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Water and Wastewater Treatment Technologies

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Preface

Energy demand has been rising remarkably due to increasing population and urbanization. Global economy and society are significantly dependent on the energy availability because it touches every facet of human life and activities. Transportation and power generation are two major examples. Without the transportation by millions of personalized and mass transport vehicles and availability of 24 × 7 power, human civilization would not have reached contemporary living standards.

The International Society for Energy, Environment and Sustainability (ISEES) was founded at Indian Institute of Technology Kanpur (IIT Kanpur), India in January 2014 with an aim to spread knowledge/awareness and catalyse research activities in the fields of Energy, Environment, Sustainability and Combustion. The Society's goal is to contribute to the development of clean, affordable and secure energy resources and a sustainable environment for the society and to spread knowledge in the above-mentioned areas and create awareness about the environmental challenges, which the world is facing today. The unique way adopted by the society was to break the conventional silos of specializations (Engineering, science, environment, agriculture, biotechnology, materials, fuels etc.) to tackle the problems related to energy, environment and sustainability in a holistic manner. This is quite evident by the participation of experts from all fields to resolve these issues. The ISEES is involved in various activities such as conducting workshops, seminars, conferences, etc. in the domains of its interests. The society also recognizes the outstanding works done by the young scientists and engineers for their contributions in these fields by conferring them awards under various categories.

Second International Conference on 'Sustainable Energy and Environmental Challenges' (SEEC-2018) was organized under the auspices of ISEES from December 31st 2017–January 3rd, 2018 at J N Tata Auditorium, Indian Institute of Science Bangalore. This conference provided a platform for discussions between eminent scientists and engineers from various countries including India, USA, South Korea, Norway, Finland, Malaysia, Vietnam, Austria, Saudi Arabia and Australia. In this conference, eminent speakers from all over the world presented their views related to different aspects of energy, combustion, emissions and alternative energy resource for sustainable development and cleaner environment. The conference presented 5 high voltage plenary talks from globally renowned experts on topical themes namely “Is It Really the End of Combustion Engines and Petroleum?” By Prof. Gautam Kalghatgi, Saudi Aramco; “Energy Sustainability in India: Challenges and Opportunities”, by Prof. Baldev Raj, NIAS Bangalore; “Methanol Economy: An Option for Sustainable Energy and Environmental Challenges”, By Dr. Vijay Kumar Saraswat, Hon. Member (S&T) NITI Ayog, Government of India;, “Supercritical Carbon Dioxide Brayton Cycle for Power Generation” by Prof. Pradip Dutta, IISc Bangalore and “Role of Nuclear Fusion for Environmental Sustainability of Energy in Future” by Prof. J. S. Rao, Altair Engineering.

The conference included 27 technical sessions on topics related to energy and environmental sustainability including 5 plenary talks, 40 keynote talks, and 18 invited talks from prominent scientists, in addition to 142 contributed talks, and 74 poster presentation by students and researchers. The technical sessions in the conference included Advances in IC Engines: SI Engines, Solar Energy: Storage, Fundamentals of Combustion, Environmental Protection and Sustainability, Environmental Biotechnology, Coal and Biomass Combustion/Gasification, Air Pollution and Control, Biomass to Fuels/Chemicals: Clean Fuels, Advances in I.C. Engines: CI Engines, Solar Energy: Performance, Biomass to Fuels/Chemicals: Production, Advances in I.C. Engines: Fuels, Energy Sustainability, Environmental Biotechnology, Atomization and Sprays, Combustion/Gas Turbines/Fluid Flow/Sprays, Biomass to Fuels/Chemicals, Advances in I.C. Engines: New Concepts, Energy Sustainability, Waste-to-Wealth, Conventional and Alternate Fuels, Solar Energy, Waste water Remediation and Air Pollution. One of the highlights of the conference was the Rapid Fire Poster Sessions in (i) Energy Engineering, (ii) Environment and Sustainability, and (iii) Biotechnology, where more than 75 students participated with great enthusiasm and won many prizes in a fiercely competitive environment. 200+ participants and speakers attended this four days conference, which also hosting Dr. Vijay Kumar Saraswat, Hon. Member (S&T) NITI Ayog, Government of India as the chief guest for the book release ceremony, where 16 ISEES books published by Springer under a special dedicated series “Energy, Environment and Sustainability” were released. This was the first time that such significant and high quality outcome has been achieved by any society in India. The conference concluded with a panel discussion on “Challenges, Opportunities & Directions for Future Transportation Systems”, where the panelists were Prof. Gautam Kalghatgi, Saudi Aramco; Dr. Ravi Prashanth, Caterpillar Inc.; Dr. Shankar Venugopal, Mahindra and Mahindra; and Dr. Bharat Bhargagava, DG, ONGC Energy Center, and Dr. Umamaheshwar, GE Transportation, Bangalore. The panel discussion was moderated by Prof. Ashok Pandey, Chairman, ISEES. This conference laid out the roadmap for technology development, opportunities and challenges in Energy, Environment and Sustainability domain. All these topic are very relevant for the country and the world in present context. We acknowledge the support received from various funding agencies and organizations for the successful conduct of the Second ISEES conference SEEC-2018, where these books germinated. We would therefore like to acknowledge SERB, Government of India (Special thanks to Dr. Rajeev Sharma, Secretary); ONGC Energy Center (Special thanks to Dr. Bharat Bhargava), TAFE (Special thanks to Sh. Anadrao Patil), Caterpillar (Special thanks to Dr. Ravi Prashanth), Progress Rail, TSI, India (Special thanks to Dr. Deepak Sharma); Tesscorn, India (Special thanks to Sh. Satyanarayana); GAIL, VOLVO, and our publishing partner Springer (Special thanks to Swati Mehershi).

The editors would like to express their sincere gratitude to large number of authors from all over the world for submitting their high quality work in a timely manner and revising it appropriately at a short notice. We would like express our special thanks to Dr. Takahiro Fujioka, Dr. Chart Chiemchaisri, Dr. Xuan-Thanh Bui, Dr. Sunita Varjani, Dr. Jaecheul Yu, Dr. Vo Hoang Nhat Phong, Dr. Ho Ngo Anh Dao, Dr. Nguyen Thanh Tin, Dr. Vo Thi Kim Quyen, Dr. Nguyen Thai Anh, Dr. Pham The Hai, Dr. Rajmohan K. S., Dr. Muthulingam Seenuvasan, Dr. Bishwambhar Mishra, Dr. Sunita Varjani, Dr. Baskar Gurunathan, Dr. Praveen R., Dr. Deepak Pant, Dr. Bharathi Raja and Dr. Ramya T., who reviewed various chapters of this book and provided very valuable suggestions to the authors to improve their manuscript.

The book covers different aspects of recent advanced technologies for water and wastewater treatment and water reuse. The technologies involve novel physio-chemical, biological and advanced oxidation processes in which they are modified processes or coupled with nano materials and/or newly developed products for improving the performance of the treatment processes. The book also contains chapters describing treatment strategies for the current pollution of complex organic matters, nutrients, toxic substances and emerging micro pollutants in different water resources. The treatment processes described the recent developed technologies for water and wastewater treatment and reuse such as coagulation using natural coagulants, biological nutrient removal, membrane separation processes, Fenton/ozone oxidation, etc. The membrane processes include recent research on the removal of challenging chemicals by various membrane bioreactors and reverse osmosis processes, and emerging techniques for evaluating membrane integrity and membrane fouling levels. In addition, the integrating water treatment and bioelectricity production by micro fuel cells are also described in the book.

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Bangkok, Thailand	Chart Chiemchaisri
Nagasaki, Japan	Takahiro Fujioka
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Chart Chiemchaisri, Ph.D. is Associate Professor and Associate Dean for Research at the Faculty of Engineering, Kasetsart University, Thailand. He received his Ph.D. in environmental engineering from the University of Tokyo. His research interests include membrane technology for water and wastewater treatment and reuse, landfill technology for solid waste disposal, greenhouse gas emissions from solid waste and wastewater management. He has published more than 100 international refereed journal papers from 1991 to date and also served as associate editor/ editorial board/guest editor for several international journals, e.g. Journal of Water Sustainability, Agricultural and Natural Resources, Bioresource Technology, Desalination and Water Treatment.

Takahiro Fujioka, Ph.D. is Associate Professor at the Graduate School of Engineering, Nagasaki University, Japan. He completed his Ph.D. at the University of Wollongong, Australia. His research interests centre on water reuse using membrane technologies, and he has published 36 international journal papers.

Dr. Sunita Varjani is Scientific Officer at Gujarat Pollution Control Board, Gandhinagar, Gujarat, India. She holds an M.Sc. in microbiology and Ph.D. in biotechnology. Her major areas of research are industrial and environmental microbiology/biotechnology. She has authored more than 60 publications, including research and review papers, books and chapters. She has won several awards and honours, including Young Scientist Award—2018 by International Society for Energy, Environment and Sustainability; Certificate of Appreciation—2017 from EPFL, Lausanne, Switzerland; Top Reviewer Award—2017 from *Bioresource Technology Journal*, Elsevier; Young Scientist Award at AFRO-ASIAN Congress on Microbes for Human and Environmental Health, New Delhi (2014); and Best Paper Awards in national and international conferences in 2008, 2012 and 2013. She is Member of the editorial board of *Journal of Energy and Environmental Sustainability* and has served as Guest Editor of special issues of *Bioresource Technology Journal*, *Journal of Energy and Environmental Sustainability* and *Indian Journal of Experimental Biology*. She is the recipient of visiting scientist fellowship from EPFL, Lausanne, Switzerland (2017).

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Part I
General

Chapter 1
Introduction to Recent Advances in Water and Wastewater Treatment Technologies

Xuan-Thanh Bui, Chart Chiemchaisri, Takahiro Fujioka and Sunita Varjani

Abstract Nowadays due to urbanization and industrialization, several pollutants and its derivatives are discharged into water environment. Most of the pollution is caused by organics, nutrients, and contaminants with low concentration but is highly toxic to human and aquatic environment. Especially, there are several micropollutants and its derivatives that exist in water and wastewater such as disinfection by-product (DBPs), endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), antibiotics, pesticides, heavy metals, etc. This book provides holistic approach in terms of measurement, monitoring, and recent advanced treatment technologies for water and wastewater treatment and water reuse. The technologies involve the novel physio-chemical, biological and advanced oxidation processes in which they are modified processes or coupled with nanomaterials and/or newly developed products for improving the performance of the current treatment processes. In addition, the membrane processes include recent research on the removal of challenging chemicals by various membrane bioreactors and reverse osmosis processes, and emerging techniques for evaluating membrane integrity and membrane fouling propensity.

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Keywords Water and wastewater treatment · Membrane · Water pollution Bioreactor · Contaminants

Water source control is one of the most important strategies for sustainable water and wastewater treatment. In the second part, the first chapter provides the fate of microcystins for drinking water applications. Water eutrophication has become one of the most challenging environmental problems in the world. The excessive nutrient loading into the surface water system is considered to be one of the major factors. As a result, massive proliferation or prolonged of toxic cyanobacteria blooms (TCBs) are increasing in both frequency and distribution. TCBs are an environmental concern due to their ability to produce a wide range of hepatotoxins, neurotoxins, and dermatotoxins. Microcystins (MCs) are the most common toxin and are considered to be one of the most hazardous groups. Indeed, some of the largest aquatic ecosystems on the earth are being contaminated with MCs. MCs pose a potential health risk for humans when occurring in freshwaters used for human recreation or drinking purposes. To ensure the safety of drinking water supplies, a variety of physical, chemical, and biological processes, such as coagulation, flocculation, sedimentation, filtration, disinfection, adsorption, and biodegradation have been applied for removal of MCs. This chapter provides an overview of the current knowledge of MCs including occurrence, distribution, as well as current methods of their removal from drinking water.

Another chapter focuses on the issues surrounding algogenic organic matter (AOM) in source water. Algogenic organic matter (AOM) in eutrophic water has become a critical problem for the sustainable operation of water treatment plants. As AOM is a high-yielding precursor of disinfection by-products (DBPs), its occurrence in water sources intensively raises public attention on the issues of safe and stable supply of drinking water. This chapter presents current advanced knowledge of AOM characterization and their applications for the prediction of DBP formation upon chlorination. Herein, two dominant classes of carbonaceous DBP (C-DBPs), trihalomethanes (THMs), and halo acetic acids (HAAs) were reviewed as major products of DBP from eutrophic water. Overall, AOM has higher yielding potential of THM and HAA precursors upon chlorination compared to terrestrial natural organic matter (NOM). Of the characterization tools, fluorescent spectrometry is an advanced proxy to trace AOM-derived C-DBP formation over traditional bulk parameters or ultraviolet absorbance because of its greater sensitivity and selectivity. However, future work may use fluorescent spectrometry technique in combination with bulk parameters, such as chlorine consumption, or MW properties to increase its predictability to AOM-DBP formation.

Regarding water treatment technologies, we have included one chapter that provides an overview of a natural coagulant called *Moringa oleifera* in water treatment. In a typical drinking water treatment, coagulation followed by sedimentation and sand filtration plays an important role in removing particulate matter. *M. oleifera* seed can be used as an alternative to chemical coagulants such as aluminium sulfate (alum) and ferric chloride. *M. oleifera* seeds contain dimeric cationic proteins, which can be extracted from *M. oleifera* seeds and used for coagulation applications. Thus, *M. oleifera* coagulation is a pragmatic option to provide safe drinking water to rural communities in developing countries. The chapter also provides the potential of *M. oleifera* coagulation as a low-cost fouling mitigation technique for membrane treatment process.

One chapter reviews on recent advances in phytoremediation for removal of heavy metals during wastewater treatment. Scientists have been succeeded in the usage of wastewater for agricultural purposes. But the discharge of effluent from the industries led to a constant increase in effluent concentration and adversely affects the health of human, plants, and animals. Phytoremediation is one of the wastewater treatment technologies used to eradicate the contaminants from marine and soil environment without disturbing the environment. The ability of plants roots to accumulate, translocate, and degrade the contaminants from environment plays a major role in Phytoremediation process. Phytoremediation follows mainly four mechanisms which are phytoextraction, phytostabilization, phytodegradation, phytovolatilization, and phytofiltration. Aquatic or terrestrial plants are used to accumulate, immobilize, or degrade the contaminants from air, soil, and water. It is an inexpensive technique and it could be applied to large contaminated areas without any significant damage to environment. Treatment of contaminated site would take long period is one of the few limitations to overcome. Chelating agents are used to enhance the accumulation ability of plants. Inorganic chelating agents are more aggressive and enhance high accumulation of contaminants. To protect the environment and to enhance accumulation ability of plant, organic acids are used as chelating agents. The success of phytoremediation is determined not only by accumulation ability but also the bioavailability of contaminants in environment and plant. This chapter discusses the potential mechanisms and strategies available to widen the application of phytoremediation.

Another chapter reports about volatile organic compounds that are of significant importance in water. In this study, volatile organic compounds (VOCs) emissions from solid wastes and leachate at a municipal solid waste dumpsite in Thailand were investigated. Due to poor upstream segregation, several volatile organic compounds such as benzene, toluene, ethylbenzene, and trichloroethylene were detected in several wastes components. Their concentrations were found varied between types of wastes, disposal ages of wastes, and disposal locations in the waste pile. Field measurement was used to assess the fate of emission of those compounds from solid waste stockpile area (7.4 ha). Benzene was the mostly emitted from the stockpile through direct volatilization to the atmosphere whereas trichloroethylene was majorly drained out with leachate and subsequently emitted from the surface of leachate storage pond. The emission was highly temperature dependent being higher during daytime during which the waste temperature may rise to 80 °C by about four times from those observed at an average ambient temperature (40 °C). These significant contaminations of VOCs should be taken into account when waste utilization and leachate treatment are to be considered.

One chapter provides an overview of membrane technologies that can play an important role for the removal of contaminants such as pharmaceuticals. In course of past few years, pharmaceutical industries have huge contribution in the economic development of the country, but concurrently the pharmaceutical pollutants can also be responsible for severe hazards to the environment. Traditional methods of wastewater treatment cannot erase these pollutants from the water due to their hostile behavior. The advent of the pharmaceutical pollutants leads a demand for assessment and depiction of the wastewater discharged from pharmaceutical industry as per the norms recommended by the official agency (Pollution Control Board). A vast number of treatment strategies are adapted by the pharmaceutical industries to reuse wastewater and regulate environmental pollution. In this chapter, the finest membrane based methodologies to abolish the pharmaceutical compounds were focused. At present, no individual technology has the potential to expel out the pharmaceutical pollutants from wastewater. Merging of traditional methods with membrane reactors leads to the best hybrid wastewater treatment technology.

Ozonation has been widely applied to water and wastewater treatment. However, the formation of by-products still remains a challenge. This chapter provides a comprehensive review about the fate of ozonation by-products with a particular focus on bromate and *N*-nitrosodimethlyamine during water and wastewater treatment. The other chemicals discussed in this chapter include aldehydes, ketones, and carboxylic acids. The chapter has shown the information about the formation mechanisms of these by-products. It has also provided a list of conventional and potential techniques that can minimize the by-product formation. Overall, this chapter provides useful knowledge on public health protection for drinking water and recycled water.

Another chapter deals with different technologies called electro-fenton for pollutant removal. In recent times, there has been a growing interest in homogeneous electro-Fenton technology for the remediation of organic pollutants in water streams. The organic compounds are ionized or oxidized by direct electrolysis on the anode in the electrolytic cell based on the generation of a very powerful oxidizing agent such as the hydroxyl radical ($^{\cdot}$OH) in solution. This section presents a review of articles on the subject of the fundament and application of Electro-Fenton as effective degradation technology for complex organic pollutants in wastewater. After a short description of the theoretical background and practical basics concerning wastewater treatment by means of Electro-Fenton technique, the most important applications for eliminating complex aqueous organic pollutants of Electro-Fenton in lab scale with suitable references are demonstrated. The huge role played by Electro-Fenton technique in removing the pollutants in textile and pesticide producing wastewater is also discussed.

Towards the end of the section on the removal of contaminants, one chapter focuses on water quality after reverse osmosis (RO) treatment of wastewater for potable water reuse. Reliable water quality assurance for the removal of trace organic compounds (TOrCs) is critical for public health protection and cost-effectiveness in potable water reuse. In particular, *N*-nitrosodimethlyamine (NDMA), which is a disinfection by-product and potential human carcinogen, can readily permeate through RO membrane, resulting in their detection above the NDMA notification levels (e.g., 10 ng/L). Thus, this chapter provides an overview of recent research for achieving high removal of NDMA by high rejection RO membranes. The chapter also introduces the latest technologies associated with online monitoring of NDMA, which could be used as potential surrogate for monitoring the rejection of many other TOrCs by RO membrane.

In the third section, the first chapter presents the recent trend and technologies about biological wastewater treatment and biological activities, which are of importance in wastewater treatment. Conventionally, activated sludge process (ASP) is most frequently practiced for wastewater treatment. However, the conventional treatment system is inefficient for the removal of biological nutrient to a greater extent. Nutrients such as nitrogen (N) and phosphorus (P) has high influence on the receiving water body and causes eutrophication and algal bloom. It leads to the depletion of dissolved oxygen level and in turn high risk to aquatic life. Eutrophication is a major problem in developing countries and is responsible for water pollution. Removal of biological nutrient in the wastewater is an essential task to lead the positive impacts on solving the environmental pollution issues. Developing the biological nutrient removal approach in the wastewater treatment is to balance the biogeochemical system of the receiving aquatic environment. Biological nutrient removal is a challenging task and number of operational parameters governs its efficiency.

Another chapter mentions about the recent trend of new membrane aerated biofilm reactor. Traditionally, biological treatment systems such as wetlands, conventional activated sludge (CAS), trickling filter processes, and rotating biological reactors were used to treat these wastewaters. The capital and operation and maintenance (O&M) costs of the process play a critical role in the final system selection. During the past decade, membrane bioreactor (MBR) has progressively replaced these biological wastewater treatment systems. For example, MBRs could be operated with higher energy efficiency of 70% compared to CAS process. Moreover, even at a low footprint, MBRs could achieve a high volume of treatment in an existing area with records of up to 50% extra capacity. Following these MBR systems, the next technological innovation was membrane-aerated biofilm reactor (MABR), which uses the bubbleless aeration through the lumen of fiber membrane. The bubbleless aeration, in fact, assists the smooth growth of microorganisms compared to the bubbled aeration in CAS process which often interferes with the microbial growth in the system. Apart from providing diffused aeration, the membrane also serves as attachment medium for microorganisms that consume organics and nitrogen, thereby purifying the wastewater. Thus, within single reactor, simultaneous nitrification and denitrification are achieved. The MABRs have been successful in the treatment of a variety of pollutants such as landfill leachate, pharmaceutical wastewater, ammonia-rich wastewater, industrial wastewater, domestic wastewater, and anaerobic digestion liquor. In addition, their applications have flourished for the treatment of high carbon and nitrogen wastewater, volatile organic compounds, and xenobiotic components. However, the major limitation of this process is maintaining optimal biofilm thickness on the membrane surface and scaling-up mechanisms to real scale plants.

One chapter works on the advances in photobioreactors for future wastewater treatment. The photobioreactor is an efficient artificial system in terms of biomass cultivation and removing pollutants. Compared to other conventional technologies, its design and operational processes are superior. Therefore, the photobioreactor specifically targets and tailors for the increasing demand for biomass and stringent pollutants removal standards. Since the early 1950s, there has been a variety of photobioreactor types, and these have been addressing the different technical issues over time and others more recently. As well, diverse applications of the photobioreactor process are becoming more widespread, and this opens for a good opportunity for future sustainable developments. This book chapter discusses advances being made in photobioreactor technology, encompassing: (1) modeling; (2) designs and classifications; (3) applications; and (4) future perspectives.

For the anaerobic process, a chapter reviews on anaerobic processes for sustainable wastewater treatment. Conventional anaerobic bioreactors have proven useful for energy recovery and efficient in removing organic pollutants from wastewater. Unfortunately, the application of most conventional anaerobic systems is limited due to their applicability over a narrow range in substrate compositions and selective type of pollutant removal. Additionally, for conventional arrangements, issues present in bioreactor operation and maintenance limit their overall efficiency in reactor performance and removal of pollutants. For a sustainable wastewater treatment strategy, the primary requirement is to remove a wide range of pollutants and organics efficiently from wastewater. Recent developments in anaerobic processes include nonconventional bioreactor designs, such as bio-electrochemical systems (BES), integration of pre-/posttreatment methods and chemical/biological additives to improve bioreactor performance. Combining these processes with traditional anaerobic bioreactors can be both efficient and sustainable for wastewater treatment.

In addition, one more chapter is associated with anaerobic digester. Anaerobic digestion (AD) is a biochemical process that involves four groups of microorganisms namely hydrolyzers, acidogens, acetogens, and methanogens. These groups function in syntrophy and have co-dependent metabolic pathways. Changes in one group (e.g., over/under-expressed population and function) can alter this delicate chain of anaerobic process and consequently AD performance. With recent progress in culture-independent techniques, an array of previously unknown and uncultured microorganisms has been recently uncovered in the AD process. New discoveries on the diversity and structure of the AD microbial community could provide critical information on digester stability and performance (e.g., biogas production). This chapter provided a critical analysis of the current knowledge on the AD microbial community, focusing on the factors affecting microbial community and the relationship between microbial community and AD performance. Overall, gaining a better understanding of microbial ecology could be the key for greater AD efficiency and biogas production capacity.

One chapter deals with industrial wastewater treatment for the removal of chromium from tannery effluent. Leather-based industries utilize nearly 90% of chromium-containing tanning agents for converting raw skin/hides into leather.

Apart from chromium, different metals such as iron, aluminum, zirconium, and titanium are also used for various tanning applications. Tannery wastewater is highly complex and contains high amount of inorganic, organic, and dissolved solids including chlorides and sulfates. The chromium present in the effluent can have adverse effects on the environment. Hence, the treatment of effluent before releasing it into the environment becomes an important issue. Bioremediation is a recent technique for treatment and disposal of industrial wastewater. This approach is advantageous as compared to conventional treatment methods which are costly, time consuming, and generate toxic end products. Bioremediation is the potential, cost-effective, environmental-friendly technique that uses several microbes in treatment of wastewater, soil, and sediments. Hence, this chapter focuses on the role of microbes as consortium in chromium remediation from tannery effluent. This chapter will also focus on the various mechanisms such as biosorption, bioaccumulation, and microbial reduction of chromium by microbial cells.

Another chapter in the section deals with biofouling detection of reverse osmosis (RO) membrane. Although many applications such as seawater desalination and water reclamation have employed RO membrane as one of the critical water treatment techniques, membrane fouling still remains a challenge. In particular, membrane biofouling can occur suddenly and cause an increase in energy consumption, which makes the water treatment application less economical. This chapter provides an overview of biofouling tests most commonly used for detection of biofouling associated with RO membrane. Because membrane biofouling cannot be readily predicted, detection methods of biofouling provided in this chapter may help to achieve successful RO system operation.

The final section is dedicated to advanced materials and technologies that could make a breakthrough for future water and wastewater treatment. Nowadays, water pollution and freshwater scarcity have become a serious problem worldwide, causing concerns to public health and the environment. To reduce these challenges, various treatment technologies have been adopted. Among these technologies, nanotechnology and biotechnology-based techniques are usually applied separately for water treatment (for domestic purposes) and wastewater (for reuse). This chapter presents the new and emerging nano/biotechnologies for the sustainable removal of pollution causing constituents during water/wastewater treatment processes. Besides, toxicological and safety aspects of different nano/biotechnologies, their current and future perspectives are discussed. However, further research is needed from a systems perspective on the integration of nanotechnology and environmental biotechnology (nano-biotechnology) in treating water and wastewater. Nano-biotechnology refers to the capability to manipulate and integrate different biological and chemical materials and processes for applications in the remediation of contaminated environment.

Regarding novel materials associated with water and wastewater treatment applications, we have included one chapter that has comprehensively reviewed advances and developments of nanofiber membranes for water and wastewater treatment. Nanofiber membranes have advantages on controlling membrane characteristics (e.g., porosity, pore size, structure, surface properties, and mechanical and thermal stability). Thus, they have the potential uses for many water treatment applications such as membrane bioreactor, desalination, groundwater recharge, water reuse, and pure water production. This chapter also includes comprehensive discussion about designs and structures of nanofiber membranes and their future prospects.

We have another chapter that provides recent trends of nanomaterials for removal of hazardous organic pollutants. The increased disposal of highly hazardous organic pollutants without appropriate treatment into the natural water bodies has become an immediate threat to the living organisms in the earth. Pollutants such as pesticides, surfactants, halogens, polycyclic aromatic hydrocarbons, microorganisms, dyes, and other contaminants need to be removed completely by facile and eco-friendly technology. With the advancement of nanotechnology, the nanomaterials have delivered effective solutions for water treatment. Especially nanofibers symbolize the next generation of nano-catalyst that offers unique properties to overcome water pollution crisis as compared to conventional catalyst. Currently, electrospinning is one of the most proficient method for the nanofiber fabrication with good physico-chemical properties. In that, composite nanofibers such as zinc oxide, titanium dioxide, and zirconium dioxide, etc. are attractive material for wastewater treatment due to their capability of total mineralization of organic contaminants under atmospheric conditions with greater removal efficiency. The synergetic effect of composite nanofibers promotes the production of hydroxyl radicals by enhancing the light absorption and better photon harvest property, thereby reducing the recombination of semiconductor surfaces and complete removal contaminant occurs. Thus, this review highlights the recent trends of nanofibers as adsorbent, photocatalyst, filter media, and sensor in water and wastewater treatment.

The other chapter provides the potential of engineered osmosis for future water treatment. The industrial revolution led to tremendous change in global population and pollution rate. Especially, polluting the available freshwater is creating unexcelled demand for water to meet the global needs. The conventional water reclamation techniques endure from energy cost and technical efficiency. Hence, there is a need for sustainable water reclamation technique with low cost, high operation flexibility, performance, and maintenance. Forward osmosis or engineered osmosis emerged has the powerful substantial technique suitable for water treatment. This chapter deals with the advantages, feasibility, challenges, and opportunities of engineered osmosis for water treatment. The significant progress of engineered osmosis in the area of water treatment, commercial availability, process configurations, and operations is discussed. Further, emanation of the potential area of improvement in near future, integrated designs and other innovative technologies for water treatment by engineered osmosis are also discussed.

Towards the end of the control section, one chapter provides a history about developments of microbial fuel cells. The overpopulation in the future will result in burning issues on our environment and negative effects of global warming, environmental pollution and habitat loss to the worldwide human community. Moreover, the nonrenewable natural resources such as fossil fuels and fresh water are consuming at the speed faster than their rate of regeneration. Global demand has increased year by year which is expected to exceed production from known and anticipated resources. Last but not least, the demands of water utilized for agriculture, industries, and supporting population growth have increased and become of the most challenges in the recent century. Under those circumstances, there are requirements for finding alternative renewable energy resources and cost-effective water treatment technologies with less energy consumption. Among various technologies have been well investigated, microbial fuel cell might be the key point to deal with the recent situation of water-energy nexus. In general, the microbial fuel cell is a cross-disciplinary technology so that the study area has extended to energy, material sciences, biochemistry, and so on. In addition, the integration between microbial fuel cells and other technologies has supposedly made great opportunities to concurrently reach to sustainable energy production, efficient wastewater treatment, and reuse. In order to introduce microbial fuel cell to practical application, it is necessary to understand step by step about mechanism and operational condition of this technology. In this chapter, we aim to communicate about the recent developments of microbial fuel cells and discuss the potential applications of this technology in the future.

The topics of the book are organized in four different sections: (i) General, (ii) Water and wastewater treatment for removal of contaminants, (iii) Biological wastewater treatment and biological activities, (iv) Advanced materials and technologies for future water treatment.

Specific topics covered in this book include:

- Introduction to Recent Advances in Water and Wastewater Treatment
- Microcystins in Freshwater Ecosystems: Occurrence, Distribution and Current Treatment Approaches
- Advanced Techniques for Characterizing DBP Precursors from Eutrophic Water and their Applications for DBP Prediction
- Application of *M. oleifera* Plant for Water Treatment
- Phytoremediation Strategies on Heavy Metal Removal
- Membrane Technologies for the Treatment of Pharmaceutical Industry Wastewater
- Recent Research on Ozonation By-products in Water and Wastewater treatment: Formation, Control, Mitigation
- Degradation of Complex Organic Pollutants in Wastewater by Homogeneous Electro-Fenton.
- Removal of *N*-nitrosodimethylamine for Potable Reuse: Reverse Osmosis Treatment and Monitoring Technologies
- Realistic Advancement in Engineered Osmosis for Water Treatment
- Recent Developments in Biological Nutrient Removal
- From Conventional Activated Sludge Process to Membrane-Aerated Biofilm Reactors: Scope, Applications, and Challenges
- Nonconventional Anaerobic Bioreactors for Sustainable Wastewater Treatment

- Advances of Photobioreactors in Wastewater Treatment: Engineering Aspects, Applications and Future Perspectives
- Microbial Community in Anaerobic Digestion System: Progression in Microbial Ecology
- Emissions of Volatile Organic Compounds from Solid Wastes and Leachate at a Municipal Solid Waste Dumpsite in Thailand
- The Role of Microbial Consortium in Chromium Bioremediation from Tannery Effluent
- Biofouling Detection on Reverse Osmosis Membrane
- Applications of Nanotechnology and Environmental Biotechnology for Sustainable Water and Wastewater
- Nanofiber Membranes for Water and Wastewater Treatment: Recent Advances and Developments
- The Current trends of Electrospun Nanofibers Applications in Water and Wastewater Treatment
- Developments of Microbial Fuel Cells: From the Beginning until Now.

To summarize, this book contains information about existing and emerging pollutants in water and wastewater. Novel analytical and diagnostic techniques have been discussed to measure and model the concentration of various contaminants in the environment. Finally, recent advanced control methods and remediation techniques for cleanup of polluted water and wastewater sources are intensively described in the book.

Part II
Water and Wastewater Treatment for Removal of Contaminants

Chapter 2
Microcystins in Freshwater Ecosystems: Occurrence, Distribution, and Current Treatment Approaches

Thanh-Luu Pham and Tran Ngoc Dang

Abstract Toxic cyanobacterial blooms (TCBs) are an environmental concern due to their ability to produce wide a range of hepatotoxins, neurotoxins, and dermatotoxins. Microcystins (MCs) are the most common toxin and are considered to be one of the most hazardous groups. The increasing occurrence and detection of MCs in recreation or drinking water sources pose a variety of challenges to water treatment. To ensure the safety of drinking water supplies, a variety of physical, chemical and biological processes, such as coagulation, flocculation, sedimentation, filtration, disinfection, adsorption, and biodegradation have been applied for removal of MCs. It is important to determine which type of MCs is present and whether the toxins reside within the cell or as extracellular to optimize treatment approaches. Conventional treatments using coagulation, flocculation, sedimentation, and filtration are effective for removing cyanobacteria intact cells. However, these methods are faced with the release of dissolved toxins as well as the requirement of regular backwashing. Dissolved MCs have been shown to be effectively removed by some techniques such as activated carbon adsorption or biological degradation. However, factors affecting the removal such as acclimation periods, biofilm composition, temperature, and water quality cannot be easily controlled. This chapter provides an overview of the current knowledge of MCs including occurrence, distribution, as well as current methods of their removal from drinking water.

Keywords Cyanotoxins · Drinking water treatment · Toxic cyanobacterial blooms
Water eutrophication

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2.1 Introduction

Eutrophication of surface water, in particular through the excessive use of fertilizer and manure in agriculture as well as through sewage discharges are the major cause for the global occurrence of toxic cyanobacterial blooms (TCBs) (He et al. 2016; Preece et al. 2017). Recent evidence revealed that warmer conditions, rising CO_2, and climate changes have enhanced TCBs in water systems (Visser et al. 2016). These blooms accumulated with high concentrations of cyanotoxins in drinking, recreational, and irrigation water bodies pose a serious hazard for wild and domestic animals as well as humans (Pham and Utsumi 2018). Among cyanotoxins, microcystins (MCs) are the most common and are considered to be one of the most hazardous groups in eutrophic freshwaters (Li et al. 2017). MCs are mainly produced by the three genera *Microcystis, Dolichospermum,* and *Planktothrix*, but they can be also produced by other cyanobacteria such as *Aphanizomenon, Anabaenopsis, Aphanocapsa, Fischerella, Gomphosphaeria*, *Hapalosiphon, Nostoc, Phormidium,* and *Pseudanabaena* in which *Microcystis* has been reported as the most common bloom-forming and the main producer of MCs in freshwater ecosystems worldwide (Preece et al. 2017).

Microcystins are cyclic peptides with molecular weight (MW) ≈800–1100 Dalton (Da). They contain seven peptide-linked amino acids, with the two terminal amino acids of the linear peptide being condensed (joined) to form a cyclic compound (Fig. 2.1). Most congeners are with the general structure cyclo-(D-alanine-X-D-MeAsp-Y-Adda-D-glutamate-Mdha) in which R_1 and R_2 are variable L amino acids, D-MeAsp is D-erythro-b-methylas-partic acid, and Mdha is *N*-methyldehydroalanine (Pham and Utsumi 2018). The amino acid Adda, (2S,3S,8S,9S)-3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid, is the most unusual structure in this group of cyclic peptide toxins. There are over 100 MC congeners have so far been reported but the three most common are MC-LR, -RR and -YR, in which MC-LR is the most toxic one (Li et al. 2017). Chemical structures of the several most common MC variants are shown in Fig. 2.1. MCs were produced non-ribosomally by a multifunctional enzyme complex that includes peptide synthetase and polyketide synthase modules, both of which are encoded by the microcystin synthetase gene (*mcy*) cluster which contains 55 kb of DNA and has been revealed in several cyanobacterial genera (Pham et al. 2015).

