44]	–
	Estradiol	5.7 [42]	0 [46]	0.17
	Ethynilestradiol	29 [45]	0.14 [44]	0.18
	Estriol (E3)	40.27 [42]	0.43 [44]	0.1

value (diclofenac). Due to widespread use of analgesics for therapeutic purposes and low removal efficiency of existing wastewater treatment plants, analgesic EOCs such as diclofenac exhibit high MEC values. Thus, innovative technologies and materials will be required for efficient removal of EOCs to decrease the MEC/PNEC values. Antibiotics, estrogens, and lipid regulators are also known as widely used therapeutic agent groups and widely studied in environmental research; however, their

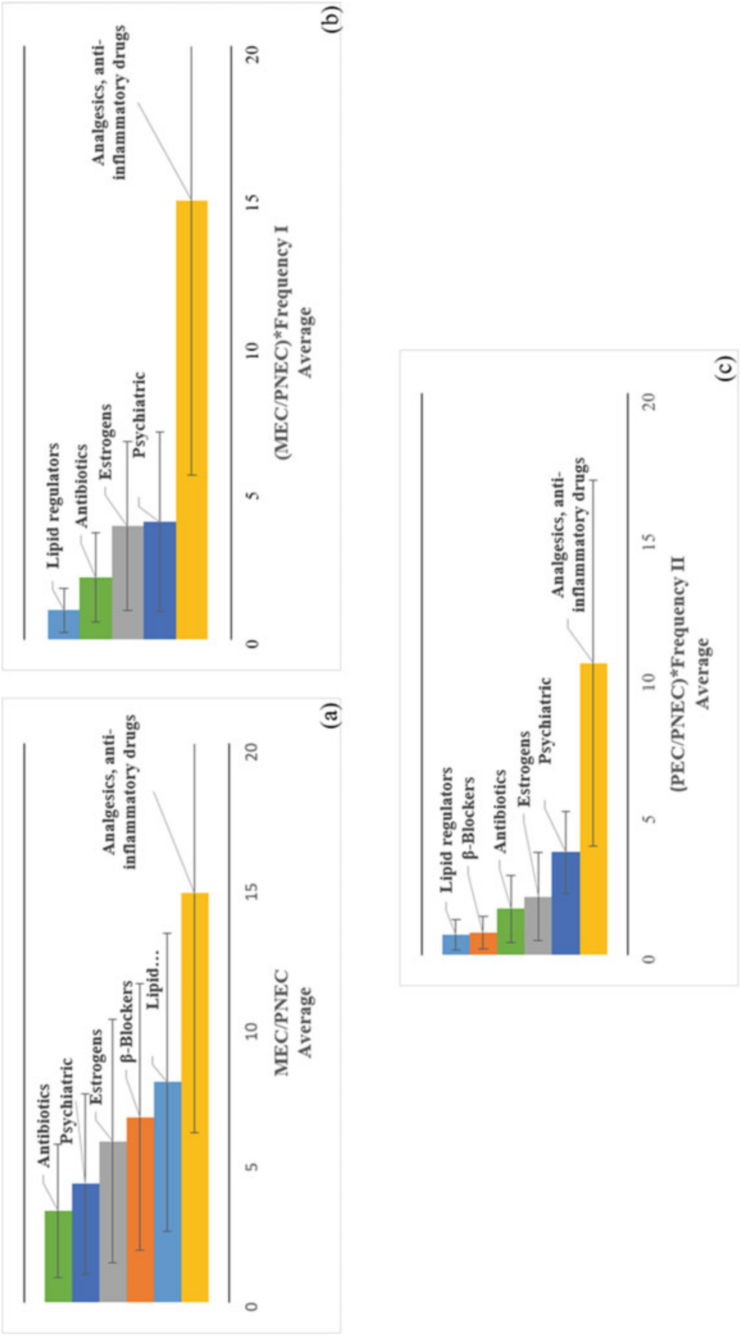

Fig. 1 Risk grouping for PhACs based on therapeutic groups by using quadratic average of EOCs shown in Table 1. (**a**) based on MEC/PNEC with the data available in the literature (maximum MEC and minimum PNEC is used for the worst-case situation) (**b**) MEC/PNEC multiplied by Frequency I (**c**) MEC/PNEC multiplied by Frequency II. Error bars show the standard deviation of MEC/PNEC values for each group

MEC/PNEC values were comparatively lower. In fact, MEC and PNEC reflect hazard levels rather than risk levels. The hazard entails the degree of harm, while risk takes into account the probability of occurrence in addition to the degree of harm (hazard). Therefore, risk could be formulized as the MEC/PNEC multiplied by likelihood [42]. Likelihood means the number of times that EOC is present in a sampling period. Although the data were limited, MEC/PNEC values were multiplied by available EOC frequencies in Table 1 and are presented in Fig. 1b. Psychiatric drug, estrogen, and antibiotic groups follow the analgesics in the risk groups based on EOC frequencies and are considered in risk calculations. Figure 1b indicates PhAC risk groups based on prioritization, in addition to highlighting the need for the innovative technologies and materials to improve the removal efficiency of respective EOCs in water media. Due to the limited sampling measurement frequency data, the percentage of EOC content in the total number of EOC removal studies was accepted as the likelihood in risk calculation presented in Table 1, and the results are presented in Fig. 1c. There was no difference between Fig. 1b, c based on the order of risk groups. This might demonstrate that the frequencies reported in studies for a certain EOC was compatible with its frequency in the environment. Thus, the frequencies reported in EOC studies could be used as an approach for the ranking of EOCs in treatment studies with innovative technologies and materials. As seen in Table 1, Frequency I was based on the number of occurrences in a certain number of sampling periods. On the other hand, Frequency II was based on the number of occurrences in published papers on EOC removal. The EOCs in Table 1 were summarized based on the rank of the most studied EOCs in the literature after 99 papers published between 2010 and 2020 were analyzed using the Web of Science (WoS) database in Quartile1 journal ranking with keywords "removal of" followed by the group names presented in Table 1.

3 Innovative Technologies and Materials Used in Combined Treatment Systems

Following the toxic and persistent properties of EOCs that pose a potential threat to humans and aquatic life, several researchers investigated EOC removal possibilities using various treatment technologies [54–56]. These technologies include aerobic and anaerobic biodegradation, chemical oxidation, adsorption, membrane separation, solvent extraction (treatment of sediments, sludge, and soil primarily containing organic compounds), photocatalysis, and ultrasonic degradation technologies. These technologies can be used as a single process in certain cases; however, the recent and innovative studies evidenced that the combination of these technologies with membrane processes would improve EOC reduction in the environment [57–60]. The combined systems provide several advantages such as high selectivity, easy upscaling, and modularity. Moreover, a treatment combined with membrane systems ensures the integration of innovative technologies and materials. The common membrane technologies for the removal of EOCs include pressure-driven membrane processes (e.g., ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO)), forward osmosis (FO), and membrane distillation [9]. In this section, a comprehensive overview is presented on the combination of membrane technologies with biological treatment technologies, adsorption, and advanced oxidation process (AOP) in EOC removal from water and wastewater.

3.1 *Biological Treatment and Membrane Combined System*

The mechanism of biological treatment is to degrade the EOCs with large molecular size to those with smaller molecular sizes using a microorganism community (e.g., algae, bacteria, and fungi). Generally, during the biodegradation of EOCs, the organic compounds act as a substrate for microorganisms [61]. Commonly, the biological processes provide promising degradation efficiency, which can totally degrade the EOCs in most cases [62]. Biological treatment could be classified as aerobic and anaerobic processes, which could be preferred based on wastewater properties. Membrane Bioreactors (MBR), Sequence Batch Reactors (SBRs), and conventional Activated Sludge (AS) can be preferred in aerobic processes [63]. Various operational conditions should be controlled during conventional AS system; i.e., temperature, pH, Sludge Retention Time (SRT), Hydraulic Retention Time (HRT), and Dissolved Oxygen (DO). Furthermore, other parameters such as Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Volatile Suspended Solids (VSS), Total Suspended Solids (TSS), nutrients (e.g., phosphorus and nitrogen), and pathogens [64] should be monitored. The AS process in EOC removal has various advantages such as low impact on the environment [65] and low operational costs [61, 65]. However, the activated sludge process could not completely remove pharmaceutical compounds [61]. A small section of EOCs could be removed by aerating volatilization, chemical precipitation, sludge absorption, and primary settling, while the major part of EOCs could be removed with biodegradation [61]. The EOCs tend to accumulate on the solid phases such as sediments or activated sludge. The structural properties of EOCs affect its accumulation in the sludge phase, and it mainly occurs due to hydrophobic interactions between the EOCs [66, 67]. K_{ow} (octanol-water partition coefficient) and K_d (soil adsorption coefficient) values are important parameters in the use of hydrophobicity of contaminants. The K_d value is used for the measurement of chemical substance adsorbed onto soil per unit of water. Higher values mean stronger adsorption to soil or organic matter (the higher sorption tendency). If there is more stability across the soil, the contaminants could be adsorbed rather by the sludge in biological treatment [59]. Therefore, it is really important to take not only the liquid phase but also the solid phase into consideration to study the fate of EOCs and their metabolites.

Anaerobic processes could be conducted with anaerobic film reactors, anaerobic filters, and anaerobic sludge reactors [63].

Comparative studies on aerobic and anaerobic degradation of organic pollutants demonstrated that aerobic conditions were more effective for the removal of organic pollutants, whereas it was assumed that anaerobic digestion was more sensitive to toxicants when compared to its aerobic counterparts [68]. The major drawback of aerobic treatment is higher energy consumption when compared to anaerobic conditions. Thus, anaerobic treatment could be preferred in the removal of EOCs [69]. Furthermore, the anaerobic process allows the treatment of high strength wastewater since it requires low sludge yield, less land area, lower operational costs, and fewer nutrients. Besides, both biogas production and energy recovery can be achieved with anaerobic treatment. Nevertheless, due to the recalcitrant and low biodegradable properties of certain EOCs, anaerobic processes are not always practical in the treatment of these types of contaminants [63]. Due to low biomass growth in anaerobic reactors, the biodegradation of recalcitrant contaminant is limited [70, 71]. The operating parameters and/or conditions play an important role in EOC removal or degradation efficiency. These operational parameters are used to analyze the performance of the anaerobic system. These parameters include pH, HRT, SRT, and Organic Loading Rate (OLR) [70]. The performance of anaerobic processes in EOC removal depends on the contaminant molecular/physicochemical properties such as hydrophobicity, polarity, surface charge, and molecular size and structure. According to Tadkaew et al. [72], there is a correlation between the level of biological degradation and the existence of certain moieties in the molecular structure of the specific organic compound. In the same study, it was reported that diclofenac and fenoprop had strong electron withdrawing functional groups (e.g., chloro, amide, and nitro) and they were resistant to biological degradation, leading to lower removal efficiency. Certain studies evidenced that the main EOC removal mechanism was biodegradation with anaerobic treatment [73]. According to a study that was conducted under anaerobic conditions by Joss et al. [74], the removal efficiency of estrogens was very low under anaerobic conditions when compared to aerobic conditions in conventional activated sludge systems. Nevertheless, conventional processes based on activated sludge are often not adequate to ensure high removal of most EOCs. Therefore, the use of only conventional biological treatment is not a practically feasible alternative to several other types of EOC removal. However, encouraging results were reported when the biological processes were combined with membrane technologies [69]. The combination of biological and membrane systems (i.e., membrane bioreactor (MBR)) could achieve higher and more consistent EOC removal when compared to conventional systems. Two MBR configurations could be applied as side-stream MBR and submerged MBR. In side-stream MBR, the membrane module is externally connected to the bioreactor, while in submerged MBR, the membrane module is placed inside the bioreactor [75, 76]. Side-stream MBR consumes more energy than submerged MBR due to pump use for biomass circulation. Furthermore, the submerged MBR system has several benefits due to the preservation of the activated sludge in suspended state and the presence of abundant oxygen in the aeration process. Moreover, the membrane fouling could be easily controlled in submerged MBR system since the membrane surface can be continuously scrubbed by aeration [75]. In MBRs, EOCs are removed with biological reactions adjacent to the surface rejection by the membrane. Furthermore, EOCs with high molecular weight are held by the bioreactor membrane that allows high retention time for the biodegradation of EOCs [77]. Recently, aerobic membrane bioreactors (AeMBRs) were upgraded to anaerobic membrane bioreactors (AnMBRs) due to certain disadvantages of AeMBR such as higher energy consumption, higher solid yield, and greenhouse gas emissions (CO_2 and N_2O) when the nitrification and denitrification processes are implemented. Thus, there is a growing interest in AnMBRs technology to eliminate the drawbacks and improve the advantages [78].

Various studies that employed biological processes and membrane technologies for EOC removal are presented in Table 2. For instance, Sahar et al. [83] investigated two configurations: (1) conventional AS-UF/RO and (2) MBR/RO for the removal of six antibiotics (erythromycin, roxithromycin, clarithromycin, sulfamethoxazole, sulfamethazine, and trimethoprim), three pharmaceuticals (ibuprofen, salicylic acid, and diclofenac), one industrial product (Bisphenol A), and one hormone (cholesterol). It was reported that the removal of hydrophobic macrolide antibiotics (Log $K_{ow} \sim 3$) with the first configuration (conventional AS/UF) was around 72% and 93%, while the removal was 89–91% in the MBR process. The high performance in MBR was explained by the higher SRT (>40 days). Moreover, the hydrophobic interactions between the contaminants and membrane surface contributed to better removal efficiency in PhACs. In higher PhAC concentrations in MBR, low K_{ow} may lead to the sorption of PhACs onto the membrane surface biofilm layer. It was also reported that RO had a positive effect on the removal of contaminants; however, the additional treatment techniques should be reviewed to ensure full removal efficiency [83].

According to pilot study conducted by Holloway et al. [80], an osmotic membrane bioreactor (OMBR) combined with UF and RO was operated to treat 20 organic trace chemicals. The removal mechanisms of contaminants were explained by biodegradation and adsorption. A mass balance in the liquid phase was reported with contaminant Log D values. It was reported that the FO membrane rejection of ionic and nonionic hydrophilic contaminants was higher when compared to nonionic hydrophobic contaminants. This finding demonstrated that except bisphenol A and N, and N-diethyl-m-toluamide, all selected contaminants were removed by the RO membrane in the study. Wei et al. [84] investigated the removal of 15 EOCs with a side-stream AnMBR (i.e., anaerobic reactor followed by ultrafiltration membrane) and an NF membrane. They found that the biological removal of biodegradable EOCs (e.g., sulfamethoxazole, amitriptyline, fluoxetine, Tris (1,3-dichloroisopropyl) phosphate, diphenhydramine, and trimethoprim) was higher when compared to the refractory EOCs (e.g., atrazine, dilantin, carbamazepine, primidone, N, N-diethyl-m-toluamide, and Tris (2-chloroethyl) phosphate). More than 80% biological removal of biodegradable EOCs was achieved, while the refractory EOC removal did not exceed 40%. Generally, the biodegradable EOCs have a strong electron donating group, while the refractory EOCs have a strong

Table 2 Some studies concern with the combination of biological processes and membrane technologies for the removal of EOCs

Treatment system	Membrane properties	Treatment Scale	Studied EOC	Treatment efficiency (%)				Reference
				Biological Reactor	Membrane	Combined	Post treatment	
MBR	Membrane type: Microfiltration (MF) module type: Hollow fiber Membrane material: Polyvinylidene fluoride (PVDF) pore size: 0.4 μm Surface area: 0.02 $m^2 \times 2$ Flux: 10.41 L. m^{-2} h^{-1}	Lab-scale	Acetaminophen	>84	–	95	–	[59]
			Naproxen	>84		97		
			Bezafibrate	70		–		
			Ketoprofen	63		87		
			Atenolol	43		59		
			Propranolol	17		29		
			Roxithromycin	33		51		
			Trimethoprim	–		36		
			Norfloxacin	–		–		
			Tetracycline	–		87		
			Sulfamethoxazole	–		55		
			Carbamazepine	–		NS[a]		
			Clofibric acid	–		–		
			Diclofenac	–		36		
MBR	Membrane type: UF Membrane module: Hollow fiber Membrane material: PVDF Surface area: 9 m^2 Flux: 14 L.m^{-2} h^{-1}	Pilot scale	Diclofenac	–	–	NS[a]	–	[79]
			Sulfamethoxazole			78.5		
			Trimethoprim			80		
			Carbamazepine			NS[a]		
			Naproxen			82.3		
			Propranolol			NS[a]		
			Ibuprofen			100		
			17β-Estradiol			100		
			Gemfibrozil			45.8		
MBR	Membrane type: MF Membrane module: Flat sheet Pore size: 0.45 μm	Lab-scale	Diclofenac	–	–	29	–	[57]
			Erythromycin			82		
			Estrone			99		
			Ethinylestradiol			95		
			Ibuprofen			92		

			Naproxen Roxithromycin Sulfamethoxazole Trimethoprim			95 70 80 52		
MBR	Membrane type: UF Membrane module: Hollow fiber Pore size: 0.045 μm	Lab-scale	Diclofenac Erythromycin Estrone Ethinylestradiol Ibuprofen Naproxen Roxithromycin Sulfamethoxazole Trimethoprim	–	–	62 91 99 96 99 90 98 74 42	–	[57]
UF-OMBR + RO	Membrane type: UF Membrane module: Hollow fiber Membrane material: PVDF Module surface area: 0.44 m^2 FO membranes material: Cellulose triacetate (CTA) Total membrane area: 1.2 m^2	Pilot scale	Acetaminophen Ibuprofen Naproxen Atenolol Trimethoprim Diclofenac Sulfamethoxazole Fluoxetine	–	–	>90 >90 >90 >90 >99 75 64 55	>90 >90 >90 >90 >90 >90 >95 >90	[80]
MBR + NF	Membrane type: MF Module type: Hollow fiber Membrane material: PVDF Pore size: 0.4 μm Total surface area:	Lab-scale	Salicylic acid Ketoprofen Acetaminophen Naproxen Ibuprofen Diclofenac Carbamazepine	–	–	97 65 87 45 96 <20 30	>95 >95 87 >95 >95 >95 87	[81]

(continued)

Table 2 (continued)

Treatment system	Membrane properties	Treatment Scale	Studied EOC	Treatment efficiency (%)				Reference
				Biological Reactor	Membrane	Combined	Post treatment	
	0.074 m^2 Flux (average): 0.07 m d^{-1}		Gemfibrozil Estriol Estrone 17α-ethinylestradiol 17β-estradiol			99 95 97 >90 >90	99 95 97 >95 >95	
MBR + RO	Membrane type: MF Module type: Hollow fiber Membrane material: PVDF Pore size: 0.4 μm Total surface area: 0.074 m^2 Flux (average): 0.07 m d^{-1}	Lab-scale	Salicylic acid Ketoprofen Acetaminophen Naproxen Ibuprofen Diclofenac Carbamazepine Gemfibrozil Estriol Estrone 17α-ethinylestradiol 17-β-estradiol	–	–	97 65 87 45 96 20 30 99 95 97 >90 >90	>95 >95 >95 >95 >95 >95 >95 >95 >95 97 >95 >95	[81]
MBR (University of Cape Town, UCT) conf.) + RO	MBR Pore size: 0.4 μm Total area: 8 m^2 RO Pressure: 10 ± 1 bar Flow rate: 179.35 ± 1.28 L.h^{-1} MWCO: 100 Da	Pilot scale	Carbamazepine Diazepam Erythromycin Sulfamethoxazole Ofloxacin Atenolol Metoprolol Propranolol Sotalol Salbutamol	–	–	51 67 75–87 69 0 87.10 71.16 67.01 70.88 79	Overall removal rates >99	[82]

MBR (UF) + RO	Membrane type: UF Membrane module: Submerged hollow fiber Total area: 2 m^2 Flux range: 10–20 L. m^{-2} h^{-1} Pressure range: 10–24 kPa	Pilot scale	Sulfamethoxazole Trimethoprim Erythromycin Roxithromycin Ibuprofen Salicylic acid Diclofenac	–	–	69.6 96 90.4 89.5 97–99 97–99 27	97.6 97.2 99.3 99.6 – – > 99	[83]
(conventional AS + UF) + RO	Membrane type: UF Membrane module: Submerged hollow fiber Total area: 1024 m^2 (24 modules) Flux range: 25–47 L. m^{-2} h^{-1} Pressure range: 6–7.4 kPa	Pilot scale	Sulfamethoxazole Trimethoprim Erythromycin Roxithromycin Ibuprofen Salicylic acid Diclofenac	29.4 54.9 46.7 66.8 – – –	–	60.3 66.4 72.2 81.4 97–99 97–99 40	97.6 93.2 99.3 99.9 – – 95	[83]
AnMBR	Membrane type: MF Membrane material: Ceramic Membrane effective area: 0.09 m^2 Pore size: 1 μm	Lab-scale	Carbamazepine Diclofenac Gemfibrozil Ibuprofen, Ketoprofen, Naproxen, Paracetamol, Sulfamethoxazole Trimethoprim	–	–	20 15 25 18 25 38 54 82 94	–	[71]

(continued)

Table 2 (continued)

Treatment system	Membrane properties	Treatment Scale	Studied EOC	Treatment efficiency (%)				Reference
				Biological Reactor	Membrane	Combined	Post treatment	
AnMBR – NF	Membrane type: UF Module type: Hollow fiber Membrane material: PVDF Pore size: 30 nm Filtration area: 310 cm^2 Flux: 6 $L.m^{-2}.h^{-1}$	Lab-scale	Fluoxetine	80	–	98	–	[84]
			Sulfamethoxazole	80		98		
			Trimethoprim	80		98		
			Carbamazepine	<40		30–80		
			Acetaminophen	40–80		80–95		
			Atenolol	40–80		80–95		
UASB + aerobic + external membrane filtration chamber	Membrane type: UF Module type: Hollow fiber Total surface area: 0.9 m^2 Pore size: 0.04 μm Flux: 12.3 $L.m^{-2}.h^{-1}$	Pilot scale	Carbamazepine,	20	20	>40	–	[58]
			Diazepam,	12	22	>40		
			Diclofenac,	15	23	>40		
			Fluoxetine	6	12	>40		
			Ethynilestradiol	0	13	>40		
			Ibuprofen,	20	62	82		
			Estradiol	0	82[b]	82		
			Estrone	0	82[b]	82		
			Naproxen,	92	NS[a]	>75		
			Trimethoprim	79	NS[a]	>75		
			Sulfamethoxazole	90	NS[a]	>75		
			Erythromycin	25	15	40		
			Roxithromycin	31	20	51		

Membrane UASB reactor	Membrane type: UF Module type: 20 fibers of hollow fiber Pore size: 0.04 μm Total area: 0.0245 m^2 Flux: 10 $L.m^{-2}.h^{-1}$	Lab-scale	Diclofenac, Estriol, Estrone, Ibuprofen, Carbamazepine, Atenolol, 17α-Estradiol, 17α-ethinylestradiol, Gemfibrozil, Ketoprofen, Trimethoprim 17β-Estradiol Naproxen, Paracetamol Sulfamethoxazole	–	–	>10 >10 >10 >10 >10 <10–50 <10–50 <10–50 <10–50 <10–50 <10–50 50–>90 50–>90 50–>90 <90	–	[85]

a*NS* Not significant

[b] Removed only by UF

electron withdrawing group. Furthermore, they found that addition of the NF membrane to the AnMBR, EOC removal (in particular, refractory EOCs) was improved to more than 98% for biodegradable EOCs and up to 80% for refractory EOCs. Moreover, atenolol, acetaminophen, and caffeine required more time (45 days) for adaptation, after which the removal efficiency was steady [84].

Alvarino et al. [58] studied an innovative treatment system that included an AeMBR and upflow anaerobic sludge blanket (UASB) reactor as a pretreatment to remove 16 EOCs in municipal wastewater. The experiments were conducted at low temperature (20–22 °C) and with an HRT of 17 h (12 h in the UASB and 5 h in the aerobic stage). Generally, the EOCs with biotransformation property had a high removal efficiency with the UASB and AeMBR when compared to conventional treatment systems. The removal efficiency in certain compounds exceeded 95% with the innovative system after the experiment (150 days). In the anaerobic step, the biodegradable EOC (e.g., trimethoprim and sulfamethoxazole) removal was 84%. The EOC removal mechanism was mainly due to biotransformation; however, musk fragrances were removed by sorption onto sludge surface. The anaerobic system, as a pretreatment phase, was found to be a promising option to improve EOC removal with biotransformation (e.g., sulfamethoxazole, trimethoprim, and naproxen). During the UASB step, it was found that sorption was a crucial mechanism in EOC removal when compared to MBR.

Innovative biological processes include specifically enzyme-based systems that utilize new material. Enzyme-based treatments are beneficial due to the fact that they operate in high and low pollutant concentrations, low amount of sludge generation, their catalytic function, applicability in a wide range of pollutants, and low energy requirements [86]. Despite the advantages of enzymatic treatment, several challenges such as high catalyst costs, inability to reuse the enzyme, loss of enzyme stability under harsh environmental conditions, and formation of hazardous soluble by-products remain. It is possible to solve these issues by immobilization of the enzyme in different solid supports. Furthermore, various examples of successfully insolubilized enzymes help eliminate the above-mentioned limitations associated with reusability and recycling. The bioremediation of wastewater depends on the use of enzyme laccase and peroxidases, which catalyze the oxidation-reduction-assisted biodegradation of various hazardous pollutants by forming radicals that degrade the parent pollutant into more biodegradable and smaller products that exhibit minimal toxicity [86, 87].

3.2 Adsorption Process-Membrane Combined System

Adsorption is a physicochemical process that could be described as a surface phenomenon. The targeted molecules or particles, usually denoted as adsorbates, immigrate from the liquid phase to the solid phase, usually denoted as adsorbents. Targeted molecules travel from the bulk liquid phase to the solid phase driven by the difference in concentration between the two phases and the solubility of the molecules in the liquid phase [88, 89]. Adsorption is categorized in two groups: physical and chemical adsorption. Physical adsorption is attributed to Van der Waals bonds, hydrogen binding, and dipole interactions without electron exchange between the liquid and solid phases. On the other hand, chemical adsorption is attributed to the link between the adsorbent and adsorbate. Furthermore, chemical adsorption includes the evolvement of chemical bonds (covalent or ionic) between adsorbent and adsorbate [88]. Adsorption is a proven process used for water and wastewater treatment, and its applications in wastewater treatment contribute to the removal of hardness ions, heavy metals, nutrients, chlorine, and various organic contaminants. Also, it is used in taste and odor control in municipal wastewater treatment. The removal of organic and inorganic chemical compounds was investigated using adsorption by different types of materials.

EOCs are part of a vast group of contaminants that could be removed with adsorption, revealing a promising and appropriate method to eliminate this persistent group of contaminants [90–92]. The removal of EOCs by adsorption is popular due to its efficiency in the elimination of dissolved pollutants that exist in biological and chemical oxidation treatment effluents. The adsorption process has numerous advantages that make it attractive for the removal of EOCs in wastewater. These advantages include (a) simple design and operation, (b) flexible operation in continuous and batch configurations, (c) environmentally friendly, (d) low investment costs, and (e) reuse and regeneration of adsorbent after exhaustion [93, 94].

Beside those aforementioned advantages, adsorption is proven to have a significant and effective performance in the treatment of dissolved contaminants that endure biological treatment or chemical oxidation [95–97]. Adsorption is preferred over other processes such as advanced oxidation with a potential of producing harmful by-products, since the targeted EOCs might be transformed without being eliminated from wastewater [91, 98, 99].

Different types of adsorbents, including activated carbon (AC) [100], carbon nanotubes (CNT) [101], clay/mineral based adsorbents [102], graphene [103], biochar [104], zeolite [105], and Mesoporous Carbon (MC) and Mesoporous Phenolic resins (MP) [106], were developed and investigated over the last decades for EOC removal in wastewater. AC is one of the adsorbents that have been extensively investigated in the literature on EOC removal using either granular AC (GAC) or powder AC (PAC) and it is proven to be significantly efficient in removing several EOCs [107–109]. Despite its significant performance in EOC elimination in water media, it was not employed in full-scale applications due to the high regeneration cost and the fact that the regenerated AC is not as efficient as the new AC [110]. More recent studies investigated the use of new adsorbents such as graphene and carbon nanotubes, indicating that these two adsorbents had higher capacity and potential for EOCs removal due to their physical and chemical properties [111–113]. Clay/mineral based adsorbents are another type of low-cost, copiously available adsorbents with satisfactory properties [114]. MC and MP resins, which have a stable nature and high affinity for organic pollutants, are promoted as innovative adsorbents. MC and MP are merged carbon and organic polymers and mesoporous materials [115]. Adsorption application as a single process in EOC removal leads to certain drawbacks that are mainly attributed to production costs and regeneration of adsorbents. Additionally, fate of exhausted adsorbents used for EOCs removal is not well addressed in the literature which raises the question about the proper disposal of exhausted adsorbents after use. The miss disposal of these adsorbents might pose a threat to the aquatic environment upon potential release of toxic compounds from their surface. The aforementioned drawbacks require further investigation in order to overcome the problems associated with EOCs removal using adsorption [116].

The employment of adsorption with membrane filtration is one of the common combinations in the literature that have been used as a posttreatment process [117] by either using a GAC column or addition of various PAC doses into the membrane system [118]. Adsorption could possibly enhance EOC biodegradability when it is combined with MBR systems due to biolayer formation on the GAC surface. It was reported that PAC addition decreased the fouling of the membrane and enhanced the removal efficiency upon the formation of biofilm on the activated carbon [119]. Table 3 illustrates different studies on the removal of EOCs using a combination of adsorption and membrane systems.