Microcystins cause toxic effects to human, animals, and plants. Their adverse effects on different living organisms have been extensively studied and reviewed (Chen et al. 2016; Elisabete et al. 2016; McLellan and Manderville 2017). The inhibition and regulation of the expression of protein phosphatases (PPs) groups are well known as the principal mechanism of toxicity of MCs (Chen et al. 2016; Elisabete et al. 2016). PPs are well known for their regulated function to maintain homeostasis in the cell, inhibition of PPs may generate hyperphosphorylation, causing severe cell damage (Elisabete et al. 2016). This is an important post-transitional modification which can lead to excessive signaling and may

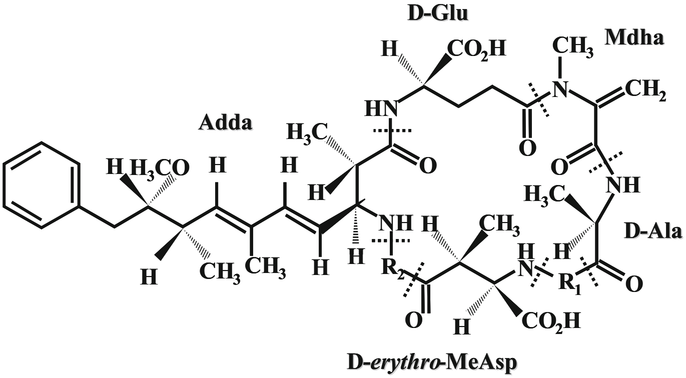

Fig. 2.1 Chemical structure of the several common microcystin (MC) variants. R_1 and R_2 positions are highly variable L-amino acids that determine the suffix in the nomenclature of microcystins

resulted in cell proliferation, cell transformation, and tumor promotion (McLellan and Manderville 2017). In addition, MCs are known to induce oxidative stress, which caused by reactive oxygen species (ROS) such as superoxide anion ($O_2^{\cdot -}$), hydrogen peroxide (H_2O_2), and hydroxyl radical (HO·), in both animal and plant (Elisabete et al. 2016). As a preventive step to protect the public health from adverse effects, the World Health Organization (WHO) recommends a provisional guideline value of 1 μg/L for MC-LR concentration in drinking water in 1998, and a chronic tolerable daily intake (TDI) of 0.04 μg/kg body mass per day for human consumption (Chorus and Bartram 1999).

2.2 The Occurrence of Microcystin in Freshwater Ecosystems

The occurrence of TCBs associated with cyanotoxins has been reported in eutrophic freshwaters worldwide, where cyclic hepatotoxic MCs are found in over 75% of cyanobacterial bloom cases (Harke et al. 2016). A summary of TCBs, toxin producers, their prevalence, and MC concentrations recorded worldwide are shown in Table 2.1. Through the literature reports, *Microcystis* is one of the most ubiquitous bloom-forming cyanobacterial genera in inland freshwaters (Lürling et al. 2017). Its blooms associated with toxins have been recorded in at least 108 countries and territories worldwide except Antarctica, and MCs have been detected in 79 of these locations (Harke et al. 2016). Due to the lower amount of publications from Eastern Europe, Africa, and South America reflecting the lack of monitoring campaigns in these regions, this may lead to the underestimation of the prevalence of toxic cyanobacterial blooms and the diversity of toxins worldwide (Merel et al. 2013).

A recent study indicated an expansion of *Microcystis*, as previous documentation noted less than 30 countries with bloom recorded (Zurawell et al. 2005), suggesting that *Microcystis* has proliferated and dominated phytoplankton communities in a wide range of freshwater ecosystems in both temperate and tropical climates (Lürling et al. 2017). Likewise, MCs in freshwater blooms are found at higher concentrations than the other cyanotoxins (Lürling et al. 2017). MC levels in lakes can vary over orders of magnitude and can be strongly related to *Microcystis* abundance. However, MCs are produced by only toxic cyanobacterial strains, and cyanobacterial blooms are often comprised of toxic and nontoxic strains. Thus, total MC concentrations generally positively correlated with quantification of toxigenic cyanobacterial biomass (Singh et al. 2015; Dong et al. 2016).

There are numerous studies about the occurrence and distribution of MCs in lakes and reservoirs throughout the world. MC concentrations in surface waters have been reported from trace to several milligrams per liter. In temperate regions, high MC levels are often recorded during the summer period when heavy cyanobacteria blooms usually occurred (Turner et al. 2018). However, in tropical environments with sustained high temperatures, cyanobacterial blooms may occur at any time and persist for months (Singh et al. 2015; Pham et al. 2017). Recent evidence indicated that eutrophication and warmer conditions have enhanced cyanobacterial biomass and MCs concentration (Visser et al. 2016; Lürling et al. 2017). For instance, field and laboratory studies showed the level of MCs in Lake Taihu, China was nearly 20 times higher than previous records (Su et al. 2018). Several large and most important inland waters on Earth are increasingly experiencing severe TCBs associated with MCs, such as Lake Erie in USA (Rinta-Kanto et al. 2009), Lake Winnipeg in Canada (Binding et al. 2018), Lake Suwa in Japan (Chan et al. 2007), Lake Victoria in Kenya (Sitoki et al. 2012), Lakes Poyang (Zhang et al. 2015), Erhai (Yu et al. 2014), Chaohu (Yu et al. 2014), and Dianchi (Wu et al. 2014) in China, Dau Tieng and Tri An Reservoirs in Vietnam (Pham et al. 2017; Dao et al. 2016). Due to the temporal and spatial variation of MCs, it is difficult to accurately assess MC contamination within and among lake systems (Su et al. 2018). Each lake or reservoir has its own limnological and meteorological characteristics, which may lead to differences in the cyanobacterial composition, dominant species and congener in the water column (Su et al. 2018; Amé et al. 2010). In addition, because of differentiation in extraction and detection methodologies, comparing MC concentrations among water bodies is challenging. Nevertheless, extremely high levels of MCs from crude extract of bloom materials or from water column have been reported worldwide. For example, MCs concentration has been reported up to 7280 μg/g dry weight (dw) from central China (Chorus and Bartram 1999), or 7100 μg/g dw in Portugal waters (Vasconcelos et al. 1996). Very high levels of total MCs (including intracellular and extracellular) in water have also been documented up to 19,500 μg/L in Lake Suwa, Japan (Harke et al. 2016), 29,200 μg/L in Lake Oubeira, Algeria (Nasri et al. 2004), or 36,500 μg/L in Lake Horowhenua, New Zealand (Wood et al. 2006) (Table 2.1).

In general, MCs are first synthesized and retained more than 95% in toxic cells (intracellular or cell-bound), but they will be then released to the water after cell

Table 1 The occurrence of microcystins (MCs) from various water bodies. Concentrations are presented in μg/L or else in μg/g dry weight (dw) as indicated

Country	Name and trophic state	Dominant species	Toxins variants	Max concentration (μg/L or μg/g dw)	References
Algeria	L. Oubeira (H)	*Microcystis*	MC-LR	29,200	Nasri et al. (2004)
	D. Cheffia (E)	*Microcystis* sp.	MC-LR	28.8	Nasri et al. (2007)
Argentina	L. Los Padres (E)	*Planktothrix agardhii*, *Anabaena* sp. and *Microcystis* sp.	MC-LR, -RR, -YR, -LA	5.6	Amé et al. (2010)
	R. San Roque (E)	*M. wesenbergii* and *M. aeruginosa*	MC-LR	48.6	Giannuzzi et al. (2011)
Australia	Southwest lakes (E–H)	*Microcystis*	MC	8428	Kemp and John (2006)
Brazil	R. Alagoinha (ND)	*M. panniformis*	MC	836.3[a]	Bittencourt-Oliveira et al. (2014)
	Argemiro de Figueiredo (E)	*M. aeruginosa*	MC-LR	27.3	Lins et al. (2016)
Canada	L. Winnipeg (E)	*A. flos-aquae* *M. aeruginosa*	MC-LR	300	Binding et al. (2018)
China	L. Erhai (H)	*Microcystis*	MC-RR, -LR	8.95	Yu et al. (2014)
	L. Chaohu (E–H)	*Microcystis*	MC	17.61	Yu et al. (2014)
	L. Poyang (E)	*Microcystis*	MC-RR, -LR -YR, -LA	7.97	Zhang et al. (2015)
	Central China (ND)	*A. circinalis, M. aeruginosa, Oscillatoria* sp.	MC-RR, -LR	7300*	Harke et al. (2016)
Chile	L. Lo Galindo (E)	*M. aeruginosa*	MC-LA, -RR, -LR -YR.	115	Almanza et al. (2016)
France	R. Grangent (E)	*M. aeruginosa*	MC-RR	15	Sabart et al. (2010)
India	L. Sankuldhara (E)	*Microcystis* spp.	MC-RR, -LR, -YR	39.60	Singh et al. (2015)
	L. Lakshmikund (E)	*Microcystis* spp.	MC-RR, -LR, -YR	128.14	

(continued)

Table 1 (continued)

Country	Name and trophic state	Dominant species	Toxins variants	Max concentration (µg/L or µg/g dw)	References
Japan	L. Suwa (H)	*M. aeruginosa*	MC-LR	19,500	Harke et al. (2016)
	L. Kasumigaura (E–H)	*Microcystis* spp.	MC-RR, -LR	9.5	Tomioka et al. (2011)
Kenya	L. Victoria (E)	*Microcystis* spp.	MC-LR, -YR	81	Sitoki et al. (2012)
New Zealand	L. Horowhenua (E)	*M. aeruginosa*	MC-LR	36,500	Wood et al. (2006)
	L. Dudding (E)	*M. aeruginosa*	MC-LR	200,000	
	L. Ngaroto (H)	*M. flos-aquae*, *A. planktonica*	MC-LR	1535	
	L. Taupo (O)	*Nostos commune*	MC-LR	708	
	Neuma Pond (ND)	*M. aeruginosa*, *M. flos-aquae*	MC-LR	12,000	
	L. Waitawa (E)	*M. aeruginosa*	MC-LR	32,000	
Portugal	Portuguese freshwaters (E–H)	*Microcystis, Anabaena, Nostoc*	MC-RR, -LR, -YR	7100[a]	Vasconcelos et al. (1996)
S. Africa	D. Nhanganzwane (H)	*M. aeruginosa*	MC	23,718	Oberholster et al. (2009)
	D. Makhohlolo (M)	*M. aeruginosa*	MC	0.317	
	R. Hartbeespoort (E–H)	*Microcystis* spp.	MC	3200	Conradie and Barnard (2012)
	R. Roodeplaat (E–H)		MC	217	
		Oscillatoria			

(continued)

Table 1 (continued)

Country	Name and trophic state	Dominant species	Toxins variants	Max concentration (µg/L or µg/g dw)	References
United States	L. Erie (E)	*Microcystis*	MC-LR	22	Rinta-Kanto et al. (2009)
	L. Pinto (E–H)	*Microcystis*	MC-LA, MC-RR, MC-LR, MC-LF, -YR	100	Miller et al. (2010)
Vietnam	R. Dau Tieng (E)	*M. aeruginosa*	MC-RR, -LR, -YR	669[a]	Pham et al. (2015)
	R. Tri An (E)	*Microcystis* spp.	MC	640[a]	Dao et al. (2016)
	L. Nui Coc (E)	*Microcystis*	MC-LR, -RR	1699[a]	Duong et al. (2014)
	L. Hoan Kiem (E)	*Microcystis*	MC-LR, -RR	46	

L Lake; *R* Reservoir; *D* Dam; *MC* Microcystin; *dw* Dry weight; *O* Oligotrophic; *M* Mesotrophic; *E* Eutrophic; *H* Hypereutrophic; *ND* No data

[a] Concentration was represented in µg/g dw

lysis or death, which results in accumulation of a high concentration of dissolved MCs (extracellular) in water column (Pham and Utsumi 2018). Thus, water column serves as an intermediate transmission compartment and is often the most contaminated with both intracellular and extracellular MCs. From here, MCs could contaminate to other aquatic compartments such as sediment, animals, aquatic, or terrestrial plants. MCs are chemically stable and can persist in water for several days or weeks after the bloom event (Preece et al. 2017). A ubiquitous distribution of MC in the aquatic environment has been summarized (Pham and Utsumi 2018). The main route of human exposure to MCs is the chronic and accidental ingestion of contaminated drinking water, although other routes such as consumption of contaminated food, dermal contact with toxins during recreational activities in recreational waters, or oral intake of cyanobacterial dietary supplements can be considered significant for some cultures and individuals (He et al. 2016).

2.3 The Occurrence of Cyanobacterial Toxins in Vietnamese Freshwaters

During the last two decades in Vietnam, most studies focused only on morphological characteristic and described the present or absent of cyanobacteria species. The most commonly cited potentially toxic cyanobacteria species is *Microcystis aeruginosa*, which has been morphologically described from Lake Thanh Cong (Hummert et al. 2001), the Huong River (Nguyen et al. 2007), and the Tri An Reservoir (Fig. 2.2a) (Dao et al. 2010). Other potentially toxic species such as *Microcystis botrys* and *Microcystis wesenbergii* have also been reported (Pham et al. 2015; Nguyen et al. 2007). Nguyen et al. (Nguyen et al. 2012) collected, morphologically characterized, and classified *Microcystis* strains in the middle and north of Vietnam, but provided no information on MC concentrations. The first report on cyanobacterial toxins in Vietnam was the study in Lake Thanh Cong, where extracts of *M. aeruginosa* contained MC-RR, MC-YR, MC-WR, and five minor compounds (Hummert et al. 2001), but no toxin concentration was given. However, during the past 10 years, the occurrence of cyanobacterial blooms and their toxin have been frequently reported from many water bodies in Vietnam (Fig. 2.2b, c). Nguyen et al. (Nguyen et al. 2007) reported a bloom of *Microcystis* spp. in a pond and several rivers in Thua Thien Hue, a central province in Vietnam, where total MC concentrations in the water were up to 76.2 μg/L. The authors also detected MC-LR and MC-RR in a culture biomass of *Microcystis* spp. with max concentration up to 4.12 mg MC/g dw (Nguyen et al. 2007). Dao et al. (Dao et al. 2016) reported MC concentrations up to 640 μg/g dw in bloom samples from the Tri An Reservoir. Duong et al. (2013, 2014) measured MCs concentration up to 1699 μg/g dw in bloom samples and 185 μg/L in water samples from the Nui Coc Reservoir and Hoan Kiem Lake, respectively. Pham et al. (2015) reported the present of three MCs includes MC-LR, MC-RR, and MC-YR with concentrations

Fig. 2.2 Map of Vietnam with some waterbody locations where microcystins have been reported **a**: 1. Nui Coc Reservoir; 2. Thanh Cong Lake; 3. Hoan Kiem Lake; 4. Huong River; 5. Tri An Reservoir and 6. Dau Tieng Reservoir. Bloom of *Microcystis* from Dau Tieng (**b**) and Tri An Reservoirs (**c**)

up to 2129 μg/g dw from either cyanobacterial strains or bloom biomass from the Dau Tieng Reservoir. Although MCs have been detected from several reservoirs used for drinking purpose, there are no facilities for removal of MCs from drinking water plant so far in Vietnam.

2.4 Current Approaches to Microcystins Removal

As TCBs and their toxins in freshwater increase in frequency, the protection of water supplies becomes more challenging (He et al. 2016). Therefore, there is a need for alternate water treatment technologies to remove MCs to reduce the risk from toxic cyanobacterial blooms in drinking water. MCs removal by common drinking water treatment (DWT) processes usually include a sequence of fundamental and optional processes. The most basic treatment steps for a high-quality surface water resource would typically consist of coarse filtration followed by clarification to remove natural organic matter (NOM) and disinfection to inactivate pathogens (Fig. 2.3). These techniques could be divided into two categories: those based on the retention of contaminants (coagulation, flocculation, sand filtration, adsorption, etc.), and those based on the degradation of contaminants (biodegradation, advanced oxidation, etc.) (Merel et al. 2013). Although multiple technologies have been developed for removal of MC, this chapter will discuss those currently in use for general water treatment.

2.4.1 Coagulation, Flocculation, and Sedimentation

Conventional methods for water treatment such as coagulation, flocculation, sedimentation, and filtration are frequently used in DWT. The traditional coagulation process involves the addition and rapid mixing of a metal salt compound (e.g., aluminum sulfate, ferric chloride) with raw water (He et al. 2016). These reactions produce a variety of precipitates that facilitate the agglomeration of suspended particles, which enhances removal during sedimentation.

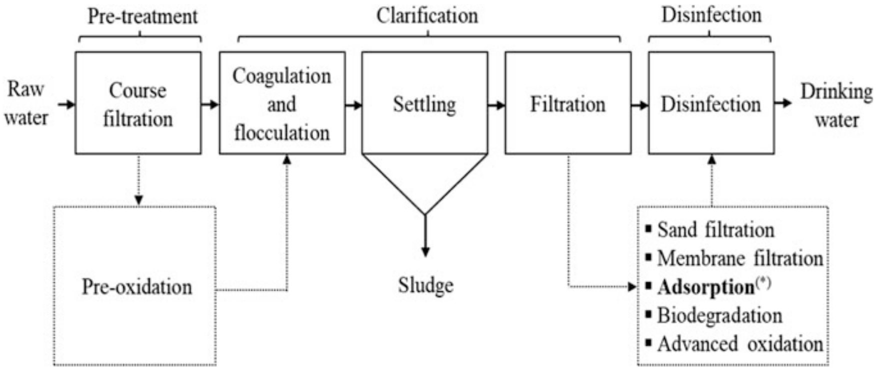

Fig. 2.3 Basic steps for microcystins (MCs) removal in drinking water treatment. (*)The barrier which is mainly responsible for MCs removal. Source: Adapted and modified from Merel et al. (2013)

Cyanobacteria are microscopic organisms with negative charges on the cell membrane that can be roughly considered as colloids and removed by conventional methods. For example, up to 90% removal can be achieved on cultured of *Microcystis* spp. (Merel et al. 2013). Due to the positive buoyancy, low specific density, motility, variable morphologies, the removal of some cyanobacteria genera may be more challenging (Merel et al. 2013). For those positive buoyancy, the application of dissolved air flotation (DAF), which uses air injected at the bottom of the reactor to carry the cells to the surface where they can be removed by scrapping, could also efficiently remove cyanobacteria instead of sedimentation (Teixeira et al. 2010). Previous studies have shown that coagulation and flocculation are effectively removed cyanobacteria cells or intracellular MC but do not remove extracellular one (Teixeira and Rosa 2007; Sun et al. 2012). In addition, physical perturbations involved in coagulation processes may result in cyanobacterial cell lysis and a direct increase in dissolved MC concentration. Coagulation and sedimentation are typically followed by the process of rapid or slow sand filtration by using sand, gravel, and/or anthracite. The traditional purpose of a rapid sand filtration is to remove any remaining particles in the water following sedimentation (He et al. 2016).

Direct and rapid filtration was not effective in removing cyanobacterial cells and extracellular MC, but slow sand filters were shown to remove both cyanobacteria and their toxins during water treatment. For example, slow sand filters can remove up to 99% of the cells of *Planktothrix agardhii* (Grützmacher et al. 2002). In addition, slow sand filtration possibly develops a biofilm on the top of the filter, due to its lower loading rate, resulting in biodegradation of extracellular MCs (Grützmacher et al. 2002; Bourne et al. 2006). Grützmacher et al. (2002) found that more than 90% of extracellular MC were removed during slow sand filtration, primarily due to the biodegradation on or inside the filter bed. Thus, rapid filtration is not enough effective method for removal of cyanobacterial cells and extracellular MC, but slow sand filtration could improve the treatment (Grützmacher et al. 2002; Ho et al. 2006). However, this water treatment requires regular backwashing of the filters and if this process is performed inadequately, plugging of the filter and toxin release from the lysed cyanobacterial cells entrained in filter beds are significant problems. Coagulation and filtration alone do not lead to a substantial reduction of toxicity but are potentially very useful if combined with other treatment techniques (Pantelíc et al. 2013).

2.4.2 Membrane Filtration

Membrane filtrations involve pressure-driven filtration through small pores to remove contaminants not typically removed through physical coarse filtration (Roegner et al. 2014). The term membrane filtration includes four categories characterized by the pore size of the associated membrane: microfiltration (MF) (0.1–10 μm), ultrafiltration (UF) (1–100 nm), nanofiltration (NF) (around

1 nm), and reverse osmosis (RO) (0.1 nm) (Merel et al. 2013). These retention techniques have received great attention for their application to remove micropollutants in DWT. MF and UF techniques are effective for removing cyanobacteria intact cells as well as intracellular toxins. For instance, Merel et al. (2013) showed that both kinds of membranes can remove up to 98% of the cells of the toxic cyanobacteria *M. aeruginosa.* Previous studies revealed that MF and UF with a molecular weight cutoff (MWCO) of 100 kDa rejected cyanobacterial cells but not the MCs (Gijsbertsen-Abrahamse et al. 2006; Lee and Walker 2008). However, MF and UF techniques are not expected to remove extracellular MC and require costly pumping of water as well as face fouling and cell lysis problems.

To date, MF and UF processes appear adequately to remove cyanobacterial biomass if backwashing, cleaning, and disinfection occur between runs (Roegner et al. 2014). Both kinds of MF and UF processes can be applied to remove extracellular toxins previously adsorbed on powdered activated carbon (PAC) (Dixon et al. 2011). On the contrary, RO and NF membranes are effective for removing MCs via size exclusion since the pore size of these membranes MWCO ~100 Da for RO, and 150–200 Da used for NF is smaller than the molecular weight of MCs (~1000 Da). For example, Teixeira and Rosa (2006) found that NF reduced more than 95% of MC-LR. Neumann and Weckesser (1998) observed that 95% and 99% of MC-LR and -RR were removed by using NF and RO membranes, respectively. Although membrane filtration seems to be a promising method to remove both cyanobacteria and MC during DWT, they require a high cost and high technique level of maintenance to prevent membrane fouling by NOM and cyanobacterial cells (Lee and Walker 2008).

2.4.3 Activated Carbon

Manufactured from wood, coal, peat, and coconut shell, activated carbon (AC) has a high porosity and a large surface area, typically ranging from 600 to 1200 m^2/g, which enables to adsorb contaminants from water (Donati et al. 1994; Huang et al. 2007). AC in both powdered activated carbon (PAC) and granular activated carbon (GAC) forms has been extensively used for decades to remove pollutants in drinking water and wastewaters (Donati et al. 1994; Huang et al. 2007; Drogui et al. 2012). Adsorption by AC, either GAC or PAC is considered as the best available technology and commonly used for trace organic contaminants removal from surface water. In particular, MCs are effectively adsorbed into AC (Donati et al. 1994; Mohamed et al. 1999). By far, as a single technology, AC most effectively removes dissolved MCs from a water source, with reported levels of up to 99% removal (Roegner et al. 2014). AC is effectively adsorbed extracellular MC but neither cyanobacteria nor intracellular MC. The removal efficiency of cyanotoxins may depend on the kind of adsorbent employed (Donati et al. 1994; Huang et al. 2007; Newcombe and Nicholson 2004). PAC with mesopores range from 2 to 50 nm in diameter is sizeable surface areas for adsorptions, while micropores

(<2 nm) hold fewer adsorption sites and limit water flow, making them less effective (Roegner et al. 2014). Indeed, Donati et al. (1994) investigated the adsorption of MC-LR on eight activated carbons, and adsorbents with the largest volume of mesopores (pore diameter in the range of 2–50 nm) were shown to be the most efficient.

Water quality has a strong influence on the removal capability of cyanotoxins by AC since NOM can compete with contaminants and limit their adsorption. Indeed, Lambert et al. (1996) observed a clear difference when compare PAC adsorption isotherms of MC-LR ultrapure water versus surface water. The isotherms obtained with surface water or previously used AC exhibit an alteration of the slope indicating much lower adsorption capacity for MC (Lambert et al. 1996). Other factors influence the removal capability of AC is the dose of adsorbent and contact time. For effective MC removal, very high doses of PAC are required (10 µg/L MC requite >200 mg PAC/L) at a contact time from 1 to 12 h (Pantelíc et al. 2013; Ho et al. 2011).

Although AC can efficiently retain cyanotoxins, AC filtration displays a limited lifetime for all contaminants including MCs (Pantelíc et al. 2013). It needs to be changed frequently vary between 2 months to 1 year depending on the type of toxin and the water quality, and the removing efficiency will decrease with time (Ho et al. 2011). Therefore, complete adsorption would require a high amount of different adsorbent types, what significantly increases treatment costs. AC filtration is safe because no by-products were produced during treatment process. Consequently, AC should not be considered as an individual remediation measure but as a part of a multi-barrier approach (Roegner et al. 2014).

2.4.4 Advanced Oxidation Processes

Advanced oxidation processes such as ozonation and UV photolysis are also a very efficient process for the rapid and complete destruction of MCs from water (Westrick et al. 2010; He et al. 2015). Ozone is one of the most commonly used oxidants in water treatment due to its effective and fast reaction agent. Ozone has been widely utilized for disinfection and oxidation purposes. It has been recently applied at a two-stage treatment including pre- and post-ozonation in water treatment plants (Pantelíc et al. 2013). Ozone is one of the most effective and fastest agents for the destruction of intracellular and extracellular cyanotoxin fraction. Indeed, Westrick et al. (2010) reported that nearly 100% of MC in natural water was oxidized by ozonation (0.22 mg/L ozone) within a short treatment time (15 s). The ability to oxidate MCs depends on pH values. At pH values below 7.0, ozone can be very effective for MC-LR oxidation; however, about pH 7.0, oxidation will be minimal and may not achieve desired removal (Pantelíc et al. 2013). By studying the intermediates and by-products pathways from ozonation degradation of MC-LR in aqueous solution, Chang et al. (2014) demonstrated that ozone reacted with two sites of MC-LR: the diene carbon bonds in the Adda side chain and the Mdha amino acid in the cyclic structure. The fragment from the Adda side chain oxidative cleavage could be further oxidized to an aldehyde.

UV irradiation is a potential process for drinking water disinfection. Although sunlight alone cannot cause the degradation of the cyanotoxins, UV light in the range 240–280 nm results in inactivating microorganisms by inducing DNA alteration (Westrick et al. 2010). UV photolysis is effective for the destruction of MCs, but high UV radiation dosage (1530−20,000 mJ/cm^2) is required for the successful UV photolysis of MCs, which is impractical for full-scale water treatment (Westrick et al. 2010). MC-LR and -RR degraded much more rapidly when the toxins were exposed to UV and UVC (100–280 nm) light at wavelengths around their absorption maxima (238–254 nm) (He et al. 2016). Recent studies suggested that the UV/O_3 process was a more effective method for the removal and mineralization of MC-LR in water, compared with UV- and O_3-alone processes (Chang et al. 2015). The degradation pathways of the MC-LR during UV/O_3 process involved isomerization, hydroxylation, and oxidative cleavage of the Adda side chain, oxidation of Mdha and decarboxylation of MeAsp and Glu, in which the oxidation of Adda moiety was the dominant reaction (Chang et al. 2015). While UV radiation mainly resulted in the isomerization of Adda moiety and the decarboxylation of MeAsp and Glu, O_3 oxidation resulted in the oxidation and cleavage of Adda and Mdha (Chang et al. 2015).

Although ozonation and UV photolysis contribute significantly to MCs removal, the potential problem of ozonation is the generation of toxic by-products due to incomplete oxidation (He et al. 2016). Due to high doses required, low to medium pressure lamp, UV treatment is not recommended as a viable treatment barrier for MCs. The disadvantages of these treatment techniques also include the high cost of ozonation equipment, highly corrosive and toxicity of ozone, as well as higher level of maintenance and operator skill (Westrick et al. 2010).

2.4.5 *Biodegradation*

Although less commonly employed compared to physical and chemical treatment processes, biodegradation is increasing attention since it has been proven as an environmentally benign and cost-efficient method for MCs removal. Current research advances for MC biodegradation were discussed in detail by Li et al. (2017). Biological treatment is most often employed in combination with the filtration process in DWT (He et al. 2016). Microorganisms capable of degrading MCs have been described in the literature for almost two decades. Nowadays, various organisms originated from diverse ecosystems including prokaryotes (e.g., bacteria) and eukaryotes with the ability to degrade MCs in water have been identified, with the majority identified as *Sphingomonas* and *Sphingopyxis* genera belonging to α-Proteobacteria class (Li et al. 2017). The degradation pathways and enzymatic processes are fully characterized for strains within α, β, and γ-proteobacteria, including *Sphingomonas, Stentophomonas, Sphingopoxyis,* and *Methylobacillus* (He et al. 2016).

Previous studies have demonstrated that aerobic biodegradation is the main natural attenuation mechanism for MCs (Bourne et al. 2006; Ho et al. 2006). However, recent researches revealed that MCs can be rapidly degraded under anaerobic condition with natural sediments as inoculum (Chen et al. 2010; Zhao et al. 2017). This suggested that both aerobic and anaerobic biodegradation are important in the natural degradation of MCs. The biodegradation pathway for MC-LR has been elucidated. Bourne et al. (Bourne et al. 1996) explored that *Sphingomonas* sp. ACM-3962 degraded MC-LR by using three enzymes. The first enzyme, microcystinase, cleaves the Arg–Adda peptide bond in the toxin and converts the cyclic MC-LR to a linear form. The second enzyme hydrolyzes the Ala–Leu bond, converting the linearized MC-LR into a tetrapeptide. And the last one breaks the tetrapeptide into smaller peptides and amino acids, which are used for constructing new proteins or enzymes (Bourne et al. 1996). The fact that the by-products from MC-LR degradation are nontoxic compared with parent MC-LR. A few years later, Bourne et al. (Bourne et al. 2001) identified a gene cluster, *mlrA*, *mlrB*, *mlrC* , and *mlrD*, involved in the degradation of MC-LR from the first isolated MC-degrading bacterium, *Sphingomonas* sp. ACM-3962. The authors determined that the *mlrA* gene encoded an enzyme responsible for the hydrolytic cleaving of the cyclic structure of MC-LR (Bourne et al. 2001). Hydrolysis of linearized MC-LR to the tetrapeptide intermediate is catalyzed by *mlrB*, a putative serine peptidase. Tetrapeptide cleavage is accomplished via *mlrC*, also a putative metallopeptidase (Fig. 2.4). The final gene, *mlrD*, encoded for a putative transporter protein that may support for active transport of MC and/or its degradation products into or out of the cell (Bourne et al. 2001).

Since more and more MC-degrading bacteria are being identified indicates that MC-degrading bacteria may be prevalent in the natural environment. Unfortunately, estimating rates of toxin removal in complex natural environments from laboratory experiments containing isolates or consortia is not straightforward (He et al. 2016), microbial consortia grown on biofilm seemed to be more effective at MC removal than isolated strains such as *Sphingomonas* sp. (Bourne et al. 2006). In addition, biodegradation is effective for only extracellular MC and degradation rates in natural environments containing a mixture of cyanotoxins could be more different than rates measured for isolates grown on individual toxins under laboratory conditions (He et al. 2016). Although biodegradation of MCs from water provides a reliable, cost-effective purification system, this treatment requires long reaction time of hours to days to complete degradation. Therefore, biological degradation should be used in conjunction with other treatment methods such as filtration, PAC, or GAC to meet the WHO recommended guidelines.

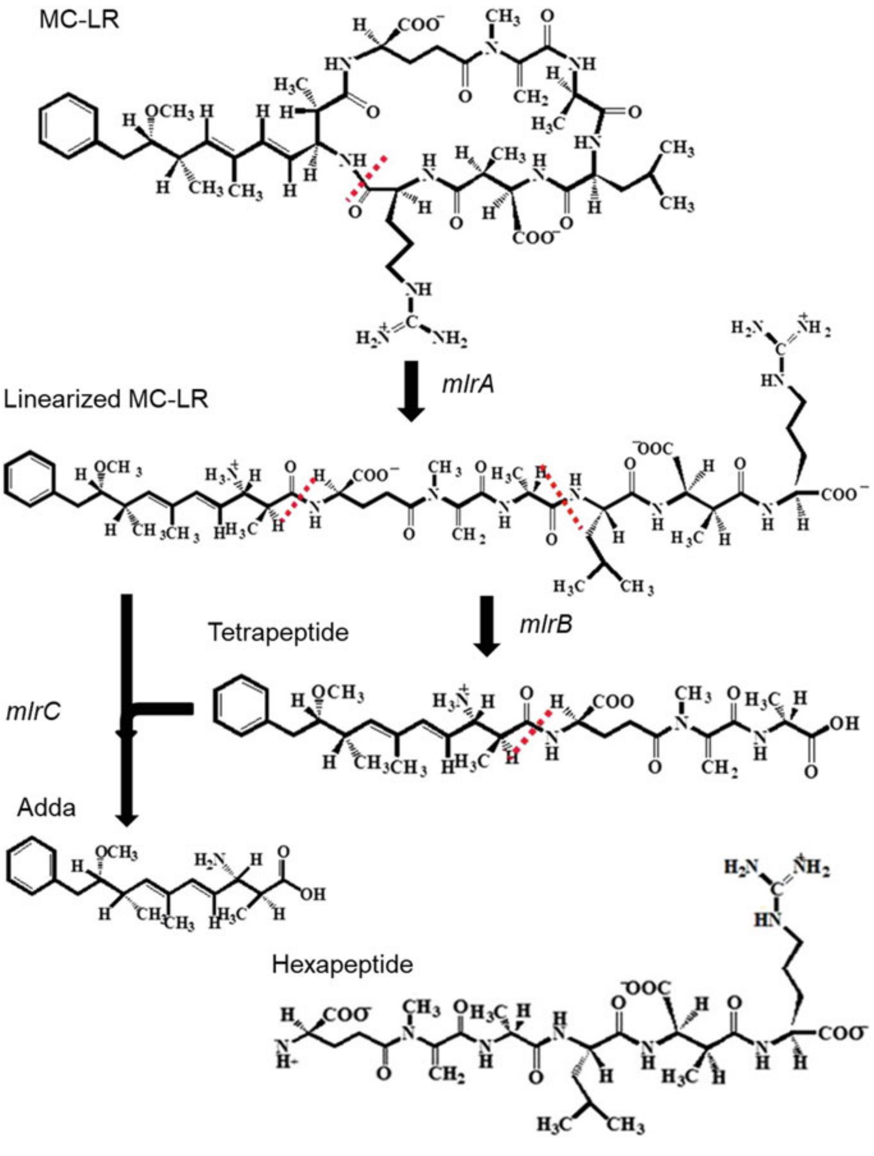

Fig. 2.4 Biodegradation pathway of MC-LR by *Sphingomonas* sp. Source: Adapted and modified from Li et al. (2017)

2.5 Conclusion

Toxic cyanobacterial blooms continue to plague eutrophic waters worldwide. The occurrence of TCBs of *Microcystis* associated with the hepatotoxic MCs appears to be expanding, with hundred countries or territories around the world. MCs are ubiquitous in the eutrophic environment. As a result, humans are increasing exposed to cyanobacterial toxins through drinking water consumption. Thus, control and abatement TCBs are critical issues faced by the scientist community. There is also a need for further efforts to curb eutrophication of freshwater resources. Numerous strategies have been emerged to prevent or eliminate blooms of cyanobacteria and MCs. To meet the WHO drinking water guideline, it is important that DWT has to remove both intracellular and extracellular MCs. While the conventional method efficiently removes cyanobacteria cells or intracellular MCs and in some case increasing extracellular MCs, combining AC absorption, biodegradation as well as advanced oxidation processes should ensure the removal of the most common extracellular MCs. However, MCs contain for hundred structures and variants, no single treatment has been proven to simultaneously remove all the MCs in a mixture. Although individual MCs can be efficiently removed or transformed by at least one treatment step during the production of drinking water, the efficient management of MCs in DWT should be based on a multi-barrier approach. Water treatment appears to be successful in the term of overcome consequence, a sustainable approach strategy should be a prevention of TCBs in surface waters.

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Chapter 3
Advanced Techniques for Characterizing DBP Precursors from Eutrophic Water and Their Applications for DBP Prediction

Lap-Cuong Hua and Chihpin Huang

Abstract Algogenic organic matter (AOM) in eutrophic water has become a critical problem for the sustainable operation of water treatment plants. As AOM is a high-yielding precursor of disinfection by-products (DBPs), its occurrence in water sources intensively raises public attention on the issues of safe and stable supply of drinking water. This chapter presents current advanced knowledge of AOM characterization and their applications for the prediction of DBP formation upon chlorination. Herein, two dominant classes of carbonaceous DBP (C-DBPs), trihalomethanes (THMs) and haloacetic acids (HAAs), were reviewed as major products of DBP from the eutrophic water. Overall, AOM is higher yielding THM and HAA precursors upon chlorination compared to terrestrial natural organic matter (NOM). Of the characterization tools, fluorescent spectrometry, i.e., excitation–emission matrix (EEM), is an advanced proxy to trace AOM-derived C-DBP formation over traditional bulk parameters or ultraviolet absorbance because of its greater sensitivity and selectivity. However, future work may use EEM technique in combination with bulk parameters, such as chlorine consumption, or MW properties to increase its predictability to AOM-DBP formation.

Keywords Eutrophication · Algogenic organic matter · Disinfection by-products Chlorination · Fluorescent spectroscopy

3.1 Introduction

Eutrophication of algae in reservoirs frequently impedes the unit operation of water treatment plants (WTPs) because of its exponential rise in a cell population in the water body (Tomlinson et al. 2016). Importantly, algal eutrophication always

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accompanies a remarkable increase in the concentration of algogenic organic matter (AOM), which is well proved as a major organic precursor to organic halogenated disinfection by-products (DBPs) upon chlorination (Nguyen et al. 2005). The formation of halogenated DBPs in finished drinking water has posed severe concerns about the safety of drinking water after treatment because of their mutagenicity and/or carcinogenicity for human (Tomlinson et al. 2016). Of the DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) are two major classes commonly formed during the chlorination in WTPs (Chang et al. 2010; Reckhow et al. 1990). They thus have been regulated worldwide. In practice, the regulated levels of THMs and HAAs in finished water is vulnerably excessed when algal eutrophication occurs (Tomlinson et al. 2016). Hence, an optimization for the treatment of eutrophic water is crucial to maintaining a sustainable water production.

AOM is an important autochthonous organic input from algae with the characteristics that are manifestly differentiated from humic substances derived from dead organic compounds of plants [terrestrial natural organic matter (NOM)] (Hong et al. 2013; Hua and Reckhow 2007; Hua et al. 2017). AOM comprises low aromatic with high nitrogenous content and mainly hydrophilic character (Hua et al. 2017, Nguyen et al. 2005). However, because of these characteristics, AOM is unamendable to remove by the traditional coagulation/sedimentation/filtration processes, increasing the risk of DBP formation after disinfection (Henderson et al. 2008a; Tomlinson et al. 2016).

The characteristics of AOM precursors vary species-by-species and depend on the origins of AOM and the phase of algal growth. These characters robustly determine the composition and physiochemical properties of AOM. Of the algal species, *Microcystis aeruginosa* and *Chlorella* sp. have been of much interest as they are the commonly blooming blue-green and green algae (Fang et al. 2010; Hua et al. 2017; Li et al. 2012; Zhu et al. 2015). It is essential to take a deeper insight into the role of a mixture of AOM precursors derived from various algal species. Speaking of the origin of AOM, it can be contributed by via extracellularly soluble organic matter arising by the metabolism and excretion of algal cells (i.e., extracellular organic matter—EOM) and cellular organic matter arising by auto cell lysis (i.e., intracellular organic matter—IOM). Because of the distinct origin and characteristics, they would yield differently DBPs. The other important character of AOM is algal growth phase. So far, there also remained unclear knowledge about the behaviors of AOM during algal growth. Thus, it is very crucial to clarify the role of these aforementioned characters on AOM precursors and their corresponding DBP formation potential (DBPFP).

To date, although current research has put efforts to investigate AOM-derived DBP formation potential intensively, there is limited relevant work that takes the prediction of AOM-derived DBP formation into account. In this chapter, we review the current knowledge of AOM physiochemical properties and their applicability for the prediction of AOM-DBP formation upon the chlorination of eutrophic water.

3.2 THMs and HAAs Formation in Drinking Water

Since the first discovery of trihalomethanes (THMs) as the first class of organic halogenated DBPs in drinking water was published in the 1970s (Bellar et al. 1974; Rook 1974), formation of DBPs in drinking water have extensively raised public concern about the safety of treated water because of their mutagenicity and carcinogenicity (Koivusalo and Vartiainen 1997). To date, hundreds of DBPs including organic and inorganic classes have been found in drinking water (Tomlision et al. 2016; Krasner et al. 2006; Singer 1994). Two major prevalent classes of carbonaceous organic halogenated DBPs (C-DBPs) are the THMs and the HAAs, which may account for >50% of a weight basis of DBPs, following by haloacetonitriles, haloketones, chloropicrin, cyanogen chloride, and chloral hydrate (Singer et al. 2002). Due to their potential carcinogenicity, THMs and HAAs are widely regulated with maximum level contaminant (MLC) levels as low as 60 and 80 μg/L (US, EPA 1998), respectively.

3.2.1 THMs and HAAs Classification

THMs are a major first class of organic halogenated DBPs, which constitutes four subclasses including trichloromethane (TCM or chloroform), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM or bromoform) (Singer 1994). These four THMs are often referred to as THM_4. The second most abundant organic halogenated DBPs in drinking water are HAAs. They comprise nine subclasses, which are monohalogenated acetic acid [monochloroacetic acid (MCAA) and monobromoacetic acid (MBAA)], dihalogenated acetic acid [dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), and bromochloroacetic acid (BCAA)], and trihalogenated acetic acid [trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA)] (Singer et al. 2002; Singer 1994). They are always referred to as HAA_9. Five of HAA_9 are currently regulated, including MCAA, MBAA, DCAA, TCAA, and DBAA. Table 3.1 gives the physiochemical properties and chemical abstracts service (CAS) number for all THMs and HAAs.

3.2.2 Toxicity and Regulation of THMs and HAAs

Numerous studies have been conducted on the toxicity of THMs and HAAs; there has been vast evidence showing that THMs and HAAs link to the cancers of colon, kidneys, and liver tumors in rat and mice and are mutagens in *Salmonella typhimurium* or fish (Boorman 1999; Condie 1990; DeAngelo and McMillan 1990;

Table 3.1 Physiochemical properties and chemical abstracts service (CAS) number for all THMs and HAAs adapted from Bougeard

Compound		Formula	Molecular weight (g/mole)	Boiling point (°C)	CAS number
THMs	TCM	$CHCl_3$	119.4	61–62	67-66-3
	BDCM	$CHBrCl_2$	163.8	87	75-27-4
	DBCM	$CHBr_2Cl$	208.3	119–120	124-48-1
	TBM	$CHBr_3$	252.7	146–150	75-25-2
HAAs	MCAA	$C_2H_3ClO_2$	94.5	189	130 79-11-8
	MBAA	$C_2H_3BrO_2$	138.9	206–208	79-08-3
	DCAA	$C_2H_2Cl_2O_2$	128.9	194	79-43-6
	BCAA	$C_2H_2BrClO_2$	173.4	215	5589-96-8
	TCAA	$C_2HCl_3O_2$	163.4	196	76-03-9
	DBAA	$C_2H_2Br_2O_2$	217.8	128–130	631-64-1
	BDCAA	$C_2HBrCl_2O_2$	207.8	NR[a]	71133-14-7
	DBCAA	$C_2HBr_2ClO_2$	252.3	NR[a]	5278-95-5
	TBAA	$C_2HBr_3O_2$	296.7	245	225,75-96-7

[a] Not reported

Dunnick et al. 1985; Koivusalo and Vartiainen 1997). To protect public health, the US Environmental Protection Agency (US EPA) released a regulation for the MCL of THMs as an annual average of 100 μg/L in 1979. In 1998, the US EPA strengthened the existed regulation by establishing the stage 1 disinfectants and disinfection by-products. The new regulation trickily strengthened the MCL for the four THMs (THM_4: TCM, BDCM, DBCM, and TBM) down to 80 μg/L and added the MCL for the five HAAs (HAA_5: MCAA, MBAA, DCAA, DBAA, and TCAA) at 60 μg/L. These MLCs for THMs and HAAs have been broadly used to control the DBPs in drinking water. In Taiwan, since chlorine-based oxidants have been commonly used as disinfectants in WTPs, the THMs and HAAs are also the mostly found organic halogenic DBPs in drinking water (Chang et al. 1998, 2010). Since 1998, Taiwan EPS has released the regulation for the MCL of THM_4 at 100 μg/L and was reduced to 80 μg/L in 2006. No regulation for HAAs was introduced at that time. Up to 2016, the MLC of HAA_5 of 60 μg/L was eventually regulated in drinking water. Table 3.2 gives the cancer activity of chlorinated by-products and their corresponding guideline and regulated MLCs by World Health Organization (WHO), US EPA, Europe, Australia, and Taiwan EPA.

Table 3.2 Toxicity and regulation of THMs and HAAs

Regulated DBPs	Cancer group[c]	WHO guideline value (μg/L)	US EPA standards (μg/L)		EU standards (μg/L)		Australian standards (μg/L)		Taiwan standards[a] (μg/L)	
Chloroform	B2	300	Total THM_4	80	Total THM_4	100	Total THM_4	250	Total THM_4	80
Dichlorobromomethane	B2	60	Total HAA_5	60	Total HAA_5	NR[b]	Chloroacetic acid	150	Total HAA_5	60
Dibromochloromethane	C	100					Dichloroacetic acid	100		
Bromoform	B2	100					Trichloroacetic acid	100		
Dichloroacetic acid	B2	50								
Trichloroacetic acid	C	200								

[a] From the new standard of Taiwan EPA released in 2016; [b] Not regulated; [c] Classification based on the carcinogen ability for human, including A: human carcinogen; B: probable human carcinogen (B1 limited evidence from epidemiological studies and B2 sufficient evidence from animal studies); C: possible human carcinogen

Adapted from Tomlinson et al. (2016)

3.2.3 THMs and HAAs Derived from NOM and Models Compounds

THMs and HAAs are formed in treated water as a result of serial oxidation-substitution and hydrolysis of natural organic matter (NOM); they are not removed effectively by upstream treatment and correspondingly react with the disinfectants, such as chlorine or chloramine (Reckhow and Singer 1985; Reckhow et al. 1990). To have a better insight into the reaction pathways and the physical parameters of DBP formation in drinking water, numerous research has been conducted with the aim to qualify and quantify the formation kinetics and pathways of DBPs form various organic precursors in water sources, such as humics/fulvic substances, common amino acids, and others (Dickenson et al. 2008; Hua et al. 2014; Liang and Singer 2003; Reckhow and Singer 1985; Reckhow et al. 1990; Scully et al. 1988).

NOM is a major source of THM and HAA precursors (Reckhow et al. 1990). Table 3.3 shows the review of TCM, DCAA, and TCAA formation potentials derived from various precursors of NOM sources and model compounds. Many studies have put numerous efforts to investigate their characteristics and corresponding roles on DBP formation (Hong et al. 2013; Hua et al. 2014, 2015; Reckhow and Singer 1985). A very early study of Reckhow et al. (1990) reported the formation of TCM, DCAA, and TCAA from extracted aquatic humics from five surface waters in the US. The average DBP results showed that the extracted fulvic and humic substances from surface waters could yield a substantial amount of TCM, DCAA, and TCAA, especially for the extracted humics because of their high content of activated aromatic rings. Hong et al. (2013) also showed that the formation potentials of these three compounds were much higher for the sediments of NOM. Because of the complexity of NOM in surface waters, several studies have been carried out with their model compounds, such as commercial humic acids, BSA, amino acids, lipids, starch, and lignin, as precursors to DBPs for a better interpretation of the formation mechanism (Hong et al. 2008, 2009; Hua et al. 2014; Scully et al. 1988). Of these model compounds, tryptophan and tyrosine, two naturally found biomolecules in phytoplankton or bacterial cells seemed to be the highest yielding precursors to TCM, DCAA, and TCAA.

The formation of THMs and HAAs within the chlorination of NOM is attributed to a serial oxidation and substitution reactions. In general, substances with aromatic moisture and conjugate system are potential precursors to THM and HAA formation. Figure 3.1 shows the typical formation pathways of three major C-DBPs including TCM, DCAA, and TCAA (Reckhow et al. 1990). DCAA and TCAA are mainly formed when NOM precursors are constituted by readily oxidizable functional groups (OFG), i.e., carbon–carbon double bond, alcohol, and amine. Otherwise, TCM is possibly formed as the final product (Hong et al. 2009; Hua et al. 2017; Reckhow et al. 1990).

Table 3.3 Reported levels of THMs and HAAs in drinking waters in Taiwan and other countries

Location		THM level[a] (μg/L)	HAA level		References
			HAA measured	Ranged (μg/L)	
US		30–44	HAA$_5$[b]	13–21	Krasner et al. (1989)
US		4–164	HAA9	5–130	Krasner et al. (2006)
UK		NR[d]–76	HAA9[c]	NR–244	Malliarou et al. (2005)
Beijing, China		3–16	HAA$_5$	1–14	Wang et al. (2007)
Canada		31–43	HAA$_5$	20–27	
Taiwan		21–42	HAA$_5$	25–68	Chang et al. (1998)
Taiwan[f]	Northern	ND[e]–63	HAA$_5$	2–37	Chang et al. (2010)
			HAA9	2–50	
	Central	2–30	HAA$_5$	1–14	
			HAA9	1–17	
	Southern	5–53	HAA$_5$	2–47	
			HAA9	3–58	
	Eastern	0.2–27	HAA$_5$	0.2–27	
			HAA$_5$	0.2–37	
	Offshore island	4–133	HAA5	2–28	
			HAA$_5$	6–42	

[a] THM level for THM$_4$ (TCM, BDCM, DBCM, and TBM)
[b] HAA$_5$ including MCAA, MBAA, DCAA, DBAA, and TCAA
[c] HAA$_9$ including all HAAs
[d] Not reported
[e] Not detectable
[f] Data during summer from July–August 2007

3.2.4 Formation of THMs and HAAs in Worldwide Practical Drinking Water

HAAs and THMs are well reported to be the most abundant halogenated DBPs during water chlorination accounting for more than 50% of total DBP yield in surface water (Chang et al. 1998, 2010; Singer et al. 2002). Nonetheless, the contribution of THMs and HAAs distinctly varies from the nature of water source, the unit operation performance in WTPs, as well as the local regulation conditions, as shown in Fig. 3.2.

Table 3.3 presents the THM and HAA levels formed in worldwide drinking water. In the US, a very early investigation of Krasner et al. (1989), which surveyed 35 WTPs in the US, reported that the total concentration THMs ranged from 30 to 44 μg/L with TCM and BDCM were the major compounds. The HAA$_5$ yield was ranged from 13 to 21 μg/L, which was twofold less than THMs. In the UK, a study

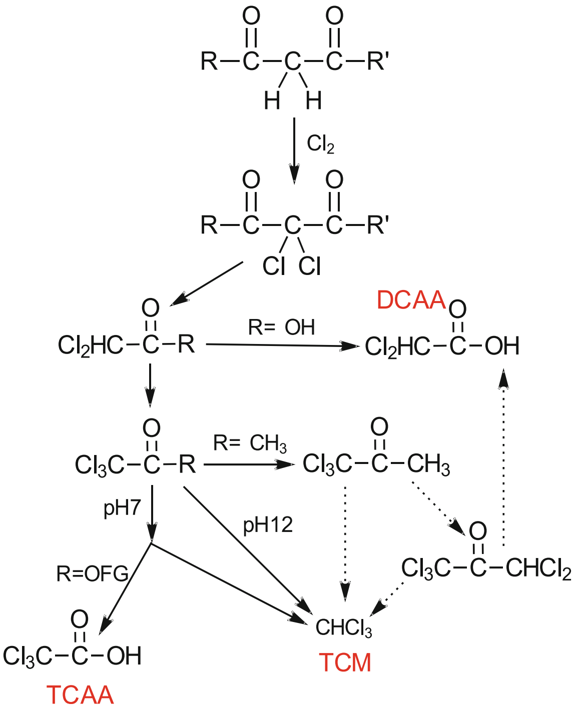

Fig. 3.1 Formation pathways of TCM, DCAA, and TCAA during the chlorination of NOM. OFG: oxidizable functional groups, e.g., –OH, $–NH_2$, –S–

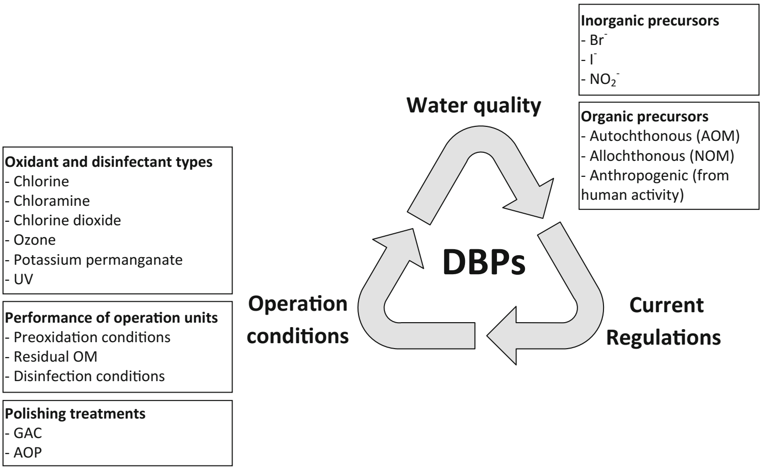

Fig. 3.2 Factors affecting DBP formation, including water quality, operation conditions, local regulation

reported that levels of HAAs yield during chlorination ranged from 35 to 95 μg/L per region and could reach up to 244 μg/L, which was much higher than the yield of THMs (76 μg/L) (Malliarou et al. 2005). In Taiwan, the first survey of Chang et al. (1998) on the formation of THMs and HAAs for six conventional WTPs in Taiwan showed that THMs formed in finished water ranged from 21 to 42 μg/L, while HAA_5 were yielded in a higher range from 25 to 68 μg/L. Thereafter, Chang et al. (2010) also conducted a comprehensive investigation on the formation of THMs and HAAs in the finished waters from 86 WTPs including mainland and offshore islands in Taiwan during winter and summer seasons in 2007. The data showed that the concentrations of THM_4 could reach up to 99.4 and 133.2 μg/L during the winter and summer seasons, respectively, while HAA_5 content could reach around 38.9 in the winter season and 46.7 μg/L in the summer season, respectively. In this latter report, the levels of HAA_5 were much lower than THM_4. This indicated a contrary result from the first study by Chang et al. (1998), but it was similar to Krasner et al. (1989). In addition, a comparable yielding rate of THMs and HAA_9 was reported by Singer et al. (2002) by examining more than 5000 water samples. Because of the complexity of water characteristics, comprehensive investigations of the nature of surface waters and DBP precursors would provide a better insight into the knowledge of the prediction and control of THMs and HAAs in drinking water.

3.3 AOM in NOM Matrix

NOM is a very complex mixture of various aromatic and aliphatic organic substances that bond to an amide, carboxyl, hydroxyl, ketone, and various minor functional groups (Leenheer and Croué 2003). Numerous works have reported that NOM is rich in aromatic and hydrophobic but less in nitrogenous organic contents (Hong et al. 2013; Hua and Reckhow 2007; Hua et al. 2015; Matilainen et al. 2010; Reckhow et al. 1990; Sillanpää et al. 2015). For instance, a comprehensive early study of Reckhow and coauthors (1990) was conducted for 10 aquatic NOM from different sources of the lake and river waters. The data revealed that about 52–56% carbon in total mass comprised of 14–19% and 30–35% of aromatic content as well as 0.8–2.1 mequiv/g and 1.5–5.4 mequiv/g of phenolic OH content for fulvic and humic fractions, respectively. Furthermore, all water samples comprised less than 2% of the nitrogenous organic content.

However, the characteristics of NOM are markedly changed when the autochthonous AOM enters water pool, especially during the eutrophication periods of algae. In general, AOM is an important autochthonous OM derivative of algae; it is produced intensively by the exudation or cell lysis during algal eutrophication. 7–50% of carbon fixed per unit area was found to be released in dissolved organic matter (DOM) by the liberation of various algae in lakes and seas into water system (Fogg et al. 1965). The amount of released AOM can contribute up to 50% of total dissolved organic carbon entering the NOM in surface water during the low rainfall seasons (Linden et al. 2004). Revsbech et al. (1994) demonstrated that the OM from three algal-rich coastal ponds and two algal-rich dry valley lakes comprised of about 2.2–4.7% of nitrogenous organic content with much lower aromatic content (11.7–16.5%) compared to terrestrial pools. The alike phenomenon was reported in another study in which nitrogenous peptides accounting for approximately 25% of all C in a eutrophic lake (Mao et al. 2007). As a result, AOM occurrence causes drastic changes in the amount and characteristics of organic matter (OM) in raw water (Coral et al. 2013). This manifestly proves the significant impacts of AOM on the variation NOM matrix.

3.4 AOM as THM and HAA Precursors

3.4.1 Importance of AOM as Precursors of THMs and HAAs

Natural organic matter (NOM) has been well accepted as a major DBP precursor in surface waters (Hong et al. 2013; Hua et al. 2015; Liang and Singer 2003; Reckhow and Singer 1985; Reckhow et al. 1990; Tomlinson et al. 2016). In contrast to allochthonous terrestrial NOM precursors that are highly aromatic and more hydrophobic contents, resulting in high DBP formation potential (DBPFP) (Hong et al. 2013; Hua and Reckhow 2007; Reckhow and Singer 1985; Reckhow et al. 1990; Trussell and Umphres 1978), AOM comprises of low aromatic with high nitrogenous content and hydrophilic character (Huang et al. 2009; Leloup et al. 2013; Nguyen et al. 2005; Pivokonsky et al. 2015). However, because of these characters, AOM is a greater yielding DBP precursors not only in terms of C-DBPs, THMs, and HAAs, but also in terms of nitrogenous-DBPs (N-DBPs) compared to NOM (Graham et al. 1998; Hoehn et al. 1980; Hong et al. 2008; Huang et al. 2009; Nguyen et al. 2005; Tomlinson et al. 2016).

3.4.2 THMs and HAAs Derived from AOM of Different Species

A summary of the EOM and IOM precursors yielding various levels of the THMs and HAAs from various algal species is given in Table 3.4. There has been a lot of information about the specific yields of blue-green algae to THMFP and HAAFP because they are commonly blooming algae. For instance, Li et al. (2012) reported that the yields of THMs and HAAs from the EOM and IOM precursors of M. *aeruginosa* during its exponential phase. The results showed that the formations of total THMFP and HAAFP were comparable, but the IOM precursors yielded more THMs and HAAs than EOM, which were two- and threefold higher for THMFP

Table 3.4 Variation in the formation of THMs and HAAs from EOM and IOM precursors for various algae and their corresponding growth phases

Algal species	Chlorination condition		THM formation (μg/mg-C)		HAA formation (μg/mg-C)		Note	References
			EOM	IOM	EOM	IOM		
Blue-green algae								
Microcystis aeruginosa	pH 7.5, RC[a] > 3 mg/L, dark, 22–24 °C, 7 days	Late exponential		64[b]		117	IOM was isolated by freeze–thaw sequence	Wert and Rosario-Ortiz (2013)
	pH 7, 5: 1, dark, 25 °C, 3 days	Exponential	32[b]	55[b]	21[b]	68		Li et al. (2012)
	pH 7, 5: 1, dark, 25 °C, 3 days	Stationary	8	15	IOM > EOM			Zhu et al. (2015)
	pH 7, 5: 1, dark, 24 °C, 3 days	Late exponential	IOM > EOM[b]					Zhou et al. (2014, 2015)
	pH 7, RC > 0.5 mg/L, dark, 21 °C, 7 days	Late exponential	28	61	66	164	IOM was algal cells	Huang et al. (2009)
	pH 8, RC > 1 mg/L, 22 °C, 1 day	Stationary		16 μg/L for 250,000 cells		6 μg/L for 250,000 cells		Coral et al. (2013)
	pH 7, RC >0.5 mg/L, dark, 21 °C, 7 days	Stationary	17[b]		11[d]			Fang et al. (2010)
Oscillatoria prolifera	pH 7, 5:1, dark, 20 °C, 7 days	NS[e]	30					Nguyen et al. (2005)
Oscillatoria sp.	pH 7, 10: 1, dark, 20 °C, 4 days	Exponential		26		72	IOM was algal cells	Hong et al. (2008)

(continued)

Table 3.4 (continued)

Algal species	Chlorination condition		THM formation (µg/mg-C)		HAA formation (µg/mg-C)		Note	References
			EOM	IOM	EOM	IOM		
Oscillatoria sp.	pH 7.5, chlorine residual >3 mg/L, dark, 22–24 °C, 7 days	Late exponential		47^{b}		121	IOM was isolated by freeze–thaw sequence	Wert and Rosario-Ortiz (2013)
Lyngbya	pH 7.5, chlorine residual >3 mg/L, dark, 22–24 °C, 7 days	Late exponential		38^{b}		101		Wert and Rosario-Ortiz (2013)
Anabaena flos-aquae	pH 7, RC, dark, 20 °C, 1 day	Exponential	0.001–0.33^{b}	0–0.43^{b}			IOM was algal cells	Graham et al. (1989)
Anabaena flos-aquae	pH 8, RC > 1 mg/L, 22 °C, 1 day	Stationary		23 µg/L for 250,000 cells^{b}		14 µg/L for 250,000 cells	IOM was algal cells	Coral et al. (2013)
Anabaena flos-aquae	pH 7, chlorine residual >0.5 mg/L, dark, 21 °C, 7 days	Late exponential	26	50	48	78		Huang et al. (2009)
Green algae								
Scenedesmus quadricauda	pH 7, RC > 5 mg/L, 20 °C, 7 days	Late exponential		98 µg/L for 200,000 cells^{c}		209 µg/L for 200,000 cells^{c}	IOM was algal cells	Plummer and Edzwald (2001)
Scenedesmus quadricauda	pH 7, 5:1, dark, 20°C, 7 days	NS^{d}	48					Nguyen et al. (2005)
Chlorella vulgaris	pH 7.2, RC > 0.5 mg/L, dark, 22°C, 3 days	Exponential	15					Yang et al. (2011)
		Stationary	13					
Chlamydomonas sp.	pH 7, 10: 1, dark, 20 °C, 4 days	Exponential		34		62	IOM was algal cells	Hong et al. (2008)

(continued)

Table 3.4 (continued)

Algal species	Chlorination condition		THM formation (µg/mg-C)		HAA formation (µg/mg-C)		Note	References
			EOM	IOM	EOM	IOM		
Diatom algae								
Cylotella sp.	pH 7, RC > 5 mg/L, 20 °C, 7 days	Late exponential		58 µg/L for 200,000 cells[c]		97 µg/L for 200,000 cells[c]		Plummer and Edzwald (2001)
Chaetoceros Mulleri	pH 7, RC > 5 mg/L, 20 °C, 7 days	NS[d]	30					Nguyen et al. (2005)
Nitzschia sp.	pH 7, 10: 1, dark, 20 °C, 4 days	Exponential		48		42		Hong et al. (2008)
Asterionella formosa	pH 7, RC, dark, 20 °C, 1 day	Exponential	0.07–0.12[b]	0.0–0.25[b]			IOM was algal cells	Graham et al. (1989)

[a] Residual chlorine

[b] THM yield as TCM

[c] Yield from algal suspension (IOM + EOM)

[d] HAA yield as DCAA

[e] Not specific

and HAAFP, respectively. A similar trend was reported by Zhu et al. (2015), where they investigated the yield of THMFP and HAAFP during the stationary phase of M. *aeruginosa* culture with the same IOM extraction method and chlorination condition. The high potential of IOM precursors to form THMs and HAAs have been supported by other studies of blue-green algal species (Nguyen et al. 2005; Wert and Rosario-Ortiz 2013; Zhou et al. 2014, 2015). This tendency is also true for green or diatom algal species (Hong et al. 2008; Plummer and Edzwald 2001) (Table 3.4). Particularly, the early study of Graham et al. (1998) reported 85% of TCM yield from algal cell precursors. Another later study by Plummer and Edzwald (2001) revealed that up to 70% of DBP precursors were attributed to the cellular materials in which 73% and 71–75% of TCM and HAA were derived from algal cells, respectively. It is clear that IOM precursors yield more THMFP and HAAFP than EOM precursors.

Table 3.4 also shows that the yields of HAAFP were higher than THMFP for different algal species (Huang et al. 2009; Plummer and Edzwald 2001; Wert and Rosario-Ortiz 2013). However, the contrary opinion has been reported by Coral et al. (2013), where the yields of THMFP for *M. aeruginosa* and *A. flos-aquae* cells were approximately twofold higher than HAAFP. This may be as a result of different algal cultures and growth phases. Thus, studies in this aspect are needed to provide more comprehensive information about the algae-derived DBPs from various species.

3.5 Physiochemical Characteristics of AOM

The physiochemical nature of AOM markedly determines not only its reactivity, but also the category and quantitative content of DBP formation. Most current studies have characterized the basic physiochemical characteristics of AOM by means of (1) organic carbon and/or nitrogen content (DOC and/or DON), (2) ultraviolet–UV absorbance and fluorescent spectrum, (3) hydrophilicity, and (4) MW profile as shown in Table 3.5.

In practice, AOM released from algae is either the exudate products in EOM (mostly low MW amino acids) (Fogg et al. 1965; Watt 1966) or is released from cells by the autolysis of senescent cells (Tomlinson et al. 2016; Zhou et al. 2015). Because of the abundance of proteins and amino acids, IOM manifestly comprises a higher content of DON compared to EOM (Hua et al. 2017; Li et al. 2012; Zhu et al. 2015). IOM thus has a lower DOC/DON ratio than has been reported for EOM. The DON content of the IOM for some species may be fourfold compared to that of the NOM in natural water (Li et al. 2012).

The most commonly used indicator for the aromaticity in OM water sample is UV absorbance, at 254 and 280 nm, which are converted to specific UV values (SUVA) for comparison (Korshin et al. 1997; Matilainen et al. 2011). For AOM samples, both EOM and IOM, in particular, have low SUVA values, mostly of <2 mg/L.m, especially in case of IOM of < 1 mg/L.m. The SUVA values of EOM

Table 3.5 Composition and physicochemical properties of EOM and IOM for various algal species in different growth phases

Algal species	Growth phase	EOM or IOM	C/N ratio	SUVA (mg/L.m)	HPI (%)	MW distribution	EEM[a] spectrum	References
Blue-green algae (Cyanobacteria)								
Microcystis aeruginosa	Late exponential	EOM	4.32	0.84	67	–	–	Zhou et al. (2015)
		IOM	6.34	0.97	79	–	–	
	Stationary	EOM	5.33	1.22	–	–	HA and SMP	Zhu et al. (2015)
		IOM	2.96	0.83	–	–	AP and SMP	
	Exponential	EOM	–	0.72	63	1–100 kDa: 85%	HA and SMP	Li et al. (2012)
	Exponential	IOM	0.23	0.84	83	<1 kDa: 27% 40–800 kDa: 42% >800 kDa: 31%	HA and SMP	Li et al. (2014)
	Exponential	EOM[b]	–	1.65	59	–	–	Henderson et al. (2008b)
	Stationary	EOM[b]	–	0.48	57	<1 kDa: 38% >30 kDa: 55%	SMP and AP	
	Late exponential	IOM	0.3	1.6	–	–	–	Wert et al. (2013)
	Exponential	EOM	–	–	75	–	–	Leloup et al. (2013)
	Stationary	EOM	–	1.07	61	–	–	
	Death	EOM	–	1.04	–	–	–	
	Exponential	EOM	–	1.6	69	–	–	Pivokonsky et al. (2014)
	Stationary	EOM	–	0.7	69	–	–	
	Stationary	IOM[c]	–	1.4	87	–	–	
	Stationary	EOM		0.34	34%	>100 kDa: 73.4%	SMP, AP	Qu et al. (2012)
Oscillatoria sp.	Late exponential	IOM	0.2	0.7	–	–	–	Wert et al. (2013)
Lyngbya sp.	Late exponential	IOM	0.3	0.3	–	–	–	

(continued)

Table 3.5 (continued)

Algal species	Growth phase	EOM or IOM	C/N ratio	SUVA (mg/L.m)	HPI (%)	MW distribution	EEM[a] spectrum	References
Anphanizonmenon flos-aquate	Stationary	EOM	–	0.79	63	–	–	Goslan et al. (2017)
Anabaena flos-aquate	Stationary	EOM	–	0.34	81	–	–	
Green algae								
Scenedesmus subspicatus	Stationary	EOM	–	1.18	54	–	–	Goslan et al. 2017
Chlorella vulgarus	Exponential	EOM[b]	–	1.29	60	–	–	Henderson et al. (2008b)
	Stationary	EOM[b]	–	0.54	71	<1 kDa: 30% >30 kDa: 62%	SMP,AP, HA, and FA	
Chlorella sp.	Exponential	EOM	2.21	1.34	–	–	HA & FA	Hua et al. (2017)
		IOM	0.54	0.78	–	–	AP & SMP	
Euglena gracilis	Exponential	EOM	–	–	75	–	–	Leloup et al. (2013)
	Stationary	EOM	–	1.95	69	–	–	
	Death	EOM	–	2.64	–	–	–	
Chlamydomonas geitleri	Exponential	EOM	–	1.2	71	–	–	Pivokonsky et al. (2014)
	Stationary	EOM	–	0.6	73	–	–	
	Stationary	IOM	–	0.3	89	–	–	
Diatom algae								
Asterionella formasa	Exponential	EOM[b]	–	1.70	73	–	–	Henderson et al. (2008b)
	Stationary	EOM[b]	–	0.54	70	<1 kDa: 81% >30 kDa: 9%	SMP and AP	
Melosira sp.	Stationary	EOM[b]	–	0.58	64	<1 kDa: 30% >30 kDa: 53%	SMP and AP	

(continued)

Table 3.5 (continued)

Algal species	Growth phase	EOM or IOM	C/N ratio	SUVA (mg/L.m)	HPI (%)	MW distribution	EEM[a] spectrum	References
Fragilaria crotonensis	Exponential	EOM	–	1.8	74	–	–	Pivokonsky et al. (2014)
	Stationary	EOM	–	0.8	74	–	–	
	Stationary	IOM	–	0.4	90	–	–	

[a] EEM spectra classification by on Chen et al. (2003), including four components with excitation/emission wavelengths (Ex/Em) of 350/435–450 nm, 250–280/425 nm, 280–285/340–350 nm, and 220–230/340–350 nm, representing humic-like (HA), fulvic-like (FA), soluble microbial-like products (SMP), and aromatic protein-like (AP) substances

[b] EOM may comprise some closely bound OM from cells and IOM due to cell lysis by centrifugation

and IOM are substantially lower than that obtained for the allochthonous NOM (SUVA > 4 mg/L.m) (Hong et al. 2013; Matilainen et al. 2011; Nguyen et al. 2005). This results from less aromatic and more hydrophilic contents in AOM compared to terrestrial NOM (Hua et al. 2015; Pivokonsky et al. 2016; Tomlinson et al. 2016), and indicates that AOM-containing water responds poorly to UV absorbance.

Excitation–emission matrix (EEM) spectroscopy is commonly used for OM fluorescent characterization (Chen et al. 2003; Coble 2007; Hidayah et al. 2017; Hua et al. 2017; Matilainen et al. 2011), which provides more useful information than UV absorbance does, in terms of OM component discrimination and their relative concentrations (Coble 2007; Matilainen et al. 2011). Many studies on AOM characterization have applied EEM to interpret the behavior of AOM during pre-oxidation (Lin et al. 2018; Zhu et al. 2015), coagulation (Lin et al. 2016), membrane filtration (Her et al. 2004; Qu et al. 2012), and especially for AOM-derived DBP formation (Hua et al. 2017; Hua et al. 2018b; Li et al. 2012). In general, EEM-AOM fluorescent spectra can be classified into four major components according to their excitation/emission wavelengths (Ex/Em) of 350/435–450 nm, 250–280/425 nm, 280–285/340–350 nm, and 220–230/340–350 nm, representing humic-like (HA), fulvic-like (FA), soluble microbial-like products (SMP), and aromatic protein-like (AP) substances, respectively (Chen et al. 2003). In particular, IOM is predominantly comprised of AP- and SMP-like substances, while EOM is abundant in SMP-, HA-, and FA-like products (Henderson et al. 2008b, Hua et al. 2017, Zhu et al. 2015). Examples of EEM spectra for EOM and IOM derived from Chlorella sp. and their corresponding four fluorescent components are given in Fig. 3.3.

Compared to NOM, AOM predominantly comprises greater amounts of hydrophilic (HPI) substances. The HPI fraction in AOM could account for more than 83% on average, which is much higher than the HPI fraction in NOM, where the HPI fraction is only about 10–20% (Hong et al. 2013; Leloup et al. 2013). In brief, HPI substances are the most dominant fraction in AOM regardless of the algal species and the growth phase. Current studies have reported that HPI fraction is more difficult to remove by traditional coagulation compared to hydrophobic (HPO) fraction (Henderson et al. 2008b; Pivokonsky et al. 2015; Tomlinson et al. 2016), which would increase the amount of AOM remained after traditional treatments.