Baumgarten et al. [128] investigated the combination of adsorption with PAC and microfiltration in MBR system. Different PAC doses (50, 200 and 500 mg/l) were investigated. PAC was tested in two configurations: (1) PAC was added to the MBR and (2) PAC was added to permeate MBR stream as a post treatment. The study findings revealed that adsorption with PAC increased the removal efficiency of the targeted EOCs from a poor removal of 27% up to almost total removal in the case of higher PAC dose additions to MBR units. According to the same study, the results for the case where adsorption was conducted as a post treatment after MBR were similar; however, total removal was not achieved with the posttreatment approach even at high PAC doses.

In another study, two hybrid systems that utilized PAC in combination with ultrafiltration (UF) were compared. One system used pressurized PAC/UF (pPAC/UF) and the other used submerged PAC/UF (sPAC/UF) [124]. Both systems were applied to remove benzotriazole, carbamazepine, diclofenac, mecoprop, and sulfamethoxazole in municipal wastewater treatment plant effluent. pPAC/UF exhibited higher flux and permeability when compared to sPAC/UF. High flux and permeability obtained with pPAC/UF was attributed to the PAC layer formed on the surface of the UF membrane where the development of coating layer helped to protect the membrane surface. Based on targeted EOC removal efficiencies, both systems reported similar removal rates within range of 60–95% at 20 mg/l PAC dose [124]. It was reported that the individual performance of the UF membrane in amoxicillin, carbamazepine, and diclofenac removal was inefficient [120]. However, a combination with PAC increased the removal efficiency to almost 100%. In the same study, PAC was deposited in the membrane system and PAC was circulated within the membrane system. High log K_{ow} and hydrophobicity of compounds had a significant impact on adsorption results where the trend was reported as amoxicillin < carbamazepine < diclofenac [120].

GAC employment in combination with UF was investigated in EOC removal [125]. In that study, several pharmaceutical compounds were investigated: 1000 ng/l

Table 3 Some studies concern with the combination of adsorption and membrane technologies for the removal of EOCs

Adsorption method	Membrane properties	Treatment scale	Studied EOCs	Treatment Efficiency (%)			Reference
				adsorption	membrane	Combined	
Adsorption by PAC	Membrane type: UF Membrane module: Hollow fiber Membrane material: Polysulfone Membrane size: 100 kDa Effective transfer area: 6.6 cm^2	Lab-scale	Amoxicillin Carbamazepine Diclofenac	–	100%	Up to 99	[120]
Adsorption by PAC	Membrane type: MF Membrane module: Flat-plate Membrane size: 0.4 μm Effective area: 0.1 m^2	Lab-scale	Fluoxetine Ibuprofen & Naproxen Diclofenac Carbamazepine Diazepam Trimethoprim, Roxithromycin Erythromycin	–	82–89 >90 NS[a] <20 <20 NS[a] 71–86 42–64	Up to 98	[121]
Adsorption by PAC (trade mark: DOTEX)	Membrane type: UF Membrane size: 100 kDa Effective area: 240 cm^2	Lab-scale	Acetaminophen Carbamazepine Diclofenac Gemfibrozil Ibuprofen Metoprolol Naproxen Sulfamethoxazole Trimethoprim	12 80 32 45 5 92 NS[a] 43 93	NS[a] 70 25 50 NS[a] 40 NS[a] 18 5	>90 for all EOC, except for acetaminophen (~20)	[122]
	Membrane type: MF Membrane module:	Lab-scale	Atenolol Carbamazepine	–	–	99 99	[123]

(continued)

Table 3 (continued)

Adsorption method	Membrane properties	Treatment scale	Studied EOCs	Treatment Efficiency (%)			Reference
				adsorption	membrane	Combined	
Adsorption by GAC (coal-based premium grade – MDW4050CB)	Hollow fiber Membrane material: Poly-acrylonitrile Membrane size: 0.10 μm Effective area: 0.044 m^2		Diclofenac Fluoxetine Gemfibrozil Ketoprofen Naproxen Paracetamol Sulfamethoxazole Trimethoprim			99 89 99 99 99 96 97 99	
Adsorption by PAC	Membrane type: MF & UF Membrane module: Flat sheet (MF), Hollow fiber (UF) Membrane size: 0.45 μm (MF), 0.045 μm (UF)	Lab-scale	Carbamazepine Diclofenac Erythromycin Estrone Ethinylestradiol Ibuprofen Naproxen Roxithromycin Sulfamethoxazole Trimethoprim	–	NS[a] (NS[a])[b] 29 (62) 82 (91) 99 (99) 95 (96) 92 (99) 95 (90) 70 (98) 80 (74) 52 (42)	95 (90)[c] 80 (95) 97 (99) 99 (99) 93 (93) 91 (98) 89 (98) 96 (99) 80 (70) 97 (91)	[58]
Adsorption by PAC	Membrane type: UF Membrane material: Polyethersulfone (pPAC/UF) & polyvinylidene fluoride (sPAC/UF) Membrane area: 0.2 (pPAC/UF), 0.94 (sPAC/UF)	Pilot scale	Carbamazepine Diclofenac Sulfamethoxazole	–	–	89 (pPAC/UF), 96 (sPAC/UF) 85(pPAC/UF), 82 (sPAC/UF) 55 (pPAC/UF), 68 (sPAC/UF)	[124]

Adsorption by GAC (Clarimex 061 CAE and Epibon YM 12X40)	Membrane type: UF Membrane material: Polyethersulfone Membrane size: 3 kDa Effective area: 90.28 cm^2	Lab-scale	Acetaminophen Diazepam Diclofenac Ibuprofen Sulfamethoxazole	12–48 68–99 94–97 43–99 54–94	NS[a] 18–19 25–42 12–26 10–20	28–58 96–99 95–98 64–99 68–96	[125]
Adsorption by PAC	Membrane type: MF Membrane material: Polyethersulfone membrane pore size:0.1 μm Effective area: 0.005 m^2	Lab-scale	Carbamazepine Clofibric Diclofenac	–	–	98–100 95–99 97–100	[126]
Adsorption by biochar	Membrane type: UF Membrane module: Flat sheet Membrane material: Polyamide thin film composite Membrane size: 3 kDa	Lab-scale	17α-ethinylestradiol, Carbamazepine Ibuprofen	–	30 10 40	Up to 45 Up to 75 Up to 75	[127]

[a] *NS* Not significant
[b] Removal % by MF (removal % by UF)
[c] Removal % by MF + PAC (removal % by UF + PAC

acetaminophen and ibuprofen concentrations and 300 ng/L clonazepam, diazepam, diclofenac, and sulfamethoxazole concentrations, which were the usual concentrations found in wastewater. The efficiency of adsorption onto GAC varied between 32 and 95% at 10 mg/l dose and between 43 and 99% at 50 mg/l dose. The same study reported a poor performance for UF with a maximum removal efficiency of 25%. The GAC + UF combination improved UF removal efficiency for all studied EOCs within the range of 58–99%, particularly at high 50 mg/l GAC dose. It was suggested that the removal mechanism of GAC + UF combination could be attributed to log K_{ow} (hydrophobicity) of the studied compounds, as well as to the adsorption onto the UF membrane and GAC surfaces [125]. Biochar was used as an adsorbent in combination with UF membrane in a recent study conducted on 17α-ethinylestradiol, carbamazepine, and ibuprofen removal [127]. The use of the UF membrane alone revealed that ibuprofen removal was the highest, while biochar + UF combination removed the 17α-ethinylestradiol the highest. The UF + biochar removal mechanism in that study entailed hydrophobicity of compounds toward biochar [127].

3.3 Oxidation Process and Combined Membrane System

It is considered that advanced oxidation processes (AOPs) are quite effective on the oxidation of various EOCs. Based on hydroxyl radical generation methods, AOPs are conventionally categorized in four groups: chemical, electrochemical, sonochemical, and photochemical methods. AOPs aim to remove the occasionally non-biodegradable recalcitrant/refractory compounds. Water and wastewater treatments are commonly carried out via several AOPs such as Photo-Fenton reactions, photocatalysis with semiconductors, catalytic oxidation, ozonation, and ultrasound processes [129]. Ozonation is the most preferred AOP in EOC removal. The ozone oxidation includes two general reaction mechanisms: direct ozone reaction and the indirect reaction by OH radicals (•OH) that are formed during the ozone reaction. The primary source for •OH formation is the effluent organic matter (EfOM). EfOM could be considered an AOP due to its high •OH generation potential. HO• is produced with a side reaction of ozone and specific groups of EfOM such as amines. The degradation of EOCs during ozonation depends on the reaction rate constants associated with the respective EOCs, ozone, •OH, and the oxidant exposure. The transformation product and oxidation by-product formation are an important problem for ozonation since the applied doses do not lead to mineralization. However, the use of ozone oxidation in treatment requires further studies on metabolites due to EOC oxidation [6]. EOC elimination with O_3 is energy efficient; however, the kinetics of pollutant removal are rather slow, especially in the removal of persistent compounds that do not include electron-rich chemicals. One way to improve the removal rate is the addition of H_2O_2 to the reaction mixture, which is also called the "peroxone process." Despite its obvious benefits in removal kinetics, the energy cost in the peroxone process is more than five-fold when compared to ozonation.

Similar to the ozonation, the UV/H_2O_2 process is among the most studied commercial oxidation processes utilized in degradation of EOCs. UV/H_2O_2 process entails the production of hydroxyl radicals through irradiation of H_2O_2 with UV light at <300 nm wavelengths. Although it was determined that the UV/H_2O_2 process is more effective when compared to UV photolysis, UV/H_2O_2 energy cost is still 4–5 times higher when compared to the ozonation. The UV/H_2O_2 process also leads to certain significant problems. The first is the requirement for high H_2O_2 concentrations due to a rather low molar absorption coefficient at 254 nm for efficient •OH generation. Furthermore, in real water matrices, •OH production efficiency is further limited by the presence of matrix components, attenuating the penetration of UV light into the solution. The method that entails decomposition of micropollutants by UV/O_3 and UV/O_3/H_2O_2 processes leads to a higher removal rate and lower energy cost when compared to the UV/H_2O_2 process [39, 130].

Several studies were conducted on Photo-Fenton oxidation in wastewater treatment due to its high efficiency in the removal of EOCs in complex aqueous matrices. The process revealed a higher reaction rate when compared to the conventional Fenton method. The Fenton process is based on the reaction of a transition metal (M) with peroxide. Metals such as Fe, Mn, Cu, and Cr are commonly used as transition metals. The reaction between Fe^{+3} and hydrogen peroxide is called Fenton-like reaction, when Fe^{+3} is used instead of Fe^{+2}.

$$M^{+n} + H_2O_2 \rightarrow M^{(n+1)} + \bullet OH + OH- \tag{1}$$

Photo-Fenton oxidation is a version of the Fenton process enhanced via photocatalytic activity. In Photo-Fenton process, UV rays ensure the increased •OH formation rate and efficiency through photo-reduction of Fe^{+3} to Fe^{+2}. Therefore, the redox cycle continues as long as peroxide is present in the environment.

$$Fe(III)OH^{+2} + hv \rightarrow Fe^{+2} + \bullet OH \tag{2}$$

Photo-Fenton method is a promising AOP in the removal of several EOCs in urban wastewater due to its environmentally friendly nature and the possibility of implementation under natural solar irradiation, lowering the operation costs significantly. The effectiveness of the Photo-Fenton method depends on several operating parameters in EOC degradation, including Fenton reagent dose (H_2O_2 and iron concentrations), pH, and wastewater organic/inorganic content [130].

Several studies investigated removal of various EOCs with heterogeneous photocatalysis. EOCs could be degraded with radicals formed by photoexcited electrons or photoinduced holes, or through direct oxidation in the catalyst surface pores. This method was employed in both bench and pilot-scale investigations, where TiO_2-based materials were used as catalysts. Two main configurations were developed in a TiO_2/UV reaction system: the suspended catalyst configuration (slurry design) or the catalyst attached to a carrier material (immobilized design) [131]. The efficiency of a heterogeneous photocatalytic slurry system is usually based on irradiation, catalyst load, initial concentration of target contaminants, and the physical-chemical properties of the wastewater (pH and dissolved effluent organic matter (dEfOM)), where matrix effects are the limiting factors in photocatalytic-based system implementation in urban wastewater treatment plants [6].

In electrochemical treatment, the efficiency is based on the electrode material. The advantages of the electrochemical method include its capacity to mineralize organic compounds and the lack of external reagent use requirement; however, this method requires electric energy. The high energy demand and low removal efficiency in the case of diluted organic pollutant solutions are two main disadvantages. All the above-mentioned technologies are considered as improvements in wastewater or natural water EOC removal. The EOC removal performance is also affected by the intrinsic presence of inorganic anions and dEfOM in wastewater, which could lead to a reaction with the electro-generated hydroxyl radicals and other reactive oxygen species [6].

$$R+ \rightarrow MO_X(OH)_Z \rightarrow CO_2 + zH^+ + ze + MO_x \tag{3}$$

where.

MOx is the oxidized anode,

MOx + 1 is active oxygen,

R is the organic compound, and.

z is the number of hydroxyl radicals adsorbed onto the anode.

Ultrasound radiation, known as sonolysis, is one of the AOPs, and it recently became popular in the literature. Sonolysis is based on a process, where acoustic cavitation bubbles produce free radicals such as •OH via water pyrolysis, and))) refers to ultrasound irradiation.

$$H_2O+))) \rightarrow \bullet OH + \bullet H \tag{4}$$

$$2\bullet OH \rightarrow H_2O_2 \tag{5}$$

$$2\bullet OH \rightarrow H_2O + O \tag{6}$$

Among different AOPs, sonolysis is a rarely investigated process in the literature among various AOPs, and even fewer studies were conducted on sonolysis EOC degradation in urban wastewater effluents [132].

Recently, innovative studies focused on AOP and membrane process combinations given the fact that the membranes efficiently separate contaminants from water but fail to degrade them. Furthermore, the combination methods could help minimize fouling problems in membrane systems. EOC removal could be optimized based on effluent quality, reliability, and operational costs with treatment method combinations. AOPs produce a strong oxidant that oxidizes the foulant and improves the permeability of membrane performance, facilitating the elimination of membrane fouling and remediating pharmaceutical compounds. The removal of EOCs by Low and Medium Pressure (LMP) processes such as microfiltration and ultrafiltration was reported to be difficult due to their low molecular weight when compared to membrane pores [133]. Consequently, the oxidation pretreatment combined with LPM has the potential of significantly improving removal efficiency. The combination of AOP and membrane processes decreases system costs and increases the removal performance. It was considered that EOCs were not effectively removed by a single AOP due to factors such as (1) uncertainties in the derivatives that form based on the wastewater matrix, (2) the uncertainties in the metabolites that occur due to AOP degradation and related ineffectiveness in their analysis, (3) higher cost of known metabolite standards when compared to EOC active substance standards, (4) lower concentrations of known metabolites, which remain below the detection threshold of equipment such as gas chromatography-mass spectrophotometer (GC-MS) and liquid chromatography-mass spectrophotometer LC-MS/MS, and (5) the higher toxicity of the known metabolites.

The combined treatment systems that utilize AOPs and membranes to remove EOCs from water and wastewater are presented in Table 4. Most studies in the literature were conducted with photocatalytic membrane reactors. Certain studies preferred to use UV-lamps in oxidation, and it was observed that their removal efficiency was high [134]. Studies demonstrated that the water matrix applied in EOC removal was also effective [137, 140]. In addition, removal efficiency depends on the catalyst content, UV-radiance power, type of the membrane, and operating conditions. In a study, Photo-Fenton and TiO_2 photocatalysis were compared and it was observed that the Photo-Fenton process exhibited a higher mineralization level [136]. Lee et al. [143] utilized a combination of catalytic ozonation-membrane filtration process to investigate the degradation of EOCs. Surface morphologies and elemental distributions across the Catalytic Ceramic Membranes (CCMs), fabricated with citrate sol-gel assisted wet impregnation method, were characterized by scanning FESEM-EDX and AFM electron micros. CeOx-impregnated CCM (Ce-CCM) exhibited higher EOCs mineralization when compared to that of MnOx-impregnated CCM (Mn-CCM). Multiple impregnation cycles increased the CeOx load in Ce-CCM and a higher HRT resulted in higher total organic carbon (TOC) removal. It was found that Ce-CCM enhanced the O_3(aq) decomposition and Reactive Oxygen Species (ROS) generation. LC-MS/MS and catalytic ozonation were used to identify the intermediate combined process by-products and the EOC degradation pathways, respectively. The proposed heterogenous catalytic ozonation with Ce-CCM mechanism and doubled membrane contact from 6.8 to 13.7 s resulted with 29% improved TOC removal with 1xCe-CCM. The effective EOCs mineralization in membrane micropores was obtained due to the catalytic O_3(aq) decomposition that led to higher ROS generation, highly dispersed surface-active sites throughout the CCM pores treated as a microreactor, and the impact of Ce(III/IV) redox pair in facilitation of electron transfer resulted in an enhanced Ce-CCM mineralization capacity. Hence, the authors argued that the proposed combination of catalytic ozonation–new membrane filtration process was effective on EOC degradation.

Table 4 Some studies concern with oxidation processes and membrane technologies for the removal of EOCs

Oxidation method	Membrane properties	Scale	Studied EOC	Treatment efficiency (%)	Reference
				Combined	
UV-Phc	Membrane type: UF Module type: Hollow fiber Area: 4.19 m^2 Membrane material: PVDF Pore size: 0.03 μm Flux: 2.4–3.7 L. m^{-2} h^{-1}	Pilot scale	Diclofenac	56–100	[134]
UV-Phc	Membrane type: MF Material: Ceramic Pore size: 10 μm	Pilot scale	Atenolol Carbamazepine Diazepam Diclofenac Ibuprofen Naproxen Fluoxetine Estradiol Estrone Ethynylestradiol Gemfibrozil Sulfamethoxazole Trimethoprim	>80	[135]
UV-Phc (TiO_2) / UV-Fenton	Membrane type: NF/RO Module type: Flat sheet Area: 139 m^2 Material: Polyamide Flux: 20 L. m^{-2} h^{-1} for NF	Lab-scale	Sulfamethoxazole Diclofenac Hydrochlorothiazide	95 <95–100 90	[136]
UV-Phc	Membrane type: UF Module type: Hollow fiber Area: 0.097 m^2 Material: PVDF Flux: 15 L. m^{-2} h^{-1}	Pilot scale	Diclofenac	>96	[137]
UV-Phc	Membrane type: UF Module type: Flat sheet	Pilot scale	Estrone Estradiol Estriol Erythromycin	90 90 90 86	[138]

(continued)

Table 4 (continued)

Oxidation method	Membrane properties	Scale	Studied EOC	Treatment efficiency (%)	Reference
				Combined	
	Area: 25 m^2 Material: Ceramic Pore size:60 nm Flux: 100 L. m^{-2} h^{-1}		Trimethoprim Sulfamethoxazole, Metoprolol Roxithromycin	86 86 86 86	
UV-Phc	Membrane type: UF Module type: Hollow fiber Area: 100 cm^2 Material: PVDF Pore size: 0.04 μm Flux: 100 L. m^{-2} h^{-1}	Lab-scale	Atenolol Carbamazepine Diazepam Paracetamol Diclofenac Ibuprofen Naproxen Fluoxetine Salicylic acid Gemfibrozil Sulfamethoxazole Trimethoprim	75 75 75 100 100 100 100 95 100 100 100 85	[139]
UV-Phc	Membrane type: UF Module type: Flat sheet Area: 0.014 m^2 Material: Polypropylene (PP) Pore size: 0.2 μm Flux: 8 L. m^{-2} h^{-1}	Lab-scale	Diclofenac Ibuprofen Naproxen	100 93 94	[140]
UV/H_2O_2	Membrane type: NF Module type: Flat sheet Area: 314 cm^2 Pore size:0.8 μm Flux: 8 L. m^{-2} h^{-1}	Lab-scale	Diclofenac, Amoxicillin	100 100	[141]
Fenton-like	Membrane type: MF Module type: Tubular Area: 0.85 m^2 Material: Ceramic Pore size:50 μm	Pilot scale	Diclofenac	65	[142]

One-pot coupling process is achieved with the combination of membrane filtration and electrochemical advanced oxidation processes [144]. Electric field enhanced membrane, obtained with electro-kinetic effects such as electroosmosis, electrophoresis, and electrostatic interaction, leads to a high permeation flux and treatment efficiency. In-situ electrochemical oxidation of the EOCs and the microflow disturbance near the electrode surface, which maintains high permeation flux and extends the membrane lifespan, reduce fouling and concentration polarization of the membrane [145]. Non-conductive membranes (polymeric or ceramic) are commonly used as the separation media in coupling systems. Commonly, an electrical potential gradient is present across the membrane when non-conductive membranes are used as the separation media and located between the anode and the cathode in one-pot coupling systems. A membrane with good water permeability and pollutant retention is essential. The one-pot process that relies on the conductive membrane as an electrode has several advantages. For instance, the coupling system becomes more compact and achieves higher removal efficiency at the same voltage, leading to lower energy consumption. Furthermore, EOCs are dragged toward the membrane/electrode surface due to the feed solution flow, resulting in an effectively enhanced mass transfer coefficient in the liquid phase. Press forming and metal powder sintering are among the common applications for the production of frequently used porous metal membranes. Various studies extensively focused on stainless steel and porous titanium membranes. Titanium membranes were widely studied due to their good corrosion resistance and feasibility for electro-catalyst loading. These membranes operate as an anode and filtration medium concurrently in wastewater treatment [144].

4 Economic Analysis of the Emerging Organic Compound (EOC) Removal with Innovative Technologies

The previous studies were focused on technical developments in innovative technologies and materials in EOC removal in water/wastewater treatment plants and their economic analysis is yet to be conducted except for a few studies. Since EOCs are usually new chemical substances, which were introduced to the market only a short while ago, they are not considered in existing wastewater treatment plants in the design stage. During the first decade of the twenty-first century, the studies focused on the development of advanced analytical methods for micro- or nano-concentration measurements. In environmental monitoring studies, EOC removal capabilities of existing wastewater treatment plants were investigated. Recently, innovative technologies and materials have been emerging due to the inefficient removal capacity of conventional biological treatment for certain high-risk EOCs; however, these studies lacked economic analyses.

The most detailed economical assessment of hybrid technologies in EOC removal was conducted by Echevarría et al. [146]. They calculated the Operational (OPEX) and Capital (CAPEX) costs for EOC removal (Carbamazepine, Diuron, Erythromycin, Diclofenac, Sulfamethoxazole, Octyl-phenol, Atenolol, Nonylphenol, and Acetaminophen) with MBR and Powdered Activated Carbon (PAC). Furthermore, they compared these approaches with the combinations of conventional biological treatment, Ozonation/UV oxidation and MBR. OPEX was the highest with the PAC and MBR hybrid (0.223 €/m^3) and the lowest with the conventional biological treatment and O_3/UV oxidation hybrid (0.158 €/m^3). Energy and reagent consumption were the highest shares in OPEX with MBR PAC hybrid. CAPEX was the reverse of OPEX with 655 €/m^3/d with the conventional biological treatment and O_3/UV oxidation hybrid and 624 €/m^3/d with MBR PAC hybrid. Although MBR PAC hybrid seemed to be more expensive, when the space is limited in the plant and wastewater recovery is limited, this hybrid produced better removal efficiency. Vela et al. [147] studied the photocatalytic treatment (ZnO and TiO_2) of bisphenols, phthalates and parabens. Treatment cost was the cheapest in ZnO with 102.98 €/m^3/year. For TiO_2 P25 and TiO_2 vlp 7,000, the costs were 148.83 and 285.34 €/m^3/year, respectively. The high cost of the TiO_2 treatment was due to its low capacity for the targeted removal efficiency (90%). Although the unit cost for all materials were almost similar, the reaction time required for 90% removal was much shorter with ZnO, making it the most economically feasible alternative.

The critical cost items in economic analysis of innovative technologies might be the operating costs associated with energy and reagent consumption. Especially in developing countries, operating costs could be higher if the reagents are imported with high duties. However, recovering energy to produce the required electricity by the plant could decrease the costs. In terms of capital costs, countries that produce technology or utilize natural materials would have an advantage. Nevertheless, there is no regulation for the control of EOCs in any country today, and only Switzerland took action to upgrade the existing plants for EOC removal capacity [6]. Since the measurement, hence the monitoring are already too expensive when compared to conventional pollutants and there are no regulations, it could be suggested that economic analysis will not be the focus until full-scale applications will be on the agenda.

5 Future Perspective and Conclusion

To raise the international awareness about the risks and hazards of EOC discharge to water media without any removal is an inevitable requirement to preserve the habitable planet in the current century. Thus, clarification of significant technological trends, filling the knowledge gaps, and wide adoption of best technological practices are extremely sensitive priorities to ensure healthy water supply. The analysis and effective treatment of emerging pollutants require high-cost techniques. Thus, reliable analysis and risk management of EOCs with a focus on the prioritization of pollution prevention would contribute not only to the selection of adequate technologies but also to improve their effectiveness. There is a trade-off between risk levels and cost-effective EOC treatments in aquatic medium. In several guidelines, various strategies were proposed to improve EOC treatment techniques. However, the emerging pollutants should be prioritized and standardized at national level, to decide on the adequate and viable treatment technology, especially in developing countries. Thus, a sophisticated integration and comprehensive coordination between benefits and costs of recommended technologies and identification of environmental control initiatives are required, and national level strategies should be developed for eco-efficient management of EOCs, allowing the sustainable preservation of the resources, healthy water supply, and controlled discharge of treated wastewater.

Prevention of EOC discharge into water resources, independent of the national economic and environmental development level, is among the most important current issues. Based on the studies on the detection of EOCs in conventional wastewater effluents, the efforts have been focused on EOC removal with innovative technologies and materials; however, expectations have not been fully met by lab- and pilot-scale studies. Conventional wastewater treatment plant and novel technological solution hybrids have been pursued at full-scale implementation levels only in a limited number of countries such as Switzerland, Austria, and the USA. For safe and robust ecosystem sustainability, categorization of the EOCs based on their undesired negative effects on nature would be one of the crucial starting points in the facilitation of the development of real scale eco-protective solutions. Developing countries could achieve further benefits from the outcomes of environmental risk categorization in the short term since they could improve R&D support for elimination of diverse EOCs without devoting further financial and temporal resources to the determination of environmental risk groups.

Most research topics on the development of novel solutions for EOC removal were conducted to include performance efficiency and technical feasibility without considering the economic aspects. The most promising combined technologies have been typical membrane treatments assembled with adsorption and advanced oxidation processes. Adsorption materials applied with PAC, GAC, or certain green chemistry products applied after membrane separation enhanced EOC removal efficiency up to 99%. The UV and Fenton are the most widely studied and the most effective advanced oxidation processes that were successfully applied in hybrid systems with membrane technologies to improve EOC removal. The analysis of the expenses of these hybrid technologies in the removal of conventional collective parameters such as organic carbon demonstrated that the operational costs may not be feasible despite no study has fairly supported this claim. Further studies are required to improve the economic perspectives in EOC removal and to invent future economic and innovative technologies and/or optimize the current ones with minimal and acceptable costs. This would contribute to facilitate the advances in full-scale implementations in developed countries. It would also allow the developing countries to develop and implement coordinated mid- and long-term sustainability plans by applying similar technologies or alternative solutions. Another action could entail the facilitation of an international discussion and agreement platform since the permanent nature of hardly removable EOCs could lead to serious legal issues between the nations, as well as health risks and even security conflicts due to their transportation potential across the borders in a not distant future. These platforms for controllable management of EOCs could encourage the collaboration between the developing and developed nations by providing operational opportunities and tools such as central measurement centers or technology sharing. Beside all these control efforts, it was also highly suggested to develop eco-protective technologies for cleaner production of consumables that release EOCs to the environment. Industry 4.0 applications, paving the way for preventing the use of environmental harmful composites, agents and active chemicals and decreasing their volumes in products, could lead to a framework of an environmental protection priority supported by artificial intelligence.

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Trihalomethanes (THMs) in Wastewater: Causes and Concerns

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Contents

Abstract Effective wastewater treatment is critical to public health and well-being. The main function of a wastewater treatment plant is to minimize the environmental impact of discharging untreated wastewater into natural water systems. Disinfection is a vital process to inactivate pathogenic microorganisms in drinking water and wastewater. It also acts as the cornerstone unit operation of the water treatment process that secures drinking water safety. Since the 1970s, it has been recognized that disinfection can produce harmful by-products and cause health concerns.

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Chlorination is the most widely used approach to achieve the disinfection of wastewater but it leads to the formation of disinfection by-products (DBPs) on reaction with the organic matter present. Trihalomethanes (THMs) are the major DBPs formed during the disinfection of water and wastewater. Several water quality operational parameters influence the formation of THMs. The presence of ammonia in wastewater leads to the formation of nitrogenous DBPs in addition to chlorinated and brominated THMs. THMs have been recognized as potential carcinogenic substances, which adversely affects the human health. Owing to the carcinogenic nature of DBPs, guidelines values have been recommended by the regulatory agencies to control their formation and subsequent discharge. The present chapter would describe all the aspects related to THMs formation in wastewater.