Table 3.5 also shows the fractionated MW for EOM and IOM. They broadly vary with algal species and growth phase. In general, the molecular substances in IOM and EOM are distributed in a range from <1 kDa to >100 kDa. It has also been shown that the MW distribution strongly relates to the aromaticity and hydrophilicity of OM; the less aromatic content presents, the smaller MW fraction (Leenheer and Croué 2003; Sillanpää et al. 2015). In relation with HPI, because of its small MW characteristics, AOM is more recalcitrant to being removed by coagulation compared to NOM, resulting in a greater amount of available residual AOM to react with disinfectants (Hua and Reckhow 2007; Pivokonsky et al. 2015, 2016; Zhao et al. 2006). Current studies have also revealed that small MW

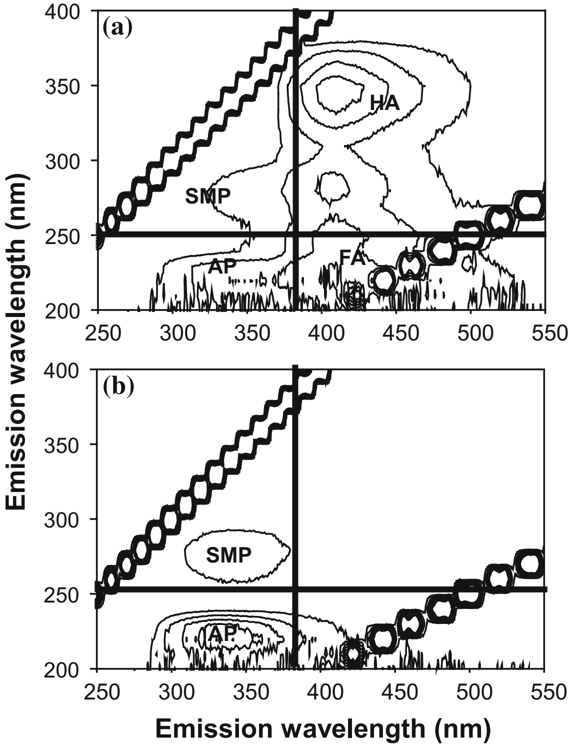

Fig. 3.3 Examples of overall fluorescent spectra of **a** EOM and **b** IOM derived from *Chlorella* sp. and their regional fluorescent components (AP: aromatic protein; SMP: soluble microbial product; HA: humic acid; FA: fulvic acid). Adopted from Hua et al. (2017)

precursors have relatively high formation potential for both C- and N-DBPs (Hua and Reckhow 2007; Zhao et al. 2006; 2015). This thus intensifies the formation potential of AOM-derived DBPs.

In brief, the basic physiochemical composition and characteristics of AOM vary study-by-study, even for the same species. This is likely due to the complex nature of AOM and its origins as well as the differences in culture conditions and algal growth phases.

3.6 Predictions of AOM-Derived DBPs

Since AOM has a great potential to produce both C- and N-DBPs (Goslan et al. 2017; Lui et al. 2011; Wert and Rosario-Ortiz 2013), the effective prediction of the formation of AOM-derived DBPs will significantly benefit the sustainable operation of water treatment facilities. Although DBP modeling and prediction have been reported in numerous studies over many years (Chen and Westerhoff 2010; Chowdhury et al. 2009, 2010; Ged et al. 2015; Hong et al. 2013; Kulkarni and Chellam 2010; Peleato et al. 2018; Reckhow et al. 1990; Sadiq and Rodriguez

2004; Sohn et al. 2001; Xue et al. 2014), little attention has been paid to the prediction of AOM-derived DBPs (Hua et al. 2018a).

In general, common surrogates of DBP formation are the bulk parameters; they are frequently used as independent variables in the prediction models of DBP (Chen and Westerhoff 2010; Hong et al. 2013; Xue et al. 2014). Bulk parameters can be traced by monitoring DOC, DON, pH, bromide, and chlorine concentrations. The models based on bulk parameters show the strong prediction of C-DBP formation (Chowdhury et al. 2009; Hidayah et al. 2017; Hong et al. 2013). However, the practical monitoring of these parameters is complicated by time-consuming and multiple analytical tasks. They are also likely comprised of a weak predictability of the formation of N-DBPs, such as N-nitrosodimethylamine (NDMA) (Chen and Westerhoff 2010). The application of bulk parameters may be insufficient to track the trends and the formation of all DBP classes derived from AOM. As the prediction of AOM-yielded DBPs still remains largely unknown, more practical work on bulk parameters of AOM water is required to clarify its applicability for DBP prediction.

Work on DBP prediction has also used the optical properties of samples as common fingerprints of DBP formation (Hidayah et al. 2017; Johnstone and Miller 2009; Pifer and Fairey 2012; Uyak and Demirbas 2014). Such optical characterization tools, i.e., UV absorbance and EEM, have been widely applied in laboratories and practical predictions of NOM-derived DBP formation (Beauchamp et al. 2018; Li et al. 2016; Peleato and Andrews 2015; Peleato et al. 2018). For AOM samples, UV absorbance (254 and/or 280 nm) should not be used to predict DBPs because it responds poorly to AOM samples where nitrogenous and hydrophilic contents are dominant (Henderson et al. 2008b; Hua et al. 2015; Hua et al. 2018a). Conversely, EEM technique is a more reliable tool for predicting AOM-derived DBPs compared to traditional UV absorbance (Coble 2007; Hao et al. 2012; Hidayah et al. 2017; Johnstone and Miller 2009; Roccaro et al. 2009; Yang et al. 2008), because of the great selectivity and sensitivity of EEM to AOM samples (Hua et al. 2018a). Table 3.6 gives a review of current applications of regional EEM information derived (average fluorescent intensity—AFI) for the prediction of DBP formation from NOM and AOM precursors. Overall, the applications of EEM well predict HAAs but is still too weak for the prediction of AOM THM formation ($R^2 = 0.323$) (Hua et al. 2018a). Nonetheless, because AOM-containing water is always subjected to serial treatments, fluorescence thus has a great advantage of long-term monitoring to track AOM precursors throughout treatment units (Matilainen et al. 2011). Future work can use fluorescence techniques in combination with bulk parameters, such as chlorine consumption, or MW properties to increase the applicability of fluorescence for predicting AOM-DBP formation.

Table 3.6 Applications of regional average fluorescent intensity (AFI) of EEM for the prediction of C-DBP formation.

Reference	Source water	Target	Component: ex/em	n	R^2	Regression equation
Johnstone and Miller (2009)[a]	River water	$CHCl_3$	AF1 & AF2: < 250/< 350[d] FA: < 250/> 350 SMP: 250–280/< 380 HA: > 250/> 380	58	0.82	$CHCl_3 = 5.164\ (AF_{AP1})^{-0.0517}\ (AF_{AP2})^{-0.167}\ (AF_{FA})^{0.464}\ (AF_{SMP})^{0.555}\ (AF_{HA})^{-0.424}\ (\Delta Cl_2)^{-0.665}$
		Cl_2AA[b]			0.86	$Cl_2AA = 0.906\ (AF_{AP1})^{-0.212}\ (AF_{AP2})^{0.211}\ (AF_{FA})^{1.000}\ (AF_{SMP})^{0.526}\ (AF_{HA})^{-0.940}\ (\Delta Cl_2)^{0.447}$
		Cl_3AA[c]			0.90	$CHCl_3 = 0.652\ (AF_{AP1})^{0.144}\ (AF_{AP2})^{0.621}\ (AF_{FA})^{-0.017}\ (AF_{SMP})^{-1.030}\ (AF_{HA})^{0.689}\ (\Delta Cl_2)^{1.19}$
		$CHCl_3 + Cl_3AA$			0.92	$CHCl_3 = 1.622\ (AF_{AP1})^{-0.087}\ (AF_{AP2})^{0.363}\ (AF_{FA})^{0.542}\ (AF_{SMP})^{0.011}\ (AF_{HA})^{-0.278}\ (\Delta Cl_2)^{0.713}$
Johnstone et al. (2009)	Coagulated water	$CHCl_3$	AF: 219 & 280/310 SMP: 219 & 304/381	30	0.77**	$CHCl_3 = -34.5 + 47.8\ AF_{SMP} - 17.3\ AF_{AP}$
Hao et al. (2012)[e]	Reclaimed water	THMs	FA: 362/415 & 237/420	10	0.992**	$THMFP = 0.186\ AF_{FA} + 143.324$
		HAAs			0.984**	$HAAFP = 0.216\ AF_{FA} + 21.350$
Hidayah et al. (2017)	Coagulated water	THMs	HA: 250/460 & 360/460	38	0.65	$THMFP = 856\ AF_{HA} + 52.69$
		HAAs	FA: 250/420 & 340/420		0.70	$HAAFP = 1053\ AF_{FA} + 16.72$
Hua et al. (2018a)[f]	AOM-containing water	THMs	AP: 220–230/340–350 SMP: 280–285/340–350 HA:350/435–450 FA: 250–280/425	9	0.323	$THMFP = 0.015\ AFI_{AP} - 0.013\ AFI_{SMP} + 0.133\ AFI_{HA} - 0.169\ AFI_{FA} - 0.24\ Total_{AFI} + 7.640$
		HAAs			0.879**	$HAAFP = 0.238\ AFI_{AP} + 0.226\ AFI_{SMP} + 0.121\ AFI_{HA} + 0.1\ AFI_{FA} - 0.97\ Total_{AFI} + 4.120$
		C-DBPs			0.846**	$C\text{-}DBPFP = 0.240\ AFI_{AP} + 0.205\ AFI_{SMP} + 0.284\ AFI_{HA} - 0.152\ AFI_{FA} - 0.107\ Total_{AFI} + 9.917$

[a] Regression models based on regional AFI and residual chlorine (ΔCl_2)

[b] Dichloroacetic acid

[c] Trichloroacetic acid

[d] AF1 and AF2 represented for two aromatic proteins regions of tyrosine and tryptophan

[e] Regression models were built by standard solution of fulvic acid

[f] Regression models based on regional AFI and total AFI ($Total_{AFI}$)

$^{**}p < 0.001$

Adapted from Hua et al. (2018a)

3.7 Conclusions

Overall, AOM has high potentials to produce a significant amount of THMs and HAAs upon chlorination compared to terrestrial NOM, especially IOM. For the practical treatment of eutrophic water, preoxidation approaches with chlorination or ozonation are frequently required to inactive algal cells prior to coagulation. It inevitably ruptures the cells and releases the IOM. The use of preoxidation should be optimized to reduce the risk of IOM release from the cell to avoid the intensification of the AOM-DBP formation during the treatment of eutrophic water

Unlike in case of NOM, the tradition indicator of DBP formation, UV absorbance at both 254 and 280 nm, is ineffective to apply for AOM-DBP prediction because of the poor sensitivity of UV to AOM samples. The regional fluorescent intensity of EEM, in contrast, has a great potential for predicting AOM-DBP formation because of its effectiveness, rapid method, and cost-effective. Although EEM information is still insufficient to predict THMs, future work can use EEM techniques in combination with bulk parameters, such as chlorine consumption, or MW properties to increase its predictability to AOM-DBP formation.

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Chapter 4
Application of *Moringa oleifera* Plant in Water Treatment

Tetsuji Okuda and Eman N. Ali

Abstract *Moringa oleifera* is a tropical plant that is native to India. The extractant from *M. oleifera* seeds can be used for water treatment, because coagulation-active components are contained in the seeds. *M. oleifera* coagulant (MOC) is traditionally extracted with water and used for the treatment of turbid water. Recently, many studies have been focused on revealing its practical application and improving its coagulation activity, including those on MOC purification or heavy metal removal by MOC. MOC has the potential for use in drinking water and wastewater treatment, especially in tropical regions.

Keywords Coagulation · Extraction · Flocculation · *Moringa oleifera* Water treatment

4.1 Introduction

Coagulation is a major technology for water treatment, and many kinds of coagulants are used in conventional water treatment processes for tap water production, wastewater treatment, and water recycling. These coagulants can be classified mainly into inorganic coagulants, synthetic organic polymers, and natural coagulants. The inorganic polymer "polyaluminum chloride (PAC)" is widely used in water treatment, especially in Japan, and the inorganic salts "aluminum sulfate (alum)" and ferric chloride, which are other famous coagulants used worldwide (Kumar et al. 2012). Synthetic organic polymers, such as polyacrylamide and its copolymer with other monomers, are widely used, especially in water treatment (Mallevialle et al. 1984).

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Natural coagulants have been demanded and studied for use in water treatment because of their low cost and safety. Coagulants containing Al or Fe as the main component remain in water treatment residuals (WTRs). WTRs are reused and recycled for various purposes, of which reuse on farmland is an important one. Al or Fe in the coagulants can combine with phosphoric acid, which is added to the soil as a nutrient, and produce $AlPO_4$ or $FePO_4$, essentially inhibiting the nutrient function in the field. This may lead to some difficulty in the acceptance of WTR recycling on farmland and would be a reason why natural coagulants should be paid greater attention.

Some famous natural coagulants are chitosan (Gassara et al. 2015; Zonoozi et al. 2011) and alginic acid (Maryam et al. 2014). Plant materials, e.g., seeds, also have been studied in order to develop natural coagulants. Among the plant materials that have been studied are *Pisum sativum* (Rajamohan et al. 2018), common oak acorn (Antov et al. 2018), *Durio zibethinus* (Suffian et al. 2018), *Jatropha curcas* (Abidin et al. 2017), *Ocimum basilicum* (Sorour et al. 2015), and *Cassia obtusifolia* (Yee and Yeong 2014). *Moringa oleifera* is a tropical plant that contains a coagulation-active component in its seeds. In a review paper written by Dr. Mustapha Hassan Bichi (Bichi 2013), the use of *M. oleifera* as a coagulant/flocculant in water treatment is well summarized. He wrote that the use of *M. oleifera* seeds for domestic household water treatment has been traditionally known in certain rural areas in Sudan and that one of the best-known uses in West Asia for *M. oleifera* is using its powdered seeds to flocculate contaminants and purify drinking water.

The *M. oleifera* tree, seedpod, and seeds before and after being shelled are shown in Fig. 4.1. *M. oleifera* belongs to the family of Moringaceae, which contains only a single genus of shrubs. The occurrence of *M. oleifera* is summarized in the review paper by Bichi (2013). As *M. oleifera* is found in nature and does not receive harmful synthetic or other treatments, even when it is not used correctly in coagulation, leading to an overdose of the natural substance, no adverse effects on public health are expected in the case of slight overdosage. In addition, given its organic nature, coagulant sludge generated through *M. oleifera* coagulation is likely safer for use as animal feed or plant fertilizer. *M. oleifera* is a fast-growth tree, commonly found in semiarid, tropical, and subtropical areas including India, South and Central America, Africa, and Southeast Asia (Olsen 1987; Jahn 1988). Thus, *M. oleifera* coagulation is a pragmatic option for providing access to safe drinking water to rural communities in developing countries worldwide, which is the Sustainable Development Goals (SDGs: “sustainable water management” in it).

M. oleifera seeds contain dimeric cationic proteins, which can be extracted from the seeds using water or a salt solution. This *M. oleifera* extract can then be used for coagulation applications. Coagulation with the *M. oleifera* extract is effective for turbidity removal, especially for highly turbid water, meaning *M. oleifera* extract can be used as a coagulant (*M. oleifera* coagulant: MOC). For example, previous studies demonstrated that water-extracted MOC achieved more than 60% removal of turbidity for highly turbid surface waters, i.e., up to 750 NTU (Bichi 2013). As described in the literature, attempts have been made to enhance the coagulation activity of MOCs, including via solvent changes and different purification processes

Tree

Pod

Seeds
(without (left) and with (right) shell)

Fig. 4.1 Images of a *Moringa oleifera* tree, pods, and seeds

in order to remove unnecessary organics. Some of this research, including that carried out by the authors, is introduced and summarized in this review paper.

4.2 Historical Coagulation/Flocculation Via *Moringa oleifera*

4.2.1 Coagulation/Flocculation Via Moringa oleifera *Seed*

Several studies have been done on the performance of *M. oleifera* seeds as an alternative coagulant or coagulant aid. Earlier studies recommended the use of *M. oleifera* seed extracts as coagulants for water treatment in African and South

Asian countries where this plant is considered indigenous (Bichi 2013; Olsen 1987). If MOCs become widely used in drinking water and wastewater treatment in other countries as well, *M. oleifera* may become a cash product, bringing more economic benefits for the producing countries.

Ndacigengesere and Narasiah (Ndacigengesere and Narasiah 1996) have studied turbidity removal by water-extracted MOC as the primary coagulant in the first stage of MOC research, and the result was up to 80–99% removal for both raw waters and synthetic turbid waters. For the application of MOC, coagulation of target materials by MOC has been investigated. Unlike inorganic turbid materials, organic suspended solids such as bacteria, algae, and organic matter were difficult targets for coagulation. Sengupta et al. (2012) reported the removal of helminth eggs from irrigation water, turbid water, wastewater, and tap water by water (tap water)-extracted MOC. Margarida et al. (2017) aimed to develop a water treatment sequence using MOC combined with an activated carbon in order to remove *Microcystis aeruginosa* and natural organic matter through an integrated process. They demonstrated higher than 80% removal of *M. aeruginosa* cells from water with 150–200 μg/L of chlorophyll *a* (indicates the algae amount), with water-extracted MOC removing them by the combination of coagulation/flocculation and dissolved air flotation (DAF) processes. MOCs has been applied in the removal of dyes, surfactants, perfluorooctane sulfonate (PFOS), and perfluorooctanoate (PFOA), too (Beltran-Heredia et al. 2009; Beltran-Heredia and Sanchez-Martin 2009; Kumar et al. 2015). For dye removal, the influences of coagulation pH, temperature, and initial dye concentration have also been tested by using the Langmuir isotherm model fitting. The ability of water-extracted MOC to remove an anionic surfactant, sodium lauryl sulfate, has been evaluated, with up to 80% removal observed via the coagulation/flocculation process. pH and temperature were found to be not very important factors in this removal efficiency, unlike the dye removal. PFOS and PFOA are persistent organic pollutants, and their occurrence in the environment can cause toxicological effects to humans. The removal efficiency of these compounds by water-extracted MOC was investigated and compared with those of alum and ferric chloride. Kumar et al. (2015) reported that water-extracted MOC was more effective in reducing PFOS and PFOA than the conventional inorganic coagulants, with reduction efficiencies up to 65 and 72%, respectively. Kumar et al. also tried a combination of activated carbon and MOC for removal as like Margarida et al. (2017). This significantly increased removal efficiency, with the maximum removal efficiencies reported as 98 and 94% for PFOS and PFOA, respectively, with low-dose MOC (with powder-activated carbon).

Regarding practical application of MOCs, some researchers have checked its coagulation activity, including direct usage of the seed itself, for real surface water and wastewater. Poumaye et al. (2012) dried and transformed into a powder the seeds of *M. oleifera* to clarify the surface water, i.e., the river M'Poko. By using sand/coal filtration with coagulation treatment with MOC seed powder, the turbidity and a quantity of organic matter could be treated to the required standards. Vieira et al. evaluated *M. oleifera* seed with a mixed culture that was used for the biodegradation of hydrocarbons present in the effluent from fuel distribution terminals contaminated with diesel oil and gasoline under different coagulation conditions (Vieira et al. 2012). The biodegradation was evaluated by varying the *M. oleifera* seed concentration, drying temperatures, and seed drying times. They compared *M. oleifera* seed with chitosan, and the results indicated that Chitosan is a superior coagulant compared with *M. oleifera* for the sedimentation.

However, MOCs does not always lead to better coagulation activity. Muyibi and Evison (1995) found that the residual turbidity of samples increased with the decrease in initial turbidity at the optimum dosage of water-extracted MOC. This indicates that water-extracted MOC may not be an efficient coagulant for low turbidity water. It is a problem for the usage of water-extracted MOC for drinking water treatment, because the turbidity of its raw water is usually low, especially in Japan. This is also mentioned by other researchers (Pereira et al. 2017). Pereira et al. mentioned another problem—an increase in the organic matter after coagulation/flocculation with MOCs. Organic matter, especially the dissolved organic carbon (DOC) component of total organic carbon (TOC), is related to biochemical oxidation demand (BOD) and chemical oxidation demand (COD) and can cause undesired colors and odors of the water. This increase is a classical problem with treated water, which is likely caused by unnecessary components eluted during extraction of the coagulation active components from the seeds, as Beltrán-Heredia et al. mentioned (Beltrán-Heredia et al. 2012).

There is a possibility that these problems can be solved by improving the method for extracting the coagulation-active components from the *M. oleifera* seeds or purification method for them. These developments are necessary for the wide use of MOCs, not only for drinking water treatment but also for other water treatment processes.

4.2.2 Isolation and Improvement in Extraction of Coagulation Active Components

The coagulation active components of water-extracted MOC were found to be soluble cationic proteins with molecular weight of about 13 kDa isoelectric with a pH value of 10–11 (Ndacigengesere et al. 1995). The amino acid sequences of this protein were revealed by Gassenschmidt et al. (1991, 1995). These studies were conducted in 1990; however, the coagulation proteins present in *M. oleifera* seeds and their characterization have been investigated recently as well. As an example, Alves et al. (2017) reported that globulin and albumin were the highest protein fractions in *M. oleifera* seeds with 53 and 44%, respectively. By using protein profile analysis, Bodlund I. et al. discovered that the major protein bands had molecular weights of around 6.5 and 9.0 kDa, respectively (Bodlund et al. 2013).

Based on the scientific information about coagulation-active components in *M. oleifera* seeds, trials to improve extraction of these components would be a reasonable development in order to improve the coagulation activity of MOCs. As an example, our research group found a better solvent for the extraction. To improve the coagulation-active components, we used a salt solution, because Olsen reported that ethanol, hexane, methanol, and acetone could not improve the extraction of the coagulation active component (Olsen 1987). It was well known that the solubility of proteins increases with salt concentration at low salt ionic strength owing to the decrease in mutual association of protein molecules by shielding with the salt molecules (White et al. 1968; Voet and Voet 1990). Because the active component for coagulation in water-extracted MOC is a protein (Gassenschmidt et al. 1991, 1995), it was possible that its solubility could be enhanced by the salt solution, thus improving the coagulation activity of MOCs. Therefore, we tried some salt solutions as a solvent to improve the extraction of the active component. The results led us to the following conclusions, which were reported in Okuda et al. (1999). First, extraction with 1.0 mol/L NaCl solution enhanced the coagulation activity of MOC. Second, the MOC extracted with NaCl solution (salt-extracted MOC) achieved seven times lower turbidity of a kaolin solution than conventional MOC extracted with distilled water could, as shown in Fig. 4.2. Third, salt-extracted MOC was an effective coagulant, with a greater than 95% decrease in the 50 NTU initial turbidity of kaolin using only 4 mL/L, whereas 32 mL/L of water-extracted MOC was necessary for only a 78% turbidity decrease. In Japan, turbidity standard is 2 mg/L for drinking water, so only salt-extracted MOC could archived this level in this experiment. The active component extracted with the salt solution was not the same as that extracted with water; its molecular weight was found to be about 3 kDa by Okuda et al. (2001a). Other research groups confirmed these results. For example, Madrona et al. revealed the coagulation properties and potential for the MOC extracted by a KCl solution (Madrona et al. 2010). Following our research Okuda et al. (2001a), other extractants, including other salt solutions and tap water, were used as the extraction solvent for the improvement of MOCs activity in some studies, in which better results compared to those with distilled water were found. Here, alum could reduce residual turbidity less than 1 mg/L at around 2 mg-Al/L without the increase of residual DOC.

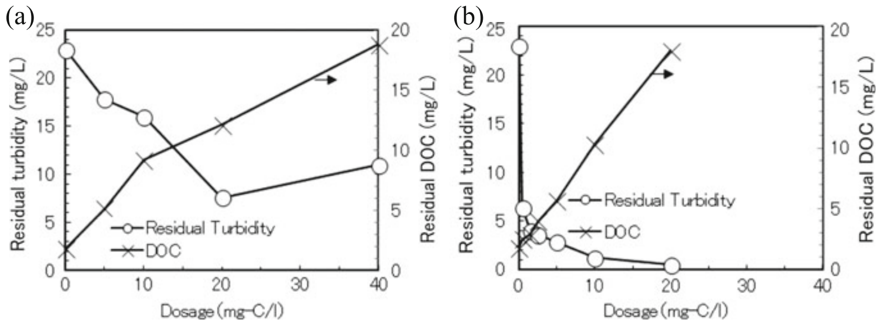


Fig. 4.2 Coagulation activity and residual DOC for two kinds of MOC (in a 50 mg/L kaolin solution at pH 7). **a** Water-extracted MOC. **b** Salt-extracted MOC (1 M NaCl)

Even in salt-extracted MOC, the problem of increasing residual organic matter still exists. As shown in Fig. 4.2, salt-extracted MOC could decrease the residual DOC from 20 mg-C/L (water-extracted MOC) to 2 mg-C/L at the dosage of MOC for around 7 mg/L of residual turbidity. For example, the standard of TOC (total organic carbon), similar to DOC in treated water, is 3 mg/L in Japan, salt-extracted MOC could meet this standard with turbidity removal. In addition to the research on improving the extraction solvents, the coagulation activity between species of *Moringa* (*Moringa stenopetala* and *M. oleifera*) was compared in order to find coagulation-active components with higher performance. Dalvand et al. compared the efficiency of *M. stenopetala seed coagulant* (*MSC*) with that of alum, and they found that a salt-extracted MSC-alum hybrid coagulant could remove a dye (Direct Red 23 azo dye) from textile wastewater. Moreover, a ninhydrin test was used to determine the quantity of primary amines in the salt-extracted MSC and salt-extracted MOC, which showed that salt-extracted MSC was much more effective than salt-extracted MOC for the dye removal (Dalvand et al. 2016).

4.2.3 Purification of Active Components from Crude Extractant

MOCs are problematic for real application, as mentioned at Sect. 4.2.1, because of the increase of organic matter in treated water, which likely is caused by unnecessary components in MOC. To remove these components from salt-extracted MOC, Ghebremichael et al. tried purification using ion exchange. They discussed the chemical characteristics, coagulation, and antimicrobial properties of purified MOC (p-MOC) (Ghebremichael et al. 2005). Dezfooli et al. reported that coagulant proteins from *M. oleifera* seeds could be purified by removing the seed oil followed by a protein salting out method with 40% $(NH_4)_2SO_4$ combined with subsequent dialysis and heat treatment (Dezfooli et al. 2016). In another study, Baptista et al. reported the efficiency of ultrafiltration for MOC (Baptista et al. 2015). They used surface water for the evaluation of salt-extracted MOC performance, and better performance in the removal of color (89%), turbidity (89%), compounds with UV254 nm absorbance (76%), and SUVA (62%) was achieved by using this p-MOC purified by membrane filtration. This same research group developed another method for active component purification, i.e., the fractionation of proteins. With it, 87% removal of color, 90% removal of turbidity, and 79% removal of UV254 nm were achieved using 13 mg/L of the globulin coagulant from *M. oleifera* seeds for treatment of low turbidity water (50 NTU) without leading to an excessive increase in the DOC of the treated water (Alves et al. 2017).

Regarding purification, our research group also tried to isolate the active coagulation component in the salt-extracted MOC and established a method for such (Okuda et al. 2001a, b). In that study, the active component was isolated (purified) from salt-extracted MOC through a sequence of steps that included salting out via dialysis, removal of lipids and carbohydrates via homogenization with acetone, and fractionation via anion exchange (Fig. 4.3) by using DOC concentration and coagulation activity as indicators. After the ion exchange fractionation based on carbon concentration, one fraction eluted at 0.3 M NaCl gradient had high coagulation activity (peak 2 in Fig. 4.3, coagulation activity was calculated as like Eq. 4.1). Specific coagulation activity of the active components (ratio of DOC to MOC dosage) in this fraction was much higher than the crude extract (salt-extracted MOC). The active component was not the same as that of the water-extracted MOC; its molecular weight was only about 3 kDa.

$$\text{Coagulation Activity} = (\text{RT}_{\text{blank}} - \text{RT}_{\text{sample}})/\text{RT}_{\text{blank}} \tag{4.1}$$

In our related research, the coagulation mechanism of the p-MOC was also studied, which seemed to involve an enmeshment by the insoluble matters formed from the coagulation-active component. Other coagulation mechanisms such as double-layer compression (Fig. 4.4), interparticle bridging, and charge neutralization were not responsible for the coagulation by the salt-extracted p-MOC based on zeta potential and molecular weight analysis. The formation of insoluble matter was affected by bivalent cations, such as Ca^{2+}, which may connect each active component molecule in the salt-extracted p-MOC to form the net-like structure shown in Fig. 4.5.

Based on the isolation and identification of the active component of salt-extracted MOC, a simple purification method was developed over a series of studies. The two-step purification consisting of (1) acetone washing of powdered

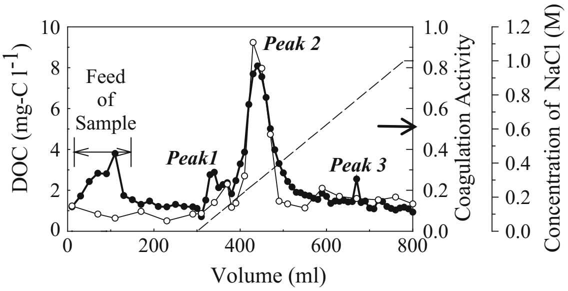


Fig. 4.3 Anion exchange chromatogram of pre-purified salt-extracted MOC. Open circles show coagulation activities, closed circles show DOC, and the dashed line shows the NaCl gradient (Okuda et al. 2001a)

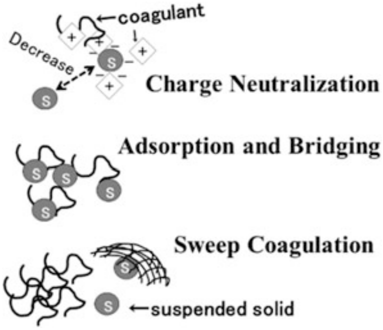


Fig. 4.4 The three types of major coagulation mechanisms

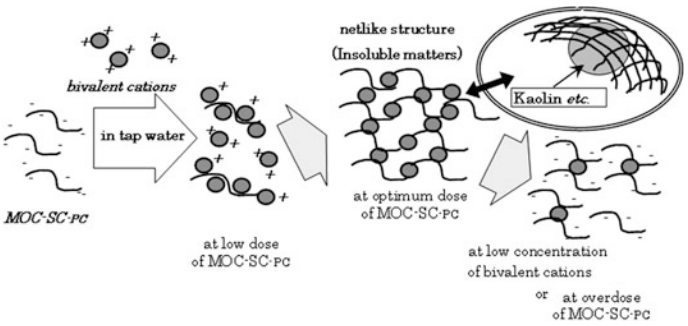
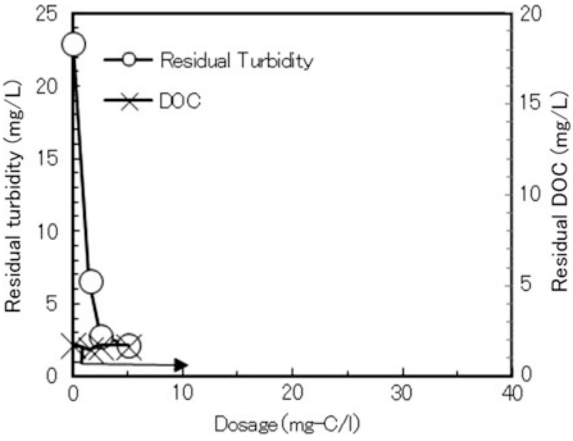


Fig. 4.5 Model for the coagulation mechanism by salt-extracted p-MOC (Okuda et al. 2001b)

Fig. 4.6 Coagulation activity and residual DOC of p-MOC (in 50 mg/L kaolin solution at pH 7)



active components insolubilized by sedimentation via dialysis and (2) their re-dissolution in NaCl solution was established as a practical purification method for salt-extracted MOC. The coagulation activity and residual DOC of this practical p-MOC are shown in Fig. 4.6. It can be seen that no residual DOC increases by keeping high coagulation activity was obtained at low carbon dosage to compare with salt-extracted MOC before purification, as shown in Fig. 4.2. This indicates that the method consisting of dialysis and re-dissolution was enough to prevent DOC from increasing in water treated via coagulation. We believe that this research was a stepping stone for other researches on the purification of MOCs.

To decrease the contamination by unnecessary components of MOC, not only the purification of the extracted solution was evaluated in our recent study, but also the pretreatment of the seed powder. Figure 4.7 shows the effect of prewashing time (washed with 100 mL distilled water per 1 g of seed powder at 5 °C) on the coagulation activity of salt-extracted MOC (extracted with 100 mL 0.3 M NaCl solution per 1 g of prewashed seeds), with oil-extracted (cold press method) seed powder used in this experiment. The coagulation activity (ratio of turbidity

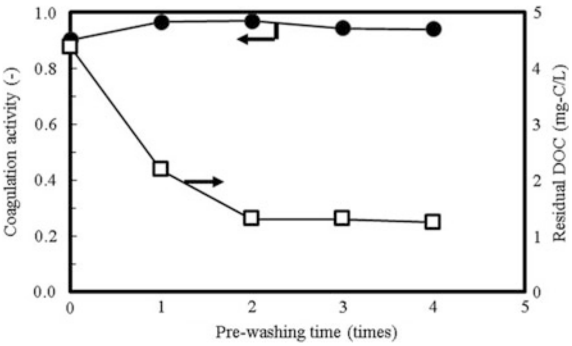


Fig. 4.7 Effect of prewashing (100 mL distilled water for 1 g seed powder at 5 °C) on coagulation activity of salt-extracted MOC (0.3 M NaCl extraction)

decreases against it in coagulation experiment without MOC) and residual DOC of the treated water are shown in Fig. 4.7. The DOC of the initial turbid water (kaolin solution with tap water) was 0.9 mg/L, and 50–60% of residual DOC could be reduced with two rounds of distilled water prewashing of the seed powder while maintaining high coagulation activity. Two rounds of prewashing seemed to be the best, as some decrease in coagulation activity was observed after three rounds of prewashing. This was due to the extraction of some coagulation-active components via prewashing. In that study, the optimum temperature and volume of distilled water for prewashing were also investigated, but no significant difference was observed in these conditions (data not shown).

4.3 Studies for Practical Use

4.3.1 Evaluation for Real Water Treatment Systems

For real-use application, it is necessary to compare the capacity and coagulation properties of MOCs to those of traditional coagulants, such as aluminum sulfate (alum). Arnoldsson et al. investigated the optimum coagulant dosage for different levels of turbidity using water-extracted MOC combined with direct rapid sand filtration after coagulation (Arnoldsson et al. 2008). They showed that coagulation with alum led to treatment that was more efficient than that with water-extracted MOC although prolonged sedimentation was necessary for the MOC to produce water of acceptable quality (WHO water guidelines). In contrast, it is mentioned that the treatment with water-extracted MOC did not change the chemistry of the treated water in their experiments. They concluded that water treatment with water-extracted MOC is a sustainable solution for coagulation in drinking water treatment. MOCs were compared with alum in other studies (Okuda et al. 1999; Madrona et al. 2010).

For the cost perspective, the direct use of seed powder for water treatment was studied in further trials for a real application. Our research group conducted one

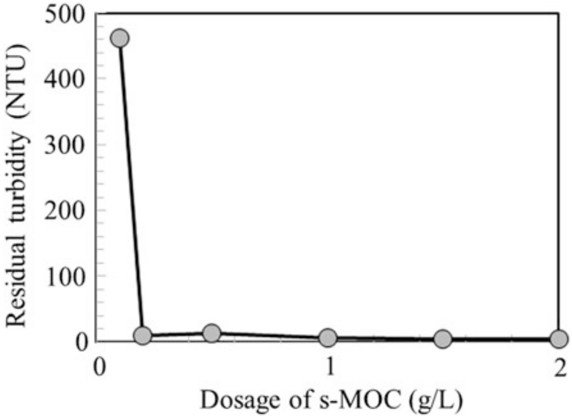


Fig. 4.8 Coagulation activity of s-MOC

such trial by using a slurry of the cake that remains after oil extraction from *M. oleifera* seeds (s-MOC), and its results are being introduced. *M. oleifera* seeds were shelled (dehusked) and grinded into powder for the oil extraction process. The oil in the seed powder was removed via Soxhlet extraction using n-hexane as the solvent for three cycles of extraction and then dried overnight in an oven at 50 °C. Oil extraction is recommended as a method for purifying water-extracted MOC, as well. Samples from the Sungai baluk river, Pahang, Malaysia, of 500 mL were placed in 500 mL beakers, and jar testing was conducted with rapid mixing of 200 rpm for 2 min, 40 rpm for 25 min, and sedimentation for 1 h. Figure 4.8 shows the comparison between the dosage of s-MOC and turbidity. The lowest turbidity value was 4.7 NTU with 1.5 g/L of s-MOC. In this method, coagulation components in seeds were extracted by sample water itself after its addition, then the extracted components would act as a coagulant. There is a possibility that some part of s-MOC remained in the supernatant and contributed residual turbidity; however, the effect was small in this experiment.

4.3.2 Additional Target Materials

For more understanding, identification, and improvement of MOCs activity for some potential treatment, targets (contaminants in water) are also important for real application of MOCs, meaning “What can MOC treat?” and “What can be removed with a concurrent decrease in turbidity?”

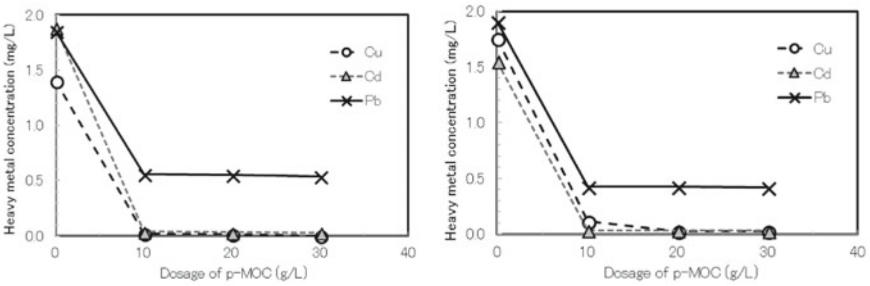
There is a difficulty in coagulation for organic particle removal, as mentioned above. Therefore, instead of its removal ability, Ghebremichael et al. investigated the coagulation and antibacterial activity of p-MOC (Ghebremichael et al. 2005). The p-MOC showed not only enough flocculating ability, but also some antibacterial effects with 1.1–4.0 log reduction of bacteria. Other reports showed that MOC prevents the growth of coliforms and pathogens (Santos et al. 2012) and bacteria

(Shan et al. 2017), and that the treatment using MOC could be met for some disinfection requirements (Srivastava 2014; Jabeen et al. 2008). Even treated water rarely is completely free of germs, so it is important to prevent the growth of microorganisms (Amagloh and Benang 2009). Our research group found that MOCs also helped to remove dirt, solid particles, and even some bacteria and fungi (Bina et al. 2010; Eman et al. 2014). In that work, filtration was not conducted during the extraction stage; rather, the suspension (slurry) of oil-free s-MOC (10–30 g/L) was used to treat the Sungai baluk river and wastewater samples. There was coagulation activity (85–94% turbidity removal) in the jar test operated with an initial speed of 150 rpm for 2 min. In addition, s-MOC helped to prevent the growth of microorganisms. The concentration of bacteria was reduced to 7.5×10^4 from 1.7×10^5 CFU/mL in river water and to 1.0×10^4 from 1.1×10^6 CFU/mL in wastewater (Shan et al. 2017) (Table 4.1).

Coagulation of dissolved targets is difficult, but it is possible that target materials are adsorbed by flocs and removed with them via sedimentation or filtration. Santos et al. tried to remove humic acids from water by using salt-extracted MOC (extracted with 0.15 M NaCl) (Santos et al. 2012). Treatment with a low salt-extracted MOC concentration removed humic acids from water, and the extract dosage determined in the study does not impart untoward odor or color to the treated water. It is most difficult to remove soluble inorganic materials such as heavy metals. We reported on heavy metal removal via direct use of *M. oleifera* seed, s-MOC (Shan et al. 2017). The wastewater samples were collected from the Sungai baluk river. s-MOC was prepared by immersing cake residue, which is seeds residue by removing oil into the distilled water, and different concentrations of s-MOC were used for the jar test. The initial and final heavy metal (Cu, Cd, and Pb) concentrations were measured, and the removal percentages were calculated. The removal of heavy metals increased proportionally with s-MOC dosage until optimum removal was achieved. s-MOC showed high efficiency in the removal of heavy metals from the Sungai baluk river samples, up to 98% Cu and Cd successfully removed. Pb was also reduced by up to 78% (Fig. 4.9). It is possible that heavy metals were removed via coagulation, which includes adsorption onto flocs produced, but it is also possible the seeds themselves absorbed them. This biosorption would become an alternative technique for heavy metals removal from water with combination of coagulation/flocculation.

Table 4.1 Effect of s-MOC concentration on the bacterial abundance of river and wastewater samples (Shan et al. 2017)

s-MOC (g/L)	Bacterial number (CFU/mL)	
	River water	Wastewater
0	1.7×10^5	1.1×10^6
10	9.5×10^4	2.1×10^5
20	8.6×10^4	9.7×10^4
30	7.5×10^4	1.0×10^4



River water wastewater

Fig. 4.9 Effect of different concentrations of s-MOC on heavy metal removal from Sungai baluk river and wastewater samples (Shan et al. 2017)

4.3.3 *Water Softening and Disinfection*

Water softening means to decrease the hardness of water, which is caused by ions in water, typically those of calcium and magnesium. Water-extracted MOC shows potential as a softening agent, as evidenced by Muyibi and Evison (1995). They analyzed 17 water samples from hand-dug wells and found that water-extracted MOC can reduce residual hardness, the process of which is influenced by water-extracted MOC dosage and the hardness components, i.e., "calcium only" or "calcium and magnesium". They also found that the absorption isotherm for softening with water-extracted MOC was linear and of approximately the Langmuir type.

4.3.4 *Novel Studies*

Some challenging and progressive approaches based on coagulation/flocculation with MOCs also were tried to exploit those substances. Santos et al. (2016) evaluated the effectiveness of the coagulation/flocculation using *M. oleifera* functionalized with magnetic iron oxide nanoparticles, which produced flakes that are attracted by an external magnetic field, thereby allowing fast settling and separation of the clarified liquid. The magnetic functionalized MOC could effectively remove 90% of turbidity, 85% of apparent color, and 50% of the compounds with absorption at UV254 nm from surface waters under the influence of an external magnetic field for 30 min. Then, the coagulation/flocculation treatment using magnetic functionalized MOC. Coagulant was able to reduce the values of the physicochemical parameters evaluated with reduced settling time.

The combination with other new technologies is also interesting. Our research group tries to use salt-extracted MOC as a pretreatment of membrane filtration to prevent membrane fouling as an application study for drinking water treatment based on past research (Katayon et al. 2007). In our novel research, coagulation was conducted for the removal of turbidity prior to each microfiltration experiment. Microfiltration treatment of river water without pretreatment resulted in a rapid increase in transmembrane pressure (TMP; an indicator of membrane fouling) from 12 to 24 kPa within three filtration cycles (60 min per cycle), including interval backwashing with clean water without pre-coagulation. Coagulation with salt-extracted MOC performed prior to micro-filtration effectively reduced membrane fouling (1–3 mL-MOC/L), with a significant reduction in membrane fouling observed (based on TMP). The fouling mitigation by salt-extracted MOC pre-coagulation was maximized with a 2 mL/L dosage, which resulted in only an increase in TMP from 12.0 to 12.4 kPa over three filtration cycles. It is possible that unnecessary DOC increased the TMP at dosages higher than 2 mL/L. This indicates that a sufficient level of membrane fouling mitigation in micro-filtration can be achieved via salt-extracted MOC pre-coagulation, even TMP increase could be more prevented by pre-coagulation with alum. It is possible that some increase in TMP (fouling) was caused by MOCs itself (data not shown).

4.4 Conclusions

The basics of application of *M. oleifera* seed for water treatment have been studied and increasingly developed in the past 20–30 years, in particular, in the areas of extraction improvement, extract purification, and scientific interest, such as the isolation of active component.

Target materials in raw water, not only “turbidity” but also others, and effect of raw water quality on them in coagulation/flocculation using *M. oleifera* seed have been energetically revealed in recently.

The most of problem for its real utilization and the usage combined with other novel technologies has been studied.

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Chapter 5
Phytoremediation Strategies on Heavy Metal Removal

Myilsamy Dineshkumar, Muthulingam Seenuvasan and Gopalakrishanan Sarojini

Abstract Over many decades, treatment and reuse of wastewater has been a key research area for environmentalists. Scientists have succeeded in the usage of wastewater for agricultural purposes. However, the discharge of effluent from the industries led to a constant increase in effluent concentration and adversely affects the health of human, plants, and animals. Phytoremediation is one of the wastewater treatment technologies used to eradicate the contaminants from marine and soil environment without disturbing the environment. The ability of plants roots to accumulate, translocate, and degrade the contaminants from environment plays a major role in phytoremediation process. Phytoremediation follows mainly five mechanisms which are phytoextraction, phytostabilization, phytodegradation, phytovolatilization, and phytofiltration. Aquatic or terrestrial plants are used to accumulate, immobilize, or degrade the contaminants from air, soil, and water. It is an inexpensive technique and it could be applied to large contaminated areas without any significant damage to environment. Treatment of contaminated site would take long period is one of the few limitations to overcome. Chelating agents are used to enhance the accumulation ability of plants. Inorganic chelating agents are more aggressive and enhance high accumulation of contaminants. To protect the environment and to enhance the accumulation ability of plant, organic acids are used as chelating agents. The success of phytoremediation is determined not only by accumulation ability but also by the bioavailability of contaminants in environment and plant. This chapter discusses the potential mechanisms and strategies available to widen the application of phytoremediation.

Keywords Phytoremediation · Heavy metals · Ethylenediaminetetraacetic acid (EDTA) · Chelating agent

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5.1 Introduction

The quality of life in today’s world is based on the environmental conditions we live. However, desolately, the quality of life is coping up with the economical progress of the society. This uneven transition puts our generation and the future generations into jeopardy. In the name of economic development, all the natural resources are being exhausted. Due to this scenario; many researchers have done research on the environmental problem.

Environmental pollution is classified into two types namely, natural and man-made. Earthquakes, flooding, tsunami, hill fire, lightning, and falling of meteors come under the natural pollution. Due to the fact that it happens at uneven timings and in large areas such pollutions cannot be controlled easily. Releasing of untreated effluents, dumping solid waste without safety steps, etc., is known as manmade pollution. This kind of pollution can be controlled easily by strictly regulating the permissible limits of effluent discharge to the environment. If not controlled and once it exceeds the threshold capacity, it will take a very long time to reduce or remove the contaminants from the environment for the comfortable life of human beings and other living organisms.

Untreated industrial effluents contain heavy metals such as mercury, lead, manganese, cadmium, chromium, cobalt, copper, nickel, selenium, silver, antimony, thallium, mercury, arsenic, zinc and they cannot be removed easily. These heavy metals are essential for living organisms but higher concentrations can cause catastrophic to the environment. So, the complete removal of heavy metal from environment is challenging and novel method must be developed because of the drawbacks in conventional effluent treatment methods (Carolin et al. 2017;

Table 5.1 Advantages and disadvantages of conventional methods (Carolin et al. 2017)

Conventional methods	Advantages	Disadvantages
Chemical precipitation	Simple and economically viable	Sludge production and process associated with sludge disposal
Coagulation–flocculation	Easy to operate, high performance in removing suspended solids	Sludge production and process associated with sludge disposal
Dissolved air flotation	inexpensive, shorter hydraulic retention time	Less efficiency as successive operations needs to be carried out for better results.
Ion exchange	Eco-friendly, less time consuming	Expensive, not suitable for all metal ions
Ultrafiltration	Require less area	Expensive, frequent maintenance is required
Nanofiltration	Easy to operate, high rejection rate	Expensive, frequent maintenance is required
Reverse osmosis	Able to withstand high operating conditions	Expensive, frequent maintenance is required

SanmugaPriya and Senthamil Selvan 2017; Mehta et al. 2015; Ganzenko et al. 2014; Luo et al. 2014; Anbalagan et al. 2016) (Table 5.1).

5.1.1 Phytoremediation

The word phytoremediation is a combination of a Greek and a Latin word. The word “phyto” means “plant” in Greek and “remedium” means “to cure” in Latin. Plants which are used to remove contaminants from soil are called phytoremediant and the process is known as phytoremediation. These plants are able to uptake, stabilize, and degenerate the contaminants present in the environment. Due to its eco-friendly technique, hyperaccumulator plants have benefited over the other treatment methodologies.

Phytoremediation is a promising and novel technology for removal/treatment of heavy metals from contaminated sites. In this method, plants are being allowed to grow in contaminated sites and harvested after a certain period of time (Das and Mazumdar 2016). Accumulated plants are harvested/removed from the contaminant soil/aquatic region. It is a green technology approach as no other by-products are formed during the period of the cleaning the heavy metal contaminated sites (Saha et al. 2017). Several researchers have identified phytoremediation of heavy metals would be a feasible technology to eradicate toxic metal ions from the environment without affecting the same.

It is evident that few heavy metals play an important role in human and plants life. Metal ions such as manganese, copper, zinc, nickel, cobalt, etc., play an important role in the growth of plant, photosynthesis, DNA transcription, hydrolysis of urea, etc., (Bokhari et al. 2016). As metal ions are closely associated/ bound with the other essential ions, some plants accumulate such metal ions, even though it is nonessential. Cadmium (Cd), Chromium (Cr), Lead (Pb), Cobalt (Co), silver (Ag), selenium (Se), mercury (Hg), etc., are some of the common metal ions that have been accumulated by the plants during its lifetime (Romero-Hernández et al. 2017). Excessive accumulation of such metal ions by the plants become toxic or alters its metabolic activities. However, some plants are able to withstand such toxic conditions by accumulating them and thrive on such contaminated sites and are called metallophytes (Chattopadhyay et al. 2012). These plants are an integral part of biodiversity to maintain the eco balance and have the ability to widespread in the region (Queiroz et al. 2017; Zhou et al. 2016). Some plants have the ability to accumulate metal ions 100 times greater than that of “normal” plants growing in the same environment and are called as hyperaccumulators. Till date, 500 plant species from 45 plant families have been found to be hyperaccumulators. Due to extensive research in this area, a number of metal-hyperaccumulating species are undeniably set to increase (García-Mercadoa et al. 2017; Riaz et al. 2017; Hatami et al. 2016). However, the practical difficulties in phytoremediation process are limiting the extensive application in the removal of pollutants from contaminated sites.

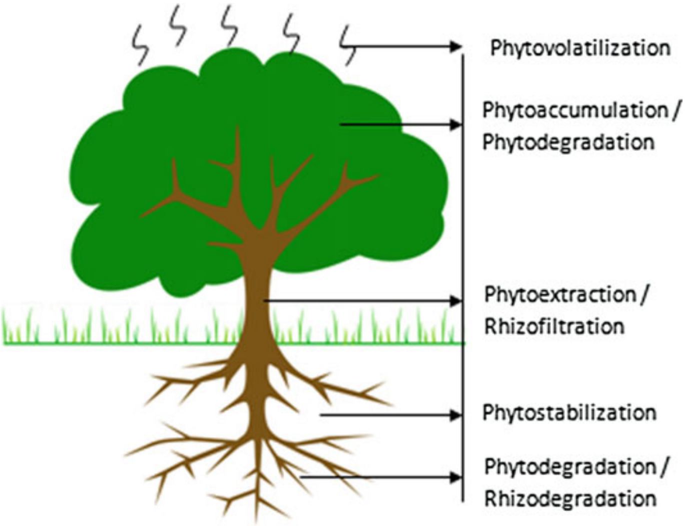

Fig. 5.1 Phytoremediation techniques (Carolin et al. 2017)

Phytoremediation is classified into five distinct types (Fig. 5.1) based on their process of reacting with the heavy metals in soil and water. In this review, the classification of phytoremediation process and their effect on the various heavy metals contaminated environment will be discussed.

5.1.1.1 Phytoextraction

Extraction of contaminants from soil and aquatic bodies through root is called phytoextraction, also known as phytoaccumulation (Venkatachalam et al. 2017). Phytoextraction is an outstanding technique to eradicate heavy metal contaminants from the environment. In this method, plant accumulates contaminants and translocates into the above ground parts from the below ground parts of the plant. It is a suitable method to remediate toxic contaminants from contaminated sites where the concentrations of contaminants are low. In phytoextracting, two innovative techniques have been developed to optimize the phytoextraction process. They are the following:

- Chelate-assisted phytoextraction, in which artificial/natural chelates are added to increase the mobility and uptake of metal contaminant.
- Continuous phytoextraction depends on the natural ability and continuous harvesting of plant.

In order to achieve this, the plant must hold a large amount of heavy metals ions in their roots and translocate them into above ground parts and produce a large quantity of plant biomass (Rodriguez-Hernandez et al. 2017). Factors such as biomass, growth rate, element specification, tolerance level would play a huge role in phytoextraction process (Chen et al. 2012). However slower growth rate, shallow root system, and small biomass production limit the phytoextraction process. Many hyperaccumulator species have been discovered which results in rising attention toward this technique.

5.1.1.2 Phytofiltration

Contaminants that are accumulated and translocated to upper parts of the body are known as phytofiltration (Verma et al. 2016). Phytofiltration is classified into two types namely, rhizofiltration and blasto filtration. Rhizofiltration is where plant roots are distributed in a contaminated environment and plants are grown from seedlings that are grown in a contaminated environment is called blasto filtration. These methods participate in the treatment of heavy metals by concentrating toxic metals from effluents to the plant. Blasto filtration is more advantageous when compared to rhizofiltration (Sung et al. 2015) It is due to that the plants were grown in the contaminated area, the chance of genetical changes is possible unlike the distribution of plant roots and also the increase in surface volume ratio after germination; seedlings tend to ad/absorb large quantities of contaminants (Gao et al. 2014). The mechanism of phytofiltration for different metals is not the same as another. Biological characteristics are important due to their tendency to slow the remediation process, translocating ability from root to shoot parts of the plants (Gomes et al. 2017). Both terrestrial and aquatic plant roots absorb contaminants from the contaminated environment.

5.1.1.3 Phytovolatilization

It is found that the plants convert metal ions into volatile matter with less toxicity and releases it into the environment. This method is called as phytovolatilization. In this process, plants uptake the contaminants from soil and aquatic bodies, transforming them into volatile compounds and release into the atmosphere. It is done by the biomethylating the contaminants to form volatile molecules (Deng et al. 2012). These contaminants are transferred to leaves and volatilize into atmosphere at relatively low concentrations. This technique is primarily used in the removal of mercury. Toxic ions are transformed into lesser toxic compounds when it is transpirated into atmosphere (Deng et al. 2012). It is found to be successful in the reducing the toxicity of selenium by transforming into dimethyl selenide (Deng et al. 2012).

5.1.1.4 Phytostabilization

In this method, pollutants were immobilized by the plants, which is known as phytorestoration. In most cases, pollutants were displaced due to water erosion and by blockage that enables hydraulic control that restricts the vertical migration of pollutants into groundwater. Phytostabilization is mostly used in the treatment of contamination present in soil, sediment, and sludges (Singh et al. 2006). This method mainly focuses on plants which are poor translocators since the upper part of the body is consumed by humans or animals. The pollutants were immobilized physically and chemically by the root sorption and chemical fixation with different soil amendments (Singh et al. 2016) This process mainly depends upon the bioavailability of contaminants and the ability of root to accumulate (Sidhu et al. 2017). Plants with dense root are more preferable as they control soil erosion. The process stabilizes the metal ions by sorption, precipitation, complex action, or metal valence reduction (Anudechakul et al. 2015). The main purpose of the plant is to reduce and retain the amount of metal ions passing through the soil by water flow. It results in a reduction of distribution of contaminants to other areas. It is effectual in order to protect water and soil characteristics of a large ground. The major disadvantage of phytostabilization is the contaminants remain in soil and necessity of continuous monitoring is a must.

5.1.1.5 Phytodegradation

It is a breakdown of organic/inorganic contaminants into simpler molecules where the plant is able to accumulate and incorporate them into their tissues. In this process, plant metabolism contributes to the transformation, break down, stabilization, or volatilizing of contaminant compounds from soil and groundwater (Ramakrishnan et al. 2010). Enzymes such as dehalogenases, oxygenases, and reductases play a major role in breaking the contaminants and convert them into wastes, chlorinated solvents (Singh et al. 2006). Microorganism such as yeast, fungi, bacteria, etc., in the soil contribute to the reduction and degradation of heavy metal contamination by consuming solvents. This is called rhizodegradation (Saxena and Saiful-Arfeen 2009; Sinha and Saxena 2006). It is a slower process compared to phytodegradation.

Phytoremediation techniques are not limited but the technologies could be used simultaneously to eradicate contamination from the environment. Heavy metal extraction mainly depends on its bioavailability.

5.1.2 Plant Response to Heavy Metals

Based on accumulation and resistance toward contaminants, it has been classified into three types. They are as follows:

5.1.2.1 Excluders

Plants that resist contaminants entering into aerial parts, maintain low concentration over high concentration of contaminants in soil. These plants restrict contaminants in their roots and alter its membrane permeability, metal binding capacity of cell walls, or exude more chelating substances to exclude contaminants (Zurayk et al. 2001).

5.1.2.2 Indicators

Plants species that actively accumulate metal in their aerial tissues and indicates the contaminant level in the soil is called as indicators. Such plants are tolerant to the toxicity of contaminants by synthesizing intracellular metal binding compounds (chelators) and utilize the contaminant compartmentalization technique for storing metals in the nonsensitive part (Zurayk et al. 2001).

5.1.2.3 Accumulators

Plants accumulate high concentration of metals in the aboveground plant parts compared to the concentration of contaminants in soil. Accumulators do not prevent metals from entering the roots and thus allow bioaccumulation of high concentration of metals (Zurayk et al. 2001) (Table 5.2).

Table 5.2 Lower limit of hyperaccumulator plants known for various heavy metals element (Hatami et al. 2016; Venkatachalam et al. 2017; Rodriguez-Hernandez et al. 2017; Chen et al. 2012; Verma et al. 2016; Gomes et al. 2017; Deng et al. 2012; Singh et al. 2006, 2016 ; Sidhu et al. 2017)

Metal ions	Hyperaccumulation lower limit (mg/l)	Hyperaccumulators
Ar	1000	*Brassicaceae, Peraceae*
Cd	100	*Brassicaceae, Asteraceae, Chenopodiaceae*
Co	300	*Lamiaceae, Scrophulariaceae*
Cu	300	*Cyperaceae, Lamiaceae, Brassicaceae, Poaceae, Scrophulariaceae*
Au	1	*Brassicaceae*
Pb	100	*Compositae, Brassicaceae*
Mn	10000	*Apocynaceae, Cunoniaceae, Proteaceae*
Ni	1000	*Brassicaceae, Cunoniaceae, Proteaceae*
Se	100	*Fabaceae, Brassicaceae*
Ag	1	*Brassicaceae*
Ti	100	*Brassicaceae*
U	1000	*Brassicaceae*
Z	3000	*Brassicaceae, Crassulaceae, Leguminosae*

5.1.3 Ecology of Metal Hyperaccumulation

Hyperaccumulation of metal ions by the plants tend to change its physiochemical and metabolic activities. Due to this ability, hyperaccumulator species have few advantages if the following propositions are convened (Verma et al. 2016):

- Ability to accumulate and impound the nonessential metal ions into shoot parts and tolerate the toxicity of metal ions. Also, these plants remove/dispose such ions from its system detaching its parts (leaves, branches, etc.,).
- Plant species is able to stabilize the metal ions in their respective root parts of the system. Due to this, the soil is enriched by the resisting the behavior of plants.
- Drought resistance makes hyperaccumulators plants to withstand any significant conditions.
- Accumulation of metal ions by the plants led to the protection of hyperaccumulator plants as the metal ions are translocated into root and shoot parts and resist the consumption by herbivores.

Although these propositions are not applicable to plants and metal ions, it provides an ecological context for phytoremediation studies of hyperaccumulators.

5.2 Factors Affecting Phytoremediation

This topic discusses the factors influencing and restricting the efficiency of the plant to accumulate metal ions and provides some alternative methods to enhance the phytoremediation efficiency in order to obtain a large and wider commercial application. The desirable characteristics of a plant species for successful phytoremediation are the following:

- adaptability to environment/sites
- distributed root system to cover large soil volumes,
- rapid growth and high biomass,
- tolerant to high concentrations of metals in plant tissues,
- high translocation factor,
- easy discarding of waste

However, the plant with all the above characteristics mentioned are difficult to uncover. Few prime factors (Fig. 5.2) play an important role in phytoremediation. Few hyperaccumulator plants have the ability to accumulate high concentration of heavy metals but its low biomass and ability to uptake 2–4 metal ions at a time restrict them to use in large-scale application. Similarly, high biomass-yielding

Fig. 5.2 Factors affecting phytoremediation process

plant species absorbs numerous heavy metal ions but is limited to lower concentrations. Irrespective of the biomass, availability of metal ions in the environment to plant roots is an important key factor in the optimization of phytoremediation. Also, the availability of metal ions would be high, only if the metal ions are present in soluble form (Table 5.3).

Few hyperaccumulator plants have the ability to accumulate high concentration of heavy metals but its low biomass and ability to uptake 2–4 metal ions at a time restricts them for use in large-scale application. Similarly, high biomass-yielding plant species absorbs numerous heavy metal ions but is limited to lower concentrations. Irrespective of biomass, availability of metal ions in the environment to plant roots is an important key factor in the optimization of phytoremediation. Also, the availability of metal ions would be high, only if the metal ions are present in soluble form.

Table 5.3 Physicochemical factors known to affect the heavy metal uptake, accumulation, and toxicity of ions (Pal et al. 2010; Luo et al. 2014)

Parameter	Effect
Temperature	More uptake/toxicity at higher temperatures
Light	Uptake is light dependent in some cases
pH	Lower pH generally increases the uptake/capacity
Salinity monovalent cations	Lower salinity increases the content/toxicity
Divalent cations	Increasing monovalent cations reduces the uptake
Divalent anions	Increasing divalent cations reduces the uptake
Nitrate(N)	Significantly reduces toxicity
Selenite(Se)	Tends to reduce metal uptake and toxicity
Sulfate	Insignificant but reduces uptake slightly
Sulfur (amino acids)	Reduces uptake and toxicity indirectly
Extracellular products	Reduces toxicity
Organic acids	Reduces uptake and toxicity
Polysaccharides	Chelate metals, reduces uptake/toxicity
Polypeptides	Reduces uptake/toxicity by complexation
Sediment fraction	Binds metals, reduces uptake/toxicity
Suspended solids	Complex metals, reduces uptake/toxicity
Heavy metals	Reduces uptake/toxicity by binding metals Complex metals, reduces uptake/toxicity Zn/Cd, Ni, Cu combinations are antagonistic. Fe can stimulate Cu accumulation

5.2.1 *Bioavailability of Heavy Metals*

Availability of metal ions in the form of the solution is the primary requirement for phytoremediation process. Plants can only extract if the metal ions are in suitable soluble fraction form. Based upon the availability of metal ions and metal fraction form, metal fractions are classified into available, unavailable, and exchangeable fractions. Free metal ions and soluble metal complexes could be accumulated by the plant at ion exchange sites. However, the metal fractions chemically bound to organic matter, precipitated as oxides, hydroxides, and carbonates and entrenched with silicate minerals are very difficult to be accumulated by the plant.

Once bioavailable heavy metal fractions are reduced due to plant uptake, they would be supplied from unavailable fractions. When bioavailable heavy metal fractions increase owing to input from external surroundings, some bioavailable and exchangeable fractions can change into unavailable fractions as a result. It is due to the external disturbance such as environmental conditions, accumulation, organic chelation, or the fluctuations in temperature and moisture. It is understood that the available metal is proportional to the metal concentration in soil solution rather than the total metal concentration in bulk soil. Heavy metals such as Zn and Cd are readily available, but in case of Pb it occurs as soil precipitates which are a less bioavailable form for accumulation.

5.3 Soil-Associated Factors Influencing Metal Bioavailability

5.3.1 Soil Type

Quality of soil plays a role in the bioavailability of metal ions. In general, a high concentration of heavy metal can be retained in fine-textured soils such as clay and clay loam compared to coarse-textured soils such as sand.

5.3.2 Soil Moisture

Usually, high metal accumulation takes place at higher soil moisture conditions. Also, plants will have larger biomass at such conditions which result in higher accumulation of metal ions from the environment. Many researchers have found that the hyperaccumulator plants grow well under high soil moisture contents and the biomass of all the tested species is found to be increased. At lower soil moisture contents, the biomass and growth of the plants are inhibited (Jain et al. 2017).

5.3.3 Soil pH

The decrease in pH leads to an increase in H^+ ions that causes an increase in the concentrations of soil solution. The exchangeable capacity between heavy metal cations and H^+ adsorbed on the surface of soil particles will increase after pH decreases. Thus, at lower pH, large quantities of heavy metal ions are desorbed from the surface of colloids and clay mineral particles and enter into soil solution (Jain et al. 2017). Soil pH not only affects the bioavailability metal ions but also has an effect on accumulation by roots. At lower pH, heavy metals act as cations and become more soluble while anions become more soluble at higher pH due to sorption on the soil. It is been found that lowering pH increases the uptake of Zn, Mn, and Co but reduces the uptake of Ni. Increase in pH reduces the uptake of Zn, Mn, and Co, but increases Ni accumulation. In general, soil pH is reduced by acidification using concentrated sulphuric acid and by application of soil nutrients which includes the addition of organic and chemical fertilizers. The addition of soil nutrients not only decreases soil pH but also increases soil fertility. It is known that the growths of most plants are hindered if the soil pH is <4. It is due to the toxicity of soluble aluminum (Al) and/or calcium (Ca) and magnesium (Mg) deficiency. It is understood that soil pH must not inhibit the growth of the plant. It is better to employ acid-resistant hyperaccumulator plants are valuable in remediating contaminants (Sheoran et al. 2016).

5.3.4 Redox Potential (Eh)

The redox potential of the soil is a measure of the tendency of the solution to accept or donate electrons. The mobility of metallic contaminants depends strongly on the oxidation states. Metals such as technetium (Tc), chromium (Cr), uranium (U), and plutonium (Pu) exhibit multiple oxidation states of which the reduced forms are quite insoluble in water and the oxidized forms are highly soluble. An increase in soil organic material can also decrease soil Eh. The method of regulating soil Eh can be conducted by farming techniques such as solar drying, intermittent irrigation of paddy fields, and crop rotation between paddy and dry fields (Sheoran et al. 2016).

5.3.5 Cation Exchange Capacity (CEC)

Soil CEC is the ability of a soil to retain metal ions. The CEC increases with increasing clay content in the soil. Higher CEC leads to greater sorption and immobilization of metals; while the lower CEC leads to an increase in availability of metals in soil. Under acidic conditions, H^+ ions displace metal cations from cation exchange complex of soil components and cause metals to be released from clays in which they have been adsorbed (Sheoran et al. 2016).

5.4 Plant-Associated Factors Influencing Metal Bioavailability

Plant-associated factors include plant root depth, root density, rhizospheric processes at root zone including various microorganisms (fungi and bacteria), root-induced changes in pH of the rhizosphere, increased root reducing capacity, quantity and composition of root exudates (organic acids), and environmental conditions that govern the translocation of metals from root to shoot (Table 5.4).

Table 5.4 Availability of metals as per their type of associations (Sheoran et al. 2016)

Type of metal association	Availability of metal
Exchangeable metals	High
Metals associated with Fe–Mn oxides	Medium
Metals associated with organic matter	Medium or high depending on time of decomposition/ oxidation of organic matter
Metals fixed in crystalline phase	Low, only after weathering or decomposition

5.4.1 Plant Root Depth and Density

The amount of metal accumulating by plants is root dependent. In general, most of the plants' root density decreases with increasing depth. Hence, selected plants should have sufficient root density and depth to cover a large area for treatment. Root absorption factor is also affected by rhizobiological activity, root exudate, temperature, moisture, pH, concentration of competing ions, and metal concentration in soil solution.

5.4.2 Transpiration Rate

The uptake of soil solution from the root zone is translocated into stems and leaves which is called as transpiration. Higher metal concentrations in roots are due to the precipitation of metal migration nearer to the root zone. As transpiration rate is also climate dependent, the plants will suck up less water during winter months in midlatitude climates. In summer, plants transpire large amounts of water to facilitate photosynthesis which causes an increase in the concentration level. It is also understood that the total amount of metal that accumulates in the plant roots is not usually equal to the soluble metal concentration in the soil.

5.4.3 Chelating Agent

To induce metal accumulation in plants even under low availability, one alternative approach is to use chelating agents. These chelating agents have influences in metal accumulation, biomagnifications of metal ions, and translocation of metal ions toward shoots (Bhargava et al. 2012). In recent years, the availability of organic and synthetic chelating agents has been widely studied and used in the field of phytoremediation process (Zhang et al. 2007). Ethylenediamine tetraacetic acid (EDTA), ethylenediamine disuccinate (EDDS), low-molecular-weight organic acids (LMWOA), humic substances (HSs) and nitrilotriacetic acid (NTA) are some of the organic chelates which help in the phytoremediation process by increasing the vacant sites in the plants functional groups using organic ligands (Zhang et al. 2007). Among these chelators, the EDTA is a strong chelator for metal ions which influences the chemical speciation, mobility, solubility, and bioavailability of metal ions in the soil solution phase for the accumulation of plants by roots (Ebrahimi 2016). Application of EDTA in the treatment was found to be an effective and efficient ligand in solubilizing complex metal ions. With the application and usage of EDTA in remediation, techniques, knowledge, and factors behind the EDTA-enhanced metal phytoextraction is in need of constant evaluation to understand the consequences of the process. Metal ions' entrance into root is not the only method to determine uptake and translocation rate. Also, the mechanism behind the accumulation of the presence of EDTA needs to be clearly explained. So, the continuous studies and assessment will help to improve the performance of phytoremediation.

Presence of EDTA in the treatment led to the formation of metal-EDTA complex, which encourages the metal accumulation into plant roots (Shahid et al. 2014). At first, metal-EDTA complex smoothens the progress of metal ions to diffusion into plant roots. It causes the EDTA-metal complex to break down to form the increase the meal ions concentration in the soil which ultimately causes the plants root system to uptake. Secondly, due to neutral charge, metal-EDTA complex are not blocked and attached by any carboxyl or polysaccharides functional groups in the rhizodermis cell surface. In this way, EDTA helps the metal ions to enter directly into the plant roots.

Even though the presence of EDTA in the phytoremediation process increases the accumulation and translocation of metal ions from contaminated sites, it could have few drawbacks. Also, it has been reported that the presence of EDTA is toxic to microbial and soil enzymatic activities (Ebrahimi 2016). Also, it affects the physiochemical properties of soil and aquatic region by forming a complex mineral structure in soil/water solution. As the EDTA and metal-EDTA complexes are nonbiodegradable with the continuous presence of contaminants and EDTA availability will continue to be present in the soil for several weeks or months. Therefore, the continuous presence of EDTA led to the negative impact in the environmental aspects and affects the soil.

5.5 Aquatic Plants in Phytoremediation Studies

Macrophytes are aquatic plants growing in the marine region. It is classified into three different types based on their existing condition namely: emergent, submerged, and floating. Even though macrophytes are known as aquatic plants, it is specifically meant for aquatic vegetation. Littoral region is a region where marine and terrestrial region coexist (river or lake shore). Aquatic plants or macrophytes are usually grown in the littoral region. Macrophytes grown in the shallower region (<1 m) are found to be rich in nutrients. It is by consuming the resources available in the terrestrial and marine region. Presence of abundant carbon dioxide and oxygen in the aquatic surface led to higher growth in plants in underwater. Non-rooted floating macrophytes (angiosperms, ferns, and some liverworts) are smaller in size; possess a rapid distribution in the water bodies. It sporadically takes over water bodies with their rapid distribution. Water depths of 1–3 m, there is a zone in the lower littoral of floating-leaved vegetation, plants growing in this region have firm roots extended to the leaves which is floating in the water bodies by long flexible petioles.