Keywords Chlorination, Disinfection by-products, Human health, Risk, Wastewater

1 Introduction

Wastewater must be disinfected to prevent the spread of pathogenic microorganisms essentially when the wastewater is to be used for activities such as irrigation or agricultural uses or groundwater recharge [1]. The main function of wastewater treatment plants (WWTPs) is to minimize the environmental impact of discharging untreated wastewater into natural water systems. Wastewater effluents are generally discharged into the surrounding water bodies such as freshwater or marine water. Recreational water activities are significant from environmental prospective and need protection. Typically, wastewater is transported via sewer pipes to WWTP, where it is treated prior to its discharge into nearby water bodies, such as stream, lakes, or rivers [2]. Domestic wastewater usually contains high level of organic matter, nutrients (nitrogen, phosphorus, and potassium), pathogens, solids, and other substances which deteriorate the water quality if released without proper treatment [3]. Disinfection of wastewater is carried out to kill harmful microorganisms and safeguard human beings from the exposure to waterborne pathogens. During the course of disinfection, inactivation of microorganisms is achieved by introducing biochemical changes in their DNA. This biochemical modification depends on the type of microorganisms present in the wastewater and the disinfectant applied.

Chlorination is the most common practice to achieve the disinfection of treated wastewater, but may produce certain cancer-causing substances and toxic by-products that are potentially harmful to human health and aquatic organisms [4–10]. In early 1970s, it was discovered that disinfection of water leads to the formation of harmful by-products, which has adverse effects on human health. Wastewater disinfection also leads to the formation of these toxic disinfection by-products (DBPs) [11, 12]. DBPs are designated as toxic by-products that are formed by the reaction of disinfectants with organic compounds present in water [13]. THMs are the most prevalent form of DBPs formed in water and wastewater treatment plants and are used as indicators of total (DBP) formation [14]. Total THMs (TTHMs) comprise four different THMs species, namely chloroform or trichloromethane ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), chlorinedibromomethane ($CHBr_2Cl$), and bromoform or tribromomethane ($CHBr_3$). Studies showed that natural organic matter (NOM) and dissolved organic matter (DOM) are the major precursors of DBPs formation in water and wastewater. In wastewater, the reaction between chlorinated compounds and DOM during course of disinfection is much more complex than those during water disinfection [12]. Presence of several classes of pathogens including inorganic and organic substances makes the disinfection of wastewater a cumbersome process compared to drinking water [15].

Formation of THMs in wastewater mainly depends on parameters like organic matter content, chlorine dose, pH, temperature, bromide ion concentration, and the presence of ammonia. High concentrations of organic carbon may result in the production of several chlorinated DBPs compounds after reaction with chlorine [16]. In addition to chlorinated DBPs, brominated or iodinated DBPs are also formed if the source water contains high level of bromide/iodide ions.

Several epidemiological studies suggested links between DBPs exposure with different types of cancers (bladder, colon, and rectal) and adverse reproductive effects [17]. Owing to the potential adverse effects of THMs on human health, THMs are designated as probable carcinogens by USEPA. In human beings, exposure to THMs not only occurs by drinking water intake, i.e. oral ingestion but also by THMs volatilization during day to day activities like bathing, showering, and cooking. Oral ingestion, dermal absorption and inhalation are the three possible pathways of THMs exposure [18]. To regulate THMs, the U.S. Environmental Protection Agency (EPA) Stage 2D/DBP rule sets the maximum contaminant level for four THMs, represented as total THMs (TTHMs) and five HAAs as 80 μg/L and 60 μg/L, respectively, for drinking water [19]. The National Health and Medical Research Council (NHMRC) specified the acceptable guideline values of pathogen indicators such as enterococci which should be considered low risk for activities such as swimming and boating [20]. Unlike the USEPA Stage 2 D/DBP drinking water rules, the Florida Department of Environmental Protection (FDEP) recommended guideline values for each THMs species for surface water discharge. Thus, disinfection of wastewater effluents is required to manage the potential risk exposure to human health.

2 Disinfection of Wastewater

Disinfection is the most crucial phase of the wastewater treatment process. It is the last and final step to remove pathogens from the treated water prior to discharge of effluent into the water system. Several types of bacteria such as *Vibrio cholerae*,

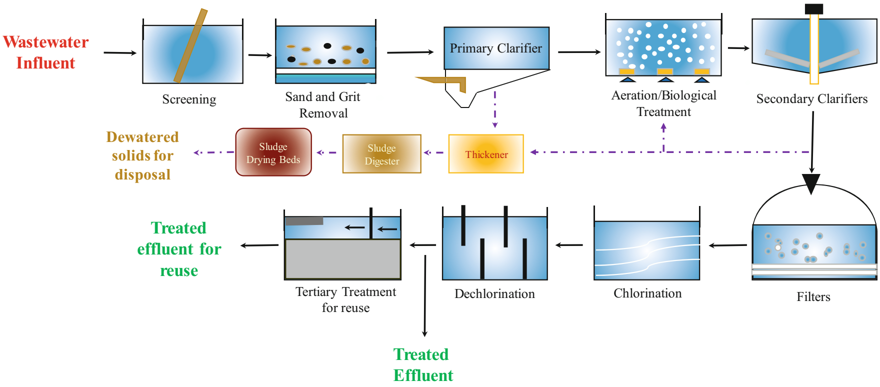

Fig. 1 Unit operations and disinfection of wastewater influent

Salmonella typhi, *Escherichia coli*), protozoa (Cryptosporidium, Giardia), viruses (Rotavirus, Poliovirus, Adenovirus), and helminth ova (Ascaris) are present in water and wastewater [21, 22]. Disinfection inhibits the growth of these harmful microorganisms by reducing their numbers to a regulated level, and thereby prevents the spread of waterborne diseases.

The goal of WWTPs is to generate an effluent which is devoid of pathogenic microbial population and possess negligible risk to human and environmental health [23] Wastewater treatment generally includes several stages, such as biological degradation of organic matter, sedimentation of suspended solids, removal of nutrients, and finally, disinfection to inactivate pathogenic microorganisms [24]. Wastewater disinfection is usually carried out after primary, secondary, and sometimes tertiary treatment. Figure 1 shows flowchart of WWTPs unit operations used for the disinfection of wastewater.

Different types of physical and chemical treatment techniques have been applied to disinfect wastewater before it is released back to the natural water course. Historically, chlorine is the most widely used disinfectant for municipal wastewater treatment owing to its high efficiency, low cost, and higher oxidation potential [10]. However, chlorine disinfection possesses detrimental effects on human health as it leads to the formation of carcinogenic DBPs such as THMs and halo acetic acids (HAAs), affecting surface water quality where the treated wastewater is discharged. In addition to this, during the chlorination process, high concentration of nitrogen in wastewater may also produce nitrogenous DBPs such as N-nitrosodimethylamine (NDMA) [25], which are usually considered to be highly toxic as compared to carbon-based DBPs [26]. The problem of storage and safe handling of chlorine led to the identification of alternative agents for the disinfection of water/wastewater. Other physical methods of wastewater disinfection such as ozonation or ultraviolet (UV) light has also been used [27–30]. Ozone, as a disinfecting agent, has additional advantage as it increases the dissolved oxygen content of the treated wastewater. But ozone needs to be generated, which adds up to the capital cost and expenditure in comparison with traditional chlorination [31]. Use of UV light as a wastewater disinfection method has gained widespread popularity over the traditional chlorine-based disinfection methods due to low construction and maintenance cost including long-term operation and also provides substantial protection to societies, plant workers, and receiving water bodies [32]. The process is advantageous as neither does it add anything to the water nor does it alter the chemical composition or the dissolved oxygen content of the water [33]. Although the above-mentioned chemicals and processes will disinfect wastewater and have certain advantages over one another, none of them are found to be universally applicable.

3 THMs Formation Mechanism

THMs are the major DBPs formed during the disinfection of water and wastewater. DBPs formation usually takes place via three common reactions, i.e. oxidation, substitution, and addition [34–36]. The majority of chlorinated DBPs are formed by oxidation and substitution reactions. In oxidation reactions, NOM especially the humic substances react with chlorinated compounds mainly chlorine and break down the annular structure. As the reaction proceeds, pseudohynol formed first followed by the electrophile substitution of C atom in α-position of carboxyl group [37, 38]. The formed carbonium ion then reacts with chlorine to form trichloromethyl ketone, which further breaks down to produce chloroform [37]. Substitution reactions are important with respect to humic substances. Aromatic compounds like phenol and aromatic acids are easily chlorinated in the water medium by $HOCl^-$ and OCl^-, producing chlorinated equivalents. Methoxyl, phenol, and keto groups are more reactive with chlorine than alkyl or carboxyl groups [38]. Chlorine undergoes an addition reaction if the organic compound has a double bond. Chloroform may be produced through a series of reactions with functional groups (such as acetyl, carboxyl, phenol, and alcohol) of humic substances. Resorcinol structure was identified as the major humic material precursor for chloroform formation and set the platform to study the mechanism of DBPs formation [35]. THMs symbolize a systemic halogenation and show a structural variation of the methane molecule (CH_4), wherein the hydrogen atoms are substituted by four halogen atoms, i.e., fluorine (F), chlorine (Cl), bromine (Br), or iodine (I). Figure 2 represents the mechanism of THMs formation.

NOM is a complex and diverse mixture of organic compounds derived from vegetation decay and animal residues or substances. It may come from natural sources such as the soil or from anthropogenic sources or discharge from sanitary landfills. NOM mainly consists of aromatic and aliphatic hydrocarbons with functional groups such as amides, carboxyl, hydroxyl, and ketones and others in smaller amounts [39–41]. During the process of disinfection, chlorine reacts with NOM especially humic substances to form THMs. Wastewater organic matter generally consists of proteins, carbohydrates, oils, and fats [42], which is considerably different from those found in drinking water. Other than organic matter, bromide ions are

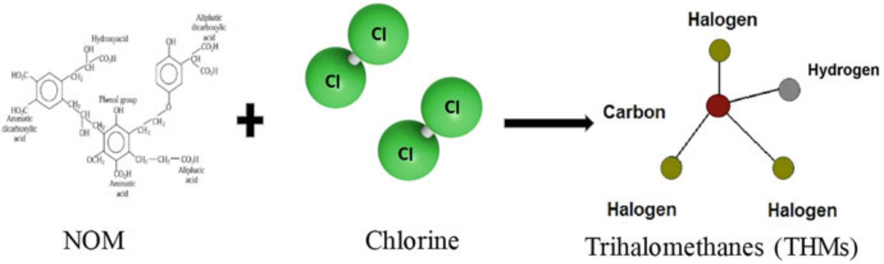

Fig. 2 Process of THMs formation

major inorganic precursors of DBPs formation. Bromide ions are omnipresent in water and wastewater and are rapidly oxidized by chlorine to bromine during chlorination which on further reaction with organic matter leads to the formation of brominated DBPs as mentioned by Eqs. (1), (2), and (3) [19, 43].

$$\mathrm{HOCl} + \mathrm{Organics} = \mathrm{DBPs} \tag{1}$$

$$\mathrm{HOCl} + \mathrm{Br}^{-} = \mathrm{HOBr} + \mathrm{Cl}^{-} \tag{2}$$

$$\mathrm{HOBr} + \mathrm{Organics} = \mathrm{DBPs} \tag{3}$$

where HOCl is hypochlorous acid and HOBr indicates hypobromous acid.

When ammonia is present in treated effluents, it reacts with chlorine to form chloramines (Eqs. (4), (5), and (6))

$$\mathrm{NH_3} + \mathrm{HOCl} = \mathrm{NH_2Cl} + \mathrm{H_2O} \tag{4}$$

$$\mathrm{NH_2Cl} + \mathrm{HOCl} = \mathrm{NHCl_2} + \mathrm{H_2O} \tag{5}$$

$$\mathrm{NHCl_2} + \mathrm{HOCl} = \mathrm{NCl_3} + \mathrm{H_2O} \tag{6}$$

where NH_2Cl indicates monochloramine, $NHCl_2$ as dichloramine, and NCl_3 as trichloramine.

Formation of NH_2Cl, $NHCl_2$, and NCl_3 depends on pH and Cl_2:NH_3 ratio. For example, monochloramine formation is predominant at 5:1 Cl_2: NH_3 ratio. Chloramines form fewer DBPs, i.e., THMs and HAAs compared to free chlorine. Figure 3 shows a conceptual mechanism for the formation of THMs from disinfecting agents such as chlorine and chloramines.

4 Factors Affecting THMs Formation

Chlorination is most widely used practice to achieve the disinfection of wastewater. As mentioned earlier, chlorine reacts with organic compounds which results in the formation of DBPs, including THMs. The formation and speciation of THMs in

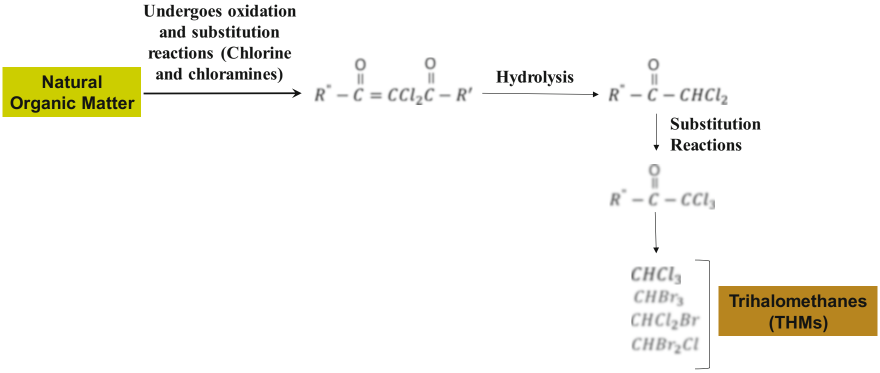

Fig. 3 A theoretical model of THMs formation

WWTP is majorly influenced by several water quality operational parameters [44], including the source, water quality, organic matter content, presence of ammonia, and bromide and iodide concentrations [45, 46]. Plant-specific disinfection variables affecting THMs formation includes contact time, pH, chlorine dose, and temperature. The effect of water quality operational parameters like pH, temperature, organic matter concentration, chlorine dose, ammonia concentration has been discussed below.

4.1 pH Effect

In general, the rate of THMs formation increases with pH [47]. For instance, a threefold increase in the reaction rate per unit pH increases THMs formation [48]. pH has two effects, viz., decreased pH results in low THM formation, and similarly, increased pH results in high THMs formation [49]. The initial attack is dependent on HClO concentration, which is related to pH. The lower the pH, the higher will be the HClO concentration and results in higher concentration of humics. THMs formation depends on the last step of THM reaction pathway, which is base-catalyzed halo form reaction. The formation of THMs increases with an increase in pH, at pH = 8 THMs production is higher than for pH = 6 [50]. Similarly, the formation of chloroform is predominant at higher pH [51–53]. THM concentration increased by a factor of 2.8 and 1.6, respectively, when pH was increased from 5 to 7 and 10 for a 24 h contact time [45]. When the pH was lowered to 7.0, the TTHMs concentration decreased by 50%. Thus, it can be said that maintaining a low pH during disinfection could help to reduce the formation of THMs [54].

4.2 Temperature Effect

Temperature is one of the most important parameters for THMs formation since it provides the activation energy required for the reaction of NOM with the residual disinfectant. TTHMs increased from 89.37 μg/L to 105.4 μg/L when temperature was augmented by 2°C, and to 139.31 μg/L when temperature increased by 4°C [55]. A 100% increase in THMs was observed when the temperature was increased from 5°C to 30°C [19]. Thus, a rise in temperature could result in an increased THMs formation [24]. Control of temperature during the process of disinfection might be helpful in reducing the formation of THMs at later stages.

4.3 Organic Matter

Organic matter is the chief precursor for the formation of DBPs in the secondary effluent from the WWTPs. Wastewater contains more DOM and suspended matter compared to drinking water. The occurrence of DOM results in chlorine decay in the reused water distribution systems, which decreases the efficacy of chlorine disinfection [56, 57]. Besides this, particles that shelter microorganisms from inactivation by disinfectants also affect the disinfection of wastewater for reuse [58]. TTHM formation increased from 6 μg/L to 8 μg/L when the total organic carbon (TOC) concentration increased from 2 mg/L to 9.5 mg/L, respectively [54]. Therefore, the organic matter concentration shows significant effect and influences THMs formation.

4.4 Effect of Chlorine Dose and Contact Time

Wastewater chlorine requirements vary considerably depending on the effluent quality. Chlorine dose influences the disinfection efficacy of wastewater. High amount of applied chlorine dose would kill more pathogens leaving a higher chlorine residual [24]. In WWTPs, increase or decrease in the chlorine dose either increases the rate of pathogen survival leading to contamination in the receiving water or increases the rate of THM formation [59]. Concentration of THMs increases linearly with increase in chlorine dose [13, 19].

The presence of diverse organic compounds in wastewater is related to THMs formation. Some of organic matter are simple and react with +1-valent halogens to form THMs and are referred to as "fast formers," while other complex molecules react with +1-valent halogens, referred to as "slow formers." Moreover, the relative yields of these "fast formers" and "slow formers" compounds are influenced by the wastewater disinfection scheme employed [7]. Chlorine added to wastewater first reacts with the "fast formers" to form THMs. Marked effect of chlorine dose varies with the different species of THMs. The effect is more considerable for $CHBr_2Cl$ followed by $CHBr_3$ and $CHBrCl_2$ whereas insignificant in case of $CHCl_3$. A logarithmic increase in the formation of $CHCl_3$ and $CHBrCl_2$ occurs with increase in chlorine dose [13]. Formation of $CHBr_3$ also increases linearly with increase in bromide ion levels, while $CHCl_2Br$ and $CHClBr_2$ increased with increasing bromide concentration from 0 to 3.2 mg/L and thereafter the increase was marginal. A sharp decline in the concentration of $CHCl_3$ takes place when the initial bromide levels were increased up to 12.8 mg/L [7]. The evolution of THMs species can be explained by the increase of the relative Cl_2/Br^- molar ratio [60]. During wastewater chlorination, higher Cl_2/DOC mass ratio leads to increased formation of THMs in which chloro-THMs formation was more predominant, and increases with an increase in the chlorine dose [61]. However, the yield of THM species did not change as the contact time was varied for each chlorine dose. This can be explained by the fact that no interconversion occurred between THMs under the specified chlorine dose [62]. THMs were formed independently with constant apparent reaction rates, indicating a minor effect of contact time on THMs speciation. Effect of reaction time is similar to that of chlorine dose in a way that a decrease in the reaction time may cause inadequate disinfection, but an increase may lead to high THM formation potential, THMFP [59]. The formation of THMs increased initially within the first few hours, followed by an insignificant increased phase [19].

4.5 Effect of Ammonia

The presence of ammonia in wastewater significantly influences the formation of THMs. If the wastewater contains high level of ammonia, the formation of combined chlorine, i.e., mono-chloramines, di-chloramines and tri-chloramines, exceeds that of free chlorine. As compared to free chlorine, combined chlorine is a weaker disinfecting agent and forms fewer DBPs [24]. Chloramines, formed by the addition of ammonia are also applied to achieve the disinfection of wastewater. Though, chloramines are used to control the formation of THMs but may elevate the concentration level of total nitrogen in the effluent. The formation of chloramines during the disinfection of water containing ammonia nitrogen and organic matter is faster than TTHM formation [63]. Ratio of chlorine-to-ammonia also plays a significant role in THMs formation. Less TTHMs will be formed if the chlorine-to-ammonia ratio is equal to 1, and a decrease in concentration levels would occur when the ratio is equal to 2 [54]. An increase in ammonia nitrogen results in a TTHM decrease [64–66] due to chloramines formation [67].

4.6 Effect of Bromide Ion

Bromide ion is one of the major parameters which influences the formation of THMs in wastewater. The disinfection process becomes complicated due to the presence of bromide (as $HOBr^-$) in wastewater. $HOBr^-$ formed in the wastewater will react with ammonia and organic substances to produce bromamines and brominated THMs. The reaction mechanism of bromide is similar to that of chlorine [68]. Bromide ions present in the wastewater will be oxidized by hypochloric acid (HClO) to hypobromous acid (HBrO), a much strong halogenating agent than HOCl. Brominated THMs will be formed first, wherein bromine occupies nearly all the existing vacant sites on DOM in the wastewater samples. Several studies advocated that the formation of bromine containing THMs was related to the bromine and chlorine incorporation into THMs [60, 61, 69]. Bromine incorporations into THMs and HAAs increased with increasing the molar ratio of bromide to DOC [70]. The formation of $CHBr_3$ increases nearly linearly with increasing the bromide ion levels, while $CHCl_2Br$ and $CHClBr_2$ increase with increasing bromide concentration from 0 to 3.2 mg/L and thereafter remain constant or slightly decrease [64, 71, 72]. Thus, with an increase in the bromide ion concentration, the formation of brominated THMs is more predominant than the chlorinated THMs. The concentration of bromide ion has been reported to be much higher in the treated effluent from sewage treatment in areas where seawater is used for sanitary purposes instead of drinking [73].

5 Risk of THMs

THMs are designated as potential carcinogenic substances and possess hazardous effect on human health and environment. Human beings can be affected if the treated wastewater discharged into the surrounding water body is used downstream as potable water supply or used as agricultural irrigation source [74]. DBPs in effluent wastewater adversely affect the aquatic life directly and the human health indirectly. Numerous epidemiological studies were conducted to identify the relation between THMs and different health effects; for instance, different types of cancers and reproductive consequences [75, 76]. Several investigations have reported that THMs exposure increases the chance of bladder, colon, and rectal cancers [73, 77–79]. Research on animal studies revealed that chronic ingestion of THMs is related to liver, kidney, and intestinal tumors [80]. In addition, spontaneous abortion and other adverse reproductive outcomes have also been reported. THMs not only cause central nervous system depression, but may also cause hepatotoxicity, nephrotoxicity, teratogenicity, and carcinogenicity [81].

Human beings can be exposed to THMs through different exposure pathways such as oral ingestion (water intake), dermal absorption (skin contact during regular indoor activities such as showering, bathing, and cooking), and inhalation

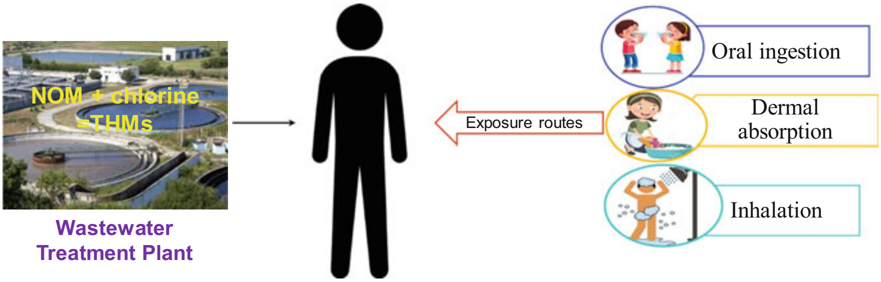

Fig. 4 Human exposure to THMs

(showering/breathing) (Fig. 4). Traditional risk assessment studies only consider oral ingestion of water as the possible route of THMs exposure but other pathways such as dermal absorption and inhalation also need to be considered for precise and accurate risk estimates [82]. Due to the possible toxic effects and impacts of THMs on human health, appropriate treatment technologies must be developed to remove these harmful by-products from water and wastewater matrices.

6 Models to Predict the Concentration of THMs

Since the detection of DBPs in the early 1970s [34, 83], significant amount of research has been carried out to characterize the influence of parameters involved in DBP formation. During disinfection process, the formation of THMs needs to be closely monitored to ensure compliance with the regulatory guidelines or standards limits. A more appropriate perspective can be attained by the application of predictive models to determine the concentration of THMs. Predictive models to determine the concentration of THMs involve establishing empirical or mechanistic relationships between the THMs levels with various water quality operational parameters. Several mechanistic and empirical models have been developed to describe the formation of THMs. The models considered total organic carbon concentration, pH, temperature, bromide ion concentration, chlorine dose, reaction time, etc. as variables. The correlation between THMs and NOM levels has been used to predict the THMs formation [84]. Correlation also exists between THMs precursors and water quality operational parameters responsible for THMs formation [85–88]. The validity of developed models is determined on the basis of R^2 values obtained. The higher the R^2 value, the more significant the model is. The accuracy and validity of the model developed is tested using field scale data. Over the past three decades, numerous models have been developed to predict DBP/THMs formation in drinking waters. A chronological review of the THMs prediction models in drinking water is provided by Chowdhury et al. [89]. But most of these models were developed to predict the concentration of THMs in drinking water supplies. Predictive models to determine the concentration of THMs on wastewater are limited [66] and have not been well explored. Hence, in wastewater treatment, this aspect needs to be considered and special emphasis should be given to develop models which can more suitably predict the concentration of THMs. A list of some of the predictive models is given in Table 1.

7 Guidelines

Even though existence of THMs has been reported in wastewater however, it is not considered as a wastewater effluent parameter even after it has been recognized as a potential carcinogenic and mutagenic substance [97]. EPA suggested that prolonged exposure to THMs has been known to cause several types of cancers in humans. For this reason, Surface Water Quality Standards have been developed and regulated at the discharge point of wastewater plants. USEPA has set the maximum allowable concentration of TTHMs in drinking water as 80 μg/L based on the probable cancer risk to human and other health effects. In order to safeguard the surface water quality, the Florida Department of Environmental Protection (FDEP) recommended guideline values of THMs for wastewater effluents discharged to surface waters. Unlike the USEPA Stage 2 D/DBP drinking water rules, the FDEP recommends the guideline values for each THMs species, i.e., chloroform (470.8 μg/L), BDCM (22 μg/L), DBCM (34 μg/L), and bromoform (360 μg/L) for Class II/III surface water discharge [98]. The European Community's (EC) environmental regulations aimed to mitigate surface water pollution triggered by municipal wastewater (Council Directive 91/271/EEC 1991 as amended by the Commission Directive 98/15/EEC of 27 February 1998) [99, 100]. The regulations make it mandatory for the European Union member states to assure that effluents discharged by wastewater and its subsequent impacts are studied regularly [101]. The current Italian guidelines suggest WWTP effluent discharge values for vast range of chemical contaminants, toxicity, and bacterial discharge to prevent the risk associated with receiving water bodies [102]. In Italy, the regulation recommends that the concentration of active chlorine and *E. coli* concentration should not exceed 0.2 mg/L and 5,000 CFU/100 mL [103]. Wastewater disinfection levels are determined by standards and recommendations that are specific to each country and region [104]. In general, these guidelines/standards are becoming more and more stringent in order to ensure better public health and environmental protection.

8 Summary and Conclusions

The presence of chlorinated DBPs, THMs in wastewater effluents is a cause of concern to public health and is a matter of major environmental problem. A wide variety of parameters influence the formation of THMs in wastewater, but it is primarily influenced by the presence of ammonia in the effluent. It is imperative to

Table 1 Models to predict the concentration levels of THMs in water and wastewater

Models	R^2	References
$\text{THMs} = 0.0412\,[\text{TOC}]^{1.098}[\text{Cl}_2]^{0.152}[\text{Br}^-]^{0.068}[\text{Temp}]^{1.069}[\text{pH}]^{0.263}$	–	[90]
$\text{THMs} = 16.9 + 16.0(\text{TOC}) + 3.319(\text{DOC}) - 1.135(\text{Temp.1}) + 1.139(\text{Reaction time})$	0.920	[91]
$\text{THMs} = -150.83 + 40.95(\text{pH}) + 6.153(\text{Temp}) - 13.876(\text{Res. Cl}_2) + 8.10(\text{Reaction time}) + 6.221(\text{TOC}) + 292.31(\text{UV}_{254})$ $\text{THMs} = 33.436\,[\text{pH}]^{0.062}[\text{Temp.}]^{0.069}[-\text{Res Cl}_2]^{-0.048}[\text{RT}]^{0.018}[\text{TOC}]^{0.079}[\text{UV}_{254}]^{0.045}$	0.955; 0.903	[13]
$\text{THMs} = 415.39 + 2.914(\text{pH}) + 2.129(\text{Temp.}) - 0.129(\text{RT}) + 9.397(\text{Cl}_2\text{dose}) - 17.753(\text{RC}) - 22.872(\text{TOC}) - 802.21(\text{UV}_{254})$	0.937	[92]
$\text{THMs} = 10 - 6.677\,[\text{TOC}]^{1.171}[\text{pH}]^{4.469}[\text{Cl}_2\text{dose}]^{1.765}$ $\text{THMs} = -0.155 + 0.017(\text{TOC}) + 0.001(\text{RT}) + 0.010(\text{pH}) + 0.017(\text{Cl}_2\text{dose})$	Not given	[93]
$\text{THMs} = 0.000395[\text{RT}]^{0.32}[\text{Cl}_2]^{1.3}[\text{pH}]^{2.62}[\text{Temp}]^{0.71}$ $\text{THMs} = 0.2[\text{Temp}]^{0.28}[\text{Cl}_2]^{1.24}[\text{NH}_4 - \text{N}]^{-0.75}$	0.973; 0.999	[66]
$\text{THMs} = 0.0101[\text{Temp}]^{0.119}[\text{Time}]^{0.337}[\text{pH}]^{3.0}[\text{TOC}]^{0.258}[\text{Cl}_2]^{1.067\times10^{-5}}[\text{Algae}]^{-1.86\times10^{-2}}[\text{Br}]^{9.534\times10^{-3}}$	0.844	[94]
$\text{THMs} = 7.07 \times 10^{-2}[\text{TOC} + 3.2]^{1.314}[\text{pH } 4.0]^{1.496}[\text{Dose} - 2.5]^{-0.197}[\text{Temp} + 10]^{0.724}$	0.986	[95]
$\text{THMs} = 3.296[\text{DOC}]^{0.801}[\text{Cl}_2]^{0.261}[\text{Br}]^{0.223}[\text{Temp}]^{0.264}$	0.87	[96]

identify and recognize the effect of DBPs in aquatic environment, as DBPs will inexorably be produced during the chlorination of wastewater. The probability of inadequate decontamination caused by these practices leads to additional risk that needs to be considered in organizing appropriate control measures for the better discharge of treated water to the receiving water bodies. Although adverse effects of chlorine can be diminished by de-chlorinating the effluent prior to its discharge into the surrounding water environment, this practice does not eliminate DBPs. To reduce THMs formation, removal of NOM as well as precursors of THMs formation needs to be carried out. WWTPs should aim to reduce the aromatic content of NOM in order to reduce the DBP precursors before chlorination of wastewater. In addition to NOM removal, the chlorine dose also needs to be regulated to control the formation of THMs.

9 Future Prospective

Formation of THMs in wastewater is widely recognized all across the globe, thus it becomes imperative to implement new approaches/practices which will help to reduce the concentration of THMs in wastewater. Certain practices or modifications/suggestions can be made in the WWTPs and disinfection approaches to control THMs formation are discussed below:

1. Generally, in WWTPs uncovered chlorine contact basins are used for disinfection which exposes the wastewater to UV irradiation from sunlight. Sunlight irradiation may lead to the dissociation of chlorine which results in chlorine loss in contact basins. To overcome this, chlorine contact basins should be covered to effectively reduce chlorine loss and THMs formation.
2. In WWTPs normally sodium hypochlorite is used for disinfection which leads to an increase in wastewater pH because of hypochlorite hydrolysis. Effective pH control in chlorine contact basins will help to reduce the concentration of THMs during disinfection/chlorination.
3. Alike chlorine, bromine is also highly effective as a disinfecting agent and may appear to be a more robust method for wastewater disinfection including THMs especially $CHBrCl_2$ and $CHBr_2Cl$ control.
4. Alternate disinfecting agents such as chloramines can be applied to achieve WW disinfection. As disinfectants, chloramines are weaker than free chlorine, but are known to be more stable and stay longer than free chlorine due to their lower oxidation potential. Thus, addition of ammonia would provide longer chlorine residual during wastewater disinfection and subsequently helps to control THMs formation especially bromoamines, formed by the reaction of ammonia with bromine.

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Part V
Wastewater Management and Sustainability

Sustainable and Green Management of Wastewater Under Climate Change Conditions

Heba Elbasiouny, Hassan El-Ramady, and Fathy Elbehiry

Contents

Abstract Climate change affects significantly the natural water cycle in many locations as projected for the future. Due to the increasing scarcity of water resources, reusing wastewater will become more crucial especially because of climate change acceleration. As well, climate change is one of the main challenges to wastewater treatment systems in the future. On the other hand, greenhouse gas (GHGs) emissions during wastewater treatment can be released into the atmosphere (such as carbon dioxide (CO_2) that results from (oxidation processes), methane

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(CH_4) that results from anaerobic processes, and nitrous oxide (N_2O) associated with nitrification and denitrification processes). The water demand increased per capita due to the pressures associated with population growth. Thus, many researchers try to address sustainable and green water management approaches that can state the root causes of such challenges. This not only mitigates the climate change impacts on water resources but also facilities using treated wastewater safely in sustainable and greenways.

Keywords Climate change, Green management, Sustainable management, Wastewater

1 Introduction

Water is a basic and valuable resource on Earth. It is necessary for human life either for direct consumption or food production [1, 2]. It is one of the world's most abundant resources; however, less than 1% of the global water supply is available and safe for human consumptions [3]. The water in the world exists naturally in many forms and locations, in the air, surface, and under the ground. The average available water per capita has been estimated that it has dropped from 3,300 m^3 (in 1960) to 1,200 m^3 (in 2002) [2]. As well, it has been estimated that by 2025, many countries will suffer chronic water stress and about 3.5 billion people will subject to water stress. Furthermore, it has been estimated that the decreasing of total actual renewable water resources will particularly affect large cities in developing countries, especially these countries suffer considerable challenges for meeting increased water demand [2].

Parween and Ramanathan [4] stated that one among five persons over the world does not safely have access to water, which gives an awful picture and pay the attention to the importance of the management of wastewater. Thus, it has been stated in the policy and technical literature as well as in national and international professional meetings that water scarcity has made the need for wastewater reuse more obvious [5]. Water scarcity has increasingly emerged as one of the most important concerns in many countries and regions. Large quantities of wastewater effluents are yearly discharged from municipal and industrial wastewater treatment plants into the adjacent water bodies (such as rivers and lakes) [6]. With population growth, urbanization, and a rise in living standards, water scarcity problems will increase, in which the previous factors will increase both water consumption and water resource pollution by releasing chemicals, energy, and other pollutants that deteriorate the water quality for other users. Therefore, policymakers are interested in developing additional water resources and preserving the existing ones. Recycling and reclaiming water is one of the important components of the national resources policy as it is considered to encourage integrated and effective use and management of water resources [7, 8]. In addition to population growth, global climate change and water pollution are the major challenges that increase the struggles met by water supply systems. Moreover, nature itself is one of the contamination sources of water through water storm runoffs, animal wastes, etc. In this context, Ibrahim et al. [8] reported that the Environmental Protection Agency-United States (EPAUS) classifies six categories of water pollution: (1) plant nutrients; (2) biodegradable waste; (3) heat; (4) sediment; (5) hazardous and toxic chemicals; in addition to (6) radioactive pollutants. Accordingly, water pollutants include pathogens, organic pollutants, industrial discharge having different anions and heavy metals, etc. that are added to the water bodies and cannot be naturally degraded tending to change the water body properties [8].

Wastewater systems (including wastewater collection – pump stations – wastewater treatment plants) play critical functions in society such as collecting, treating liquid organic wastes, and discharging seepage water of satisfactory quality for protecting the public health and environment [9]. However, the health concerns of water pollution are increasing for both citizens and policymakers. Also, the unaddressed health impacts at regional and global levels pose major policy challenges. In general, rising environmental awareness associated with more strict regulation standards has prompted numerous industries to challenge themselves in pursuing appropriate technologies for wastewater treatment [10]. Consequently, one of the major challenges facing the globe is to provide convenient access to clean water under rapidly increasing water demands [8]. When the demand for freshwater increases, treated wastewater becomes an important water source that can be reused not only for agricultural usages such as crop irrigation, but also for other uses such as groundwater recharge, landscape irrigation, and even several recreational purposes [5]. Thus, the application of wastewater is becoming popular in the regions where the water shortage is common and water demand is rising [11]. In addition, for sustainable existence, wastewater treatment, reuse, and safe disposal have become crucial [12] and wastewater should be considered as a resource that must be recovered and included in the water budget [1]. Treated wastewater can be used for replacing freshwater in agricultural irrigations and can decrease the pressure of water scarcity [6]. Therefore, wastewater management plays a key role in achieving world water security in the future. Inadequate/inefficient wastewater management can severely threaten human health, ecosystems, and economic activities [4]. There is an urgent need to establish many plants for wastewater treatment and removing contaminants from water to be suitable for irrigation and other uses [13].

Wastewater comes from different sources, for example, the agricultural wastewater used for irrigation comes in different qualities from different sources, varying from raw to diluted. Domestic wastewater comes from kitchens, bathrooms, laundries, and any other wastes that people may intentionally or accidentally pour down the drain. Sanitary wastewater contains domestic wastewater and water discharged from institutional, commercial, and similar facilities. The properties of wastewater discharges vary from location to location based on the population and the sector served, land uses, groundwater levels, as well as the degree of separation between stormwater and sanitary wastes. Industrial wastes will be varied because of varying industries that generate the wastes [2]. Typically, wastewater contains organic pollutants, such as pesticides, pharmaceuticals, detergents, processed foods, and inorganic pollutants such as salts and heavy metals. Mainly, heavy metals (HMs) come from the Earth's crust, are not degradable, or cannot be destroyed. Some metals such as Cu and Zn that are found in limited concentrations are essential to maintain the human body metabolisms. However, the accumulation of non-biodegradable heavy metals such as Fe, Pb, Ni, Cd, Cr, As, Se, and Hg in different oxidation forms by humans and plants causes severe health and environmental problems. Thus, there is also an urgent need to remove these pollutants from wastewater to be able to be reused [14].

Climate can significantly affect the hydrological cycle and water resources evolving from changes in precipitation intensity and frequency, which result in extensive flooding and expanded drought. As well, socio-economic changes like population increase and urbanization have put other stress on water resources that can worsen the concerns of water scarcity and food production. Although climate change (CC) is a global issue, its impact is probably to be severe in agricultural-based rural economy countries [15]. Therefore, the wastewater treatment sector is addressing now the challenges posed by CC, including pressure for reducing emissions, the adapting challenge to a changing climate, alongside regulatory burdens. The range of challenges interrelated to CC and cities regarding water supply and wastewater treatment systems is very wide and varies according to economics, geography, administrative capacity, and demography. Many of these challenges are general, while some of them are more specific to particular places [16]. As well, CC is one of the major challenges to urban wastewater systems in upcoming decades. It is estimated that CC has a double impact on wastewater treatment plants. The processes in these plants are then affected by CC. Further extreme weather events and earlier snowmelt runoff may result in more untreated sewer flows, increased flooding, etc. As a result of increased water scarcity, the need for wastewater reuse will be more necessary as accelerating CC. Conversely, throughout wastewater treatment, greenhouse gases (GHGs) such as carbon dioxide (CO_2) resulting from oxidation processes, methane (CH_4) resulting from anaerobic processes (approximately 3–19% of global anthropogenic CH_4 emissions), in addition to nitrous oxide (N_2O) (about 3% of N_2O emissions) related to nitrification/denitrification processes (as an intermediate product) can be released to the atmosphere [15]. Although several studies have been performed on the effect of CC on water resources, there is a lack of available information on the potential impacts of CC on wastewater treatment [17]. Thus, this chapter focuses on the effect of CC on wastewater treatment and thus addresses some of the sustainable and green treatments of wastewater to avoid the negative impacts of CC on the wastewater treatment sector.

2 Common Methods of Wastewater Management

The most commonly applied systems for wastewater disposal, mostly in rural areas, are small boreholes, cesspits, septic tanks, simple pits, and ventilated adjusted pit latrines. Cesspools, although they are usually badly managed in most cases, they are the most familiar alternative for wastewater dumping. The strong concern is now paid to seepage from cesspools because they have contaminated the scarce freshwater resources creating several negative impacts for health and the environment. Also, the opportunity of reusing wastewater is lost as it is discharged and buried away in these deep pits [7]. Adhikari and Mandal [18] reported that in developing countries, a simple system as having a stabilization pond is proposed as a cost-effective for waste recycling. Sewage water has high organic matter content, heavy metals, and essential readily available inorganic nutrients for fish-pond fertilizing.

Essentially, the wastewater treatments involve physical, chemical, and biological methods and it commonly occurs in four steps: (1) preliminary, (2) primary, (3) secondary, and (4) tertiary advanced treatments as in Fig. 1 [8, 12]. The technologies that are usually used to purify water are coagulation and flocculation, sedimentation, dissolved air float, filtrating, steam distillation, ion exchange, deionizing, reverse osmosis, and sterilization. Sediment filters, coagulants, activated carbon, ceramics, ion exchangers, organic polymers, activated alumina, and several hybrid materials are usually used in these technologies. Nevertheless, the traditional water treatment methods might be expensive and could release toxic contaminants into the environment. Recently, nanotechnology supports extremely efficient, flexible, and multifunctional processes providing a promising route, to retrofit aging infrastructures and developing high-performance and inexpensive treatment solutions that depend less on large infrastructures. Thus, the current progress in nanotechnology highlights great opportunities for developing the next generation of water supply systems and exposing the probabilities to afford modern and cost-effective treatment capabilities. This can overcome the main challenges facing current treatment methods to expand water supplies [8].

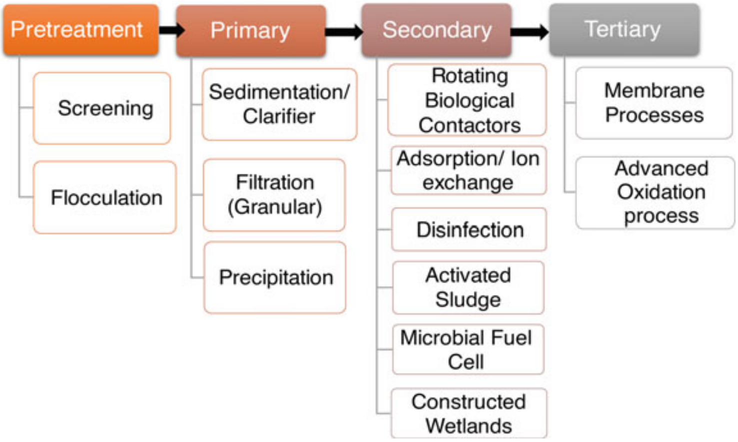

Fig. 1 Wastewater treatment designs and technologies included in each stage. Source: Yenkie [12]

3 Vulnerabilities of Wastewater Management Sector by Climate Change

The CC is one of the major challenges for wastewater systems in the future decades. As a result of increasing CHGs concentrations in our atmosphere, temperatures are expected to rise from 2 to 5 °C globally by 2050 [16, 19]. Depending on the projection data by the Intergovernmental Panel on Climate Change (IPCC), about 7% of the global population will suffer a decline in renewable resources of water. CC augments the complication of managing water resources. Undoubtedly, the uncertainty factor is associated with the CC impacts hydrological variability. Nevertheless, considering the intensity of the unseen crisis, preparation is crucial. Thus, strategies must be planned to flexibly suit the expected changes aiming also at causing no further deteriorations in CC [4]. Furthermore, the wastewater treatment, distribution, disposal, and reuse are subject to the effects of CC through increased energy costs and wastewater volumes and stormwater that enters treatment facilities in the increased precipitation areas, as well through increased requests for reuse when drought becomes more prevalent [16]. Heavy rains and floods, in the UK, for example, overwhelmed wastewater systems putting hundreds of systems out of service [9]. This failure suggests struggling wastewater systems to manage recent extreme storms since climate change is possible to cause things worst with further frequent extreme expected events of precipitation in the future [9]. Zouboulis and Tolkou [16] also stated that CC affects the hydrological cycle in various ways. Thus, updating the infrastructure to afford the increasing water is an urgent need [20].

The impact of CC on hydrology has been investigated widely, with a focus on water quantity. Several approaches have been offered to assess the potential changes in water quality because of CC and indicated a direct effect on water quality through numerous climate-related mechanisms either in the short or the long term. These include influences on air temperature increase, also changes in hydrological factors (such as limited dilution of point source emissions in the period of low river flows), and some other factors including terrestrial factors (such as changes in soil structure and vegetation) and resource-use factors (such as increased water use and water demand for cooling water) [21]. According to IPCC guidelines on GHGs, inventories, collecting, and treating wastewater in centralized systems can be related to the reduction of GHG emissions compared to no collection and untreated discharges [20]. The IPCC argues that wastewater in closed underground sewers is not supposed to be a considerable source of CH4. However, in open sewers, the situation is unalike closed one because it heats by the sun and the sewers may be sluggish allowing anaerobic conditions to emit CH_4. Likewise, centralized treatments allow capturing biogas as an energy source and using sewage sludge either in agriculture or as an energy source also, which decreases, in both cases, the role of fossil fuels in GHGs emission processes [20].

3.1 The Effect of Temperature on Wastewater Treatment

Temperature: Temperature plays a crucial role in some processes of treatment, particularly the natural-based and non-mechanized processes. Warm temperatures decline the land area requirements, improve conversion processes, enhance removal efficiencies, and make the utilization of some treatment processes feasible. As well, some treatment processes, like anaerobic reactors, may be applied in diluted wastewater (such as domestic sewage) only in warm climate areas [16]. Conversely, Martínez et al. [22] reported that the high temperatures in the industrial zone in the coastal Mexico region affect negatively the performance of the different wastewater plants, where it increases the pollutants discharge into the river in the high temperatures period in the year (35–38 °C). Other processes (such as stabilization ponds) may be operated in lower temperature areas but they engage much larger areas and subject to a decrease in performance in the winter. However, other processes (such as activated sludge and aerobic biofilm reactors) are less reliant on temperature; thus, they require higher technological inputs and mechanization levels. Furthermore, the warmer temperature can indirectly cause more severe weather, aggravated by urban heat islands that consequently could result in further hail, convective thunderstorms, cyclonic events (such as cyclones, tornadoes, and hurricanes), in addition to higher winds which may exceed the infrastructure design capacity. Moreover, the increasing temperature will raise the probability of sewer corrosion and odor problems [16].

Specifically, biological wastewater treatment is greatly affected by climate [16]. Higher temperature will increase the wastewater biological activity; the microbial population growth will increase, which will elevate the biological oxygen demand (BOD) of wastewater [18]. Martínez et al. [22] reported also that the high temperatures affect the air temperature at the exit of the compressor increasing a considerable air temperature up to 82° C or higher. When the air goes into the diffusers, it activates the temperature increase in the bioreactor liquor. The actual temperature within the bioreactor reaches 32° C in their area in October/November and 41° C in August/September. The microorganism's activity is influenced due to the effect of high temperature; thus, temperature acts an important role in the biological system performance. Therefore, this must be considered in dynamic process modeling. Ahsan et al. [23] stated that wastewater with quite high temperatures, from 40 to 50 °C, is sometimes discharged from industrial factories. At room temperature, it is very effective to treat the wastewater; thus, it is needed to cool the wastewater down to ambient temperature. On another side, the wastewater quality could be declined with expected higher temperatures because higher water temperature will promote excessive algal bloom growth in wastewater, which will, in turn, reduce the concentration of dissolved oxygen. The organic matter decomposition could also increase due to higher temperature, and thus the nutrients release such as N and P in water will in turn increase the eutrophication chance in wastewater. Simultaneously, the heavy metals availability and pesticides in the wastewater could be higher to the organisms in the wastewater [18].

3.2 The Effect of Precipitation on Wastewater Treatment

The CC is not just a temperature change, also the whole water cycle is affected. A warmer globe means that the atmosphere capacity for holding moisture is increasing in addition to the intensification of the water cycle. Thus, there are changes in the water vapor amount, rainfall, and water circulation in the atmosphere [16, 17, 24]. The CC affects the hydrological cycle in various ways. Atmospheric water vapor and evaporation are increasing, precipitation patterns are changing, and snow and ice are melting [16, 17]. As evaporation increases due to surface heating and increased temperature, the atmospheric water-holding capacity increases. Since atmospheric moisture content affects directly precipitation, stronger rainfall events are expected with CC. For every increase of 1 °C in global temperatures, there is an increase of 7% in the atmospheric moisture-holding capacity. Then, more atmospheric moisture ultimately causes changes in rainfall patterns [16].

Heavy rains and high winds, besides hurricanes, are enough to cause many problems such as flooding, widespread power outages, and the passing of billions of gallons of partially treated or untreated sewage into neighboring waterways [9]. Thus, wastewater systems are potentially influenced by intensive rainfall, aggravating flooding, as well combined sewer overflows affecting wastewater treatment plants efficiency The wastewater industry is beginning to address the challenges posed by CC, including regulatory burdens, the pressure to reduce emissions, and the challenge of adapting to a changing climate [16]. Conversely, if the wastewater quality is declined by higher temperature and excess rainfall, the wastewater will be diluted. Thus, the negative quality of wastewater will be decreased, and the wastewater will be used for agriculture practices with no problems. Conversely, if the precipitation is reduced especially in the tropics, the deterioration chance of wastewater quality will increase [18].

3.3 The Effect of Sea-Level Rise on Wastewater Treatment

Climate change is expected to exacerbate the wastewater systems failures by rising sewer floods, lessening the absorptive capacity of receiving waters, changing treatment efficiency, and subjecting more infrastructures to damage and inundation by sea-level rise. Subsequently, because wastewater systems are old and vulnerable to sea-level rise and the impacts of extreme events, they are gradually at risk of failing to protect the environment and public health [9]. Cao et al. [25] reported that sea-level rise has been widely recognized as one of the biggest challenges that humankind will be confronting in the twenty-first century. Mean sea levels are presently rising in the globe by approximately 3.2 mm yearly; however, the speed of sea-level rise is expected to gradually increase with time to be between 0.98 and 2.92 m more than the current by 2,100. Higher levels of water would heighten the flooding risk to coastal communities and infrastructure located in low-lying areas

[25]. Zouboulis and Tolkou [16] reported that with the rising of sea levels, flooding threatens many water utilities, which can have several negative impacts. These impacts will depend on the degree of rising. Flooded and damaged wastewater facilities may lead to release of untreated wastes into the ecosystem for an extended time until fixing the plant. This causes significant damages to the environment and humans. Thus, flood damages would be costly to municipalities of wastewater either regarding financial loss or regarding the threats to public health. It is assumed that only facilities that lie near tidally influenced water bodies will be affected shortly. Furthermore, sea-level rise endangers the location of many plants. Furthermore, the rising downstream water level may make pushing effluent a requirement and increase energy need. As well, the rising sea-level can decrease the hydraulic capacity of downstream sewers and increase salt-water intrusion. Therefore, careful planning is essential to take care of the consequences of sea-level rise and flooding [16].

3.4 Drought Conditions on Wastewater Treatment

Regional and global scale studies reveal that CC may cause increases in intensity and frequency of heatwaves and droughts. Water quality may weaken to critical values in the prolonged low-flow periods that are associated also with high-water temperature. So, insight and understanding of the impact of drought periods on the quality of water are essential [21]. Wastewater agencies are interested in reliably eliminating pollutants from water discharged to sewers, even with declining water quality and quantity. Drought as climate pressure poses a major challenge for the wastewater management sector [26]. van Vliet and Zwolsman [21] assessed the effects of droughts on the water quality of the river Meuse in Western Europe. They examined time series of water quality at two monitoring stations in two severe drought periods; 1976 and 2003 compared to water quality in reference periods, representing similar hydrological conditions and chemical pollution. They also assessed the effects of discharge changes and water temperature on the concentration of the chemical substance through establishing empirical relationships between discharge and concentration and between water temperature and concentration. Their results indicate a deterioration of the water quality of the river during droughts, concerning water temperature, major elements, some heavy metals and metalloids, and eutrophication. They primarily attributed the decline in water quality to the favorable conditions for the algae bloom's development (i.e. high-water temperatures, high nutrient concentrations, long residence times) and the reduction of the dilution capacity of point source effluents. This direction should be considered also in wastewater treatment.

Hur et al. [27] reported that effluents of municipal sewage and industrial wastewater can have major effects on chemical loads in surface water downstreams of developed urban areas and these effluents may have greater impacts on streams and rivers during drought periods. They reported that previous investigators have stated high nutrients concentration in the wastewater treatment plants effluents, demonstrating that wastewater treatment plants can be a major point source of pollution in urban-impacted watersheds. They cited from Marti et al. [28] based on data about 15 streams that receive effluents from wastewater treatment plants that P loads from these plants were, averagely, higher 10 times than the upstream loads and provided about 90% of the total P measured downstream of the wastewater treatment plants. They also cited that Andersen et al. [29] described the effects of wastewater treatment plants' effluent discharge on the water chemistry and nutrients concentration. They demonstrated that wastewater treatment plant effluent affects the chemistry of downstream water chemistry. These effects could be considered in a watershed in temperate climate regions under severe drought conditions. The influence of wastewater inputs on river nutrients load may be motivated in highly populated areas due to higher water demands for consumption or irrigation, associated with the long drought periods expected under CC scenarios in semiarid areas. Additionally, during drought periods, the influence of wastewater treatment system inputs on the chemistry of streams may increase whereas that of diffuse nutrients source (e.g. from agricultural activities) may decline. In contrast, the wastewater treatment system loads are quite constant regardless of hydrologic conditions, while the inputs from diffuse sources increase with precipitation and runoff [30].

4 Greenhouse Gas Emissions from the Wastewater System

The treatment of domestic wastewater can be a large source of both direct and indirect anthropogenic GHG emissions such as CO_2, CH_4, and N_2O [31, 32]. It is globally estimated that the entire wastewater sectors contribute up to 1.5% of total GHGs and 5% of non-CO_2 GHGs emission [32]. GHG emissions from wastewater treatment systems are often classified as on-sites and off-sites based on the emission point. Very few studies, however, are available about the GHGs emission from wastewater treatment plants on a country scale, maybe due to scarcity of the appropriate data and the complexity of the models [31]. For instance, despite about 20% of the population depend on on-site wastewater treatment and disposal in the European Economic Area and the USA, only a few studies have been performed based on the direct measurements of GHG emissions from on-site and decentralized wastewater treatment sectors [32].

Furthermore, GHG emissions from wastewater treatment sectors are classified as direct and indirect emissions. Direct emissions are related to biological processes. On the other hand, indirect internal emissions are related to energy consumption, and indirect external emissions are associated with the outside of the activities of wastewater treatment plants (such as wastewater and biosolid disposals, chemicals production, and biosolids' transportation). Among released GHGs, biogenic and nonbiogenic CO_2 is essentially associated with the processes of applied wastewater and sludge treatments and through energy consumption for operating wastewater treatment plants. CH_4 is mostly released during the sludge treatment processes (i.e. sludge anaerobic digestion, sludge disposals to the soil or the landfill).

Conversely, the biological processes connected to ammonia-oxidizing bacteria and the denitrification process essentially contribute to the emissions of N_2O emissions. The global warming potential of CH_4 and N_2O is 28 and 265 times higher, respectively, than CO_2 in a period of 100-year. It has been reported that the emissions of CH_4 from municipal and industrial wastewater are approximately 5% of the global CH_4 production, while direct emissions of N_2O during wastewater treatment contribute by 2% of the global warming potential of the water cycle [31]. Also, Koutsou et al. [31] cited that Zhou et al. [33] evaluated GHG emissions from domestic and industrial wastewater in China from 2003 to 2009 and reported that N_2O emissions from domestic wastewater were estimated to be almost 50% of the total CO_2e emissions. As well, they cited that Chen and Kuo [34] approximated, in Taiwan, the annual emissions of GHG from sewage sludge management and stated that sludge incineration is the source of CO_2e. Conversely, sludge dewatering recorded the lowest C footprint. Thus, the quantification of GHG emissions at a country scale is essential for both scientific and social awareness levels. This is because it aims to a better understanding of how to reduce GHG emissions from wastewater treatment plants and to increase public awareness about the role of wastewater treatment sectors as important sources of GHG emissions [31]. Adhikari and Mandal [18] reported that big cities are sources of concentrated wastewater. They added that the CH_4 emission during wastewater transporting, treating, and disposal, including sludge, was assessed by 3–19% of the global anthropogenic emissions of GH_4. The main source of N_2O is wastewater treatment and human sewage and the N_2O and CH_4 emissions from wastewater are estimated to increase by almost 25 and 50%, respectively, in the next decades. Accordingly, the GHG emissions can be mitigated through improvements in the collection and management of urban wastewater, using technologies that are most suitable to the economies and situations involved in these processes.

5 Sustainable and Green Management of Wastewater: Concepts and Approaches

The wastewater that is treated as waste should be eliminated by consuming a huge amount of energy and materials, regardless of the potential value of wastewater components. For example, P fertilizers production from easily accessible phosphate rock could be exhausted in about 50–100 years causing worldwide food security issues. Therefore, high-priced treatment technologies are performed for removing P as waste from wastewater for reducing eutrophication in receiving water bodies. Recently, emerging biological and chemical contaminants from wastewater penetrate the water bodies, making the water treatment more technically and economically challenging. These nasty cycles become worse with the growth of the cities, the intensity of agricultural practices, and condensing material flows [35]. Furthermore, wastewater has been considered, for a long time, as a human health issue and environmental hazard. However, currently, a paradigm shift is proceeding from perspective of seeing wastewater as a waste that should be treated to a proactive concern in recovering energy and materials. Thus, treated wastewater can be reused for many purposes for providing ecological benefits, reducing the potable water demand, and augmenting water supplies [36] (Figs. 2 and 3).

Sustainable development indicators are receiving growing acceptance globally as they enable a simpler monitoring and advanced assessment toward specific targets. The No. 7 of Millennium Development Goal (MDG) on ensuring environmental sustainability contains one target linked to drinking water and sanitation. The world challenges are to reduce, by 2015, the percentage of people with no sustainable supply of safe drinking water and basic sanitation [39]. The sanitation part of this target is assessed by the indicator of "proportion of the population using an improved sanitation facility" [40]. Also, in the future, further attention should be paid to existing and emerging pollutants sources regarding human health and environmental perspectives, socio-economic perspective, and both sustainable investment strategies and affordability. To do this in the context of global and climate changes, unremitting research, innovation efforts, and investments are required, particularly to (1) develop progressive and resilient monitoring and treatment solutions, (2) support cost-effective micropollutants management, and (3) better incorporate circular systems for water/sludge reusing and recovery of components [20]. The transition toward reusing wastewater derived resources in wastewater treatment plants is considered a promising solution toward shifting wastewater treatment from standard treatment way to the current emphasis on sustainability [36]. In developing countries, water management should look alternative, cost-effective, and more sustainable strategies that perhaps depend on the natural services provided potentially by ecosystems such as nutrients and organic matter removal by fluvial stream communities. However, the retention efficiency of N and P declines as increasing the proportion of the pressure of urban land use. For such reason, restoration tasks should be addressed in the management plans for these stressed streams to maximize this ecosystem service [30].