5.5.1 Classification of Macrophytes (Saha et al. 2017)

- **Aquatic macrophytes**—These plants are grown in the shallow water region with vegetative parts/leaves above the water surface for photosynthetic activities, roots in the rock/soil emerging from the stratum and such macrophytes are fruitful as they make the best use of all three possible states (sediments/rock, water, atmospheric air).
- **Emergent macrophytes**—Aquatic plants which grown under submerged soils of water bodies with the roots of such plants are distributed at the depth of 0.5 m.
- **Floating-leaves macrophytes**—Plants which grown under submerged soils of water bodies at the depths of 0.5–3 m. Aerial parts of such aquatic plants act as reproductive organs and floating leaves attached to flexible petioles to flutter in the wind (e.g., the *Nuphar*, *Nymphea*, *Braseniam*, and *Potamogetonnatans*).
- **Submerged macrophytes**—Plants whose roots are submerged into the sediments of >3 m is known as submerged macrophytes. It is also often called as pteridophytes and charophytes.
- **Free-floating macrophytes**—Macrophytes are non-rooted to the substratum but grown in the aquatic bodies with the root unattached to water. Such plants have long shoots, floating leaves, and well-developed submerged roots (e.g., *Eichhornia, Trapa, Hydrocharis*), minute surface floating or submerged plants with few or no roots (e.g., *Lemnaceae, Azolla, Salvinia*).

Water hyacinth (*Eichhornia crassipes*); pennywort (*Hydrocotyle umbellate L*); duckweeds (*Lemna minor L.*), water velvet (*Azolla pinnata*) have the ability to eradicate heavy metals by uptaking/accumulating them into root and shoot parts and volatilize them into atmosphere as less harmful ions. *Eichhornia crassipes* is a renowned aquatic plant in the application of wastewater treatment by accumulating toxic metal ions through roots and eradicate such ions by metabolic process. It is documented that metal ions such as Cd, Pb, Fe, Mg, Mn, Ar, Cr, etc., are found to be removed effectively by *Eichhornia crassipes, Lemna minor,* and *Azolla pinnata.*

5.5.2 Advantages in the Use of Aquatic Macrophytes

Macrophytes have the ability to uptake nutrients from aquatic bodies directly and incorporated them into their body. In addition to the accumulation of such contaminants or toxic ions, plants are able to degrade, destabilize, volatilize them into less toxic ions making the environment much cleanlier compared to the conventional methods. Treatment of such contaminated terrestrial/aquatic bodies seems to be more attractive.

In the phytoremediation process, aquatic plants which accumulate heavy metal ions should be harvested periodically to increase the process. The proper management and disposal of such biomass is a challenging task. Hence, various strategies are employed by the researchers and entrepreneurs to utilize the waste biomass into a valuable product. Consequently, it led to an increase in the application of phytoremediant treatment. Usually, aquatic plants biomass is employed in the field of fodder, bioenergy, and fertilizer production and paper manufacturing. It has been reported that even though these methods are feasible, it is very difficult to employ when considering the economy, time, and space required. Like most terrestrial plants, aquatic macrophytes posses sugar resources in the form of carbohydrate polymers, including cellulose, hemicellulose, and starch which can be fermented for the production of ethanol, lactic acid, and other valuable fermented products as a result of carbohydrate hydrolysis. Production of such fermented products is a cheaper and alternative option with a high source of income from plant biomass. Studies indicate that various chemicals have been used to find the optimum enzymatic hydrolysis. Alkaline/oxidative (A/O) pretreatment is one such method where sodium hydroxide and hydrogen peroxide are used to improve the enzymatic hydrolysis of *Pistia stratiotes L.* and *Eichhornia crassipes*. It is found that the *Pistia stratiotes L.* is more efficient (1.8 times) in the enzymatic hydrolysis process compared to *Eichhornia crassipes*. It is understood that the large amounts of polysaccharides (cellulose and hemicellulose) in roots produce less amount of monosaccharides compared to other parts of the plant.

Inorganic feed additives are characterized by low bioavailability and high toxicity. Also, organic feed additives are used, including amino acids chelates, in which bioavailability was greatly improved and toxicity was reduced. However, these products are still expensive (the cost is 10 times higher than inorganic salts). ICP-OES multielemental analysis has been used to investigate the process of production of mineral feed additives based on the biomass of *Lemna minor*, and the competence in the processes of accumulation of metal ions by L. minor was studied which demonstrated its potential as animal feed.

5.6 Limitations

Success of phytoremediation mainly depends on the growth rate, biomass, bioavailability of metal ions, and accumulation ability of plants (Ling et al. 2017; Falusi et al. 2016). However, the major disadvantage in phytoremediation process is that the time required to remediate contaminated site is higher than the conventional technologies. Since the period of remediation is high, it poses a serious concern to human as well as the ecological cycle (Sarathambal et al. 2017). A large amount of biomass produced from phytoremediation process may take too much time to incinerate and requires enormous land to landfill. It is known that the excessive presence of heavy metal concentration leads to the inhibition of plant growth and controls the efficiency of remediation (Feng et al. 2017). Despite being an eco-friendly technique, many researchers are working toward overcoming such difficulties to obtain better phytoremediation.

5.7 Utilization of Biomass

The rapid growth of population and consumer demands led to the massive growth in industries to fulfill the needs. At the same time, adequate supply of important metal ions such as platinum, gold, palladium, silver put major demands on electronic, pharmaceutical, and other related industries (Ojoawo et al. 2015). However, pollution and exploitation by these process industries to meet the consumer needs, affected large areas of aquatic and terrestrial region. Consequently, the situation forces the researchers/scientists to work toward an alternative and cleaner approach to overcome this hurdle. Dealing of exploiting natural resources will be discussed briefly in the relevant chapter. Recovery of such metal ions from industrial waste is carried out by many methods such as absorption, precipitation, filtration, and biological techniques. However, these conventional methods are economically not feasible, have high operating and maintenance cost, disturb ecosystem and sludge disposal. Phytoremediation provides a reliable and eco-friendly approach with less expensive and reduced labor cost in the bio-recovery of some precious metal ions from industrial wastes. Due to the synergistic effects of microbes, aquatic plants tend to accumulate, translocate and incorporate metal ions in its system which led to ease the environmental concerns.

Presence of functional groups, such as carbonyl, carboxyl, hydroxyl, etc., and the chemical composition of proteins in plant tissues provide multiple sites for the assimilation of metal ions. Due to a massive rise in pollution, many countries make strict laws against industries which release huge wastes to the environment and. Several laws were passed to reduce greenhouse gas emissions and induce the sustainable energy development. Biofuel is a promising renewable fuel which limits the exhaust gas; it degrades into a nontoxic manner compared to the conventional one and addresses the requirement of green energy. Bio-refinery technology plays an important role in the development of the future commercial transportation. Although biomass from different feedstock posses different properties, the production of bioenergy have been developed through many methods and tested to be more cost-effective. Therefore, choosing a feedstock with high-quality properties of bioenergy production is an important aspect. Many hyperaccumulator plants could be used in the production of biofuel.

5.8 Biodiversity Prospecting and Genetic Diversity Conservation

Plants, microorganism available in the biodiversity offer several opportunities to treat industrial wastes. As the treatment of industrial waste by conventional methods has some difficulties, the prospect of biological methods has led to saving a variety of ecosystems. Phytoaccumulators could clean polluted sites and the successive studies in the field of phytoremediation led to the discovery of various plant species that have the ability to accumulate the contaminants. Even though the technology is in the developing stage, this method has a great commercial application toward the treatment. To achieve this feat, some inducing agents or gene therapy will be introduced to the plants to enhance the metal tolerance and accumulation ability. This genetic modification in the plants influences the chemical interactions between metal ions and functional groups present in the plant systems, increase the chelating activities, alters the accumulation rate, translocation, and storage. A significant approach has been identified in recent years to enhance the metal tolerance and metal binding properties of plants by over-expressing metal binding peptides such as glutathione (GSH) or phytochelatins (PCs). Genetic engineering is one of the important aspects of study to protect the endangered genera of macrophytes as major wetlands are destroyed by rapid industrialization and anthropogenic activities. Such studies are in the earlier stage to maintain and a certain level of existing genetics in plants species, which are exceptional for phytoremediation process or produces high biomass but low accumulation rate or threatened to danger of extinction. Also, the plants which are grown under the polluted sites have genetic variation and possess the ability to tolerate toxic metal ions in the contaminated site (Table 5.5).

Table 5.5 Aim of genetic engineering (Shahid et al. 2014)

To enhance	To encode
Metal tolerance and translocation	Change in oxidation state metals
Plant growth and biomass	Metal transporters and chelators
Microbial activity	Metal sequestration proteins (MTs and PCs)
Root exudates and secretions	Transport proteins (ZIP family, ZnT family, etc.)

5.9 Conclusion

In recent years, enormous research has been anticipated in the removal of contaminants from the environment. Many advanced technologies such as adsorption, oxidation, and membrane processes have been introduced in the removal of contaminants. Expensive to operate, by-product formation, technical difficulty, etc., are some the major drawbacks in conventional methods. Application of plants in treating industrial wastes is a cheaper and eco-friendly approach. Since this method is gaining interest since the past decade, to understand better, a detailed study is need to be carried out on both aquatic and terrestrial plants and regions. Another important factor to induce the accumulation is by the application of chelating agent in the treatment. Genetic modifications of plants are more encouraging for obtaining higher accumulation and translocation rate. Also, few plants have high biomass production rate but low accumulation rate and vice versa. To overcome this hurdle genetic modification in plants are more preferred to remove the contaminants in polluted sites. It led to the discovery of new genes to tackle the issue of environmental cleanup. These transgenic plants are more superior to the naturally available hyperaccumulator plants in tolerance, enhanced metal accumulation, translocation, and compartmentalization. Researches also need to be carried out in the production of biomass with many utilized products can be derived. Since phytoremediation process is in the budding stage, extensive research is required for a longer period of time but also possess a greater opportunity if the technique is applied commercially in large scale.

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Chapter 6
Membrane Technologies for the Treatment of Pharmaceutical Industry Wastewater

Ankush, Mrinal Kanti Mandal, Manisha Sharma, Khushboo, Shailesh Pandey and Kashyap Kumar Dubey

Abstract In course of past few years, pharmaceutical industries have huge contribution in the economic development of the country, but concurrently the pharmaceutical pollutants can also be responsible for severe hazards to the environment. Traditional methods of wastewater treatment cannot erase these pollutants from the water due to their hostile behavior. The advent of the pharmaceutical pollutants leads a demand for assessment and depiction of the wastewater discharged from the pharmaceutical industry as per the norms recommended by the official agency (Pollution Control Board). Vast number of treatment strategies are adapted by the pharmaceutical industries to reuse wastewater and regulate environmental pollution. In this chapter, we mainly focus on the finest membrane based methodologies to abolish the pharmaceutical compounds. At present, no individual technology has the potential to expel out the pharmaceutical pollutants from wastewater. Merging of traditional methods with membrane reactors leads to the best hybrid wastewater treatment technology.

Keywords Pharmaceutical pollutant · Reverse osmosis · Nanofiltration
Microfiltration · Ultrafiltration and MBR

6.1 Introduction

In the present days, the disease burdens are increasing due to anti-microbial resistance (AMC), with regards to this the market of antibiotics, drugs, and other pharmaceutical compounds are also growing. So, the release of these pharmaceu-

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tical active compounds (PhACs) in the water sources is major concern for the public health (Jayasiri et al. 2013). Pharmaceutical compounds are synthesized stepwise through Smf and SSF, extraction, chemical synthesis, formulation, and packaging (Ince et al. 2002). Among them, chemical synthesis as well as fermentation process results in the production of wastewater with high concentration of solvents, rebellious organic compounds, and salts as well (Chen et al. 2008). Researches have been performed various method to analyze the concentration of PhACs and its removal in various water sources (Li and Randak 2009). But, the current approaches for the wastewater treatment are not suitable for the removal of these contaminants. The European Union Water Framework Directive tallies some PhACs in the major pollutants agenda in 2014. In this framework, we should focus on the eradication of these PhACs from wastewater including the organic matter. Conventionally, physical separations, chemical transformation, and physicochemical as well as biological approaches are recommended for the treatment of wastewater generated from pharmaceutical industries. The aerobic and anaerobic biological processes are quite excellent choice for the treatment of pharmaceutical wastewater due to commercial benefits of latest treatment method. The high solubility of these compounds in wastewater in turn release to nearby water sources and the presence of these PhACs have a negative impact on human as well as on the environment (Li and Randak 2009) (Fig. 6.1).

Pharmaceutical wastewater contains a huge amount of organic pollutants, biotoxic, and saline compounds. According to Cetecioglu et al. (2015), the pharmaceutical wastewater contains a high amount of chemical oxygen demand (COD) [4410–40,000 mg/L] with huge concentration of nitrogenous compounds (Cetecioglu et al. 2015; Shi et al. 2014). The behavior of dissolved organic nitrogen (DON) restricts the efficiency of biological treatment (Hu et al. 2017). The high concentration of saline is a major hindrance in the wastewater treatment due to change in osmotic potential across the membrane (Shi et al. 2015). The

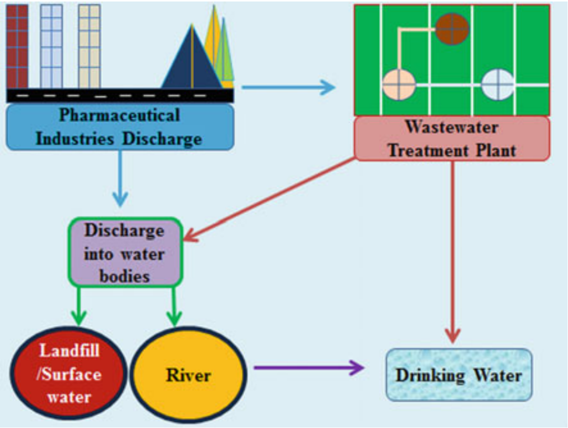

Fig. 6.1 Occurrence of pharmaceutical compound in water environment

antimicrobial action of the antibiotics also restricts the removal of PhACs from water via biological treatment (Aydin 2016).

In the era of advanced technologies, the membrane processes are recommended for the treatment of wastewater due to high efficiency for removal of organic pollutant (Lee et al. 2008). Membrane bioreactors (MBRs) are profusely used for the removal of PhACs from wastewater because of specific assets over the conventional methods. The MBR is perfect for the removal of organic as well as inorganic impurities from wastewater. The MBR has become prominent due to the draconian legislation of the environment and the reuse of water is flourishing in the present situation (Cicek 2003).

In spite of several advantages, the major challenge is that the filtration processes are not constructed to vitiate the pollutants from wastewater. Moreover, the non-degraded pollutants get accumulated (fouling) on the permeable side of membrane as a result of which the outcome of the process would be decreased (Kim et al. 2008a). Due to various concern and failure of conventional system, research is required to understand all the issues related to the removal of PhACs with membrane technologies.

6.2 Membrane Processes for the Removal of PhACs

The aided wastewater via the conventional methods may be reused for a number of operations or may be discharged in surroundings but that water may still hold an ample amount of unwanted compounds like plasticizers, pharmaceuticals, pesticides, by-products of detergents, etc. The filtration process of almost all the membranes is dependent on the pore size (Martina Hamingerova and Beckmann 2010). The separation of chemical contaminants from the wastewater is an eternal area of the target with the obligation of directive extent. The eradication process of the sighted components via polymeric membrane relegated to a number of factors like physicochemical properties, kind of membrane as well as practical situations (Van der Bruggen et al. 2008).

Execution of the membranes is enhancing at a very fast rate for the water treatment. Low-pressure membranes are suitable for the eviction of microbial contaminants devoid of enhancing disinfection vintage (Snyder et al. 2007). RO performs substantial function as pretreatment process for the desalination or to reuse water (Kimura et al. 2005). In case of space restriction or arbitrary water quality, MF or UF are firmly endorsed (Adham et al. 2005). Generally, NF and UF are used for the augmentation of wastewater as well as to remove micropollutants. The researchers studied that NF membrane holds more EDC/PPCPs as compared to UF, entailing that holding ability depends on membrane pore size. A number of studies indicated that RO and NF are the better option for the efficient elimination of substantial pharmaceutical compounds. But the further analysis of the resulting concentrate is required to remove the retenate.

Membrane distillation is a very crucial technique for the demineralization of water with provocative properties (Gryta 2012, Hausmann et al. 2011). Yet, very elegant water is provided by the membrane distillation process but fouling of membrane is extensive problem of this technique.

On the basis of membrane architecture, membrane composition, driving force, and the process of separation along with size of constituents to be evacuated, the membrane processes can be allocated in various grades. Mainly, four types of membranes explored for wastewater treatment which are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) (Martina Hamingerova and Beckmann 2010, Tchobanoglous et al. 2013).

6.2.1 Microfiltration and Ultrafiltration Membrane Processes

The researchers studied a number of membranes along with MF, UF, RO, NF, electrodialysis reversal, MBRs, etc. and their utilization for the eradication of PhACs at pilot scale as well as commercial level. The pore size of MF and UF generally varies from 100 to 1000 times greater than a micropollutant, that iss why the UF and MF are not frequently used for the removal of organic contaminants. The membrane processes based on applied pressure like NF and RO have drawn the attention of the researchers for the potable water treatment (Deegan et al. 2011). Although the research related to the utilization of RO/NF for the eradication of pharmaceutical compounds is restricted to the tertiary treatment of the water (Yoon et al. 2006). According to Deegan et al. (2011), the UF with differential symmetry can be utilized for the eviction of pharmaceutical personal care products (PPCPs, antibiotics, hormones, lipid regulators, etc.

6.2.2 Reverse Osmosis and Nanofiltration-Based Membrane Process

Usually, PhACs have the molecular weight greater than 250 Da and can be removed via membrane technologies. The membrane technologies like RO, UF, and NF are economically beneficial. NF is the currently developed technique based on the principle of derived pressure to separate the compounds and its utilization is increasing at a very fast rate from the last decade. NF has been used extensively for the eradication of antibiotic compounds from the aqueous system (Sun et al. 2000; Zang et al. 2003). Shahtalebi et al. (2011) studied the eviction of amoxicillin from pharmaceutical wastewater by utilizing NF technique. The eradication of amoxicillin via NF membrane exceeded up to 97% while COD achieved up to 40% elimination.

The complex compounds cognate with organic matter may be evacuated via microfiltration or ultrafiltration (UF). According to Adams et al. (2002), a vast number of antibiotics are removed via RO. The organic compounds with high molecular weight are separated adequately via RO membranes. The use of RO membrane reduces the BOD and COD as far as 98 and 96% respectively, while reduces the TOC up to 96% (Rodriguez et al. 2009). The eviction of organic solutes like PhACs is imperative for the potable reuse of water but the elimination fluctuates between solutes and membranes (Judd 2016). Urtiaga et al. (2013) executed the pilot-scale examination of 12 pharmaceutical compounds exclusion via RO and UF analysis of wastewater discharge. All the analyzed compounds had 99.3% elimination. The researchers also studied the removal of PhACs by utilizing RO and NF techniques in a complete potable water treatment. Maximum number of compounds eliminated up to 85% by RO but a very few were eradicated up to 30–70% (Radjenovic et al. 2008). Some of the micropollutants like 1, 4-dioxane with low molecular weight were not eliminated during high-pressure membrane utilization (Rodriguez et al. 2009). A bulk of compounds has been removed to the level profound to the limit of determination via RO membranes. However, a number of compounds like gemfibrozil musk ketone, meprobamate, pentoxifylline, etc. have been diagnosed in the infiltrate of the RO membrane with differential symmetry. Bellona et al. (2004) explained the possible cause for this, which are short circuiting in the membrane and collapsing of the membrane support. The PhACs can be eradicated via NF and UF membranes on the basis of three parameters like size and charge exclusion and physiochemical interaction between solute, solvent, and membranes (Radjenovic et al. 2007). Amy et al. (2005) described more than 90% eradication of ketoprofen and diclofenac by utilizing NF-90 membranes whereas Kimura et al. (2003) explained 95% eviction of diclofenac via RO membrane utilization. Polar and charged particles can easily be removed via NF/RO approaches because of interaction with membrane (Braeken et al. 2005) (Fig. 6.2).

6.2.3 Membrane Bioreactors

MBR is becoming more prominent from last two decades because of the advancement in the technology as well as high reduction in the cost of the membranes. The economically beneficial nature of MBRs has drawn the attention as an alternative method for the treatment of pharmaceutical wastewater because of immense sludge retention time (SRT) (Radjenovic et al. 2007). MBR system may be organized by two units, i.e., a bioreactor tank with a sidewise membrane module termed as external MBR. In the submerged membrane system, the membrane is arranged inside the bioreactor tank. MBRs propose better retention of sludge with great efficiency and higher compactness. MBRs are unified with some traditional approaches to appreciate the potency of the additives and peculiar strategies like electro-coagulation and advanced oxidation process in contrast to a precise class of pharmaceuticals (Hena and Znad 2018).

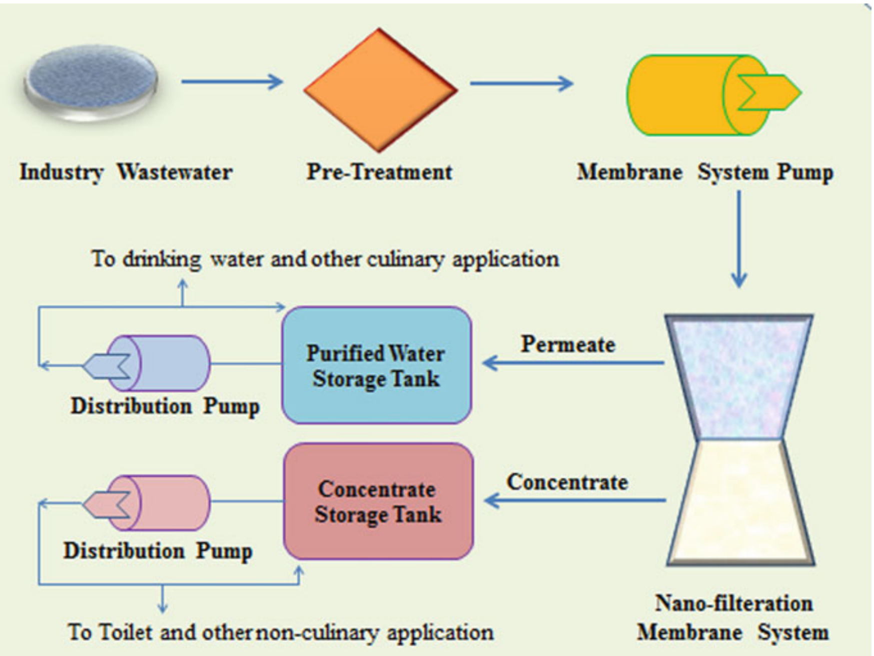

Fig. 6.2 Nanofiltration membrane system for removal of industry wastewater

MBRs eradicate the pharmaceutical compounds via adsorption, eco-friendly degradation, volatilization, and photo-degradation. Eco-friendly degradation is usually followed by polar as well as hydrophilic compounds while the mechanism of adsorption is restricted for these. The nonpolar and hydrophobic compounds get eradicated by sorption mechanism mainly on activated sludge. That is why; retention on the membrane is the central approach for the eviction from the aqueous media (Simpa et al. 2010). The physiochemical properties of the micropollutants, functioning parameters as well as augmenting consequences of MBR regulate the eviction performance of the MBRs. The researchers found that the compounds possessing electron donating functional group like aromatic alcohols, esters, primary amines, nitriles, etc. diminished without any difficulty while the compounds with electron withdrawing functional group like aromatic amines, halides, nitro, etc. (Tadkaew et al. 2011) (Fig. 6.3).

The pH of the wastewater effects the eviction of compounds from WWTPs. The solubility of the pollutants as well as performance of microbes is frequently dependent on the pH of wastewater. The pH from 4.3 to 5 is advised as the most suitable condition for the eradication of micropollutants under the MBRs process (Urase et al. 2005). The removal of some acidic compounds like diclofenac, ketoprofen is considered to be greatly dependent on the pH (Tadkaew et al. 2011). The temperature of the wastewater also controls the eradication of the PhACs in MBRs. The pollutants with hydrophobic nature and strong electron withdrawing

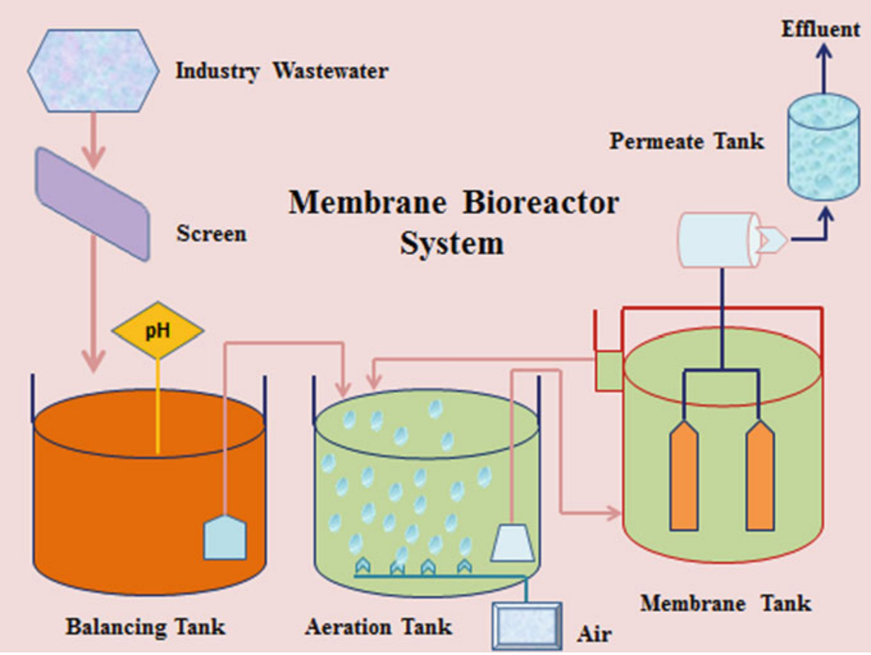

Fig. 6.3 Membrane bioreactor for treatment of pharmaceutical wastewater

group can be evicted more strongly at high temperature, i.e., up to 45 °C. The researcher concluded that the biodegradation of PPCPs is usually inversely proportional to the temperature and therefore, the eradication of micropollutants is favored at the temperature range from moderate to low (Grandclement et al. 2017).

Membrane fouling is the biggest issue related to MBR treatment process where unwanted dethroning of the microorganisms, colloidal particles along with dead cell debris on the membrane surface (Meng et al. 2017). Transmembrane pressure gets increased and permeate flux gets decreased due to membrane fouling. More air is utilized by the MBRs during biological as well as membrane cleaning process as a result of which more energy consumption is there (Hena and Znad 2018).

The concentration of microbes can be escalated up to 20 mg/L. The suspended solid particles can be easily separated by membranes which in turn overcome the limitation related to the settling aspects of the sludge (Urase et al. 2005). The researchers executed coupling of MBR with traditional methods to accomplish the treatment of pharmaceutical wastewater involving antibiotics, anti-inflammatory drugs, analgesics, etc. and achieved 90.4% COD rejection value (Radjenovic et al. 2007). Though, the absolute eradication of all the PhACs cannot be attained via MBR or any other single application. Tambosi et al. (2010) studied that compounds like acetaminophen and ketoprofen had the effective rejection rate in comparison to roxithromycin and sulfamethoxazole showed protraction to the microbial load and were eradicated with lesser intensity. Usually, the confinement of the MF and UF

Table 6.1 Types of membrane processes for pharmaceutical compounds removal on the basis of pore size

S.No.	Membrane processes	Pore size	Particle size range
1	Reverse osmosis	2–7 Å	Atomic/ionic range
2	Electrodialysis	1Å–1 nm	Atomic/ionic range
3	Forward osmosis	2Å–6 nm	Atomic/ionic, low molecular range
4	Nanofiltration	8Å–6 nm	Atomic/ionic, low molecular range
5	Ultrafiltration	6–100 nm	Low molecular, high molecular range
6	Membrane distillation	10 nm–1 μm	High molecular, microparticle range
7	Membrane bioreactor	14–400 nm	High molecular, microparticle range
8	Microfiltration	90 nm–2 μm	Microfiltration

membranes can be spurned. However, the better eradication was attained for greater SRTs. The treatment of wastewater via unification of MBR with UF was moderately successful and that is why the incessant PhACs at low concentration were delivered into the environment with wastewater. The advanced treatment techniques like ozone oxidation, NF, RO, and advanced oxidation process could be used to diminish the effluent. Generally, the membrane processes used to purify the water of pharmaceutical industry are based on the size of pollutants, i.e., is used for the separation of bacteria while for macromolecules and viruses, UF is utilized and NF is used for divalent ions and RO for monovalent ions separation. The elimination efficiency of the contaminants via the secondary treatment can be stimulated at high speed by utilizing advanced techniques as the primary treatment processes. Membrane technology, membrane distillation as well as activated carbon adsorption comes under the advanced treatment methods (Table 6.1).

6.3 Factors Affecting the Eradication Process of Membranes

6.3.1 Role of Hydrophobicity

The eradication of PhACs by NF usually depends on the hydrophobicity of the compounds. Compounds with high hydrophobicity can easily be adsorbed on the membrane surfaces or disseminated into the matrix. Retention of the hydrophobic compounds on the membrane surface leads to great removal but by the time equilibrium of the solutes results in decrease of rejection as compared to the same size of hydrophilic compounds (Verliefde et al. 2007a). At the equilibrium state, to factors, i.e., size exclusion and charge repulsion play key role for the eviction of PhACs (Yoon et al. 2007). According to Braeken et al. (2005), the compounds with hydrophilic properties are dissolved very effectively in aqueous phase, as a result of which their diameter would be larger. As a result, the hydrophilic compounds can easily be eradicated as compared to hydrophobic ones. The electrostatically neutral compound with great hydrophobic nature leads to higher eradication via great adsorption on the membrane (Ganiyu et al. 2015). Log Kow defines the hydrophobicity of nonionizable compounds whereas in case of ionizable compounds it is expressed by log D.

The NF membranes having pore size are large as compared to the membrane with smaller ones which can effectively take the advantage of hydrophobic nature of the compound. Researchers also described that most influential adsorption occurs when the approach of UF is followed by NF/RO membrane. Eradication of neutral as well as positively charged compounds with high hydrophobicity gets reduced on the negatively charged NF membrane because of their great ability to be adsorbed on the surface of the membrane (Taheran et al. 2016).

6.3.2 Role of Electrostatic Interaction

The membrane surface of NF and RO is frequently negatively charged in the neutral solutions due to deprotonation of their functional groups. That is why the PhACs with positive charge get concentrated on the surface of the membrane and reduces the eradication because of the attractive force of interaction between the PhACs and membrane. Consequently, the repulsion between negatively charged compounds and membrane surface results in decrease in the concentration of compound at the membrane surface and improves the rejection (Verliefde et al. 2007b). Some researchers also studied uncharged molecules with high dipole moment and described that these molecules can easily pass through the membrane by aligning towards the membrane pores due to electrostatic interactions (Nghiem et al. 2005, Yoon et al. 2006).

Nghiem et al. (2005) described the increased impregnation of ionizable PhACs like ibuprofen and sulfamethoxazole on the NF membrane with negative charge at pH above 5. On the other hand, the nonionizable compounds like carbamazepine were nearly independent on the chemistry of the solution. Researchers also proposed that for the rejection of neutral solutes, the size exclusion parameter plays an important role whereas for the positively and negatively charged solutes, the electrostatic interaction is the major attribute (Verliefde et al. 2007b). Bellona et al. (2004) examined the eradication of acidic solutes via charged NF membrane and analyzed that calcium present on the sample water can reduce the surface charge of the membrane but the eradication of negatively charged compounds gets reduced for the high MWCO membranes as compared to that of solutes (Heberer 2002).

6.3.3 Role of Size Exclusion

The accumulation of PhACs compounds at the membrane surface should not be deliberated a straightforward filtration approach as it is not merely operated by molecular geometry. Along with sieving parameter, the net absorption at the membrane solute junction and transit inside the membrane can play a major role in the eviction of PhACs (Taheran et al. 2016). Usually, the size exclusion is liable for the eradication of uncharged and hydrophilic compounds and nearly 85% rejection can be achieved for the solutes with molecular weight higher than molecular weight cutoff (MWCO) of the membranes. Taheran et al. (2016) explained that the elimination of neutral solutes with hydrophilic property can be precisely correlated with their molar volume and molecular length without any correlation between the eradication and equivalent width. Researchers described the enhanced removal rate of some compounds via intrication with some acids like oxalic acid, uric acid, humic acid, etc. Kim et al. (2008b) improved the hydrophilicity, steric hindrance and negative charge of the membrane surface by utilizing methacrylic acid, succinic acid, and ethylene diamine in order to increase the ibuprofen and salicylic acid. However, reduction in surface charge of the membrane by cross-linking with ethylene diamine had an adverse effect on the eradication of charged compounds.

6.3.4 Role of Membrane Fouling and Deterioration

The researchers tried to analyze the components of foulants on the NF membranes supplied by the bio-treatment discharge and they concluded that the fouling layer was derived from a mixture of natural organic and inorganic matter. They examined two different fouling phases. One was the allegation of calcium sulfate and calcium carbonate because of the great amount of inorganic ions in NF feed and other was accession of complex organic foulants with carboxyl acid, amide as functional group due to retention of cations to the membrane surface (Taheran et al. 2016). Linares et al. (2011) examined the activity of forward osmosis (FO) process for the eradication of PhACs and found out that elimination of neutral compounds with hydrophilic nature get decreased in fouled membrane because of great MWCO induced by membrane swelling. According to their study membrane flux was not affected by fouling in a situation to treat the inorganic synthetic solution whereas the secondary wastewater discharge affected the flux by 20%. Because of fouling, the filtration of sulfamethoxazole and carbamazepine lowered from 10 to 2% and from 23 to 6% respectively in case of forward osmosis (Xie et al. 2013). The retention of PhACs can be affected by NF membrane fouling by three mechanisms termed as pore restriction, alteration of membrane charge, and cake improved polarization effect. The NF membrane was more delicate to chlorine degradation due to large pore size (Simon et al. 2009; Urase and Sato 2007).

6.4 Significance of Membrane Process for PhACs Removal

Among various wastewater treatment steps, the improvement of membrane-based procedures is important, since this innovation or technology offers different points over conventional methods.

1. Most effective technology for removal of recalcitrant compounds from Wastewater.
2. Separation is accomplished without the necessity of a phase change. In this way, it is more effective than distillation.
3. Membrane process for removal of PhACs from wastewater does not require additional chemical unlike conventional removal which depends on chemical addition.
4. Membrane process operates continuously without require any regeneration cycle under steady state because there is no accumulation occurs.

6.5 Limitation of Membrane Process for PhACs Removal

1. Membrane fouling is the main drawback of membrane process which expands treatment cost.
2. Membrane including partial elimination of certain trace level dissolved compounds by advanced treatment, which may require extra treatment units or, if not a hygiene or consistence concern, makes public awareness challenges.
3. Awareness in public about reuse of wastewater for drinking purpose after treatment.
4. Management that can be complicated relying upon the feasible administrative structure in the area where the project is executed.
5. Use of high vitality during designing of new membrane, process, and module.

6.6 Conclusion

The adequate treatment of the industrial wastewater is a matter of special interest worldwide. The great organic strength and intense physic-chemical properties along with toxic contaminants result in a number of difficulties for the conventional method of the wastewater treatment. MBR technology is expected to be effective for the treatment of industrial wastewater. The economic benefits of MBR technique are frequently growing at the global scale. But the membrane fouling, microbial characterization, and accession of the working parameters are the main issues related to the MBR system. The economic feasibility and advancement in the MBR technology provide a better option as an alternative over the traditional methods.