Indeed, 50% of the population in the world lives in cities with inadequate infrastructures and resources and cannot manage wastewater efficiently and sustainably. To be successful and sustainable, there is no option except to consider wastewater as part of the solution. Thus, wastewater management must be integrated into rural and urban development planning, through all sectors. This can sustainably offer greater returns within multiple sectors than the water infrastructure development and the promotion of improved wastewater management. Wastewater's successful and sustainable management needs a mixture of inventive approaches that consider the private and public sectors locally, nationally, and transboundary [41]. Judicious water use and minimizing in the release of wastewater are equally important because of the water resource scarcity and energy costs in the wastewater treatment sector. Considerations may include overall quantity reduction, pollutant strength reduction, or a combination. This can have a considerable impact on the technical capacity, flow/loadings of wastewater treatment plants, operation/maintenance costs, energy requirements, and ecological impacts. About, 20–30% water

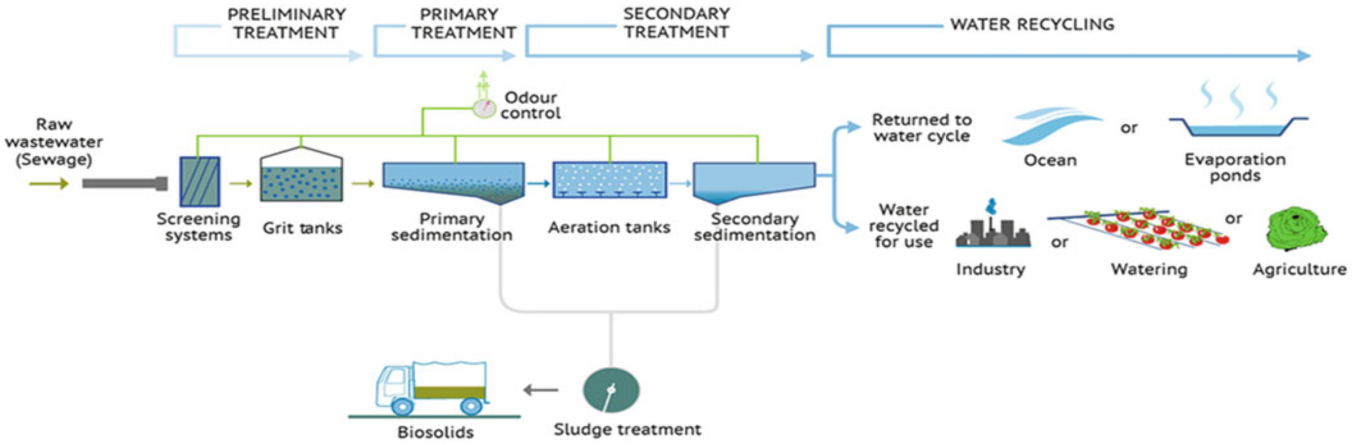

Fig. 2 Wastewater treatment process. Source: https://water.fanack.com/specials/wastewater-treatment-reuse-mena-countries/ [37]

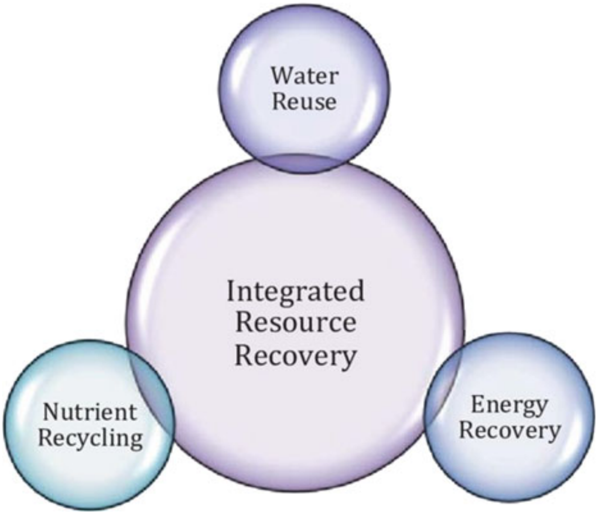

Fig. 3 Integrated resource recovery from wastewater. Source: [38]

savings can be done with flow reduction devices such as sensors for fault detections and concentration measurements and efficient controllers. Industrial plants can achieve the volume of wastewater reductions by using multi-point waste collections, reuse, and eliminating sludge discharges. Finally, wastewater treatment plants need efficient design and evaluation metrics to minimize costs, energy requirements, and subsequent environmental impacts while meeting the regulatory guidelines [12]. Yenkie [12] summarized the most modern developments in the fields of wastewater characterization, treatment technologies, modeling, and optimization framework for designing efficient wastewater treatment plants, economic analysis, and sustainability assessment in Fig. 4. Yenkie [12] mentioned that the complexity is in (1) the selection of suitable technologies for treatment network synthesis depending on contaminants in different wastewater sources, then in (2) the cost valuations, and in (3) the sustainability assessment.

Vasantha and Jyothi, [42] reported that sustainable wastewater treatment comprises the following safeguards**:**

– *Health safeguards* including accepted features standard for microorganisms in water bodies that contribute hygienically harmless water.
– *Water safeguards including* the eutrophication reduction through nutrient elimination (P and N) to the highest feasible scope, elimination of nanoparticles, micropollutant, and microplastics for both of the precautionary health care and safeguard of marine fauna.
– *Resource safeguards through* the diminution of sources used for wastewater treatment and decreasing ecological impact.

In the context of sustainable and green management of wastewater, some concepts and approaches should be recognized:

Fig. 4 An integrated approach for designing treatment networks of wastewater. Source: Yenkie [12]

The Concept of Sustainable Vs. Green

According to Spacey [43]:

- *Green* is called to the practice applied to protect the environment.
- *Sustainable* is called to the practice applied to protect the environment and improve life quality.

Although various conventional methods are used for water treatment they are not economical and not environment-friendly, innovative green materials and technologies are being used currently to overcome these problems [42, 44]. In this context, the concepts of green chemistry and green technology should be recognized.

- *Green Chemistry*: A promising alternative to produce biocompatible and stable nanoparticles that are nontoxic and eco-friendly [44].

- *Green Technology* refers to the development and expansion of the practices, processes, and applications that improve or replace the current technology and enable society to meet their requirements while substantially decreases the human impacts on the globe amid environmental scarcity and ecological risks. Environmental Sustainability and Green Technologies are focused on the goals of green technologies giving progressively more importance to guaranteeing sustainability. Thus, Green Technology is an ecological remedial technology that reduces the ecological damage caused by the products and technology for citizens' conveniences. Green technology can enhance materials along with waste consumption, energy efficiency, and recycling. The design of green technologies focusing on reducing, reusing, recycling principles (3Rs). Regarding wastewater treatment, green technology can remove the contaminants and undesirable components from domestic, industrial, and polluted water to safely reuse it and return it to the environment for many usages such as drinking, irrigation, industrial, and others. This could be accomplished through: Developing clean alternate technologies to replace those that have negative impacts on health and the environment and improving human manufacturing and expenses behavior to decrease the pollution resulted from releasing the waste release and contamination [42].

6 Conclusion

Water is necessary for human life; however, 1% of the global water supply is available and safe. One among five persons over the world does not safely have access to water, which pay the attention to the importance of the management of wastewater. Also, because climate can significantly affect the hydrological cycle and water resources, climate change will put threats on wastewater systems and their treatments including pressure for reducing emissions. Sustainable development indicators are receiving growing acceptance worldwide, thus further attention should be paid to existing and emerging pollutant sources regarding human health and environmental perspectives, socio-economic perspective, and both sustainable investment strategies and affordability. Eco-friendly and sustainable technologies in addition to green chemistry should be recognized as safe wastewater treatment for human health and the environment under the pressure of water scarcity and climate change.

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Microbial Biosurfactants and Their Implication Toward Wastewater Management

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Contents

Abstract Environmental problems associated with water sanitation are gradually on increase by superfluous human activities and also due to developmental issues. Wastewater contains various types of pollutants such as pesticides, heavy metals, dyes, and petrochemicals. This has become a global issue for balanced ecosystem since different types of pollutants are responsible for health hazards, owing to their

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toxicity and poor biodegradability. The removal of these pollutants as well as their sources from water is one of the biggest challenges for both researcher and community. Recently, methods using microbes and microbial products have been employed for the removal of petrochemicals, heavy metals, and pesticides from the water and soil. These methods have been positively used to treat different wastewater types like sewage, sludge, and industrial effluents. There are other treatment approaches also, such as chemical, physical, and other conventional methods, but some of them are not cost effective and some result in secondary pollutants and therefore unsafe to the environment. In this chapter, we will discuss the effective biological treatment approaches, which is bioremediation using microbial biosurfactants. Biosurfactants are the surface-active biomolecules that have several unique properties such as amphipathic in nature, biodegradable, emulsion forming property, tolerant to extreme conditions, and biological origin. Biosurfactants have a great potential for the removal of complex hydrophobic pollutants and pesticides from wastewater because they can be easily interact with those pollutants by their amphipathic nature. It is an extracellularly produced bio-product, and also considered as microbial secondary metabolite which is being produced in the stationary phase of the growth pattern of microbes. Here we have also briefly discussed the production of biosurfactants.

Keywords Biosurfactants, Hydrophobic organic compounds, Pesticides, Remediation, Wastewater

1 Introduction

Generally, surfactants are emulsifying, surface-active, and amphipathic molecules obtained from the commercial sources. Surfactants synthesized chemically or artificially are known as synthetic surfactants; these might be toxic and pose adverse effects to the environment. Surfactants isolated from microbial sources are called microbial surfactants, biological surfactants, or biosurfactants and they are considered quite safe from the environmental perspective compared to the synthetic surfactants. Therefore, nowadays, biosurfactants are gaining a worldwide research interest [1]. Biosurfactants are eco-friendly with long-established abilities for contaminant removal from the soil and wastewater by the bioremediation processes [2]. They are highly desirable because of their huge advantages such as low environmental impact, high specificity, surface tension reduction, biodegradability, solubilization, low toxicity, stable at extreme conditions, and emulsion forming properties [3, 4].

Biosurfactants are heterogeneous and their structures contain diverse groups of microbial secondary metabolites, which are extracellularly secreted by microorganisms in the stationary phase of their growth. They are synthesized by a huge group of microbiotas like bacteria, fungi, algae, and yeast [5]. Glycolipids (rhamnolipid and sophorolipids) and surfactin are the most extensively studied biosurfactants produced from *Bacillus* and *Pseudomonas* genera, respectively [6].

Various research works have been conducted based on the production, extraction, and purification, characterization and optimization of new biosurfactants producing microorganisms [7]. Based on their chemical composition, biosurfactants are divided into six major classes as follows: (1) glycolipids, (2) phospholipids, (3) fatty acids, (4) lipopeptides and lipoproteins (5) neutral acids, and (6) polymeric and particulate surfactants [8, 9]. Owing to some special or unique properties of biosurfactants, these are considered as future promising biomolecule for environmental sustainability. For example, biosurfactants are used as (1) dispersive or wetting agent (they have hydrophobic and hydrophilic end that is why they are easily interacting with hydrophobic molecules and disperse them), (2) great emulsion forming property (biosurfactants have lower critical micelle concentration (CMC); therefore, they form micelles at lower biosurfactants concentration with water-insoluble pollutants and reduce their surface tension), (3) stable in extreme conditions (at either very low or high temperature and pH, biosurfactants are stable and their properties also persist unchanged), (4) low toxicity (biosurfactants are generally isolated from non-pathogenic microorganisms; therefore, toxicity issue is near to negligible) [3, 10, 11]. Keeping all the above-mentioned properties in view, biosurfactants have remarkably potential applications in the restoration and protection of environments. The acceptance of biosurfactants for effective use toward environmental bioremediation is considered one of the best properties of biosurfactants, since they are eco-friendly in nature [12].

This chapter does not attempt to elucidate the several applications of biosurfactants, but rather its effort will be to focus through the sustainability lens on the applications of biosurfactants in reducing environmental pollution mainly toward wastewater treatment or its management.

There are a number of microbes (bacteria, fungi, algae, yeast, and also from plant sources) which are producing biosurfactants that can be utilized in wastewater treatment. For example, Saponins are one of the group of biosurfactants, having soap like activity. Biosurfactants have a great potential to clean-up contaminated water sites. Table 1 shows the list of microorganisms which produce biosurfactants, which is being employed in wastewater management.

2 Production of Biosurfactants

Production processes of biosurfactants depend on metabolic pathways or cultivation process of bacteria and carbon sources present in the growth media. Several metabolic pathways are associated with the production of precursors of biosurfactants according to the substrates used. Lipogenic and glycolytic pathways regulate the flow of carbon and secrete hydrophobic and hydrophilic moiety of the biosurfactant molecules, respectively. A series of enzymes are involved in the synthesis of

Table 1 Microorganisms producing biosurfactant and their applications in wastewater

S. no.	Microorganisms	Biosurfactants	Application in waste water treatment	References
1	*Pseudomonas aeruginosa*	Rhamnolipid	Bioremediation, heavy metals floatation	[13]
2	*P. fluorescens, Serratia rubidaea, Agrobacterium* spp.	Viscosin	Emulsion stabilization and food industry	[14]
3	*Bacillus subtilis*	Lipoprotein	Removal of Ca^{2+} and Cr^{3+} in aqueous solution	[11]
5	*P. chlororaphis*	Rhamnolipid	Bioremediation	[13]
5	*S. marcescens*	Serrawettin	Biocontrol agent	[15]
6	*Bacillus subtilis*	Surfactin	Bioremediation, inactivation of herpes and retrovirus	[16]
7	*Bacillus Licheniformis, B. subtilis*	Lipopeptides, Lichenysin	Chelating agent	[16]
8	*Rhodococcus erythropolis, Corynebacterium* spp.	Trehalose lipid	Reduce surface and interfacial tension, dispersive agent	[17]
9	*Agrococcus terrus*	BS produced but not determined	Oil degradation from water	[18]
10.	*Candida bombicola*	Sophorolipid	Removal of heavy metals from water	[19]
11.	*Candida bombicola*	Sophorolipid, rhamnolipid	Removal of phenol from wastewater	[20]
12.	*Starmerella bombicola*	Sophorolipid	Removal of petroleum pollutants and MEOR	[21]
13.	*Trichosporon asahii*	Sophorolipid	Shows higher solubility	[22]
14.	*Nocardiopsis alba*	Lipopeptides	Bioremediation and emulsifying property	[23]
15.	*Y. lipolytica*	Liposan	Emulsification activity and emulsion stabilization	[24]
16	*Bacillus subtilis*	Lipoprotein biosurfactants	Fish processing waste water	[25]

precursors of biosurfactants (trehalose, sophorose, rhamnose, and phospholipids) [26, 27].

Some multienzyme complexes are required to overall process for the formation of lipid and sugar moieties of biosurfactants. Among all the reported biosurfactants, the molecular biosynthetic regulation for rhamnolipid by *Pseudomonas aeruginosa* and surfactin synthesized by *Bacillus subtilis* were the earliest biosurfactants to be encoded [27].

According to [27], rhamnolipids biosurfactants (Fig. 1) are manufactured through two sequential glycosyl transfer reactions, which are catalyzed by an enzyme rhamnosyl transferase. The production of surfactin is catalyzed by surfactin

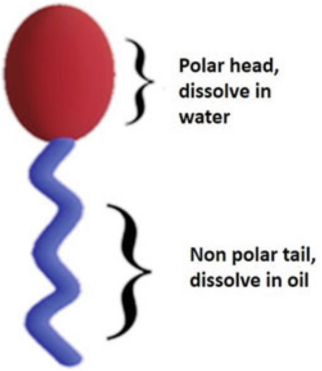

Fig. 1 Biosurfactant structure with the hydrophilic and hydrophobic end

synthetase, which is a peptide synthetase complex [28]. In case of lipopeptides, they are generally synthesized with non-ribosomal peptide synthetases in a ribosome-independent manner [29]. Generally, biosurfactants producing microorganisms are heterotrophs, whereby they utilize organic components solely from the growth media [30]. For the production of secondary metabolites such as biosurfactants at large and commercial scale, the use of cheaper and renewable feedstock will reduce the production cost. Basically, there are three types of carbon sources being used in biosurfactants productions, viz., (1) hydrocarbon groups, (2) carbohydrate, and (3) oils and fats.

3 Types of Biosurfactants

Biosurfactants are many diversified biomolecules, on the bases of their chemical composition and structures. Generally, biosurfactants have come under the glycoconjugates group, which is formed by carbohydrates covalently linked with the non-carbohydrate constitutes. The non-carbohydrate moiety may be amino acids, protein, and lipids. As per these associated moieties, the biosurfactants differ in their glycoconjugate name such as amino sugar (glucosamine), glycoproteins or peptido-glycan and glycolipids, respectively. On the bases of chemical composition biosurfactants are divided into six major classes, given below:

3.1 Glycolipids

Glycolipids consist of sugar and lipids molecules. The most common types of glycolipids are rhamnolipids, sophorolipids, and trehalolipids, which are given below in detail.

3.1.1 Rhamnolipid

These are made up of one or two units of rhamnose connected to one or two β-hydroxyl fatty acids. It is the widely studied biosurfactants, which are the principal glycolipids produced by *P. aeruginosa*. The maximum production of rhamnolipid was 22.5 g/L, obtained in batch fermentation [31]. Rhamnolipid biosurfactants have huge potential and future in environmental applications for wastewater clean-up, including the bioremediation of petroleum hydrocarbons, heavy metals, and pesticides from the wastewater sites [11].

3.1.2 Sophorolipids

These are formed by dimeric carbohydrate sophoros molecule connected to a long-chain hydroxy fatty acid by a glycosidic bond [9]. Sophorolipids are the most extensively studied microbial biosurfactants produced by *Starmerella bombicola.* Sophorolipids are generally preferred for many applications in the wastewater clean-ups techniques. It has shown good stability toward temperature and pH fluctuations. Its surface-active properties are consistent at pH values about 6–9 and at a temperature ranging from 20 to 90 °C [32].

3.1.3 Trehalolipids

These are composed of disaccharides trehalose linked to two long-chain α–branched β-hydroxy fatty acids. These are produced by many spp. of *Corynebacterium Nocardia*, and *Mycobacterium* [31].

3.2 Lipoproteins or Lipopolypeptides

These consist of proteins or amino acids covalently linked with the lipid part (mostly, hydroxyl fatty acid). Lipoprotein biosurfactants were produced from the lipid layers taken from fish processing wastewater [25]. The common examples are lichenysin, viscosin, and surfactin, i.e., these are lipoproteins which are also playing a major contribution in wastewater treatment [33].

3.2.1 Surfactin

The chemical assembly of the surfactin molecule is comprised of seven amino acids that are connected to hydroxyl and carboxyl groups on long-chain fatty acids (C13–C15). Surfactin is one of the most potent biosurfactants formed by the endospore-forming and Gram-positive bacteria like *Bacillus subtilis*. The future prospective uses of these biosurfactants are for environmental cleanliness and also for its sustainability [34].

3.2.2 Lichenysin

Lichenysin biosurfactants are quite similar to the surfactin. These biosurfactant molecules are produced by *Bacillus licheniformis,* which shows exceptional steadiness under high salt, pH, and temperature situations. These are anionic lipopeptide biosurfactants, including gramicidin, polymyxa, ornithine, taurine, cerilipin, viscosin, and arthrofactine [16].

3.3 Fatty Acid, Phospholipids, and Neutral Lipids

These biosurfactants are cell membrane constituents and possess surface activity. These biosurfactants have the potential to manufacture an optically transparent micro-emulsion of alkane in aqua solution. The phospholipid and fatty acid surfactants are generated by numerous bacterial and yeast species in huge amounts, utilizing n-alkanes as carbon source produced from *Thiobacillus thiooxidans*. Such biosurfactants consisted of complex C 12 to C 14 that are saturated fatty acids having alkyl and hydroxyl [16].

3.4 Polymeric

Different genera of microbial species produce exocellular polymeric biosurfactants which consist of either lipopolysaccharides, proteins, and polysaccharides or a multifaceted combination of these biological polymers [26]. *Acinetobacter* spp. produces phosphatidyl ethanolamine-rich vesicles that are capable to form an optically clear micro-emulsions of alkanes in water [35]. These vesicles are micro-emulsions comprised of a backbone of polysaccharide to which covalently linked are fatty acids side chain. The best investigated polymeric biosurfactants are liposan, emulsan, and alasan. The emulsan is an active emulsifying agent for petro-hydrocarbons contaminants in water. *Candida lipolytica* synthesizes an extracellular water-soluble emulsifier and their significant role in food industries as an emulsifier has been well established [36].

3.5 Particulate Biosurfactants

These are of two types, viz., total microbial cell and vesicles, which are extracellular. Extracellular membrane vesicles break the petrohydrocarbons and convert it into micro-emulsions. These micro-emulsions play a significant role in attaching hydrocarbons by the cells of microbes. Strains of *Acinetobacter sp.* form micro-emulsion vesicle, which has a diameter of 20–50 nm and thickness of 1.158 g/cm^3. This vesicle is composed of proteins, phospholipid, and lipopolysaccharides [37].

4 Biosurfactants and Decontamination

Globally, about 842,000 people and children die each year from various diseases caused by unsafe drinking water, as well as the contamination of water bodies with unwanted chemicals. To prevent this type of dangerous consequence due to contaminated water, there is a crucial need for wastewater treatment. In this process, hydrophobic contaminants, heavy metals, and pesticides from wastewater are removed. This results in clean water which can be returned back to the natural water cycle; therefore, this process will help in environmental cleanliness. Because, the excess amount of heavy metals in soils could accumulate in the food chain and will cause hazard to human health.

Biosurfactants are the candidate, which possess a huge potential to treat wastewater having different types of unwanted contaminants. In previous investigations carried out by [15, 38–40], the biosurfactants bear some unique properties, which make this biomolecule as one of the important molecules for environmental sustainability and restoration in the twenty-first century [11]. An imperative function of biosurfactant on the decontamination of wastewater containing pesticides, petrochemical, and heavy metals is shown in Fig. 2.

5 Petrochemical in Wastewater

Increasing the society demand and concerns on environmental sustainability relating to the storage of hydrocarbons and its transport has led to the creation of innovative storage and pipeline technologies, as well as environmentally appropriate remediation processes. Due to the geographical location of coastlines, marine sectors play a significant role in delivering ecosystem goods and services [41]. Therefore, the marine ecosystem can be negatively affected by urban development and movement of crude oil ships [16]. Wastewater is associated with petrochemical and toxic organic compounds, which are again a major concern to the balanced ecosystem. Moreover, several health concerns, depletion of natural water sources, and negative

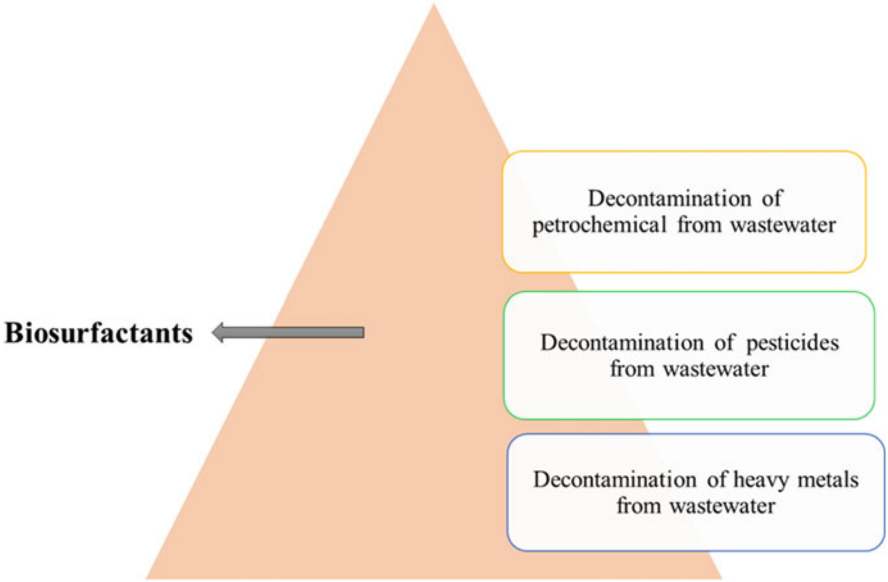

Fig. 2 Biosurfactant in decontamination of petrochemicals, pesticides, and heavy metals in wastewater

ecological impacts have resulted in wastewater generation by petrochemical pollutants; and this problem is increasing day by day [42].

Oilfield industries are also linked to petrochemical wastewater, which is being produced regularly during the extraction of oil in oil fields. Petrochemical wastewater usually contains various organic pollutants such as polymer, radioactive substances, benzenes, phenols, humus, polycyclic aromatic hydrocarbons (PAHs), complex recalcitrant, and some heavy mineral oil [37, 43].

Oil and gas exploration by the industry generates petrochemical wastes that has been identified as a key source of water and soil contamination.

(a) *Drilling wastes*: Drilling waste is majorly generated by the drilling operation or drill cuttings. Drill cutting is the major by-products of oil and gases, which pose a major waste management problem. Drill cuttings discharges are the second-largest waste generated at the water sites from oil and gas activities [44]. Furthermore, drill cuttings possess several organic and inorganic contaminant contents, which are extremely toxic to humans and nature and a key potential source of oil pollution in the marine world [45, 46].

(b) *Hydrocarbon-contaminated soil*: Hydrocarbon-contaminated soils are also a major issue. The erosion of hydrocarbon-contaminated soils into water bodies has resulted into secondary problems. Freshwater, especially river water contaminated by hydrocarbon products becomes a serious challenge [47]. This challenge is further aggravated by the addition of metals and other obnoxious chemicals. Industrial activities, which include spillage of crude oil from exploration and transportation, pipeline leakages, and leakages from underground storage tanks in stations, as well as the release of oil that occurs accidentally during drilling operations leads to the accumulation of hydrocarbon-contaminated soils from where the contaminates leached or slipped to the water bodies [48, 49]. Petro-hydrocarbon contamination occurs in any stage of crude oil processing and use [50]. It is not a country-specific problem but rather a global issue; therefore, the contamination by petro-hydrocarbon remains a contemporary concern.

6 Management and Treatment by Biosurfactants

In addition to the wastewater treatment by biosurfactants, various other bacterial metabolic processes are also always ‘on’ to manufacture enzymes, which play a major role in biodegradation of petrochemicals in water. Therefore, enzymes plus biosurfactants degrade or decontaminate the pollutants in a better and efficient way. Furthermore, biosurfactants play a significant role for the extraction of petroleum products, in transportation, up-gradation, refining and manufacturing of petrochemicals. This results in preventing the wastage of petro products, thus there is a reduction in environment pollution in water bodies [51, 52].

In biological treatment process, the incorporation of different microorganisms and their bio-products into wastewater treatment results in stabilizing hazardous pollutants in petrochemical wastewater. Biosurfactants are secondary metabolites of microbes which usually lead to the emulsification of the heavy oil from the petrochemical wastewater. It facilitates the transport of substrate via membrane [53–55]. Biosurfactants enhance the surface area of oil pollutants present in wastewater, resulting in greater bioavailability of pollutants by the micelles formation, so that hydrocarbons are easily metabolized by the microbial cell, as shown in Fig. 3. Apart from that, there are numerous other treatments, viz., physical, chemical, and

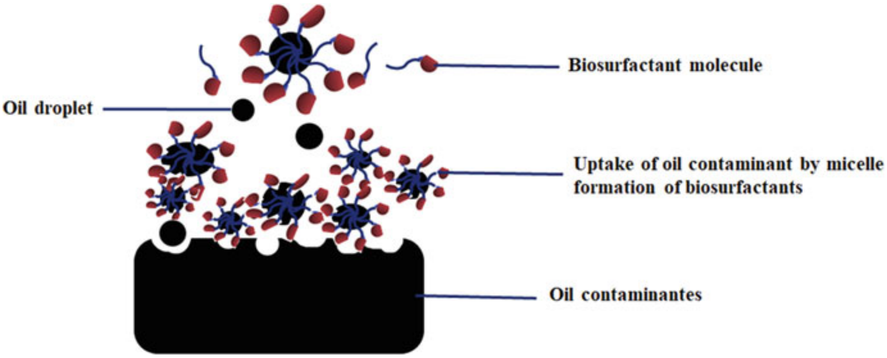

Fig. 3 Petrochemical contaminants uptake by bacterial biosurfactants with the help of micelle formation

physico-chemical, but these are not enough to solve the issue. The treatment processes of wastewater containing petrochemicals depend on the source of contaminant, discharge requirement, and treatment efficiencies [56].

7 Non-biological Wastewater Treatment

Before biological treatment, various primary treatments are used to remove gross solids and free oil by filtration, flocculation, flotation, sedimentation, and microelectrolysis [57].

Physical treatment includes adsorption by active carbon, copolymers, and zeolite, based on the characteristics of wastewater. Microfiltration (MF) and ultrafiltration (UF) can also be used to remove hydrocarbons and oil/fats, as well as suspended solids in the petrochemical wastewater; however, all these processes increase the cost of treatment [58]. Chemical treatments are also used before biological treatments. Three major chemical treatment processes are listed here:

Micro-aeration: This process breakdowns the hydrocarbon components in wastewater, and converts it into organic group which are easily biodegraded.

Ozonation: The appropriate ozone dosage and reaction time of pre-ozonation treatment conversion have been determined to be 100–200 mg O_3/h and 30 min, respectively. However, the change of pH in pre-ozonation treatment was unremarkable [59].

Coagulation-flocculation: Ferric chloride is a most effective coagulant and addition of it along with a polyacrylamide improves the sludge filtration [60].

8 Heavy Metals in Water

Expansion of mining resulted in the wide use of heavy metals in various sectors, therefore, discharge of industrial, urban, household waste and agricultural soils are often contaminated with heavy metals. The excess amount of heavy metals in soils could pollute the environmental water bodies and potentially damage human health through accumulation in the food chain, since contaminated water is also used for irrigation purposes [61]. There are several causes of heavy metal contamination in water sites such as contact with industrial discharge, improper disposal of waste, biofertilizers (metal corrosion), domestic sewage, mining drainage, acid mining drainage, ores, paints, and incidence of spills. Lead is one of the most common contaminants at the battery disposal and recycling sites [62]. The contamination of groundwater by heavy metals like lead, cadmium, zinc, chromium, arsenic, and mercury has potential to cause toxicological impact on human health. Studies carried out by [63, 64] showed that these heavy metals could cause carcinogenic, teratogenic, acutely toxic, mutagenic disorders, and damage to red blood cells, the liver, and the kidneys [65]. Heavy metals are the contaminant that causes long-term effects on the environments because they cannot be degraded or readily detoxified. They have the potential to not only disturb the microbial communities but also cause long-term threat to environments [66]. Sophorolipids produced by *Starmerella bombicola* have been capable of removing Cd and Pb from contaminated soil and water. The removal process of Cd and Pb from soil and water has been affected by the types, concentrations, and pH of the sites [11, 14].