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Chapter 7
Recent Research on Ozonation By-products in Water and Wastewater Treatment: Formation, Control, Mitigation, and Other Relevant Topics

Keisuke Ikehata

Abstract Ozone is a powerful oxidant and disinfectant widely used in water and wastewater treatment. Unlike chlorine, ozone does not produce chlorinated and brominated organic disinfection by-products, such as trihalomethanes and haloacetic acids. However, ozone-based treatment produces its own disinfection by-products, namely bromate, nitrosamines (such as *N*-nitrosodimethylamine or NDMA), aldehydes, ketones, and carboxylic acids. According to the International Agency for Research on Cancer, bromate and NDMA have been classified as possibly carcinogenic to humans (Group 2B) and probably carcinogenic to humans (Group 2A), respectively. Because of its relevance in drinking water, bromate has been regulated in many countries as a primary drinking water contaminant. The formation and control of these compounds during water and wastewater treatment using ozone has been an active research topic in the water and wastewater industry. Recently, the use of ozone in advanced water purification and reuse has attracted much interest and is adding new aspects in ozonation-by product research. In this chapter, recent research on these ozonation by-products is reviewed. The emphasis will be given on two of the ozonation by-products, bromate and NDMA, because of their relevance in drinking water and recycled water and the difficulty of their complete removal/mitigation with currently available technologies.

Keywords Bromate · Ozone · *N*-Nitrosamine

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7.1 Introduction

Ozonation is an important unit process using ozone (O_3), which is a highly reactive gaseous oxidant and disinfectant, and has been widely used in water and wastewater treatment in many countries since the beginning of the 20th century (Loeb et al. 2012; Oneby et al. 2010; Rakness 2005; Rice 1999; von Gunten 2018; Ikehata and Li 2018). Ozonation can be used as a primary disinfection process towards pathogens and/or as an oxidation process towards a variety of inorganic and organic contaminants, including iron and manganese, colored organics, hydrogen sulfide, geosmin and 2-methylisoborneol (2-MIB), and endocrine disruptors, pharmaceuticals and personal care products (PPCPs). Ozonation has a number of advantages over conventional water and wastewater treatment processes such as chlorination and permanganate oxidation, including stronger oxidation potential owing to highly reactive molecular ozone and hydroxyl radical, wider applicability to different contaminants and pathogens, and reduced halogenated disinfection by-products (DBPs) formation potential. One of the main drivers of the use of ozone in drinking water treatment in the United States has been the reduction of halogenated DBPs formation by chlorination (Thompson and Drago 2015). It is well known that the chlorination with free chlorine generates trihalomethanes (THMs) and haloacetic acids (HAAs) that are regulated drinking water contaminants by reacting with dissolved organic matter (DOM) in source water (Krasner et al. 2006; Shah et al. 2012). For example, four chlorinated and brominated THMs, including chloroform, bromodichloromethane, dibromochloromethane, bromoform, are regulated as a group with a maximum contaminant level (MCL) of 0.080 mg/L, while five chlorinated and brominated HAAs, including monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid, are regulated with a single MCL of 0.060 mg/L in a similar manner in the United States (US EPA 2010). Ozonation could oxidize DOM in source water and reduce its concentration, as well as the DBP formation potential, to prevent the excessive THMs and HAAs in drinking water distribution systems (Rakness 2005; Shah et al. 2012).

However, ozonation can also produce its own by-products, including bromate (BrO_3^-), nitrosamines such as *N*-nitrosodimethylamine (NDMA), and smaller organic acids, ketones and aldehydes. Because of the occurrence and toxicological relevance of these ozonation by-products in water and wastewater treatment, the formation and control of these compounds have been a major research topic in the last several decades (Ikehata et al. 2014; Shah and Mitch 2012; Krasner et al. 1989; von Gunten 2003a). In recent years, more research attention has been paid to explore the technologies to monitor the by-products, as well as to mitigate their impacts in the emerging area of potable reuse of recycled water (von Gunten 2018; Gerrity et al. 2014). Therefore, the main objective of this chapter is to summarize the recent research activities on the formation, monitoring, and mitigation of the ozonation by-products. Recent update on the toxicology and risk assessment of these compounds in water and wastewater treatment are also reviewed and discussed. Although the ozonation by-products may be considered as DBPs, the term "ozonation by-product" will be used in this chapter because the primary objective of ozonation may not always be disinfection.

It should be noted that the majority of ozonation by-product studies conducted to date and covered in this chapter dealt with drinking water treatment because of more direct health implication of such by-products as aldehydes and bromate in finished water, although many of the earlier studies on NDMA were done in wastewater matrices where its formation was more prevalent and distinct. In fact, the formation of all the ozonation by-products may occur in both drinking water and wastewater, and the same formation and control mechanisms are applicable. The by-product formation and control become more significant in the ozone-based potable water reuse schemes which are gaining their popularity in recent years as noted above. Therefore, this topic will be highlighted later in this chapter.

7.2 Basics of Ozonation in Water and Wastewater Treatment

Ozonation can be used in several different locations within water and wastewater treatment trains depending on the treatment objectives. Figure 7.1 shows three typical locations of ozonation in drinking water treatment in the United States. In the pre-ozonation scheme, ozone is introduced prior to coagulation-flocculation to achieve various treatment objectives, including disinfection, organics oxidation, halogenated DBP formation potential reduction, coagulation enhancement, and taste and odor control (Rakness 2005; Thompson and Drago 2015). Water treatment plants with pre-ozonation followed by direct filtration (i.e., no sedimentation) has been seen in some cases (Liang et al. 1991). The intermediate ozonation and post-ozonation can achieve all the treatment objectives listed for pre-ozonation except for coagulation enhancement, although post-ozonation is less common as compared with pre-ozonation and intermediate ozonation because a filtration process is typically required after ozonation (see below). The two-stage ozonation, which is a combination of pre- and intermediate ozonation, is common. In the case of two-stage ozonation, pre-ozonation is employed to achieve organic and inorganic oxidation (including taste and odor control) and coagulation enhancement, while intermediate ozonation is primarily for disinfection. Where the source water requires very elaborate contaminant oxidation to prevent halogenated DBP violations and taste and odor problems, multi-stage ozonation including pre-, intermediate, and/or post-ozonation with hydrogen peroxide addition for an advanced oxidation process (AOP) capability has been used as well (Bollyky 1996).

In certain situations where source water quality is exceptionally good in terms of DOM and the risk of halogenated DBP formation and pathogen regrowth in the distribution system is not a concern, ozonation can be used without subsequent filtration. However, the use of post-ozone media filtration is typically required in

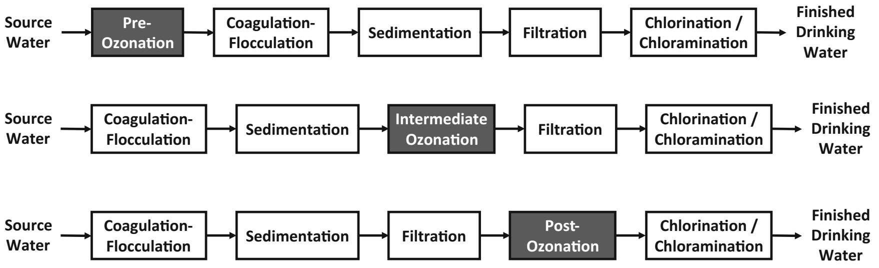

Fig. 7.1 Pre-, intermediate and post-ozonation in drinking water treatment

the United States. Silica sand, anthracite, or granular activated carbon (GAC) could be used as a filter medium in the filtration process in Fig. 7.1, although the use of GAC is sometimes mandatory depending on the countries and jurisdictions. For example, in Japan the downstream GAC filtration is currently required in the water treatment facilities where ozone is used (Japan Ozone Association 2016).

In municipal wastewater treatment, ozone is typically added after tertiary filtration to provide disinfection, color removal and organics oxidation. Since ozonation is an expensive technology to be used in municipal wastewater treatment, it is less widely used these days although ozone was a popular wastewater disinfectant back in the late 1980s and early 1990s in the United States (Ikehata and Li 2018). A new opportunity for ozonation in advanced reclaimed water treatment has been realized recently as the need for direct and indirect potable water reuse has been increasing in arid and semi-arid regions of the country, such as California, Texas, and Arizona. Ozonation can be used to as an important barrier to pathogenic microorganisms and organic contaminants in potable reuse schemes as shown in Fig. 7.2. The first and second schemes are modifications of very well-known advanced water purification scheme using microfiltration/ultrafiltration (MF/UF) followed by reverse osmosis (RO) and ultraviolet (UV) AOP. It is desirable to add biological filtration such as biological activated carbon (BAC) filtration after the ozonation process to remove ozonation by-products (the second scheme in Fig. 7.2), which will be discussed further in the following sections. Another variation of ozone-based advanced water purification scheme is ozone or ozone/hydrogen peroxide (O_3/H_2O_2) AOP followed by biological filtration, which is getting its popularity in the United States (the third scheme in Fig. 7.2) (Ikehata and Li 2018), although a similar, but more elaborate water reclamation scheme using the two-stage ozonation and BAC filtration has been used at the Goreangab Water Reclamation Plant in Windhoek, Namibia since 2002 (Lahnsteiner and Lempert 2007).

It should be noted that in contrast to the drinking water treatment schemes (Fig. 7.1), the media filtration processes are more clearly labeled as biological filters in these advanced water purification schemes (Fig. 7.2), which highlights the importance of biological degradation of ozonation by-products to mitigate their impacts on the finished water quality.

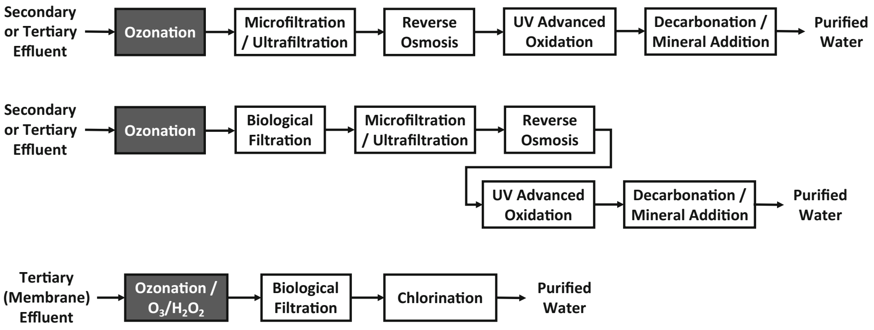

Fig. 7.2 Locations of ozonation in advanced water purification facilities for potable water reuse

The chemistry of ozone in water and wastewater treatment, including the chemical reactions pertinent to ozone-based AOPs such as the O_3/H_2O_2 process, has been described in detail in many literatures (Rakness 2005; Ikehata and Li 2018; von Gunten 2003a, b; Beltrán 2003). The readers should consult those references for basic information and terminology such as molecular ozone and hydroxyl radical reactions, including initiation, propagation, termination, and inhibition, under different treatment conditions, as well as ozonation kinetics of various inorganic and organic water constituents.

7.3 Ozonation By-products—Occurrence, Formation Mechanisms, Drinking Water Regulations, and Control Measures

As described in the previous sections, ozonation is used in various locations within the modern water and wastewater treatment facilities to achieve various treatment objectives ranging from disinfection and coagulation enhancement to DOM and trace organics oxidation. At the same time, numerous unintended side reactions occur simultaneously, which leads to the formation of various by-products during the treatment process. This is inevitable as the ozone molecule and its decomposition products (free radicals and other reactive oxygen species) are highly reactive and oxidize different inorganic and organic constituents in the water and wastewater to be treated. The extent of by-product formation varies significantly depending on the water quality parameters, such as pH, temperature, concentrations of precursors, and presence or absence of other oxidants/reductants that act as radical scavengers and/or ozone decomposition initiators. Therefore, the ozonation by-production formation potential and actual occurrence may exhibit temporal variations, as well as site-specificity. In this section, the fundamentals of the ozonation by-product formation are reviewed. The current regulatory status of these compounds in the United States, Canada and Japan, as well as the carcinogenicity classifications and the water quality guidelines by World Health Organization (WHO), is also briefly covered in this section.

7.3.1 Formaldehyde and Acetaldehyde

Ozone possesses both electrophilic and nucleophilic characteristics because of its unique chemical structure with three oxygen atoms. Since one of the major treatment objectives of ozonation is DOM oxidation, it is very reasonable to expect ozone reactions towards organics to occur during the water and wastewater treatment. Ozonation of organics in an aquatic system can be initiated by the oxidation-reduction, dipolar cycloaddition, and electrophilic substitution reactions, which subsequently lead to additional reactions such as cleavage reactions via the Criegge mechanism, ozonide decomposition, and abnormal ozonolysis, as well as further oxidation of degradation products by molecular ozone and hydroxyl radical (Beltrán 2003). Although it is possible to achieve complete mineralization which transforms organic molecules into inorganic compounds, such as carbon dioxide (CO_2), carbonate/bicarbonate ($CO_3{}^{2-}/HCO_3{}^{-}$), water (H_2O), nitrate/nitrite ($NO_3{}^{-}/NO_2{}^{-}$), chloride (Cl^{-}), and sulfate ($SO_4{}^{2-}$) by ozonation and ozone-based AOPs, the treatment only proceeds to partial oxidation of parent organics because the complete mineralization is cost-inhibitory and unnecessary. This results in generation of various transformation products with one or more oxidized functional groups such as hydroxyl, carboxylic, and carbonyl groups (i.e., alcohols and phenols, carboxylic acids, ketones and aldehydes). Among them small aldehydes such as formaldehyde and acetaldehyde are the most common ozonation by-products found in ozonated drinking water (Can and Gurol 2003; Weinberg et al. 1993; Yamada and Somiya 1988). Generation of other aldehydes and dialdehydes such as propanal and glyoxal were also reported (Weinberg et al. 1993; Yamada and Somiya 1988).

The concentrations of formaldehyde in ozonated drinking water were found to be as high as 30 μg/L based on a study in the United States, while acetaldehyde concentrations were typically less than 10 μg/L (Krasner et al. 1989). A study in Canada showed that the concentrations of acetaldehyde in drinking water could range from <0.7 to 31 μg/L (Huck et al. 1990). It should be noted that plant influent typically contained small levels ($\sim$10 μg/L) of formaldehyde and acetaldehyde and that other oxidant/disinfectant such as free chlorine could generate aldehydes as well. More recently, Dabrowska et al. (2005) demonstrated that the aldehyde production could be related to the total organic carbon (TOC) concentration in the source water and that a relationship of 2–10 μg of aldehydes production per 1 mg of TOC by ozonation, as well as chlorination and chlorine dioxide treatment, was shown.

Among the wide range of small organic ozonation by-products, those with possibly significant public health implications include acetaldehyde and formaldehyde because of their widespread detection and known genotoxicity. Formaldehyde is currently listed as a Group 1 carcinogen (carcinogenic to humans) by the WHO International Agency for Research on Cancer (IARC), while acetaldehyde is currently listed as a Group 2B carcinogen (possibly carcinogenic to humans) (IARC 1999a, 2012). Carcinogenicity of these two compounds via inhalation is well recognized by animal studies; however, there is little evidence of carcinogenicity by the oral route via drinking water consumption (WHO 1994, 2005). According to the International Programme on Chemical Safety (IPCS), the tolerable concentration of formaldehyde in drinking water is 2.6 mg/L based on the no-observed-effect level (NOEL) of 260 mg/L with an uncertainty factor of 100 (IPCS 2002). No formal health-based guideline value has been derived for formaldehyde or acetaldehyde in drinking water because of the significant difference between the tolerable concentration and actual concentration of these compounds in drinking water (IARC 1999a; WHO 2005).

While neither of these two aldehydes in drinking water are currently regulated in the United States, formaldehyde is regulated in Japan. The current Japanese water quality standard for formaldehyde is 0.08 mg/L (MHLW 2015). Formaldehyde is also currently listed on the Guidelines for Canadian Drinking Water Quality; however, it says a guideline value not necessary because the concentrations typically found in drinking water are below the level at which adverse health effects may occur (Canada Health 2017), which is consistent with the conclusion of the background document for development of WHO Guidelines for Drinking-water Quality (WHO 2005). Although there are no standard or guideline values for acetaldehyde in drinking water to date, it has been listed as one of the priority compounds that would require further considerations for regulation by the Japanese Ministry of Health, Labour and Welfare (MHLW 2003).

In fact, the generation of oxidized, smaller and more biodegradable organic compounds like aldehydes, carboxylic acids, and ketones is one of the treatment objectives of ozonation. These biodegradable organic compounds can be easily removed by subsequent biological processes such as BAC filtration (Weinberg et al. 1993; Huck et al. 1990). Therefore, the practical mitigation method for the aldehyde formation is to provide an effective biological process after ozonation.

7.3.2 Bromate

Bromate is an oxyanion of bromine and an important inorganic ozonation by-product in drinking water treatment. During ozonation, bromate is generated by the oxidation of naturally-occurring bromide (Br^-) in a number of steps (von Gunten and Hoigné 1994; Haag and Hoigné 1983). Other sources of bromate in drinking water also include the electrolytic generation of sodium hypochlorite using brine containing bromide (Weinberg et al. 2003), bromide oxidation by hypochlorite at an elevated temperature, and photochemical oxidation of bromide by hypochlorite (Xin et al. 2008). Siddiqui et al. (1995) reported that ozonation of natural water containing bromide ion could lead to bromate formation at concentration ranging from 0 to 150 μg/L based on several earlier studies. Rakness (2005) suggested that if the bromide concentration in source water was higher than 50 μg/L, there would be a risk of bromate formation above the regulated value (10 μg/L) depending on other water quality and treatment objectives.

Bromate formation during ozonation has been recognized since the early 1980s (Haag and Hoigné 1983; Richardson et al. 1981). A commercial bromate chemical, potassium bromate ($KBrO_3$) has been widely used as a food additive, a dough conditioner in bread baking, and an ingredient of permanent wave and hair straightening products. However, the carcinogenicity of potassium bromate was realized in the late 1980s (Kurokawa et al. 1986, 1990). Bromate is currently classified as a Group 2B carcinogen like acetaldehyde by the IARC (1999b). As a result, its formation in ozone-based drinking water treatment has become a critical issue. A provisional WHO guideline value of 0.025 mg/L for bromate was first created in 1993, which was subsequently lowered to 0.01 mg/L in 2004 (WHO 2011). A health-based value of 0.002 mg/L associated with the upper-bound excess cancer risk of 10^{-5} has been derived as well. In many developed countries, including the United States, Canada and Japan, bromate in drinking water is currently regulated at a concentration of 0.01 mg/L (US EPA 2001).

In the 1990s and 2000s, a great deal of research was performed to investigate the mechanisms of bromate formation, including the reaction kinetics, intermediate formation and pathway elucidation, and control measures toward bromate formation. Detailed reviews and discussion on the earlier works can be found in Siddiqui et al. (1995), Amy and Siddiqui (1999), von Gunten (2003a), Rakness (2005), and Ikehata et al. (2014). Bromate formation is typically initiated by the oxidation of bromide to hypobromous acid (HOBr) by molecular ozone or to bromine atom (Br·) by hydroxyl radical, followed by oxidation of several intermediates such as hypobromite (OBr^-), hypobromous radical (OBr·), and bromite $\left(BrO_2{}^-\right)$ to bromate (von Gunten and Hoigné 1994; Buffle et al. 2004). Since the bromate formation occurs via multiple pathways that involve both molecular ozone and hydroxyl radical, several bromate formation control methods have been developed by blocking either molecular ozone or hydroxyl radical pathway as summarized in Table 7.1. Figure 7.3 shows the reactions involved in bromate formation and chlorine-ammonia addition bromate control (Buffle et al. 2004). In addition, the ammonia-chlorine process was found to be an effective bromate control method (Wert and Rosario-Ortiz 2010; Ikehata et al. 2013). Although it was reported that GAC/BAC filtration after ozonation could reduce bromate to bromide (Kirisits and Snoeyink 1999), the performance was inconsistent and/or suffered by a limited service life (Siddiqui et al. 1995; Asami and Aizawa 1999).

Table 7.1 Bromate control methods for drinking water treatment

Method	Typical procedure	Mechanisms	Notes	Technology status
pH depression	Lower pH to about 6.5 prior to ozonation (Krasner et al. 1993)	Prevent the formation of bromite by reduce the dissociation of hypobromous acid to hypobromite ($pK_a = 9$), reduce hydroxyl radical conc.	The need of raising pH after ozonation to prevent corrosion	Demonstrated and used at water treatment plants
Ammonia addition	Add about 0.5 mg/L of ammonia-N prior to ozonation (Krasner et al. 1993; Siddiqui and Amy 1993)	Prevent accumulation of hypobromous acid and hypobromite by producing monobromamine	Inconsistent effect, bromide regeneration by bromamine decomposition with ozone, no effect on the hydroxyl radical pathway	Demonstrated and used at water treatment plants
Chlorine-ammonia addition	Add about 1 mg/L of free chlorine and 0.4 mg/L of ammonia-N prior to ozonation (Neemann et al. 2004)	Lower bromide concentration by hypobromous acid, formation, followed by monobromamine formation, hydroxyl radical scavenging by monochloramine	Low chemical cost, brominated disinfection by-product formation, organobromine compound formation	Demonstrated and used at water treatment plants
Chlorine dioxide (ClO_2) addition	Add about 1 mg/L of ClO_2 prior to ozonation (Zhou 2004)	Lower ozone demand by pre-oxidation with ClO_2, additional impact of chlorite	Requires on-site generation of ClO_2	Demonstrated and used at water treatment plants
Hydrogen peroxide (H_2O_2) addition	Add H_2O_2 to destroy ozone residual (Siddiqui and Amy 1993)	Inhibit the molecular ozone pathway by decomposing molecular ozone by H_2O_2, reduction of hypobromous acid	AOP, good taste & odor control, disinfection *Ct* cannot be obtained, inhibit color removal	Demonstrated and used at water treatment plants

(continued)

Table 7.1 (continued)

Method	Typical procedure	Mechanisms	Notes	Technology status
Ozone dose control	Reduce (optimize) ozone dose/ozone residual	Reduce bromate formation by minimizing ozone residual and oxidant exposure	No additional cost, most practical, may not provide enough *Ct* or disinfection credit for *Cryptosporidium*	Commonly used at water treatment plants
Bromide removal	Ion exchange (Wert et al. 2004)	Lower bromate formation potential by reducing the concentration of bromide	High capital and operation costs, competition with other anions	Lab/ pilot-scale
Bromate reduction	Various chemical, electrochemical, biological methods	Bromate reduction to bromide	High capital and operation costs, no commercial process available	Lab/ pilot-scale

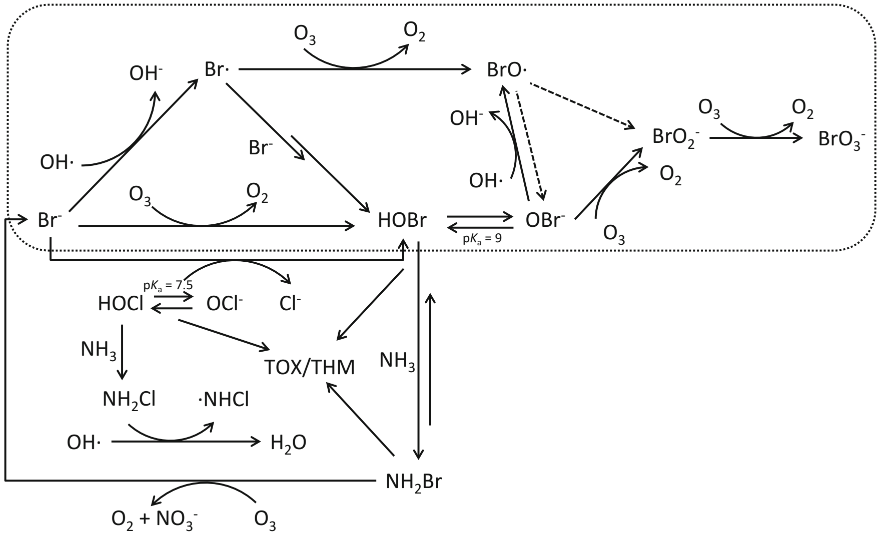

Fig. 7.3 Bromate formation during ozonation and and control by the chlorine-ammonia process (Buffle et al. 2004)

7.3.3 NDMA

NDMA is a semi-volatile organic compound that belongs to a group of potent carcinogens called *N*-nitrosamines. *N*-nitrosamines are also found in food and tobacco products, as well as discharge of industrial facilities that use nitrate and/or nitrites and amines, such as rubber manufacturing, leather tanning, pesticide manufacturing, food processing, foundries and dye manufacturing (IARC 2007; WHO 2008). NDMA is currently classified as a Group 2A carcinogen according to IARC (2007). NDMA has been detected in treated sewage, as well as drinking water (WHO 2008; Najm and Trussell 2001), and several NDMA formation mechanisms has been reported such as biological and chemical transformation of alkylamines in the presence of nitrate or nitrite (Ayanaba and Alexander 1974), chlorine disinfection of drinking water and recycled water (Mitch and Sedlak 2002a, b; Richardson 2003) and strong-base anion exchange treatment in the presence of chlorine residual (Kimoto et al. 1980). NDMA has been found, along with other nitrosamines, in surface water and sewage treatment plant effluent at concentrations ranging from <0.001 to 0.27 µg/L (WHO 2008). NDMA was also found in groundwater in Northern California, although its concentrations in treated drinking water were typically less than 10 ng/L (Najm and Trussell 2001).

As a nitrogenous organic compound, NDMA formation in drinking water treatment is typically associated with certain precursors containing nitrogen present in the source water (e.g., dimethyl amine) and/or used in the treatment processes (e.g., amine-based flocculant polymers such as polyDADMAC and quaternary ammonium-based ion exchange resin) and mediated by chlorine/monochloramine (Shah and Mitch 2012). Ammonia that can be present in treated sewage or can be added for chloramination of drinking water treatment was also attributed to the NDMA formation (Najm and Trussell 2001; Mitch and Sedlak 2002a, b). In addition, ozonation has been implicated as an alternative source NDMA in drinking water (Kosaka et al. 2009; Padhye et al. 2011; Schmidt and Brauch 2008; von Gunten et al. 2010). It is known that different NDMA precursors are involved in ozonation as compared with those involved in chlorination and chloramination, such as *N*,*N*-dimethylsulfamide (DMS) (Fig. 7.4) (Shah and Mitch 2012), which is a decomposition product of fungicide tolylfluanide (Schmidt and Brauch 2008) and several semicarbazide derivatives [such as 4,4′-hexamethylenebis(1,1-dimethylsemicarbazide) and 1,1,1′,1′-tetramethyl-4,4′-(methylene-di-*p*-phenylene) disemicarbazide] (Kosaka et al. 2009).

Despite its toxicological relevance and widespread occurrences in the aquatic environment and drinking water sources, no federal drinking water standard for NDMA currently exists in the United States (US EPA 2017), while the US EPA has calculated the NDMA concentration in drinking water representing a 1×10^{-6} cancer risk level as 0.7 ng/L and included on the Contaminant Candidate List (CCL) along with several other nitrosamines, and actively monitored their occurrences under the second Unregulated Contaminant Monitoring Rule (UCMR 2) between 2008 and 2010 (US EPA 2017). Currently, NDMA is listed on the fourth CCL (CCL 4) along with *N*-nitrosodiethylamine (NDEA), *N*-nitroso-di-*n*-propylamine, *N*-nitrosodiphenylamine, and *N*-nitrosopyrrolidine for potential future regulations in drinking water (US EPA 2016). Japan is also taking a similar regulatory action to the United States towards NDMA. The Ministry of Health, Labour and Welfare, Japan currently lists NDMA as one of 47 items that require considerations for regulation with a target concentration of 0.0001 mg/L or 100 ng/L (MHLW 2015). NDMA is currently regulated in Canada with a maximum acceptable concentration of 0.00004 mg/L or 40 ng/L (Canada Health 2017).

As of November 2017, fifteen individual states have established various drinking water and groundwater guideline values, ranging from 0.00069 (Colorado) to 0.018 μg/L (Texas) (US EPA 2017). The lower guideline values coincide with US EPA's calculation for the NDMA concentration in drinking water representing a

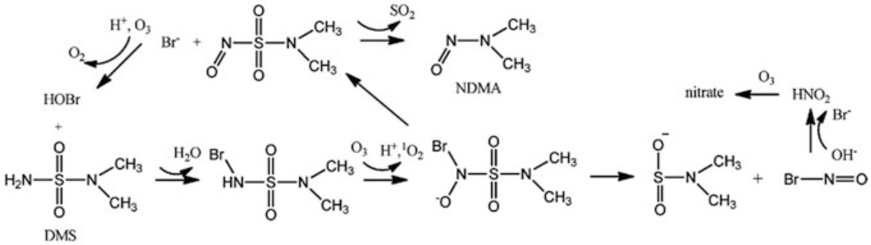

Fig. 7.4 Formation of NDMA from DMS during ozonation (Shah and Mitch 2012)

1×10^{-6} cancer risk level. California has been one of the leading states in terms of NDMA regulation and has established a notification level of 0.01 μg/L, a public health goal of 0.003 μg/L in drinking water, and a California cancer potency factor of 0.0022 μg/L (SWRCB 2017). Although these values are not enforceable water quality standards, they, especially the notification level (0.01 μg/L or 10 ng/L), have been acting as practical treatment goals set by the individual utilities in California that have known source(s) of drinking water contaminated with NDMA and/or have an advanced water purification facility for indirect potable reuse.

A number of control and mitigation methods are available for NDMA in drinking water and disinfected wastewater. The most common method to destroy NDMA is photolysis by UV irradiation (Fujioka et al. 2017; Mitch et al. 2003; Plumlee and Reinhard 2007). RO followed by UV treatment (including UV/H_2O_2 AOP and other photocatalysis) has been used extensively in advanced water purification facilities, such as Orange County Water District's Groundwater Replenishment System in Southern California. However, the re-formation of NDMA within the advanced water purification scheme in the presence of chloramines has been reported (McCurry et al. 2017) and has become an important concern in the potable water reuse. Biological treatment can also be used as NDMA is biodegradable (Fournier et al. 2006). Ozonation and AOPs can also destroy NDMA, as well as its precursors, although there is a risk of additional NDMA formation (Shah et al. 2012). In order to prevent the formation of NDMA during water and wastewater treatment, source control (i.e., elimination of the use of certain known NDMA precursors, such as cationic polymers) was found to be effective, although this is not always possible.

7.4 Recent Studies

Although ozonation is a relatively mature technology for water and wastewater treatment, its application in water reuse has drawn great interest in recent years because of the emerging need for alternative water resources due to climate change and drought events in many parts of the world, such as the extreme drought in California (Mann and Gleick 2015) and Australia (Nicholls 2004). Ozonation followed by biological filtration has been recognized as a key technology to achieve safe and reliable potable reuse of reclaimed water, especially where an additional barrier is required for treatment redundancy in direct potable reuse (DPR) projects, and where the conventional advanced water purification scheme using RO is not feasible because a mean for brine disposal is not available in inland projects (Ikehata and Li 2018; Gerrity and Snyder 2011).

Advanced water purification (Fig. 7.2) is somewhat analogous to conventional water treatment. However, its source water, treated sewage effluent, typically contains more inorganic, organic, and biological contaminants than the conventional sources such as surface water and groundwater. As reported earlier, bromate, NDMA, aldehydes, ketones and other small organics are all detected in ozonated secondary and tertiary effluents. Therefore, more rigorous quality control is required and effective by-product formation and control strategies, including monitoring and removal, should be developed and installed. In this section, recent studies dealing with ozonation by-product formation and control published in the last six years are reviewed and discussed. For bromate, new research on analytical and monitoring methods is covered as well. Since there is a chapter dedicated to NDMA analytical technologies and removal by RO authored by Fujioka (2018) and a review article on NDMA destruction by UV and UV-based AOP by Fujioka et al. 2017), these topics are excluded. Also, the recent research works on NDMA formation by monochloramine only (without the involvement of ozone) are excluded because that is beyond the focus of this chapter. Interested readers should consult the review articles published elsewhere (Shah and Mitch 2012; Krasner et al. 2013).

7.4.1 Bromate

7.4.1.1 Control and Removal

Echigo et al. (2012) showed that the use of anion exchange process as a pre-treatment of drinking water ozonation could reduce the bromate formation by a combination of two different mechanisms, namely bromide removal and DOM removal. Three types of anion exchangers with various bromide and DOM removal efficiencies were tested in this study. Approximately 60% reduction in bromate formation (reduced from 3.5 to <1.5 μg/L) was demonstrated by all three anion exchangers, while the bromide removal varied significantly, indicating the importance of different DOM fractions removed by/remained after the ion-exchange pre-treatment. Liu et al. (2017) proposed the use of natural and chemically-modified chitosan adsorbents for aqueous bromate removal. The bromate chemical adsorption capacity ranged from 23 to 43 mg/g chitosan.

Freitas et al. (2015) prepared zeolite-based catalysts that could be used to reduce bromate to bromide in water. The zeolite ZSM5 was modified with four metals including palladium, copper, thorium, and rhodium by either the ion-exchange method or the incipient wetness method, followed by drying, calcination, and hydrogen reduction. Rapid reduction (<10 min) of 10 mg/L aqueous bromate was achieved by using the bimetallic catalysts containing palladium and copper with hydrogen gas. The structural characterization of the zeolite-based metal catalysts was performed by Soares et al. (2016) using several techniques including N_2 adsorption isotherm analysis, powdered X-ray diffraction patterns, scanning electron microscopy, and Fourier transform infrared spectroscopy. Dong et al. (2018) reported the reductive removal of bromate using a catalyst composed of ruthenium oxide (RuO_2) supported by activated carbon, which was prepared previously (Dong et al. 2012). They found that the removal of bromate by the catalyst was faster at lower pH (~5) and higher temperature (40 °C) than higher pH (~9) and lower temperature (15 °C). The bromate reduction was relatively slow (>50 min for the reduction of 200 μg/L bromate at pH 5 and 25 °C) in this study although no external reductant (such as hydrogen gas) was needed. Pandey et al. (2018) described the use of lamellar two-dimensional titanium carbide also known as MXene ($Ti_3C_2T_x$) where T_x could be –O, –OH, and/or –F to reduce aqueous bromate. Like the case of RuO_2-activated carbon catalyst, bromate removal was faster at lower pH and higher temperature. The capacity of MXene for bromate removal was 322 mg/g.

In addition to the chemical reduction approaches, biological reduction of bromate and nitrate using a membrane biofilm reactor was reported (Lai et al. 2018). Bromate (~800 μg/L) could be reduced to bromide along with nitrate in the membrane biofilm reactor with denitrifying bacteria such as *Meiothermus*, *Comamonadaceae*, and *Anaerolineaceae* using methane as an electron donor. Although the bromate reduction and removal was enhanced by the introduction of low-level nitrate (~1 mg/L), it could be also inhibited by a high influent concentration of nitrate (~5 mg/L) because nitrate was the preferred electron acceptor. Vorotyntsev and Antipov (2018) described an electroreduction of bromate to bromide at rotating disc electrode, which could be applicable to water treatment.

Gerrity et al. (2014) showed minimal bromate formation (<5 μg/L) during the ozonation of chlorinated tertiary effluent. This is likely due to the chlorination prior to ozonation has converted bromide to hypobromous acid or bromine to sequester bromide, which is analogous to the chlorine-ammonia bromate control process (Table 7.1). On the other hand, Sundaram et al. (2014) showed elevated bromate formation (~20 μg/L) by ozonation in an ozone-based advanced water purification scheme tested in Reno, Nevada when influent ammonia concentration in the tertiary effluent became lower than 0.2 mg/L. The addition of hydrogen peroxide gave a limited effectiveness in this case. Lee et al. (2016) also reported significant bromate formation (ranged from ~4 to 370 μg/L) in ozonated secondary effluent samples from 10 wastewater treatment plants in United States, Switzerland, and Australia. They suggested that the hydrogen peroxide addition could be useful for the bromate control in wastewater ozonation and advanced water purification.

7.4.1.2 Analytical Methods

Several research articles have been published recently in the area of bromate analysis to improve the detection and analytical efficiency. Bromate analysis is typically done by ion chromatography followed by conductivity detection, UV/vis absorbance detection, or inductively coupled plasma-mass spectrometry (ICP-MS) with or without chloride removal by a silver cartridge (WHO 2005). The typical method detection limits (MDLs) for bromate in these methods are <1.5, <0.2, and 0.3 μg/L, respectively. Michalski and Łyko (2013) reviewed the bromate analytical methods for different sample matrices, including water. The methods covered include ion chromatography, gas chromatography, flow injection, capillary electrophoresis, and spectrophotometric methods. Alsohaimi et al. (2012) reported a bromate analytical method using reversed-phased ultraperformance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) to analyze various municipal drinking water samples, as well as bottled water samples in Saudi Arabia. The new method was more sensitive and rapid compared with the conventional methods. The MDL was 0.01 μg/L with 0.4 min analysis time. An improved ion chromatography-ICP MS method was also reported by Peng et al. (2016). The MDL for this method was 0.013 μg/L. Li et al. (2018) described a new chemiluminescence-based method for bromate detection and quantification, using carbon quantum dots and sulfite. Although the MDL for bromate was improved from 2.0 μmol/L in previous works to 0.1 μmol/L (12.8 μg/L), it is still too high for sensitive drinking water analysis.