9 Biosurfactants in Hazardous Chemicals Removal

The remediation and treatment process of heavy metal-contaminated wastewater is particularly a big challenge. As such, remediation methods must focus on either altering the redox state of a metal to a less toxic form or should focus on removal of metal from the water [67]. Therefore, biological processes play a crucial role for the removal of heavy metal from contaminated water and sludge. Microbes are well studied to interact with an extensive range of toxic and non-toxic metals and change their properties [2]. For example, metals are mostly used as electron donors and electron acceptors for the production of energy within the cell. So that is why it may be used to shuttle or transport electron within organisms in syntrophic relationships and also used as a cofactor for enzymatic reactions [11, 16]. Biosurfactants producing microbes can influence the mobility of heavy metal indirectly by affecting pH. According to [11], the mechanism behind metal removal from soil could be the binding of biosurfactants molecule with metal adsorbed substrate, forming metal-biosurfactant complex by the incorporation of the metal into micelle followed by mineralization. Figure 4 demonstrates the mechanism of metal removal from water body. These mechanisms are helpful for the prevention of groundwater contamination.

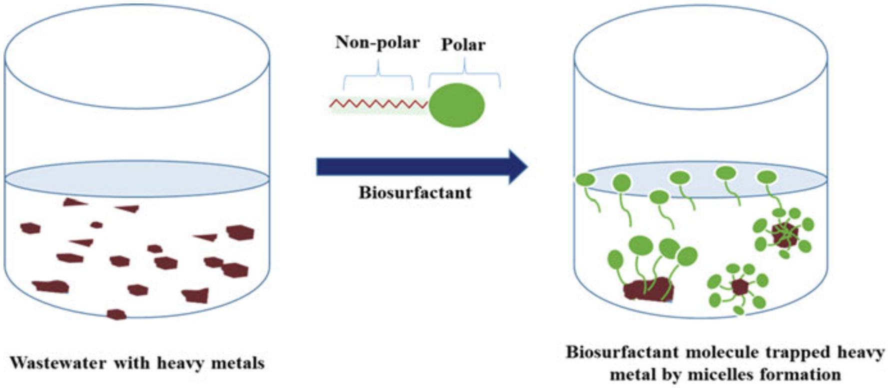

Fig. 4 Heavy metal removal from wastewater by the formation of micelles of biosurfactants

Heavy metals present in aquatic and terrestrial environments lead to groundwater contamination. In such conditions, treatment using biosurfactants is an appropriate way for heavy metals removal from such environments. Banat et al. [14] studied the effect of sophorolipid on heavy metals like Cd and Pb which are removed in batch soil washing by artificially created contaminated soil sample. Sophorolipids are an extracellular glycolipid biosurfactants which are produced by various microorganisms. Sophorolipids produced by the *Starmerella bombicola* have shown great efficiency than synthetic surfactants.

Moreover, it has been observed that a specific amount of biosurfactants needs to remove a particular concentration of heavy metals present in soil. So according to that, 44.8% of Pb and 83.6% of Cd have been removed by 8% crude acidic sophorolipids [68]. Acidic sophorolipid (SLs) has good solubility property while lactonic sophorolipids (SLs) are better in enhancing remediation of heavy metal-contaminated soils. The complexion of Cd with the free carboxyl group of the acidic SLs has been observed by Fourier-transform infrared spectroscopy (FTIR) [69]. Similarly Ramani et al. [70] investigated the microbial lipoprotein biosurfactants produced from a slaughterhouse lipid waste and used the microbial surfactants for removing the metal ion from the slaughterhouse waste aqueous solution, which resulted in sequestering the metal ions from the aqueous solution.

10 Pesticides in Water

Nowadays, farmers use different pesticides for crop protection and improving crop productivity and yield by controlling pests, weeds, and rodents. Pesticides are the chemically derived compounds that contain sulfur, chlorine, nitrogen, oxygen, phosphorous, and bromine as well as heavy metals such as copper, sulfates, arsenic, mercury, and lead. All these elements are toxic, carcinogenic, and non-degradable which are simply used in the agriculture sector in large quantities [71]. The leftover residues of these pesticides accumulate in agricultural soil particulates and other organic matter for long period, resulting in a major disturbance of environmental conditions and water pollution [72]. There are three main pesticides which are mostly observed in wastewater, these are malathion, triazophos, and dimethoate, since these chemicals are widely used in agriculture. Pesticides are one of the reasons for groundwater contamination, i.e., when pesticides are sprayed on crop plant, there are chances that pesticides come in the contact with surface water and finally leach down or runoff into water bodies and then the contaminated streams can be highly lethal to aquatic life [73]. Industries involved in manufacturing pesticides are also responsible for polluting the environment, since wastewater is not properly treated up to the desirable level.

Biosurfactants are the biological agents that can control pests and pesticides related to contamination from the environment. Köck-Schulmeyer et al. [73] evaluated the removal of pesticides by wastewater treatment plants. The same group also studied the environmental relevance of this treatment of pesticides into the aquatic ecosystem. They have studied not only the pesticide concentration but also their toxicity against three aquatic microorganisms: algae, daphnia, and fish. Since long time, people have used different physical and chemical techniques for the management of wastewater containing pesticides and several other contaminates. Considering the high toxicity and cost of these conventional treatments, biological treatment comes in the trends due to its uncountable benefits. Their applications would cause significant results for wastewater treatment and the prevention of water pollution.

11 Indirect Reduction in Agro-Chemicals by Biosurfactants

It is well known that use of pesticides especially insecticides leads to the contamination of field soils, which ultimately resulting in pollution of groundwater or surface water. An effective substitute of harmful agro-chemicals could be the employment of potential biosurfactants molecules. Mnif and Ghribi [74] judiciously reviewed the function of *Bacillus* and *Pseudomonas* bacterial species for the formulations of biopesticides in the management of the pests. The *Bacillus* species are well known for the huge production of biosurfactants. They produce lipopeptides, surfactin, fengycin, bacillomycin, iturin, and lichenysin [75]. These all biosurfactants are bioactive metabolites that can lead to hemolysis with strong larvicidal activity [31]. *Bacillus amyloliquefaciens* produce surfactin, a type of biosurfactant that has showed insecticidal potency. This potency of bacteria is helpful for fighting against green peach aphid in *Myzus persicae*; here, biosurfactants induce significant dehydration of insect cuticle membrane that may result in insects' death. Besides, lipopeptide produced by *B. amyloliquefaciens* may regulate the *Tuta absoluta* larvae. Lipopeptides act by binding to the receptor which is located in the brush-border membrane vesicles of the larvae. Similarly, biosurfactants produced by bacterium *B. thuringiensis* and *B. amyloliquefaciens* also have shown insecticidal potency against *Spodoptera littoralis* which is a cotton leaf worm; i.e., a species of the moth in the family Noctuidae [76]. Biosurfactants are successfully replacing various chemically synthesized pesticides. Although dozens of bacterial and fungi species have been reported to produce biosurfactants which act as pesticides, only a few species like *Bacillus* species have been well studied. Bacterial species, their biosurfactants, and the insecticidal properties of respective biosurfactants are given in detail in Table 2.

12 Limitations of Biosurfactants Application

Despite well studied and identified beneficial aspects of biosurfactants application in various fields, especially in wastewater management, desired results have not yet been attained. In literature, a common theme is that the biosurfactants are the

Table 2 Pesticidal properties of some biosurfactants producing bacterial spp.

Bacterial species	Biosurfactants	Insecticidal potency against insect	References
B. amyloliquefaciens	Lipopeptides	Larvicidal, against *Tuta absoluta*	[77]
B. subtilis	Surfactin	Larvicidal against mosquito	[31, 78]
B. thuringiensis	Not given	Larvicidal Colorado potato beetle	[79]
Bacillus thuringiensis	Not given	Larvicidal against *Spodoptera littoralis*	[80]
Bacillus subtilis	Cyclic lipopeptides	Larvicidal *Aedes aegypti* L.	[81]
B. amyloliquefaciens	Lipopeptides Surfactin	Insecticidal *Myzus persicae*	[82]
B. amyloliquefaciens	Cyclic lipopeptides	Pupicidal	[31]

biomolecule which compete with their synthetic counterparts. However, the high cost of production of biosurfactants and sometimes low yield make them more costly to use. In comparison to the synthetic surfactants, biosurfactants are 20–30% more expensive as reported by Hazra et al. [83]. To address the cost aspects of biosurfactant production that could be covered in three key aspects, one is the choice of cost-effective substrate, second finding or making a microbe to produce higher amount and the third one is purification processes, which increase the production cost. All the three points are responsible for biosurfactants production cost and yield [2, 84].

13 Conclusion

Whatever have been discussed above, it can be concluded that biosurfactants are noticeable agents and are causing exciting waves across research and industrial sectors, particularly in environmental clean-up aspects of wastewater treatment and some other clean-up strategies. In this chapter, the authors have tried their best to put concrete or reliable information about the key role of biosurfactants in wastewater treatment planning. Biological treatment using biosurfactants is more effective and appropriate than the other conventional approaches. In terms of pesticides, biosurfactants can be formulated to be employed as biopesticides. Biopesticides are far better than synthetic pesticides in the environmental sustainability perspective. In terms of heavy metals, biosurfactants molecules bind with metal adsorbed substrate and form a metal-biosurfactant complex by the incorporation of the metal into micelle and mineralize them. In terms of petrochemical contaminants in wastewater, biosurfactant molecule can act as a tensioactive compound and decrease the surface tension between oil/water that make them easy to access by microbes.

The regular discharge of organic and inorganic contaminants, especially the pesticides, heavy metals and petrochemical products and their accumulation in the aquatic and terrestrial environment are the major source of contamination. There are uncountable advantages behind biosurfactants biodegradation processes instead of using conventional methods for wastewater treatment. Many approaches are suggested, including physical and chemical but the use of live microbes to restore and decontaminate polluted sites is a well suitable and sustainable tactic. It has been observed that the efficacy and potency of these conventional processes are limited. Biosurfactants offer an attractive choice to remediate the non-soluble pollutants; the reason being self-biodegradability, ecological safety, and flexibility and overall its environmental acceptance. To conclude, it is very clear that there is no ambiguity that biosurfactants are multifunctional substances, which will certainly restore the sustainability of the environment not only in the present but also in future conditions.

14 Future Perspectives

The choice of using biological surfactants over synthetic surfactants is also important because surfactants having biological origin do not produce secondary contamination. Moreover, they are low or non-toxic to environments. The major issue with biosurfactants is that they are not cost effective. Also we are not able to produce sufficient quantity to fulfill our requirement. Therefore, it becomes necessary for us to develop efficient microbial strains which can produce a huge amount of biosurfactants on cheap raw materials. Furthermore, research work has to be carried out under laboratory conditions, and then finally in field for concrete results to prove the worth of biosurfactants. A positive report from the field is required to finally evaluate the effectiveness and efficiency of biosurfactants in situ. In future, there is a need to assess the long-time stability of biosurfactants and micelles synthesized by potential microbes. Genetic changes in potential microbes to produce more amount of biosurfactants using cheap substrates will make this process cost effective. Moreover, biosurfactants purification process also needs to be simplified and improved so that cost of production process should be cost effective.

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Best Practices in Wastewater Management in Poland with Particular Emphasis on Swimming Pool Waters

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Contents

Abstract Growing demand for water with its limited resources requires rational water management. The problem of proper water management is not only decreasing fresh water resources, but also its quality deteriorating to an extent that prevents natural self-purification processes. The paper presents the state of water and sewage management in Poland. Particular attention was paid to the issues related to water

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recovery and reuse. The current state of water and sewage management in Poland, including infrastructure and growing demand for water by various sectors of the national economy requires special attention to water quality. The paper provides a short review of technological processes used in wastewater treatment in Poland. As a case study the issue of recovery of water used in swimming pools and possibilities of its further use were discussed.

Keywords Poland, Sewage, Swimming pool water, Water and sewage management, Water treatment

1 Introduction

The rapid increase in demand for water with limited water resources requires rational water management at national, regional, and local levels [1]. Water supply depends not only on the amount of geologically available water, but also on the legal, economic, and social framework related to the system of its distribution [2]. It is possible to reduce water abstraction and consumption by obtaining effective technologies and relevant technical infrastructure related to water abstraction and wastewater disposal [3]. Significant progress has been made in this respect in EU countries with the adoption of common EU legislation, in particular the Water Framework Directive [4], the Urban Wastewater Directive [5], and the Drinking Water Directive [6]. These key legislative acts form the basis for improving water quality and sustainable use of the aquatic environment in Europe. Poland is among these countries as it acceded to the European Union on 1 May 2004. The common goal of the EU Member States is to significantly reduce the negative effects of pollution, excessive water abstraction, and other factors exerting pressure on water and to ensure that there is sufficient good-quality water for both human and environmental use [7]. It is particularly important for Poland to achieve this goal due to its small water resources compared to other EU countries [8]. Poland's water resources are characterised by considerable spatial diversity which is a consequence of high variability of natural environment conditions shaping the hydrological cycle (precipitation, evapotranspiration) and anthropogenic factors (high water abstraction). Water shortages are more and more frequent, especially during meteorological drought, which affects various regions of Poland [9–11]. Being aware of the limitations of water resources, authorities take appropriate measures to reduce risks. Therefore, the rational use of those resources for the needs of the population, economy, and ecosystems is extremely important [12]. Water and wastewater management is one of the key areas of Poland's development. This is evidenced by documents which present the main trends, concepts of the country's development, and challenges in the short and long term, such as the National Urban Wastewater Treatment Programme [13], the National Development Strategy 2020 [14], the Long-term National Development Strategy 2030 [15].

This paper discusses the state of water and wastewater management in Poland over the last several years, including the infrastructure and demand by various sectors of the national economy. Bearing in mind the particular importance of rational water management and water purity, a brief review of the technological processes used in wastewater treatment in Poland was carried out. In addition, due to the growing demand for water, attention was paid to issues related to water recovery and reuse and the respective legal solutions. As a case study, we discussed the issue of recovering swimming pool water and possibilities for its further use.

2 Methods and Data

The study is based on statistical information, legal regulations in force in Poland and reports on the implementation of national programmes available on ministerial websites. The paper uses the data collected from the Central Statistical Office of Poland (CSO) [16] and the Environmental Protection yearbooks [17]. Data on water and wastewater management in Poland are presented in general terms for the years 2002–2018. The study also uses the information contained in the Report on the Implementation of the National Urban Wastewater Treatment Programme [13].

Based on the available literature, the water treatment process and wastewater treatment technologies used in Poland were discussed. The use of water in swimming pools and the attempt to recover it were presented as a case study. On the basis of data from the Lumi-tech company, the technological process and technical possibilities of effective water recovery were discussed. We then analysed, on the basis of four selected swimming pool facilities, the economic viability of installing the original Lumi-ultra Hybrid Membrane Reactor technology.

3 The State of Water and Wastewater Management in Poland

The problem of proper water management lies not only in decreasing the fresh water resources whose consumption exceeds the possibilities of their renewal, but also in water quality deteriorating to an extent that precludes its natural self-purification processes. The development of the economy, especially the increase in industrial production, intensification of agriculture, and the emergence of large urban agglomerations, is conducive to the emergence of new types of pressure on water ecosystems. However, surface waters are most vulnerable to contamination. The biggest threat are discharges of industrial and municipal sewage into surface waters or to the ground [17].

All natural waters, before being used for drinking and industrial purposes, must be properly prepared, which is achieved through treatment processes. The types of individual processes used and their arrangement depend on the type of substances that must be removed from the water. The choice of the suitable water treatment process must be preceded by a water quality analysis. Depending on the results obtained, an appropriate treatment method is selected. Further technological research is carried out into the removal of contaminants, as well as the disposal of concentrations generated during the treatment of water, wastewater, and sludge.

The main source of water supply for the national economy in Poland is surface water. Its abstraction in 2017 was 8.4 km^3 and covered 83% of needs. Surface water was used mainly for the industrial production purposes. Groundwater abstraction reached 1.7 km^3 and as water of much better quality than surface water, it was mainly used to supply the population with drinking water. Poland is a country with relatively low water consumption. The water consumption indicator in 2015 was 292 m^3 per inhabitant [17].

Water consumption for the national economy and population is closely linked to the volume of water abstraction. The greatest threat to the aquatic environment is the discharge of industrial and municipal wastewater into surface water or to soil. Therefore, surface water is both a source of drinking water supply and a wastewater receiver. Water pollution is understood as any adverse changes: physical, chemical, and biological, reducing its quality.

According to the Central Statistical Office of Poland [17], in 2017, water consumption in Poland was 9656.3 hm^3. The largest share in water consumption for the national economy and population was held by the industrial sector (73%) (mainly the energy and chemical industries). Water consumption by the municipal sector through the operation of the water supply network amounted to 16%, while in agriculture and forestry, it reached about 11% of total water consumption for the national economy.

The current quality and quantity of discharged wastewater is a result of the state policy in the field of water management. In order to identify the actual needs in terms of wastewater management rearrangement and to prioritise the implementation of respective actions, the National Urban Wastewater Treatment Programme was established [13]. This programme was adopted by the Council of Ministers on 16 December 2003, and it has been regularly implemented and updated.

In recent years, a change in approach to wastewater treatment has been observed. Methods oriented exclusively towards mechanical removal of pollutants are displaced by highly efficient and complex wastewater treatment technologies with the deepened removal of nitrogen and phosphorus compounds. According to CSO data [17], in 2017, the amount of wastewater subjected to advanced treatment processes was 1138.0 hm^3 (54.5% of wastewater subjected to treatment processes), while the amount of wastewater treated mechanically was 497.4 hm^3 (23.8%). However, still some of the wastewater requiring treatment was not treated (4.9%).

In order to improve the country's water and wastewater management, further development of municipal wastewater collection and treatment systems took place. This manifested itself in the commissioning of new wastewater treatment plants (WWTPs), the modernisation of existing plants, in particular in terms of removing biogenic compounds from wastewater, as well as the expansion of the water supply

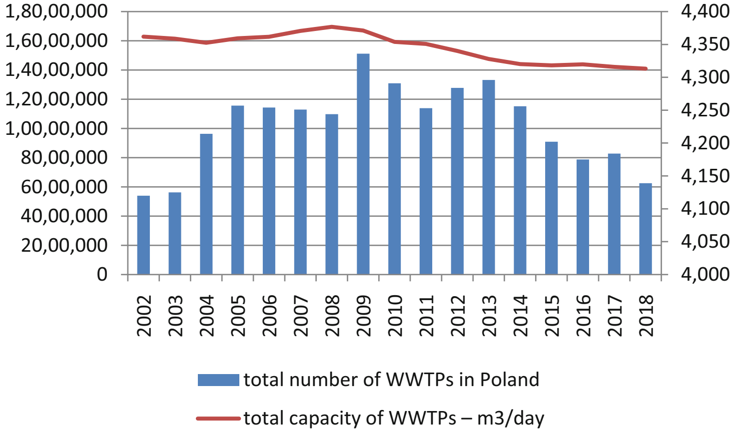

Fig. 1 Total number of WWTPs in Poland and their overall capacity (according to data [16])

and wastewater networks, and decommissioning of obsolete and inefficient facilities. The result of these activities is an increase in the total amount of treated wastewater (including a rise in treatment with increased removal of nutrients) and a decrease in the amount of untreated wastewater [17].

The most important task in improving water quality is to enhance the processes of wastewater collection and treatment. These activities aim at removing pollution from wastewater to an extent that allows water to be reused and reduces the burden on the natural environment. Due to the type of wastewater treatment methods and processes used, WWTPs are divided into the following groups:

- mechanical: only removing insoluble contaminants, i.e., solids and fats that settle or float, by means of grids, racks, and grit chambers.
- chemical: treating wastewater by precipitation of certain soluble compounds or neutralisation of wastewater by chemical methods such as coagulation, and sorption onto activated carbon.
- biological: removing organic pollutants, biogenic and refractory compounds from wastewater using the biodegradation process through the action of microorganisms and microbes.
- with increased nutrient removal: enabling increased nitrogen and phosphorus reduction.

The total number of WWTPs in Poland in the years 2002–2018 ranged from 4,120 in 2002 to 4,336 in 2009 (Fig. 1) [16]. In 2017, the number of industrial WWTPs was 926, while the number of municipal WWTPs was 3,258. Over the last few years, there has been a systematic increase in the number of municipal WWTPs (there were only 2,417 plants in 2000) and a decrease in the number of industrial WWTPs (1,626 in 2000). This change is dictated by the decommissioning of a portion of industrial WWTPs together with the closure of industrial plants or reorganisation due to the launch of industrial wastewater pre-treatment plants.

Industrial wastewater pre-treatment plants produce wastewater with a preliminarily lowered pollutant load, to the extent that it can be discharged to municipal WWTPs or WWTPs in individual factories.

The significant increase in the number of municipal WWTPs results from the systematic implementation of Directive 91/271/EEC through the National Urban Wastewater Treatment Programme [13]. It provided for equipping urban agglomerations with collective sewage systems and municipal WWTPs. Between 2000 and 2017, the number of cities covered by WWTPs increased from 801 in 2000 to 921 in 2017. Out of a total of 923 cities in Poland in 2017, two cities were not served by WWTPs.

According to CSO data [17], the share of the population using WWTPs increased from 53% in 2000 to 81% in 2017, while in cities it increased from 79% to about 95% and in villages from 11% to 42%. In the European Union, the share of population covered by WWTPs of at least 95% was recorded in seven countries (Luxembourg, the Netherlands, the United Kingdom, Spain, Germany, Malta, Austria) [17]. The lowest percentage of the population served by WWTPs was recorded in Cyprus (30%), Romania (48%), and Croatia (55%).

Also noteworthy is the increase in the number of people using WWTPs with increased nutrient removal. In 2017, twenty-one WWTPs with a total capacity of 68,000 m^3/day (including 18 municipal WWTPs with a total capacity of 5,000 m^3/day) were put into operation. The newly commissioned treatment plants were located in rural areas [17].

In the case of rural areas with dispersed development, running a sewage system is not cost-effective. One of the methods of wastewater treatment there is the use of household wastewater treatment systems [18–21]. The method of wastewater discharge and treatment in non-urbanised areas depends on the development structure and may vary in individual parts of a locality or commune. Constructing a sewage collection system for an entire village is not economically viable [22]. Household wastewater treatment systems should be used when the average length of the gravity sewer per one household exceeds 10 m [23]. Among the technologies used for the treatment of small amounts of wastewater, we can distinguish treatment systems with leach drains, tunnels or boxes, sand filters, and hydrophyte beds, as well as container treatment plants: with activated sludge tanks (including a sequencing batch reactor), with biological beds, and hybrid treatment systems which are a combination of activated sludge and biological bed technologies [24]. To obtain a permit for the construction of a household wastewater treatment system the household must meet specific criteria [25]. Household wastewater treatment systems are an important element of the wastewater infrastructure, as their use in areas with dispersed housing complements collective wastewater systems. At the same time, they are more economical, especially in the light of construction costs [26].

4 Selected Wastewater Treatment Technologies

According to the Act on Collective Water Supply and Collective Wastewater Disposal of 7 June 2001 [27], the sources of wastewater are classified into domestic, municipal, or industrial.

Domestic wastewater is wastewater from residential buildings, collective housing, and public utilities, resulting from human metabolism or household functioning, and similarly composed wastewater from these buildings.

Municipal wastewater is domestic wastewater or mixture of domestic wastewater with industrial wastewater or rainwater or snowmelt resulting from atmospheric precipitation, discharged by means of equipment used to carry out the municipality's own tasks in the field of sewage system and municipal wastewater treatment. Industrial wastewater is wastewater that is not domestic wastewater or rainwater or snowmelt resulting from precipitation, arising in connection with the commercial, industrial, storage, transport, or service activities of a plant, as well as a mixture of the above and wastewater of another entity, discharged by the sewage system of that plant.

Industrial wastewater arises in connection with the undertaking's commercial, industrial, storage, transport or service activities and which is mixed with the wastewater of another undertaking, and which is discharged by the sewerage system of that undertaking.

Other types of wastewater include

(a) water used for domestic or commercial purposes
(b) liquid animal faeces, excluding manure and slurry intended for agricultural use
(c) Landfill leachate

the extractive waste in which the extractive waste is storedhazardous and non-hazardous and inert extractive waste, storage locations

(d) water from cooling circuits of power plants or combined heat and power plants
(e) water originating from the dehydration of mining plants
(f) water used, discharged from the fish-farming facilities in flow facilities
(g) water used, discharged from fish-farming facilities or other aquatic organisms in ponds with standing water.

Details on the classification of wastewater into particular groups can be found in the Act of 7 June 2001 [27] and the Water Law Act of 2017 [28]. Depending on the types of sewage, different sewage treatment processes are used.

Physical, chemical, and biological methods are used in wastewater treatment processes. They can be combined into systems, e.g. physico-chemical and physico-biological. Each process also removes other contaminants in addition to the main purpose for which it is used. Depending on the type of wastewater, the treatment process should be selected to achieve the highest possible treatment outcome at minimum cost. One or more methods are used for this purpose. The processes of aeration, coagulation, sedimentation, flotation, filtration, ion exchange, chemical precipitation, sorption, chemical oxidation, membrane processes, and disinfection are used for water treatment [29, 30].

One of the methods is mechanical purification consisting of grinding, straining, filtering, sedimentation (settling of contaminants at the bottom), centrifugation, and flotation (flowing of contaminants onto the water surface in the form of foam). Water aeration is used to rid water of dissolved gases affecting its taste and smell, as well as volatile organic compounds. Aeration increases the content of dissolved oxygen in water, creating conditions for the oxidation of iron and manganese compounds and prevents the formation of a reducing environment. In water and wastewater technology, coagulation is used to remove colloids, colour, slowly settling suspensions, and other micro-pollutants. Different coagulants can be used in the coagulation process, which, occurring in ionic form, adsorb on the surface of colloidal particles (in the adsorbed layer) and reduce their electrokinetic potential to a value at which there is no significant influence of electrostatic repulsion. Sedimentation and flotation processes ensure the removal of suspensions present in the water both before treatment and after other processes, e.g. coagulation and chemical precipitation. During the sedimentation process, suspensions with a density higher than water are removed, while flotation eliminates particles with a density lower than water, but also higher when aeration is used. Filtration is the expulsion from water of solid-phase particles on the surface or in intergranular spaces of a porous material. The process can be used for the pre-treatment of raw water and to support other technological processes such as coagulation, de-ironing, and de-manganisation.

Biological wastewater treatment has been of great interest in recent years. It is associated with biochemical changes in which microorganisms play an essential role. Wastewater treatment with this method is carried out by the mineralisation of organic pollutants contained in the wastewater through microorganisms that are part of activated sludge. The classic active sludge is a flocculent suspension composed mainly of bacteria, protozoa, and other organisms [31]. The applied technical solutions allow for creation of optimal conditions for their development and reflect the intensified self-purification processes that take place in natural waters. The main purpose of biological wastewater treatment is to convert biodegradable pollutants into desired end products. It is particularly important to rid the treated wastewater of biogenic substances (mainly nitrogen and phosphorus compounds) causing an increase in eutrophication. Biological wastewater treatment processes used in WWTPs can be divided into aerobic, anoxic, and anaerobic. Microorganisms used in the biological wastewater treatment processes can be attached to the ground (fixed or mobile) as a *biological membrane* (sedimentary biomass, biological beds) or exist in the open space of the tank in the form of flocs (agglomerates or clusters of various types of bacteria and other organisms and pollutants, i.e. suspended biomass and activated sludge). Pollutants are converted into: internal energy stored in the bacterial cell, the final products of decomposition discharged at the wastewater outlet, and new biomass [32].

Treatment plants using the activated sludge technology are operated in large agglomerations as well as in rural settlement units. Wastewater treatment with activated sludge consists in creating in the wastewater flocculation of 50–100 μm with a very strongly developed surface. The flocs are made of a mineral nucleus and on the surface in a mucous membrane, they contain numerous heterotrophic bacteria such as *Acinetebacterium, Pseudomonas, Zoogloea, Enterobactericeae, Aeromonas, Flavobacterium, Achromobacter,* and *Micrococcus*. Organic pollutants are absorbed on the surface of the flocs and mineralised during the metabolic processes of the microorganisms. This process can also be used to remove ammonia, hydrogen sulphide, and other gases dissolved in wastewater through the operation of autotrophic bacteria such as *Nitrosomonas, Nitrosococcus, Nitrobacter,* and *Beggiatoa, Thiothrix.*

The effects of wastewater treatment vary depending on the technological solutions used [33, 34]. At present, in modern WWTPs that neutralise sludge in the fermentation process, it is becoming good practice to use the biogas generated in fermentation chambers for the combined production of heat and power in the cogeneration process. In it, the biogas obtained during sludge digestion is directed to cogeneration units for the cogeneration of electricity and heat. The treatment plant thus covers part of the electricity demand from its own production. The heat released when the biogas is burned in the generator's gas engine feeds the heating network through heat exchangers. Polish WWTPs are producing more and more sludge every year. Currently, more than 650,000 Mg s.m. are built in Poland annually (dry matter) of sludge in municipal treatment plants. It is expected that in 2020, over 780,000 Mg s.m. of sewage sludge will be generated in municipal treatment plants. As a result, and due to the option to intensify biogas production and the increasing efficiency of cogeneration units, more and more WWTPs are starting to generate both heat and electricity in the cogeneration process and are increasingly securing their own energy needs [35]. In turn, gasification residues are a valuable source of phosphorus and macroelements which can be used for fertiliser production [36].

5 Modern Wastewater Treatment Methods Used in Poland: Water Recovery on the Example of Swimming Pool Water Treatment

5.1 Swimming Pools in Poland and Pool Water Treatment Methods

The reuse of treated wastewater plays an important role in water and environmental management for economic and social reasons [37]. Under Polish conditions, only a small amount of water is recovered and reused. The best example is the water used to fill swimming pools. Bathing water is subject to strict quality requirements. The standards that must be met by water in swimming pools in Poland were established in the Regulation of the Minister of Health of 9 November 2015 [38]. The supervision of swimming pools in terms of water health safety has been regulated by the Act on the State Sanitary Inspectorate of 14 March 1985 [39]. The functioning of swimming pools has been regulated by the Act on the Safety of Persons Staying in Water Areas of 18 August 2011 [40]. According to the said Act, a swimming pool is understood as an indoor or outdoor facility, with flowing water, intended for swimming or bathing, having at least one swimming pool basin, with a permanent edge and bottom, equipped with sanitary facilities, changing rooms, and showers.

In 2016, the register of the State Sanitary Inspectorate included a total of 1849 swimming pools. The most numerous class of swimming pool facilities comprised indoor swimming pools (including water parks) totalling 1,420, which accounted for about 77% of all facilities. The number of outdoor swimming pools was 366 (ca. 20%), while mixed (indoor-outdoor) swimming pools constituted the least numerous class of 63 facilities (ca. 3%) [41]. In 2018 (as of December 31), the State Sanitary Inspectorate supervised water quality surveys for 1889 swimming pools in Poland, and in that number 82% were indoor swimming pools [42]. This means that the number of swimming pools in Poland is systematically increasing. The decision on the choice of pool water treatment technology should be made as early as at the facility design stage and adapted to the function and type of facility. In the case of existing pools, multiple methods of pool water treatment are most often used, which allows them obtaining water with satisfactory parameters. According to Wyczarska-Kokot [43, 44], we can distinguish the following methods of cleaning through:

- filtration in sand filters + chlorine disinfection + pH correction
- coagulation + filtration in multilayer or hydroanthracite sand filters + chlorine disinfection + pH correction
- coagulation + filtration + ozonisation + sorption filtration + chlorination + pH correction
- coagulation + ozonisation + filtration in a multilayer bed (including with a sorption layer) + chlorination + pH correction
- ozonisation + sorption filtration + chlorination + pH correction
- coagulation + filtration in a multilayer bed + ozonisation of part of the circulating water stream + chlorination + pH correction
- coagulation + filtration in a multilayer bed + UV irradiation + chlorination + pH correction.

If there are impurities in the water pool that cannot be removed by means of coagulation, filtration, and disinfection, they can be quantitatively reduced only by replacing the used pool water with fresh water. The supply of fresh water to the pool contributes to the dilution of water in the pool and therefore reduces the concentration of individual parameters. Disinfection is required in public swimming pools according to sanitary and hygienic guidelines. Most often water is disinfected with chlorine compounds. The basic water purification system for sports and recreation pools should include the process of filtration, or rather surface coagulation, carried out in sand and gravel bed filters and the process of chlorine disinfection using sodium hypochlorite produced on site by membrane electrolysis.

In the field of water treatment for public swimming pools in Poland and Europe, the German DIN 19643 standard has become widespread. It indicates the need to apply the following processes in swimming pool systems: filtration, coagulation, water pH correction, and chlorine disinfection. The length of the filtration cycle, filter rinsing, the dosing of coagulant, disinfectant, and water pH corrector, as well as the measurement of basic parameters controlling and demonstrating the effects of pool water treatment (measurement of free and bound chlorine concentration, redox potential, water pH, and temperature) should be fully automated in all types of public swimming pools.

All the pool water treatment methods described above cover only issues related to the quality of swimming pool water. Yet, they do not solve the problem of recovering the water that was already used but does not meet accepted standards and is disposed of as wastewater.

5.2 *Lumi-Ultra Technology for Pool Water Recovery*

One of the technical solutions used for water recovery is the Lumi-ultra technology which can successfully replace an MBR biological WWTP. However, the process of biological disposal of contaminants has been replaced by an original solution of the Hybrid Membrane Reactor in which, depending on the nature and content of contaminants, the type of chemical reaction, its duration, and membrane separation technology are individually selected (Fig. 2).

The water recovery process based on the Lumi-ultra technology can be divided into several stages.

- measurement of initial parameters affecting the planned chemical process
- correction of these parameters if they do not comply with the assumptions
- introduction of reagents into the wastewater
- support for the chemical process through physical methods

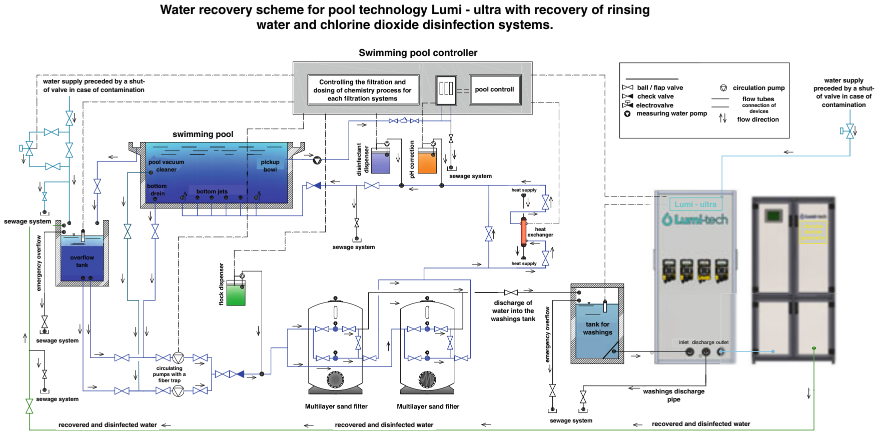

Fig. 2 Wastewater treatment technology scheme

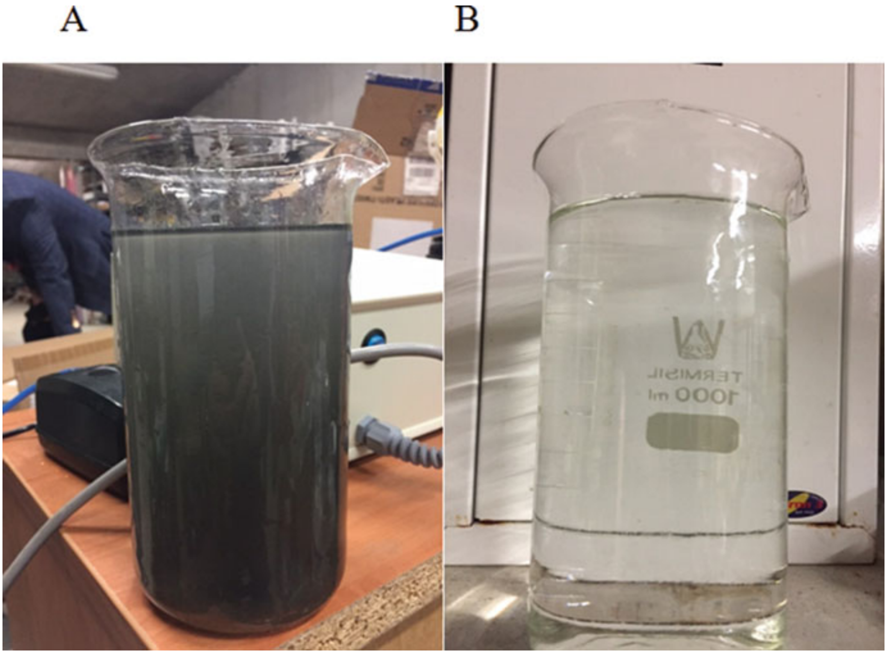

Fig. 3 Pool washings (**a**) and post-treatment water (**b**)

- coagulation or flotation of chemical reaction products
- fraction separation by suitable membrane technology, also multistage
- permeate polishing (photochemical method)
- re-measurement and correction of basic parameters and disinfection with ClO_2 if necessary.

The starting point is the selection of an appropriate method that will effectively arrive at the assumed outcome and determine the feasibility of the task. This can be achieved through water quality tests directly at the customer's premises with a mobile set.

The attached photographs show samples of washings from a swimming pool (Fig. 3) and a saline jacuzzi (Fig. 4), and the water after passing through the installation. Water quality tests include such parameters as: the number of *Escherichia coli*, the number of coagulase-positive staphylococci, the number of *Pseudomonas aeruginosa*, and the total number of microorganisms in 36 ± 2°C. According to the Regulation of the Minister of Health of 2017 [45], water in a swimming pool must meet the same requirements as drinking water. The results of microbiological analyses are assessed in a 0/1 system where 0 means that the water meets the standards, while 1 means that the standards provided for in the Regulation are not met, so the water is unfit for consumption.

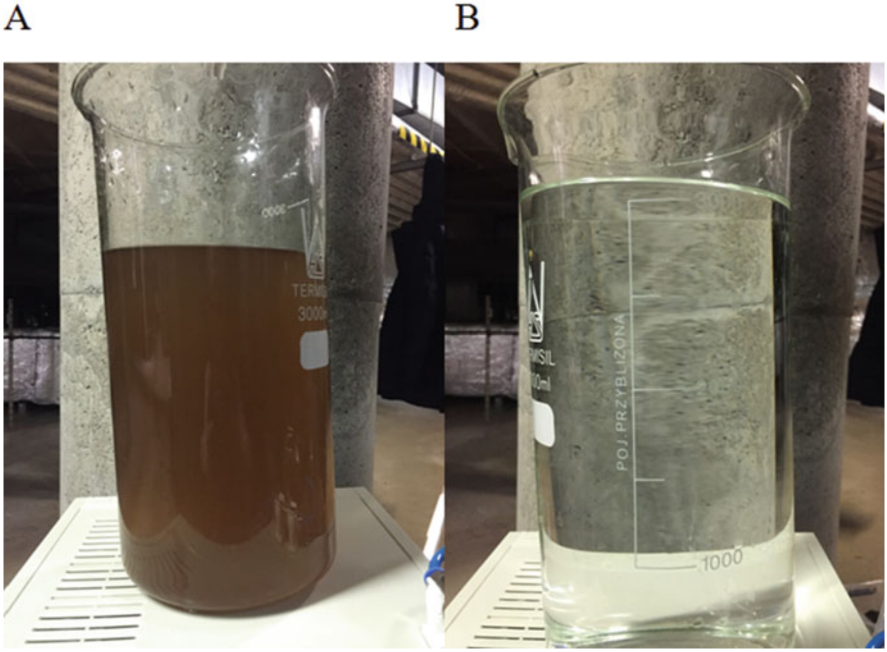

Fig. 4 Saline jacuzzi washings (**a**) and recovered water (**b**)

5.3 Economic Benefits of the Solution

Each installation is designed individually for each facility. This study presents economic calculations made in 2019 for four swimming pool facilities (Table 1).

Investments in process water recovery installations in swimming pool facilities pay for themselves within a period of over a year to a maximum of 3 years, depending on the volume of water used, the amount of washings disposed of, the price of water, wastewater, and the price of the heating agent used to heat the water. Of pivotal importance is the economic calculation, and it shows that thanks to the operation of modern installations, the cost of water, wastewater disposal, and heat energy required to heat water is reduced by up to 75%.

The above summary gives an example of how much water can be saved. Assuming that there are 1,700 indoor swimming pool facilities in Poland and each of them pours about 15,000 m^3 of water into the sewage system each year, this gives a total of 25,500,000 m^3 of water, i.e. over 61 million $USD (250 million PLN) on average. The replenished water must be heated on average by 20°C, which uses about 2,200,000 GJ of heat. Its production releases 198,000 Mg/CO_2 (tons of CO_2) into the atmosphere. In short, the amount of water wasted only during the operation of swimming pools would meet the needs of a city with a population of 100,000 for more than a year (on average, a resident of Poland uses 24 m^3 of drinking water). Meanwhile, the proposed treatment technology helps the environment and the

Table 1 Investment analysis for four swimming pool facilities (based on Lumi-tech data)

	Pool 1		Pool 2		Pool 3		Pool 4	
Parameters of process water recovery installations	Currently	With the designed recovery installation	Currently	With the designed recovery installation	Currently	With the designed recovery installation	Currently	With the designed recovery installation
Net price of UF installation ($)		414,634		53,659		73,171		60,976
Monthly amount of wastewater entering the UF installation (m^3/month)		9,150		950		1,500		1,200
Percentage of water recovered from wastewater		0.85		0.85		0.85		0.85
Amount of water recovered per month (m^3/month)		7,778		808		1,275		1,080
The cost of operating the UF installation per m^3 of wastewater introduced into the installation ($/$m^3$		0.56		0.56		0.56		0.56
The cost of operating the UF installation per m^3 of recovered water ($/$m^3$)		0.66		0.66		0.66		0.66
Fees for water abstraction and wastewater discharge		*Fee*		*Fee*		*Fee*		*Fee*
Net price of water from the network ($/$m^3$)		1.09		1.14		1.47		0.81
Price for wastewater disposal ($/$m^3$)		1.68		1.32		2.08		1.66
The cost of heating water by 19°C ($/$m^3$)		1.05		1.18		1.03		0.95
Total cost of water abstracted and discharged and the cost of its heating ($/$m^3$)		3.82		3.64		4.59		3.42

Basic parameters and calculations	*Currently*	*With installation*		*With installation*		*With installation*		*With installation*
Amount of wastewater processed by the installation (m^3/h)		16		4		4		4
Annual cost of water abstraction, wastewater disposal, and water heating in basins ($)	419,126	72,704	41,451	7,424	82,676	15,313	49,324	6,695
Annual operating cost of the UF installation ($)	–	53,561		6,395		10,098		8,078
Annual savings on water abstraction, wastewater, and heating ($)	–	346,422		34,027		67,362		42,629
Annual energy outcome (savings) (PLN) ($)	–	83,157		9,612		12,094		9,769
Annual savings on expenses with UF installation ($)	–	292,861		27,632		57,265		34,551
Payback period of the UF installation (months)	–	17		24		16		22
Comparison of the current and future situation – Annually	*Currently*	*With installation*	*Currently*	*With installation*	*Currently*	*With installation*	*Currently*	*With installation*
Cost of water abstraction, wastewater disposal and heating ($)	419,126	72,704	41,451	7,424	82,676	15,313	49,324	6,695
Cost of operating the UF installation ($)	–	53,561	–	6,395	–	10,098	–	8,078
Cash expenses ($)	419,126	126,265	41,451	13,819	82,676	25,411	49,324	14,773
Depreciation of the UF installation (10% per year) ($)	–	41,463	–	13,816	–	28,632	–	17,275
Charge to the accounting result ($)	419,126	167,728	41,451	27,635	82,676	54,043	49,324	32,049
Quality factors of the UF installation – annually		*Savings*		*Savings*		*Savings*		*Savings*
Heat savings (GJ)		6,995		875		1,463		1,239

(continued)

Table 1 (continued)

Parameters of process water recovery installations	Pool 1		Pool 2		Pool 3		Pool 4	
	Currently	With the designed recovery installation	Currently	With the designed recovery installation	Currently	With the designed recovery installation	Currently	With the designed recovery installation
Reduction of CO_2 emissions		585		74		124		106
Water savings (m^3)		93,330		9,690		15,300		12,960
Reduction of the volume of discharged wastewater (m^3)		93,330		9,690		15,300		12,960
Summary								
Installation cost including financial bonus from the sale of White Certificates ($)		353,449		46,510		61,220		50,853
Payback period including financial bonus from the sale of White Certificates (months)		14		20		13		18
Amount increasing the accounting result ($/year)		*257,517*		*22,981*		*51,143*		*29,465*

1 $USD exchange rate 4.1 PLN

pockets of facility managers and owners, who can save over 85% of the costs associated with water abstraction, wastewater discharge, and water heating. For the time being, however, local governments, which are most often the operators of swimming pools or Aquaparks, are not interested in this or are probing the topic. They show far-reaching distrust of new technologies, hiding behind regulations and the fact that water used in swimming pools must be drinking water. And in fact, it is only potable at the entry into the tank where it is prepared before being discharged to the pool basin. It should be noted that currently the cost of building an indoor swimming pool, depending on the standard, size, number, and type of swimming pool basins and other attractions, ranges from ten to several hundred million PLN for aquapark facilities, and the estimated monthly maintenance cost of the facility starts at 12–14 thousand $USD (about 50–60 thousand PLN).

6 Summary

Poland's water resources are small compared to other European countries. There still is a conviction among Polish citizens that since Poland has a well-developed river and lake network, and groundwater resources, the problem of water shortage is not important. The increase in awareness of the Polish society is very slow and unfortunately it is connected with the droughts that have swept the country in recent years. The main problem in the use of water resources and wastewater treatment is the lack of appropriate legal standards governing the design and operation of water recovery installations. Water recovery is not only important for environmental protection, but can also bring measurable financial benefits. The use of recycled water will reduce both the need for drinking water and the generation of wastewater.

As a case study, the authors presented the possibilities of recovering water from washings from sand filters in swimming pools using the original Lumi-ultra solution. As the presented economic analyses show, the water recovery system is a financially advantageous option for swimming pool facilities. The investment payback period can range from over a year to about 3 years. The system can be successfully used in buildings such as hotels and spas. Unfortunately, high installation costs still do not allow for the spread of this technology in households. In many cases it requires state support and should be part of a long-term policy on wastewater treatment and water recovery. The activities should first of all be addressed to industry as the largest water user in Poland. However, not all production plants are aware of the extent to which it is possible to reduce the costs associated with water abstraction and wastewater disposal using modern water treatment technologies. Agriculture will also potentially benefit from water reuse. The recovered water can be employed for watering crops. Such solutions have been used for a long time in Israel, Spain, Italy, Greece, the United States, and Mexico, among other countries. Solutions of this type are not widely used in Poland. A wide range of educational and informational activities in this area are therefore advisable.

7 Recommendations

The content of this chapter is important for sustainable water management on a local and regional scale in Poland. The information presented is addressed to water users, designers, and decision-makers responsible for developing appropriate wastewater treatment policies. Making decision-makers aware of the technical possibilities of water recovery, installation costs, and the lack of legal solutions will indicate the directions of work that will help to fill the gaps in this area. The support of the state administration and the establishment of a multi-annual programme will allow greater interest in modernising existing water installations and building new facilities using new water recovery technology. These activities will contribute to the increased interest of users and designers and, consequently, to the improvement of water quality in the environment.

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Towards the Global Rise of Zero Liquid Discharge for Wastewater Management: The Mining Industry Case in Chile

Sergio Santoro, Ahmet H. Avci, Marco Aquino, Lorenzo Pugliese, Salvatore Straface, and Efrem Curcio

Contents

Abstract The depletion of water has been recognized as the most pressing challenge to socioeconomic and human development. The implementation of Zero Liquid Discharge strategies is essential to drive the transition from linear to circular water management.

Mining ventures require enormous amounts of water and energy in the extraction and transformation phases while generating tremendous volumes of wastewater with a detrimental impact on the environment. By modernization of mining process and implantation of novel technologies (i.e., membrane technologies), there are opportunities such as reduction of water and energy consumption, and extraction of water and valuable components from mine tailings.

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For instance, Chile, an arid country experiencing a mega drought, has established the mining sector as the central pillar of its sustainable economic development. However, the intensive mining activities have exacerbated the water-energy nexus. Therefore, a new approach for optimization of water and energy consumption is a necessity for Chile.

This chapter provides the prospects of the exploitation of membrane technologies in the Chilean mining industry, coherently with the Zero-Liquid Discharge paradigm. Besides the traditional practices for freshwater production and remediation, possible applicable strategies are discussed taking into account the recent achievements in membrane technologies for the wastewater valorization by the recovery of valuable minerals.

Keywords Antiscaling agents, Circular economy, Desalination, Reverse osmosis, Zero liquid discharge

1 Water-Energy-Raw Materials Nexus in Chile

Water crisis represents one of the most severe global challenges of our time imposing to find a balance between the economic and the demographic growth and the water footprint of humanity [1, 2]. Under this scenario, Chile calls for more attention as figurehead in the mining sector (in particular as largest Copper producer) experiencing a dramatic mega-drought (Fig. 1a) [3, 4]. Despite the mining sector is a pillar of the Chilean economy accounting since the 1960 from 5 to 15% of the gross domestic product (GDP), of which 88% raises from Copper production, extraction activities put intense pressure on the water-energy nexus because of the enormous demands required in the extraction and transformation phases [5]. In fact, water is essential in different stages of mining activities such as dust suppression, mineral processing, mainly for grinding and flotation, and hydrometallurgical extractions. Moreover, the water management in mining sector is based on the linear economy producing 1.6 million tons of tailings every day in Chile implying dire environmental risks, such as acidification and heavy metal contamination of groundwater [6].

The alarming future scenario foresees a deficit of water resources in the coming 30 years [9–11] caused by the negative trend in rainfall (−40%) observed in the last decade [12] coupled with an increase of around 4.5% in consumptive water use by 2030 [13]. As a result, a socio-environmental conflict and the rise of a popular resistance to mining ventures are inevitable [14]. Antofagasta region represents a good example to describe the picture of the situation since copper extraction contributes to the 65% of the local GDP demanding the 59% and the 91% of regional water and electricity consumption, respectively [8] (Fig. 1b).

Definitively, the water crisis imposes an urgent need to rethink the Chilean copper mining chain from water provision to wastewater treatment with the aim to integrate

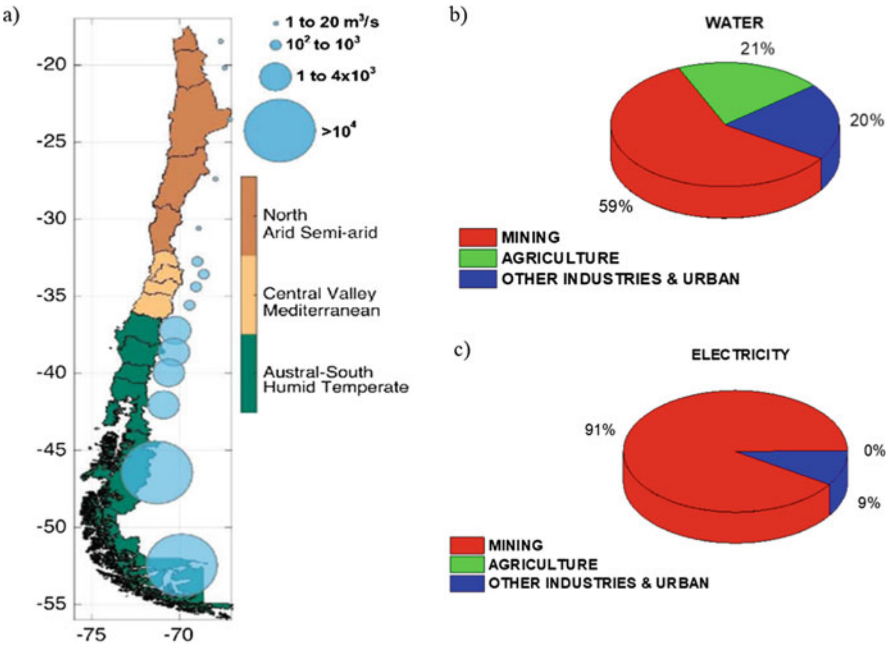

Fig. 1 (**a**) Climatic maps and water supply of Chile [7]. Available under a Creative Commons Attribution License. Water (**b**) and electricity (**c**) demand in different economic sectors in the Antofagasta region (data from [8])

sustainable water management solutions. Herein, we describe a series of membrane technologies reaching the maturity to alleviate the water-energy nexus and to implement the paradigms of the zero liquid discharge (ZLD) and circular economy in Chilean copper mining industry.

2 Water Provision and Brine in Chilean Mining Industry

Desalination technology, in particular reverse osmosis (RO), is widely recognized as a sustainable and feasible solution to address water scarcity. Recently, Chilean institutions have launched a 5-year strategic plan able to guarantee an improvement of freshwater production from seawater from 5.6 $m^3 s^{-1}$ to 14.5 $m^3 s^{-1}$ [15]. This challenging goal will be achieved due to the development of 22 new desalination projects added to the 23 active plants. Overall, the long-term programming forecasts that seawater consumption will expand up to 47% by 2030 [16, 17] (Fig. 2).

RO dominates the business of the desalination because of its technical, economical, and energetic feasibility in comparison with thermal evaporative processes. However, valid concerns have recently arisen about the severe negative impacts of RO on the environment. In fact, the osmotic pressure and the concentration polarization phenomena limit the water recovery factor at values less than 50% resulting

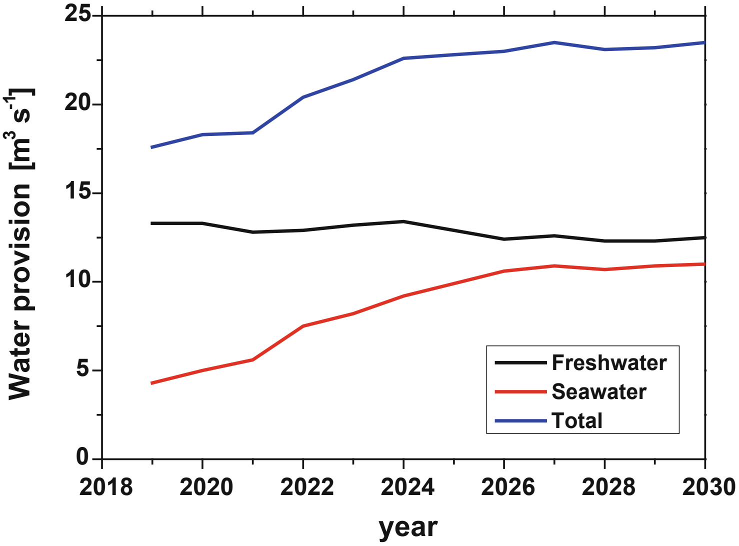

Fig. 2 Forecast of water provision and consumption by the Chilean copper mining industry 2019–2030 (data from [16])

in the production of enormous volume of hypersaline solutions (e.g. brine) as byproduct. Brine is usually discharged into the ocean causing detrimental environmental effects due to its high salinity, superior temperature with respect to the seawater, and presence of chemicals (i.e. antiscaling agents) [18, 19].

A look at available data helps to understand the seriousness of the situation: 1.6 $\text{Mm}^3\ \text{day}^{-1}$ of brine was directly discharged into the sea between 1997 and 2018 by Chilean desalination plants [20]. Moreover, the topography of Chile amplifies the question related to the energetic sustainability of desalination since the mining sites in Northern Chile are located at high altitudes. Thus, pumping freshwater from coastal area drastically increases the energetic demand of the mining industry.

Concisely, the cost for pumping to Chilean mining sites (adsorbing nearly 90% of the energy input) accounts for 77.4% of the desalination process [21] raising the freshwater production cost to US$ 5.00 per cubic meter, one of the highest value in the world [22]. These stressing issues encourage a step change in desalination for water supply to Chilean mines and ores by potentially improving the water recovery factor and minimizing the environmental impact and the energetic footprint of RO.

3 Mine Tailings and Acid Mine Drainage (AMD) in Chile

Mining activities generate significant amounts of highly concentrated wastewater disposed in tailings dams or stored in impoundments. Chile produces 1,400,000 tons day^{-1} of mine tailings and ca. 8,300 million m^3 of tail slurry that are presently

Table 1 AMD composition from Chilean mining industries [27]

Element	Ionic form	Concentration range [mg L^{-1}]
Aluminum	Al^{3+}	5–1,500
Arsenic	AsT	0–3
Calcium	Ca^{2+}	50–400
Carbonates	${CO_3}^{2-}$	0–50
Chloride	Cl^-	0–200
Copper	Cu^{2+}	60–2,500
Total iron	FeT	0–800
Magnesium	Mg^{2+}	100–800
Manganese	Mn^{2+}	5–350
Potassium	K^+	0–10
Sodium	Na^+	0–15
Zinc	Zn^{2+}	0–200
Sulfate	${SO_4}^{2-}$	800–16,000
pH	–	2–6
Total dissolved solids	–	1,500–22,000

disposed in 742 tailing deposits [23], hitting over 915 million tons per year in 2026 [24].

Severe apprehensions emerged about tailings generated from metal-sulfide mines containing large amounts of non-valuable sulfide minerals, able to generate acid mine drainage (AMD) in water upon the exposure to oxygen. As an example, chalcopyrite, the major source of copper, oxidates according to the following reaction [25]:

$$2\mathrm{CuFeS}_{2(s)} + \frac{17}{2}\mathrm{O}_2 + 5\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{Cu}^{2+} + 2\mathrm{Fe(OH)}_{3(s)} + 4\mathrm{SO}_4^{2-} + 4\mathrm{H}^+. \qquad (1)$$

AMD is a serious environmental problem because of its acidic nature (pH in the range of 2–4) and the leaching of hazardous heavy metals and toxic metalloids with adverse impact on the aquatic ecosystems [26, 27], whereas AMD soil infiltrations lead to serious implications for plant growth and human health [28] (Table 1).

Washing steps for the flue gas and/or the treatment of flue dust in smelting plant are another source of wastewater characterized by high acidity and the presence of heavy metals such as arsenic, usually neutralized by lime and resulting in a massive production of waste sludge [29, 30].

In the last decade the Chilean institutional framework has been committed to protect the environment by imposing stringent standards aiming to mitigate the environmental footprint of mining industry [31]. However, AMD is a worldwide problem and solely a radical rethinking of their disposal will meet the global challenge of a sustainable mining industry.

4 Membrane Technology: A Key Technology for the Implementation of the Paradigms of Zero Liquid Discharge (ZLD) and the Circular Economy in Chilean Mining Industry

Brine and AMD have been erroneously recognized for a long time as high volume-low value waste. Recently, water crisis and the urgent need for sustainability have changed this perception and both brine and AMD have been considered as valuable resources of water, minerals, and energy.

In fact, brines from RO are essentially concentrated seawater (salt concentration: 44.0–75.2 g L^{-1}, twice concentrated than seawater) containing basically almost all elements of the periodic table dissolved in water [32]. Similarly, mine tailings are rich of valuable minerals (among them critical raw materials such as rare earths, vanadium, and antimony) and recent studies demonstrated the feasibility to recover sulfuric acid from AMD [33].

Mechanical/thermal evaporation is economically and energetically prohibitive, whereas well-established and innovative membrane technologies have paved the way for a sustainable post-treatment and valorization of brines and AMD aimed to recover a large amount of water and valuable minerals from waste effluents according to the zero liquid discharge (ZLD) paradigm [34]. An economic assessment carried out by the Ministry of Mining of Chile estimated a profit of US$ ten million per one million tons of post-treated tailing with a tremendous economic impact considering the 525 million tons of tailings produced each year by mining sites [35].

Noteworthy, mining is an energy intensive industry with a considerable carbon footprint demanding roughly one-fifth of the total electricity consumption in Chile [36]. Conversely, Chile ratified the Paris Agreement and committed to reduce greenhouse gas emissions by 30% from 2007 levels by 2030 [37]. This challenging goal will be achieved by the reduction of the energy demand of mining ventures by the rational exploitation of renewable energy; mostly considering that Chile has the best worldwide solar energy potential for energy generation reaching an irradiation of 9–10 kWh m^{-2} per day in the northern regions [37]. With this in mind, membrane technology plays a key role because of their low carbon and energy footprint, easy integration with traditional renewable energy, and the unprecedented opportunity to generate blue energy from brine by exploiting their superior salinity [38, 39].

Hence, membrane technologies opened up new horizons to implement the ZLD strategies in Chilean mining industry (Fig. 3) ensuring a suitable water management and its valorization through the production of:

1. Water from tailings and hyper-concentrated brine via solar-driven membrane distillation (MD);
2. Valuable raw materials from AMD, thanks to the implementation of membrane crystallization (MCr).

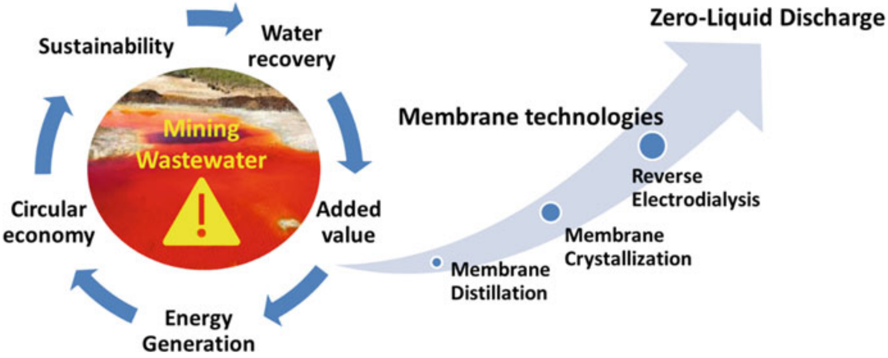

Fig. 3 Membrane technologies for wastewater valorization according to ZLD and circular economy

5 Solar-Driven Membrane Distillation (MD) for a Sustainable Water Management

A MD process is considered as a membrane-thermal hybrid process because water is firstly vaporized at 50–70 °C and then permeates through the micro-porosity of the membrane, whereas the hydrophobicity of membrane surface ensures the rejection of liquid water and dissolved non-volatile salts. On the basis of the principle of condensation, MD can be categorized into four main configurations: (1) direct contact MD (DCMD), (2) air gap MD (AGMD), (3) sweeping gas MD (SGMD), and (4) vacuum MD (VMD).

The low sensitivity of MD towards the high salinity offers a unique opportunity in brine post-treatment according to the ZLD paradigm. In fact, MD easily treats feed solution with a salinity up to 350,000 mg L^{-1} (one order of magnitude higher than seawater) [40], ensuring as a consequence a water recovery factor of 90% [41]. Roughly, the cost for water production via DCMD with heat recovery is 1.17 \$ m^{-3} [42].

Analogously, MD has been recently investigated to AMD and acid rock drainage (ARD) treatment opening the door for a shift of paradigm from linear to circular economy reaching water recovery factor of 80% (Table 2). Interestingly, the

Table 2 Performance of DCMD in water recovery from mining wastewater

Feed	Membrane	J [kg m^{-2} h^{-1}]	Water recovery (%)	Ref.
Synthetic AMD	PTFE	14.5	80	[43]
Synthetic AMD	PTFE/PP	20–36	>80	[44]
Synthetic ARD	PVDF	38	80	[45]
Synthetic AMD	PVDF	2.5	50	[46]
Gold-mining effluent[a]	PTFE	14–10	80	[47]

[a] Pre-treatment: ultrafiltration

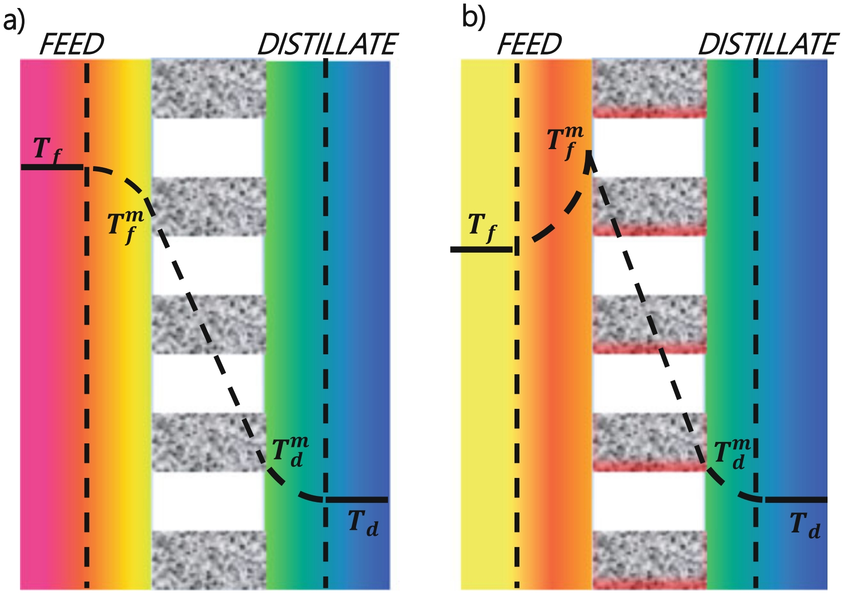

Fig. 4 (**a**) Temperature polarization in DCMD; (**b**) Reversing of temperature polarization due to photothermal effect in DCMD

retentate consists of concentrated valuable materials and the versatility of MD guarantees their recovery by the integration with other technologies. For instance, DCMD ensured a recovery of 80% of water from AMD obtaining a retentate concentrated more than 2.5 fold in terms of Cu concentration, subsequently absorbed by mesoporous silica tailored with Mn and amine to enhance the adsorption capacity and selectivity [43]. Analogously, the integration of DCMD with solvent extraction (SX) enabled the effective recovery of water and H_2SO_4 [44].

DCMD dominates with respect to other configurations because the condensation is obtained by basically flowing the cold distillate directly in contact with the membrane (Table 2). On the other side, the implementation at large scale of MD processes, included DCMD, is hampered by the thermal polarization phenomenon caused by the heat losses due to the vaporization of the water and the thermal conductivity of the membrane [48, 49] (Fig. 4a). In the last decades efforts have been focused on the exploitation of the solar energy converted into heat by solar collector to satisfy the energetic demand of MD (30.6–241.8 kWh m^{-3}) [50]. A single loop solar stand-alone AGMD set-up (membrane area 10 m^2) equipped with a solar collector of 5.73 m^2, used to supply the energy required for heating and pumping the feed, proved to produce 120 L day^{-1} of freshwater [51].

Interestingly, the recent achievements of thermoplasmonics in membrane technology have radically changed the perception of heat harvesting: photothermal materials immobilized into/onto the membranes efficiently absorb the radiation and guarantee high light-to-heat conversion heating in situ the membrane surface [52], reversing the temperature polarization (Fig. 4b).

A pioneering study of Politano et al. (2017) proved the advantages of implementing thermoplasmonics in MD processes: Ag nanoparticles dispersed into PVDF acted as hot-spots resulting in a boosting of the process performance [53]. In fact, the flux increased by 11 times under the exposure of the resonant UV radiation because the light-to-heat conversion at membrane surface ensured a reversing of the thermal polarization opening unprecedented horizon for a sustainable solar-driven MD. Since then, efforts have been devoted to improve the economic and technological feasibility of photothermal MD by the employment of inexpensive materials able to convert the natural radiation [54, 55].

6 Membrane Technologies: A New Route for Mining from Wastewater

Although desalination has strengthened the water-energy nexus in Chile, freshwater production from wastewater is currently more cost-beneficial (US\$ 0.40–1.26 m^{-3}) [56]. Traditional pressure-driven processes, such as RO or nanofiltration (NF), were found to be beneficial in AMD wastewater treatment, process water reusing, and metal recovery. A critical assessment clarified that NF is preferable to RO because of superior flux combined with lower operating pressure and excellent rejection over multivalent ions [57]. For instance, NF showed higher flux (86.6 L m^{-2} h^{-1}) with respect to RO (10 L m^{-2} h^{-1}) in treating wastewater from a Brazilian gold-mining company [58]. From an economic point of view, US\$ 131,250 of total capital cost (CAPEX) are required for NF system with a total operational cost (OPEX) of 0.263 US\$ per m^{-3} of treated effluent [58]. Similarly, systematic studies demonstrated the opportunity to treat via NF 100 kL h^{-1} of AMD (typical flow rate of mine water treatment plant) recovering more than 57 kg h^{-1} of Cu^{2+} and the 70% of water [59]. Unfortunately, the long-term stability of NF in AMD treatment is limited by the fouling and the scaling, especially related to precipitation of calcium and magnesium sparingly soluble salts, hindering the economic feasibility at large scale [60]. From a practical point of view, studies demonstrated the opportunity of the production of vanadium pentoxide by the valorization of Chilean mine tailings for an investment of 14 years with a return rate of US\$ 76 million [6].

In this scenario, an emerging application is membrane crystallization (MCr) able to ensure a precise control on the supersaturation and the subsequent crystallization of the solutes leading to the recovery of dissolved salts by taking the advantage of the mechanism of working of MD characterized by low sensitivity to feed concentration. In fact the morphological and physico-chemical properties of the membrane (e.g. porosity, contact angle, and roughness) represent a unique and powerful tool to control the kinetics of crystallization, thanks to the heterogeneous nucleation on the polymeric surfaces [61, 62]. MCr was found to be beneficial in the recovery of a wide variety of salts, such as NaCl, $MgSO_4 \cdot 7H_2O$, Na_2SO_4, and LiCl, from seawater and brine [63–65].

Also the selective diffusion of ions through ion exchange membranes was explored to induce the crystallization: Nafion N-117 cation exchange membrane facilitates the transport of Ca^{2+} into Na_2CO_3 solution driving the crystallization of tube-structured $CaCO_3$ on its surface [66].

In general, the immobilization of carriers into/onto the membranes for the ion target facilitates their transport and therefore their recovery. In the case of supported liquid membranes (SLMs) the polymeric membranes play the passive role to support the organic stripping phase (i.e. alkaline tertiary and quaternary amines or thiadiazine derivatives, acidic and chelating extractants, neutral or solvating carriers, and ionic liquids) dispersed in appropriate solvent (typically kerosene, toluene, n-dodecane, etc.). Despite their efficiency in the extraction of heavy metals and rare-earth elements from hydrometallurgical wastewaters [67], the leaching of the carrier from the membrane hampered their practical exploitation. Anchoring the carrier to the polymeric structure is the solution to ensure long-term stability offered by polymer inclusion membranes (PIMs) [68], whereas plasticizers may play the role to improve the flexibility and the homogeneity of the membrane [69]. Mixed matrix membranes (MMMs) consist in alternative candidates based on the immobilization of inorganic active fillers into the membrane. Among the myriad of inorganic nanoparticles, metal-organic frameworks (MOFs) have gained more attention because of their hybrid organic–inorganic nature based on metal ions and bridging organic ligands organized in well-defined structure with chemically tailored nanochannels [70, 71]. The promising recent results in removing metal ions (e.g. Cu^{2+} and Pb^{2+}) [72, 73] or in the recovery of valuable metals such as Au [74] from wastewater combined with the facile routes of synthesis and modification of MOFs has increased the confidence in the scalability of MMMs.

7 Outlooks

The growing Chilean water crisis affected by the mining footprint and the mega-drought imposes the urgent need to identify sustainable solutions to drive the transition from linear to circular blue economy. Even though copper extraction has relevant weight on the Chilean GDP, the depreciation of water bodies and the detrimental environmental impacts related to AMD disposal expose the mining companies to social resistance and restrictive policies. Desalination technologies, particularly RO, have been adopted to mitigate issues related to water provision, but serious environmental concerns emerged about the effect of brine disposal on the marine ecosystem.

Membrane technology has the potentials to implement circular practices in treating brine, AMD, and mining effluents ensuring high recovering factor according to the ZLD paradigm. Moreover, MCr has recently emerged as a feasible route for the recovery of valuable minerals from wastewater ensuring extra-profit, whereas innovative nanotechnologies such as thermoplasmonics and MOFs will play a key role to favor the exploitation of the renewable solar energy and to enhance the selective recovery, respectively.

Overall, the evaluation of membrane technologies for mining wastewater valorization is in an early stage but the promising results demonstrated their relevant position in the blue growth of the copper mining industry of Chile.

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Part VI
Conclusions and Recommendations

Updates, Conclusions, and Recommendations for "Cost-efficient Wastewater Treatment Technologies: Engineered Systems"

Mahmoud Nasr and Abdelazim M. Negm

Contents

Abstract Recently, increasing the population growth rates has been associated with substantial evolution in urbanization, municipal activities, and the agro-industrial practices. These current progress and developments have contributed to the increase

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of wastewater disposals, carrying pathogenic organisms and several organic and inorganic pollutants. The design and implementation of wastewater treatment technologies have been upgraded to maintain pollution reduction strategies and cost-saving opportunities. Wastewater treatment systems could be classified into either natural (ecological) or mechanized (equipped) based, mainly according to resource utilization and operating conditions. The natural wastewater treatment systems, such as ponds, wetlands, and retention soil filters, are commonly constructed outdoor from simple and ecological material (sand, gravel, plants, etc.). The engineered systems are used to treat wastewater (primary, secondary, and tertiary processes) by installing several reactors connected to equipment such as pumps, diffusers, heaters, etc. This chapter contains some updates and conclusions acquired from the application of the engineered-based processes in wastewater treatment. Some recommendations that could enhance the performance of mechanized systems in treating different wastewater types to meet the strict national and international regulations are given.

Keywords Biological wastewater treatment, Mechanized units, Pre- and post-treatment, Recycle and reuse, Water quality regulation

1 Introduction

Recently, various domestic, municipal, agricultural, and industrial activities have been substantially increased as a result of rapid population growth [1, 2]. The expansion of these practices is associated with disposing of large volumes of waste discharges [3]. The released wastewater carries various inert materials, toxic/hazard elements, persistent/emerging substances, micro/nano-particles, and organic and inorganic contaminants [4, 5]. Once these pollutants reach the environmental dimensions (water, soil, and air), they cause negative and adverse impacts on human health [6, 7]. Various infectious diseases and symptoms (neurologic, hematologic, and immunologic) are observed due to exposure to wastewater [8, 9]. In this regard, environmental engineers, scientists, and researchers are exerting extra efforts to develop wastewater treatment methods that could reduce waste and achieve additional benefits such as energy and fertilizer productions [10, 11].

The wastewater treatment plants (WWTPs) can be designed, implemented, and operated to remove pollutants via three sequential stages [12]. Some contaminants are removed in the primary step through screening, floatation, and/or precipitation. Other pollutants with biodegradable characteristics are removed in the biological (secondary) treatment process, where microorganisms tend to utilize/oxidize the organic substances for their maintenance and growth [13]. Moreover, nitrogen species are removed in this stage via a sequential nitrification/denitrification process. Certain pollutants related to heavy metals, pathogenic organisms [14], nonbiodegradable compounds, and other species not utilized by microorganisms are removed in the tertiary phase. This step includes disinfection (chlorination), ion exchange, micro/ultra-filtration (e.g., membrane separation technology), and adsorption (activated carbon as adsorbent). It's essential to gain knowledge about these wastewater treatment phases to recover main resources (e.g., water, energy, and nutrients) and have a final effluent complying with the reuse standards [15, 16].

To highlight the idea and concept of engineered wastewater treatment systems, representing the primary, secondary, and tertiary stages, the following sections briefly describe the main updates, conclusions, and recommendations of this book volume titled "Cost-efficient Wastewater Treatment Technologies: Engineered Systems."

2 Aerobic Biological Treatment of Sewage

Aerobic treatment technologies, including suspended and attached growth bioreactors, could convert a wide range of organic pollutants into carbon dioxide and settleable substances such as bacterial biomass [17]. Some aerobic-based treatment systems are also used to oxidize ammonium and nitrite to form nitrate via a nitrification process [18]. Aerobic systems could also be integrated with anaerobic and anoxic treatment processes for nitrogen and phosphorus recovery from wastewater [19]. The anaerobic/anoxic/aerobic integrated scheme is used to have a final effluent complying with the disposal of regulations and guidelines and applicable for reuse in agriculture and aquaculture [20]. Although the aerobic treatment systems have been broadly employed for pollution reduction, they suffer from both excess energy utilization (due to air supply) and high sludge production [21]. Moreover, they are inefficient in completely removing color/dyes with complex chemical structures recalcitrant toward degradation [22]. Furthermore, the aerobic process is not recommended for treating high-strength wastewater with a low biological oxygen demand (BOD): chemical oxygen demand (COD) ratio (e.g., 0.3:1). In addition, a post-treatment step is required to remove micropollutants, antibiotic-resistant bacteria, and waterborne pathogenic microbes. Hence, more studies are required to optimize the process configuration (suspended, attached, or hybrid), feed condition (batch, continuous, or semi-batch), and oxidation state (use oxygen as an electron acceptor).

3 Anaerobic Biological Treatment of Sewage

Anaerobic digestion is an environmentally valuable process used in waste management [23]. This technology is developed to treat both domestic and industrial wastes combined with green energy generation. Some points related to the anaerobic digestion of wastes should be discussed and evaluated, as follows:

- Environmental, techno-economic, and policy of biogas production by anaerobic digestion.

- Biogas-based cooking technology is considered a smart investment for gender empowerment and livelihood enhancement.
- Integration of heat, power, and biogas as an effective solution for carbon emission reduction.
- Identifying microbial communities involved in the conversion of organic matters into bioenergy via an anaerobic digestion process.
- Collaboration and information-sharing between scientific research entities, private industries, and governmental agencies for encouraging bioenergy production [24].
- The application of clean and renewable energy should be promoted for better human empowerment and livelihood.

4 Membrane Technology for Wastewater Treatment

Membrane distillation is an emerging technique used to enable a sustainable wastewater management strategy [25]. Membrane distillation is operated under temperature difference (vapor pressure difference), where a hydrophobic membrane separates the volatile solutes from the nonvolatile liquid. In particular, the vapor from the liquid phase passes through a hydrophobic membrane and further condensates (as a high-quality product) on the other side of the membrane. Solar-driven membrane distillation systems are beneficial for the dual benefit of water desalination and energy-saving [26]. The distillation process is used not only for desalination but also for heavy metal removal and valuable substance recovery. The implementation of membrane distillation for resource recovery (e.g., water, energy, and raw materials) complies with the zero liquid discharge and the circular economy paradigms [25].

Membrane bioreactor (MBR) is another application of membrane technology for water treatment. In this system, ultra- or microfiltration membranes are used to separate the solid phase (suspended biomass) and liquid phase (water), equivalent to the secondary settler of the conventional biological treatment system [27]. The configuration of MBRs could be either immersed MBR (the membrane module is submerged in the aeration basin) or cross-flow MBR (the membrane module is separated from the aeration tank). Although the immersed MBR occupies a smaller area of land, it requires larger energy inputs to supply air for maintaining both aerobic conditions and membrane surface scouring/cleaning. The MBR system has the advantages of producing a high-quality effluent, reducing the plant footprint, enhancing the control of hydraulic retention time (HRT) and sludge retention time (SRT), and enriching the nitrifying bacteria [28].

5 Electrochemical Methods of Wastewater Treatment

Electrochemical methods depend on the interrelation between the electrical and chemical routes for pollutants removal from wastewater. For example, electrocoagulation is a process that depends on the application of electric current between metal electrodes (Al and Fe), resulting in the dissolution of a sacrificial anode; and further coagulant species are formed [29]. These species include colloidal particles of $Al(OH)_3$ and $Fe(OH)_3$, attaining adsorption (physically or chemically) with pollutants. In parallel, pollutants could be removed due to the cathodic reaction via (1) flotation (hydrogen gas (H_2) evolution at the cathode) and/or (2) deposition on the cathode electrode. The enhancement in these pathways depends on the optimization of various operational factors such as current density, solution pH and temperature, electrode design (arrangement, surface area, and inter-distance), and water conductivity [30].

Some points related to the electrochemical processes should be discussed and evaluated, as follows:

- More efforts should be put into manufacturing new electrode material and selecting the proper oxidants, catalysts, and reagents.
- Enhance the understanding of the pollutant degradation kinetics and routes.
- Optimize the operational factors, including electrode surface area, solution pH and temperature, and current density, which affect gas evolution during electrochemical treatment of wastewaters.
- By-products generated from the degradation process should be recycled for sustainable development, especially in real wastewater treatment systems.
- Develop and evaluate new and inexpensive catalytic materials, with fast preparation pathways, to comply with the continuous expansion of industrial practices.

6 Disinfection for Pathogen Reduction

Disinfection is generally employed at the tertiary stage to inhibit or destroy the microbial pathogens before final disposal [31]. This process is achieved via chlorination (adding chlorine, chlorine dioxide, or chloramines), ozonation, and ultraviolet (UV) light radiation. However, the dose of disinfectants should be optimized because excess chlorine addition would generate trihalomethanes (THMs); i.e., the main disinfection by-products (DBPs) [32]. The occurrence of THMs in water bodies might cause risks to the public's health. Hence, it's essential to develop efficient predictive models for determining the levels of THMs. Moreover, the chlorine contact tanks should be properly designed and constructed to avoid chlorine loss and reduce the formation of THMs.

7 Improving Bioremediation Using Biosurfactants

Biosurfactants are biomolecules produced by different microorganisms for improving the relevant bioremediation, biodegradation, and detoxification performances [33, 34]. Biosurfactants could enhance the bioavailability of substrate for microbial species, offering various applications in environment protection (e.g., oil recovery, and treatment of agro-industrial and animal wastes) [35]. It's essential to:

- Well define the popular microbes and substrates involved in biosurfactant production [36].
- Highlight the challenges in biosurfactant production and its application in different industries [37]
- Evaluate the economic feasibility of the large-scale application of biosurfactants in wastewater treatment.
- Predict and demonstrate the biosurfactants' performance for oil recovery.
- Use cheap and green materials for developing efficient microbes to produce more amounts of biosurfactants with lower expenses.
- Ensure the implementation of guidelines and regulations for maintaining adequate biosurfactant purification technologies.

8 Emerging Organic Contaminants (EOCs) Removal

Emerging organic contaminants (EOCs) include any chemicals or microorganisms that enter the environment synthetically or naturally but are not commonly monitored in the environment [38]. This group of newly discovered contaminants has the potential to pose risks to human health and ecosystems, even if they are present in the aquatic environment with trace levels (ng/L or μg/L). Several groups of EOCs are most completely persistent to common biological degradation processes, which take place in nature or during conventional wastewater treatment [39]. The complexity, persistence, and concentration of EOCs are the main barriers for selecting the most suitable water/wastewater treatment systems. It's required to:

- Investigate innovative technologies, with economic analysis, for the elimination of EOCs.
- Raise awareness among citizens about the risks associated with increasing the EOCs levels in the aquatic environment.
- Fill the knowledge gaps and clarify key ideas and technological trends for adopting the best EOCs removal methods.
- Perform further studies to improve the socio-economic perspectives in EOC removal and optimize the current innovative technologies, with acceptable costs.

9 Nanotechnology for Wastewater Treatment

Nanotechnology has been recently used for tackling the global issues of water and soil environmental pollution [40]. The nanotechnology applications include [41, 42] (1) adsorption and biosorption (e.g., carbon, metal, and polymer based), (2) nanofiltration, (3) photocatalysis, (4) disinfection and pathological control, and (5) sensing and monitoring. Future studies associated with nanotechnology applications for environmental remediation should include:

- Overcome the challenges of nanoparticles transfer, (eco)toxicity, and cost-effectiveness.
- Develop advanced characterization of nanomaterial before and after application.
- Green synthesis of nanomaterials, such as using green tea leaves extract, is essential to maintain environmental sustainability [43].
- Due to their biocompatibility, biodegradability, and eco-friendless, nanoparticles fabricated from the plant biomass could be used in various biomedical and biotechnology applications [42].
- Identify the concentrations (levels), physicochemical properties, and reactivities of nanoparticles in the environment.

10 Biochar Synthesis and Applications to Treat Wastewater

The thermochemical treatment of biomass feedstock under an oxygen-limited condition is used to prepare a solid material, known as biochar [44]. Biochar has been progressively used in several industrial and agricultural activities due to its unique physical, mechanical, and chemical properties [45]. These properties depend on the type and source of biomass feedstock and the pretreatment method [46]. Moreover, the biochar properties depend on the pyrolysis operating factors (e.g., residence time, temperature, heating rate, and reactor type). Biochar could be modified using chemical or thermal treatment processes to improve its tendency to adsorb more quantities of pollutants from wastewater [47]. Biochar application in wastewater treatment has been broadly increased, mainly depending on its degree of carbonization [48]. Biochar's ability to treat wastewater also relies on its surface area, pore size distribution, surface functional groups, and the target pollutants to be removed. The sorption mechanisms vary mainly based on the properties of both contaminants (adsorbate) and biochars (adsorbent). The adsorption of heavy metals by biochar occurs by multiple mechanisms, including [44] (a) electrostatic attraction between cations and negatively charged function groups, (b) complexation with π electron-rich domain or surface functional groups, (c) ion exchange between positive metal ions and alkaline earth metals (or protons), and (d) pore-filling/co-precipitation as insoluble compounds. Biochar could be used as a low-cost material to maintain the adsorption process, either by mixing (batch) or fixed-bed column methods. Adsorption process could be integrated with the conventional wastewater treatment plants to enhance the removal of heavy metals and inorganic pollutants. The desorption, reactivation, and regeneration of biochars exhausted with the organic and inorganic compounds should be well defined. Techno-economic analysis of engineered biochar should be conducted to better understand its sustainability for large-scale applications.

11 Wastewater Management

The exponential growth in the world population has recently increased the gap between water supply and demand [49]. The collection, treatment, and reuse of wastewater are essential tasks to protect and conserve water resources. These processes require additional work such as GHGs emissions control, monitoring and regulation activities, and material recycling and composting. Some points should be considered for achieving the best wastewater management practices, as follows:

- Decision-makers should be aware of the technical possibilities of water recovery, installation costs, and the lack of legal solutions.
- Water recovery and reuse issues and the respective legal solutions should be highlighted [50].
- Overcome the lack of appropriate legal standards governing the design and operation of water recovery installations.
- Water, nutrients, and energy recovery is not only important for environmental protection, but can also bring measurable financial benefits.
- The use of recycled water will reduce both the need for drinking water and the generation of wastewater [11].
- The support of the state administration and the establishment of a multi-annual program should be integrated for maintaining new water recovery technologies.

12 Life Cycle Assessment (LCA)

Life cycle assessment (LCA) is an advanced evaluation tool used for analyzing the environmental impacts accompanied by project implementation; hence, it's considered a cradle-to-grave or cradle-to-cradle analysis technique [51]. Life cycle assessment (LCA) should be applied to evaluate the environmental burden of recycling wastewater generated from various residential, governmental, commercial, and public activities [52]. The scope of the LCA includes evaluation of primary, secondary, and tertiary treatments, with sludge management. Policies, public awareness, and supporting the legislation are essential factors used to address freshwater scarcity worldwide and achieve water sustainability [13]. Wastewater should be subjected to appropriate treatment techniques for adhering to the four stages outlined by the ISO 14040/44 LCA standards. More LCA studies are essential to solve the most significant issues influencing the development of a combined reclaimed water use scheme in the agro-industrial applications.

13 Conclusions

In this chapter, some of the major updates and conclusions covered by the book volume “Cost-efficient Wastewater Treatment Technologies: Engineered Systems” are highlighted. In addition, a set of recommendations for enhancing the performances of primary (physical), secondary (biological), and tertiary (advanced) processes for treating wastewater was developed. The recommendations include the design, implementation, and operation of engineered wastewater treatment systems, giving a final effluent obeying the reuse standards. The key information and findings of this chapter would encourage environmental researchers, engineers, managers, and scientists in selecting practical and cost-effective mechanized systems for wastewater treatment.

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