7.4.1.3 Toxicity and Carcinogenicity

A series of new bromate toxicity and carcinogenicity study led by Bull and Cotruvo was completed to re-visit the low dose bromate toxicity, mode of action, and carcinogenicity (Bull and Cotruvo 2013; Cotruvo et al. 2010, 2012). The new study revealed the non-genotoxic mechanisms of bromate kidney carcinogenicity in rats, which may have an impact on the bromate risk assessment in drinking water, the WHO guidelines, and regulations in the future. Liu et al. (2015) also reported the results of a range of short-term toxicity tests, including rat acute toxicity test, mice cumulative toxicity tests, Ames test, mice bone marrow cell micronucleus test, mice sperm aberration test, and 30-day rat oral toxicity study. Although there were obvious signs of acute toxicity at higher doses, no mutagenicity or significant genotoxicity was found in the Ames test, micronucleus test, and sperm aberration test in this study.

7.4.2 NDMA

7.4.2.1 Formation by Ozonation

The formation of NDMA and other nitrogenous DBPs in water and wastewater treatment, including ozonation, have been reviewed by Shah and Mitch (2012). Padhye et al. (2013) investigated the formation of *N*-nitrosamines from two dithiocarbamate pesticides, namely dimethyldithiocarbamate and diethyldithiocarbamate, by different drinking water oxidants, including ozone, free chlorine, monochloramine, and chlorine dioxide. While the former compound was the precursor of NDMA, the latter was the precursor of NDEA. Nine different of model NDMA precursors were screened for their NDMA formation during ozonation in synthetic water, as well as in treated sewage effluent (Marti et al. 2015). In addition to those precursors that were already known, the six compounds with hydrazone and carbamate moieties were found to be new NDMA precursors. Also, the NDMA formation from some of the compounds, including DMS, unsymmetrical dimethylhydrazone, and acetone dimethylhydrazone, were enhanced by the presence of bromide. Lv et al. (2015) studied the generation of NDMA upon ozonation of aqueous chlorpheniramine was reported. Dimethylamine, which is an intermediate of NDMA formation, was also detected during the ozonation of chlorpheniramine. It was also noted that the NDMA formation from this compound could be reduced by lowering the solution pH and reducing hydroxyl radical exposure, while the addition of humic acid promoted the NDMA formation.

In addition to these trace organic compounds, it has been suggested that carbon nanotubes modified with nitrogen-containing functional groups (Verdugo et al. 2014), as well as intracellular organic matter from cyanobacteria such as *Microcystis aeruginosa*, *Oscillatoria* sp., and *Lyngbya* sp. (Wert and Rosario-Ortiz 2013; Xie et al. 2013; Zhou et al. 2015), could be precursors of NDMA by ozonation and chloramination. It was also shown that pre-ozonation increased the formation potential of NDMA and NDEA in the water containing the intracellular organic matter, while it reduced those of other nitrogenous DBPs during subsequent chloramination (Wert and Rosario-Ortiz 2013).

The generation of NDMA and other *N*-nitrosamines in effluent samples from six different wastewater treatment plants in Nevada, California and Georgia by ozonation was investigated by Pisarenko et al. (2015). It was found that NDMA was the dominant compound formed by ozonation in these effluent samples and the highest concentration was 77 ng/L at an O_3:TOC ratio of 1.0. In some of the samples, significantly higher NDMA was formed by the O_3/H_2O_2 AOP than the ozonation alone, while the addition of *tert*-butanol as a hydroxyl radical scavenger yielded enhanced NDMA formation in certain other samples, indicating the importance of both molecular ozone and hydroxyl radical pathways in the NDMA formation.

7.4.2.2 Impact on Formation Potential

The impact of ozonation on the destruction of NDMA formation potential has been documented very well (Shah et al. 2012; Hanigan et al. 2012; Wu et al. 2014). Shah et al. (2012) investigated the impact of peroxidation on the destruction and formation of NDMA formation potential in different water samples. Among the pre-oxidant tested, ozone could reduce the NDMA formation potential at the greatest extent. Hanigan et al. (2012) also reported the significant destruction of NDMA formation potential by ozonation followed by BAC filtration in the surface water in China, as well as in the RO concentrate from an US advanced water purification facility. Ozonation was also found to be one of the key factors that could reduce the NDMA formation potential during drinking water treatment in a multivariate analysis and modelling (Leavey-Roback et al. 2016). Chuang and Tung (2016) investigated the removal of nitrogenous DBP formation potentials in drinking water chloramination by ozonation followed by biofiltration. The formation potential of trichloronitromethane increased by the ozone-BAC treatment, while those of haloacetonitriles and HAAs decreased. The impact of ozonation on the NDMA formation potential was inconsistent and affected by the type and characteristics of organic matter in the source water.

7.4.2.3 Destruction by Ozonation

Lv et al. (2013) investigated the destruction of aqueous NDMA by ozone (Fig. 7.5). Interestingly, the NDMA removal efficiency was better at higher NDMA concentrations. For example, more than 60% of 800 ng/L NDMA was destroyed with 4.8 mg/L of ozone, while about 30% of 50 ng/L NDMA was destroyed with the same ozone dose. The recalcitrant nature of NDMA upon ozonation at lower concentrations (<40 ng/L) in treated wastewater was also noted in McCurry et al. (2016). Lv et al. (2013) also found that the NDMA destruction occurred via the hydroxyl radical pathway, and that the primary degradation product was nitromethane, although small concentrations of other compounds such as methylamine and dimethylamine were found. Fujioka et al. (2014) studied the destruction of eight different *N*-nitrosamines by ozonation (up to 45 mg/L) in a synthetic solution containing 250 ng/L of each *N*-nitrosamine and RO concentrate from an advanced water purification facility in Australia. The result of synthetic solution treatment revealed that the susceptibility of *N*-nitrosamines towards ozonation increased as the number of aliphatic carbon increased and that NDMA, which is the smallest compound, was the most recalcitrant. In addition, significant NDMA (and NDEA) formation occurred during the ozonation of RO concentrate, while the concentrations of other *N*-nitrosamines with larger molecular weights decreased with increasing ozone doses.

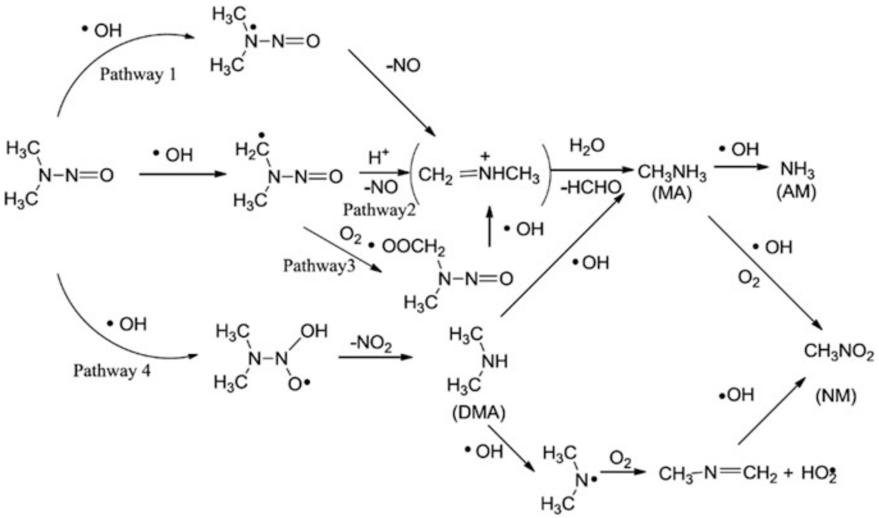

Fig. 7.5 Degradation of NDMA by ozonation (Lv et al. 2013)

7.4.2.4 Formation in Ozone-Based Advanced Water Purification Schemes

Formation of NDMA in advanced water purification facilities using ozone has been frequently reported (McCurry et al. 2016; Yoon et al. 2013; Dai et al. 2015). Dai et al. (2015) showed major generation of NDMA by ozonation in an advanced water purification facility in California that uses the first scheme shown in Fig. 7.2. The NDMA concentration in the ozonated secondary effluent was as high as 500 ng/L, which further increased to >1000 ng/L in the post-MF water. The NDMA removal occurred through the RO and UV AOP processes. A smaller concentration of NDMA (~100 ng/L) was found in the ozonated secondary effluent from another facility that employed the second scheme in Fig. 7.2. The effective removal of NDMA, as well as other *N*-nitrosamines, through BAC filtration was observed in this study, implying the importance of BAC as a polishing step.

In addition to the RO-based schemes, the non-RO potable reuse scheme (the third scheme in Fig. 7.2) has been studied actively in the recent years. For example, Gerrity et al. (2014) showed significant NDMA formation (95–125 ng/L) upon bench-scale ozonation of secondary effluent from the San Jose Creek Water Reclamation Plant in Whitter, California, while Sundaram et al. (2014) showed modest formation of NDMA (up to 11 ng/L) during a pilot study in Reno, Nevada. Blackbeard et al. (2016) reported an increased concentration of NDMA after ozonation (31.4 ng/L), which is twice as high as the concentration prior to the ozonation (15.3 ng/L) at the Eastern Treatment Plant in Melbourne, Australia, which produce “Class A” wastewater effluent for non-potable reuse. The treatment plant treats the secondary effluent produced by the conventional activated sludge process with a series of advanced treatment including pre-ozonation, BAC filtration, post-ozonation, UV disinfection, and chlorination. No further details were provided about the possible precursors and relative contribution of pre- and post-ozonation steps to the NDMA formation. Chuang and Mitch (2017) studied the impact of ozonation followed by BAC filtration on the formation of various DBPs, namely THMs, HAAs, bromate, NDMA, as well as several groups of unregulated halogenated DBPs, including haloacetaldehydes, haloacetamides, haloketones, and halonitromethane, in nitrified effluents from two municipal wastewater treatment plant in northern California. This is a laboratory-scale study and treatment parameters including the ozone dose with respect to dissolved organic carbon (DOC) concentration and the empty-bed contact time of the BAC filtration were tested. Ozonation was able to lower NDMA formation potential, while significant concentration of bromate and NDMA was formed by ozonation, especially at the higher ozone dose (1 mg O_3/mg DOC). The BAC filtration combined with ozonation could effectively remove the halogenated DBP precursors, as well as DOC (up to 72%) in this study. The NDMA formed during the ozonation was also removed by BAC (Fig. 7.6), which is consistent with previous studies such as Sundaram et al. (2014).

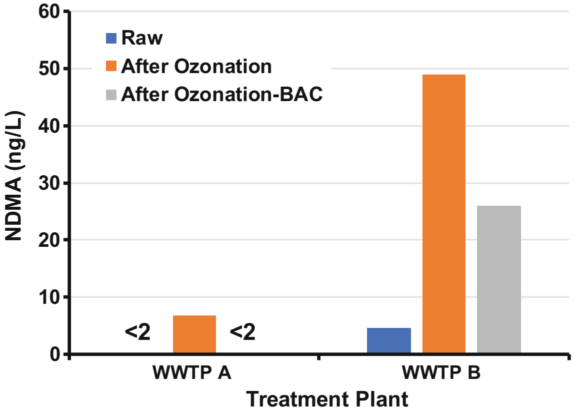

Fig. 7.6 NDMA formation ozonation and removal by BAC (Chuang and Mitch 2017)

In addition to NDMA, other types of *N*-nitrosamines have been found in ozonated recycled water. Dai et al. (2015) reported the presence of *N*-nitrosodiethanolamine in the recycled water samples collected from three out of four advanced water purification facilities. Two facilities utilize ozone before the MF-RO-AOP treatment like the first and second schemes in Fig. 7.2.

7.4.3 Other Notable Ozonation By-product Studies

In addition of bromate and NDMA, some research works have been done on the formation and removal of aldehydes in wastewater ozonation (da Silva et al. 2015; Yan et al. 2014). Da Silva et al. (2015) investigated the disinfection of anaerobically-treated wastewater using ozonation followed by chlorination. The formation of four types of aldehydes, including formaldehyde, acetaldehyde, glyoxal, and methylglyoxal, were confirmed in this study. As much as 287 ± 151, 388 ± 212, 33 ± 46, and 10 ± 14 μg/L of these aldehydes were generated by ozonation, which were decreased by subsequent chlorination. Formation of small organic by-products, including formaldehyde, acetaldehyde, ethyl glyoxal, and methyl glyoxal, was reported in a pilot-scale investigation of ozone-based advanced water purification in Reno, Nevada (Sundaram et al. 2014). Although up to 120 μg/L of formaldehyde was detected in the ozonated effluent, the subsequent BAC filtration could remove most of the aldehydes generated. Among the aldehyde tested, ethyl glyoxal was the most persistent in the BAC filtration.

Several recent studies focused on the impact of ozonation on the formation of non-regulated halogenated DBPs, including such as haloacetonitriles and haloacetamides during subsequent chlorination and chloramination (De Vera et al. 2015; Kosaka et al. 2018; Yang et al. 2012). De Vera et al. (2015) studied the impact of ozonation on the formation of halogenated DBPs including THMs, HAAs, haloacetonitriles, trihaloacetamides, and trihalonitromethanes, chloral hydrate, and haloketones in drinking water treatment. Although ozonation generally reduced the halogenated DBP formation, it increased the formation of chloral hydrate and haloketones. They also found that the addition of hydrogen peroxide to ozonation (O_3/H_2O_2 AOP) increased the formation potentials of all the tested DBPs, except for haloacetonitriles, while the addition of tert-butanol, a hydroxyl radical scavenger, showed better DBP formation potential reduction as compared with ozonation. This result suggests that the hydroxyl radical pathway (i.e., AOP) generates more organic molecules that act as precursors of those halogenated DBPs. More recently, Kosaka et al. (2018) reported the removal of haloacetamide formation potentials in drinking water treatment, including coagulation/flocculation/filtration, magnetic ion exchange, ozonation or O_3/H_2O_2, and BAC filtration, at two drinking water treatment facilities in Japan. Haloacetamide formation potential removal occurred throughout the treatment scheme with overall removal of 50–75%; the contribution of ozone-BAC treatment was relatively minor compared with those of the conventional treatment steps. It was also found that the formation potentials of chlorinated acetamides were more preferentially removed than those of brominated ones.

It has been reported that pre-oxidation using ozone could induce the cell damage in cyanobacteria and releases halogenated DBP precursors in water (Wert and Rosario-Ortiz 2013; Xie et al. 2013). Xie et al. (2013) showed that increased formation potentials of dichloroacetonitrile, trichloroacetonitrile, dichloronitromethan, and trichloronitromethane were increased, as well as various THMs and HAAs.

7.5 Concluding Remarks

In this chapter, the recent research works on ozonation by-products have been reviewed. Among the ozonation by-products reviewed, aldehydes and bromate have been extensively studied in 1990s and 2000s in terms of the formation mechanisms. Their behaviors in water and wastewater treatment are well understood. Aside from some occurrence data confirming the formation of these ozonation by-products in bench- and pilot-scale studies of water reclamation and advanced water purification, the recent works focused on the improvement on bromate analytical techniques, development of novel bromate removal methods, and additional toxicological research to clarify uncertainties in bromate toxicology and carcinogenicity. More research is desired on the development of scalable, more cost-effective bromate removal processes because they are currently absent. On the other hand, a great deal of research has been done on NDMA formation and control in the past six years, in relation to advanced water purification and potable reuse. There are still uncertainties in NDMA formation in a complex matrix such as treated sewage effluent. Elucidation of its formation mechanisms and pathways is still desired in order to understand, predict, and minimize the formation of NDMA and other potentially hazardous *N*-nitrosamines. Another major uncertainty is the regulatory outlook of

NDMA. A uniform standard or guideline value for NDMA and other related compounds in drinking water is still lacking, and the site-specific treatment goals have been set and used in case-by-case basis. This is ironic because the human health effects of NDMA is less questionable than those of bromate and the occurrence of NDMA in drinking water sources is real. Fortunately, the removal of NDMA is not as challenging as the removal of bromate, and there are several cost-effective and commercially-available treatment technologies such as biological filtration, RO, and UV treatment for NDMA removal. It is clear that ozonation alone cannot address the complex issue of NDMA formation and control in drinking water treatment and advanced water purification, including precursor removal and generation, NDMA formation and destruction, and NDMA re-formation and control. The use of multiple treatment technologies would be definitely required, and ozonation can be one of the critical components because of its proven effectiveness and efficiency in precursor destruction. The impact of ozonation on the formation of other non-regulated DBPs such as haloacetonitriles and haloacetamides is an interesting research area, depending on their implications in public health risks and future drinking water regulation. More research would be needed to eliminate any uncertainties to ensure safe drinking water regardless of water sources, including surface water, groundwater, desalinated water and reclaimed water.

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Chapter 8
Degradation of Complex Organic Pollutants in Wastewater by Homogeneous Electro-Fenton

Ha Manh Bui and Xuan-Thanh Bui

Abstract There has been a recently increasing interest in homogeneous electro-Fenton technology for the remediation of organic pollutants in water streams. In the electro-Fenton process, organic compounds are oxidized by direct electrolysis on the anode in the electrolytic cell based on the generation of a very powerful oxidizing agent, such as the hydroxyl radical ($^{\bullet}OH$) in a solution. This chapter presents a review on the fundamentals and realistic application of electro-Fenton as an effective degradation process for complex organic pollutants in wastewaters. The classification of this technique, along with the effect of influencing factors such as current density, concentrations of H_2O_2, Fe^{2+}, anions, etc. are also discussed in this chapter. In addition, the existing challenges and the most important techniques for eliminating complex aqueous organic pollutants in industrial wastewaters are discussed.

Keywords Electrochemical advanced oxidation processes (EAOP)
Electro-Fenton · Organic pollutants · Wastewater treatment

8.1 Introduction

Treatment of complex organic pollutants in wastewaters has attracted many environmental researchers around the world. Most complex organic pollutants contain high chemical oxygen demand (COD), toxic substances, complex components and recalcitrant substances such as textiles (Sharma et al. 2007), pesticides

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(Wauchope 1978), pharmaceuticals (Kolpin et al. 2002), etc. Evidently, if the polluted wastewater is directly discharged into water bodies without effective treatment, the balance of aquatic ecosystems will be severely altered and will pose a serious threat to all living organisms along the food chain (El-Shahawi et al. 2010).

At present, the wastewater treatment technologies used for removing the complex organic pollutants mainly include physical and chemical treatment methods (Erkurt and Basibuyuk 2017; Ahmed and Hameed 2018; Martínez et al. 2018; Norte et al. 2018).

The physical method is often used as a pretreatment step for recovering raw materials, intermediates, or by-products that mainly utilize extraction and adsorption. The extraction method is only a physical transfer process, so consequently, the organic matters in wastewater require further treatment (Rott et al. 2017). The adsorption method is used for the advanced treatment of wastewater mainly through highly active absorbents, but the adsorption performance is often ineffective due to the strong polarity and water solubility of the organic substances present in wastewater (Ahmed and Hameed 2018).

The chemical method is often used as a pretreatment process for biochemical treatment to improve the biodegradability of wastewater. The coagulation (Ahmed and Hameed 2018) and advanced oxidation processes (AOPs) (Bilińska et al. 2017) can effectively remove pollutants and improve the biodegradability of wastewater as well as its coagulation and oxidation. However, the coagulation is only effective on ‘colloidal paticles’ and mainly depends on the type of coagulants that generate a large amount of sludge in practical applications (Verma et al. 2012).

Some studies reported that AOPs effectively involve in removing persistent organic pollutants from wastewater by its strong oxidizing property that involves the breakdown of the functional groups of the organic substances (Chung and Kim 2011; Ganesan and Thanasekaran 2011; Bilińska et al. 2017). AOPs are based on the generation of highly reactive radical species (especially the hydroxyl radical $HO^{\cdot}$) that can react with a wide range of compounds as well as compounds that are otherwise difficult to degrade, e.g., dye molecules (Glaze 1987; Bilińska et al. 2017), pesticides (Saini et al. 2017), pharmaceuticals (Cerro-Lopez and Méndez-Rojas 2018; Kıdak and Doğan 2018).

Compared to various AOPs treating complex organic pollutants from wastewater, Fenton’s reagent involves adding Fe^{2+} and H_2O_2 to generate $HO^{\cdot}$ radical in order to enhance the biodegradability of wastewater. The Fenton process is considered as one of the most effective AOPs in wastewater treatment plants. Many Fenton studies have been successfully applied for degrading organic pollutants (Ramesh et al. 2017; Saini et al. 2017; Cheng et al. 2018). However, one of the distinct drawbacks of the conventional Fenton process is the excess use of Fe^{2+}, which releases a large amount of iron sludge and wastage of H_2O_2 in practical applications due to its radical scavenging effect.

Recently, some oxidation processes based on a Fenton reaction have been developed to overcome drawbacks including heterogeneous Fenton (Niu et al. 2018), photo-Fenton (Clarizia et al. 2017), electro-Fenton (Diaw et al. 2017), etc. Among these, homogeneous electro-Fenton is a highly promising technology because it not only highly degrades persistent organic pollutants but also significantly reduces the generation of waste sludge compared to other Fenton methods. The electro-Fenton process has been known to efficiently treat various wastewaters containing high concentrations of persistent organic pollutants. At present, there are about five types of homogeneous electro-Fenton processes (EF) that have been identified as powerful for water and wastewater treatment (Plakas and Karabelas 2017). Many factors should also be optimized during the electro-Fenton process, namely pH, current density, electrode materials, etc., for practical applications.

Taking all the above into consideration, the objective of this chapter is to summarize and evaluate the current achievements in the field of electro-Fenton application for degrading various complex organic pollutants in wastewater. This subject has been previously considered in several reviews, the most recent of which was published in 2018 (Ganiyu et al. 2018; Poza-Nogueiras et al. 2018). However, the prior reviews describe mainly issues related to heterogeneous electro-Fenton as one kind of EF and its application in water treatment. The issue of applying homogeneous EF in wastewater treatment as well as the trends of EF used in complex organics containing wastewater have not been discussed yet. Current publications aim to show new areas of the application of homogeneous EF in eliminating complex organic pollutants in wastewater.

8.2 Fundamental Elements of Electro-Fenton Process

8.2.1 Conventional Fenton

The first article discussing the Fenton process of oxidizing tartaric acid in the presence of iron was published more than 120 years ago (1984). Fenton's reagent has become widespread to both water and wastewater treatment applications. The Fenton process routinely involves three states: oxidation, neutralization–coagulation and precipitation; thus, organic substances are removed both by oxidation and coagulation (Bigda 1995). However, the Fenton process is most commonly recognized by its oxidation state. This process has been demonstrated through a connected radical reaction that generates many active free hydroxyl radicals with the increasing effective reaction area in order to degrade organic pollutants. The oxidation potential of hydroxyl radicals, which reaches 2.80 V, can degrade organic pollutants into smaller low-toxic or non-toxic molecular substances. These radicals can even directly mineralize the pollutants into CO_2 and H_2O, thereby improving the biodegradability of wastewater and reducing biotoxicity. The oxidation degradation mechanism of organic pollutants using conventional Fenton is illustrated by the following equations:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^{-} \tag{8.1}$$

$$RH^{*} + HO^{\cdot} \rightarrow R^{\cdot} + H_2O \tag{8.2}$$

$$R^{\cdot} + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \tag{8.3}$$

$$R^{+} + HO^{-} \rightarrow R - OH \tag{8.4}$$

Remark: *RH represents organic pollutants

Although Fenton's reagent could nearly degrade complex organic pollutants, as indicated in the equations above, the process requires a high consumption of iron ions and H_2O_2, and it must also react under an acidic condition (normally at pH 3–4). Moreover, the lack or excessive chemicals during the process (i.e., H_2O_2) also leads the reaction less efficiently, as described by the following equation:

$$Fe^{3+} + H_2O_2 \rightarrow HO_2^{\cdot} + Fe^{2+} + H^{+} \tag{8.5}$$

Equation (8.5) implies that the reduction of Fe^{3+} to Fe^{2+} consumes H_2O_2 and requires an excess of iron ions, which results in the production of a large amount of ferric hydroxide sludge following the neutral state of the Fenton process. Electro-Fenton process has been developed to overcome this issue.

8.2.2 Electro-Fenton

Electro-Fenton could be described as Fenton combining the application of electricity, which gives the Fenton better control through the alteration of electrodes belonging to an emerging technology called electrochemical advanced oxidation processes (Ganiyu et al. 2018). In the simplest form, EF could be described by applying an electric current to a sacrificial iron anode and carbon-based cathode to generate in situ H_2O_2 and Fe^{2+} ion that reacts with pollutants in water as a peroxi-coagulation (PC) process at an acidic condition (Qiang et al. 2002; Panizza and Cerisola 2009; Gökkuş et al. 2018). In an EF experiment, the electrode or electrode assembly is usually connected to an external DC source (Fig. 8.1) by a monopolar- or multipolar-like electrocoagulation process.

Other complex EFs which do not have in situ H_2O_2 formation and/or Fe^{2+} ion have been discussed in some practical studies (Huang et al. 2009; Shih et al. 2013). According to Plakas and Karabelas (2017), homogeneous EFs could potentially be classified into five configurations from class (I) to (V) depending on the Fenton reagent addition or formation in the EF systems as follows:

- Type I: Peroxi-coagulation (PC) process: H_2O_2 and Fe^{2+} are generated in situ by means of an oxygen sparging cathode and a sacrificial iron anode.

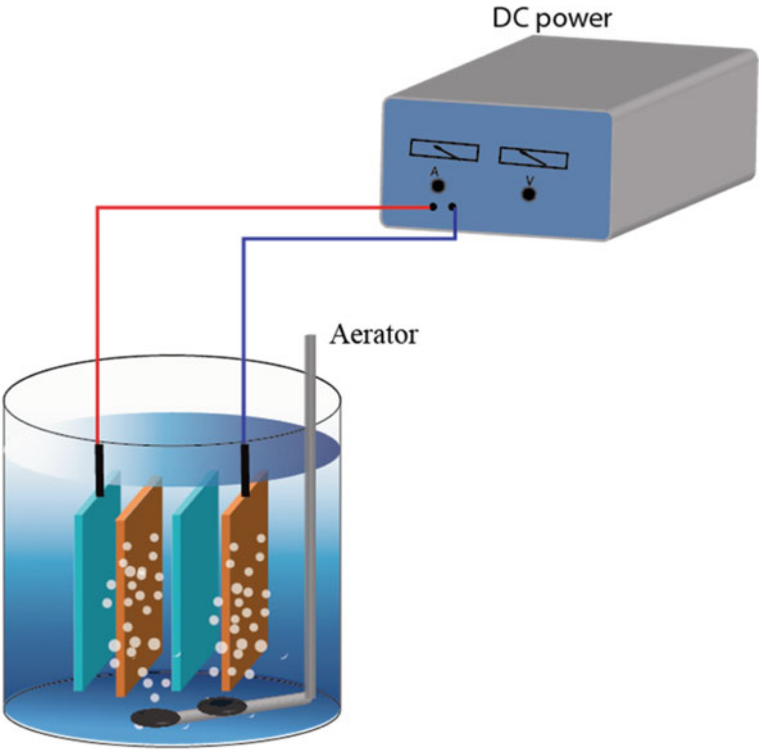


Fig. 8.1 Bench scale electro-Fenton reactor with aerated bipolar connection

- Type II: Peroxi-electro-coagulation (PEC) process or anodic Fenton treatment (AFT) process: Fe^{2+} is continuously supplied by a sacrificial iron anode while H_2O_2 is added externally.
- Type III: H_2O_2 is continuously electrogenerated on an oxygen sparging cathode while Fe^{2+} is externally added.
- Type IV: This type is similar to type III but differs in that Fe^{2+} is regenerated through the reduction of Fe^{3+} on the cathode.
- Type V: Fered-Fenton process: both H_2O_2 and Fe^{2+} are externally supplied with in situ regeneration of Fe^{2+} through the reduction of Fe^{3+} at the cathode.

In the wastewater treatment plant, the use of each EF configuration depends on the characteristics of the wastewater and the function of EFs on the systems. For example, type I is very suitable for some specific organic contaminants as a post-treatment to improve the removal efficiency of the wastewater treatment system. However, this type is negligible if conducted as a pretreatment process to enhance the biodegradability of the recalcitrant compounds and lower the toxicity for the biological treatment unit in a wastewater treatment plant. On the contrary, type V is widely used as a pretreatment method (Huang et al. 1999).

The key to an effective EF is using the proper type of electrode, particularly the cathode containing the development of carbon cathode material. For example, in the cases of type I and III regarding EFs—with carbon cathode and O_2 sparging—H_2O_2 is produced at the cathode surface as follows:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{8.6}$$

This process plays an important role because it allows to control over the concentration of H_2O_2 in EF systems. Moreover, it could potentially avoid storing and transporting this chemical in order to reduce the treatment cost.

In most EF types, an anode electrode—where most oxidation reaction occurs, including pollutants—is a sacrificial iron anode because it can produce Fe^{2+} for a Fenton reaction in the cases classified as type I and type II. However, the high excess concentration of Fe^{2+} after Fenton treatment leads not only to excessive iron sludge but also exceeds the standard limit of 2 mg/L, according to the European Union requirement for discharging wastewater into the environment (75/440/EEC). Moreover, as described in Eqs. (8.1–8.5), the Fe^{2+} contributes to the Fenton process as a catalysis (Poza-Nogueiras et al. 2018). Therefore, some researchers have reported that type III, IV and V of EFs not only decrease the wastage of Fe^{2+} but also improve the treatment capacity. The anode electrode is normally prepared by high oxidation power material like a boron-doped diamond (Canizares et al. 2005) or a dimensionally stable anode (Sopaj et al. 2016). Along with the improvement of the electrode's material, the development of the reactor design in EF systems allows the EF process to be involved in many fields relevant to water and wastewater treatment (Plakas and Karabelas 2017).

Compared to conventional Fenton process, the degradation mechanisms of organic pollutants using EF could move more quickly, be controlled more easily, and be priced less expensively (Gümüş and Akbal 2016). In the bulk phase, the EFs could easily and continuously degrade most organic pollutants at ambient conditions. However, to retain the oxidation capacity, EFs have been adjusted to narrow the pH scale from 3 to 4 and then increase it to a neutral pH for precipitation step. This typical EF removal process is illustrated in Fig. 8.2.

8.2.3 Effect of Operating Factors

Electro-Fenton combines two processes: electrochemical control and Fenton reaction; therefore, all influencing factors relative to the two processes could affect the efficiency by which pollutants are degraded. However, the effects of the operational factors significantly depend upon the type of EF.

The current (I) and voltage between electrodes (U) have significant effects on the release of H_2O_2 and Fe^{2+} concentration during the EF process. The relationship between U and I could be calculated by Ohm's Law (Zongo et al. 2009):

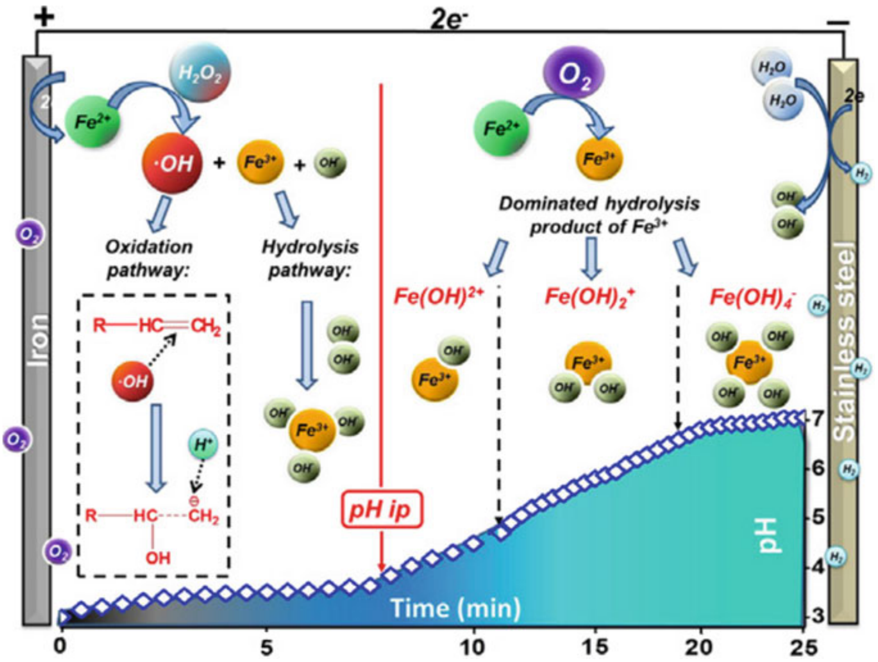


Fig. 8.2 Removal mechanism of organic pollutants from wastewater using type II electro-Fenton (Sun et al. 2015)

$$U = I \times R \tag{8.7}$$

where R is the resistance of wastewater.

While voltage determines the releasing capacity of iron in an anode (voltage of greater than 0.447 V is required for Fe changing to Fe^{2+}), current determines the velocity of a Fe^{n+} ion to an anode to a cathode or electron and H^+ with O_2 generates H_2O_2. During the EF process, only one of the two factors could be chosen for adjustment, while others will follow these changes (Daneshvar et al. 2006).

The remnant factor in Eq. (8.7), the resistance of contaminated pollutants with fixed EF design (shape and type of electrode), could be adjusted to improve the removal efficiency of the EF process by altering some parameters such as distance, electrode arrangements, pH, temperature, pollutant concentration, etc.

The presence of $HO^{\cdot}$ scavengers, i.e., $CO_3{}^{2-}, HCO_3{}^{-}, H_2PO_4{}^{-}, HPO_4{}^{2-}$, H_2O_2, etc., may also decrease the degradation rate of pollutants.

a. *Temperature*

Temperature can affect the removal efficiency. When temperature increases, the ion and electron in a solution will be more flexible or reduce resistance (R) of the solution, which gives the Fe^{2+} a greater chance for reacting with H_2O_2 (Xu et al.

2014). However, this increase also reduces the O_2 concentration in wastewater by Henry's law (Pray et al. 1952), which results in a decrease of H_2O_2 concentration in an electrolysis solution. At a high temperature, H_2O_2 also favours the decomposition of O_2 and H_2O. This trade-off effect of temperature could be found in many studies, and the suitable temperature for EF ranges from 20 to 30 °C (Özcan et al. 2008; Wang et al. 2008; Wang et al. 2010).

b. *Electrode distance*

Normally, the greater the distance between electrodes results in a greater decrease in voltage or current during EF. Essentially, the gap increase between an electron or ion makes reaching the opposite electrode difficult, which consequently decreases the *U* and *I* in a solution (Daneshvar et al. 2004). In the study focusing on removing COD from landfill leachate, Zhang et al. (2006) found that the COD removal efficiency retained the electrode distance range from 1.3 to 2.1. The removal significantly decreased following this range.

c. *Current density*

Electric current density (*J*), defined as the electric current per cross-sectional area at a given point in space, is a critical operational parameter in EC due to its attributes that include coagulant dosage rate, bubble production rate and size of the forming flocs. Generally, with an increase in power of the current density, the dissolution rate of the anode and H_2O_2 generation on the cathode enhances through Faraday' s law shown in Eq. (8.8) to determine the concentration of iron generated in the solution (Khaoula et al. 2013):

$$C\left(g_{\mathrm{Fe}}/\mathrm{m}^3\right) = \frac{I \times t \times M}{z \times F \times V} \times 10^3 \tag{8.8}$$

where *F* is Faraday's constant (96,485 Coulomb/mol); *t* is operation time (s); *M* is the molecular weight of iron (56 g/mol); *z* is the number of an electron transfer (assumed here $Z_{\mathrm{Fe}} = 2$); *V* is the treated volume (*L*); and I is the electric current (*A*).

However, an increase in current density leads to an increase in the EF energy. The energy consumption per cubic metre of wastewater can be calculated by the following equation (Ozyonar and Karagozoglu 2011):

$$\text{Energy consumption}\left(\mathrm{kWh}/\mathrm{m}^3\right) = \frac{U \times I \times t}{3.6 \times 10^3 \times V} \tag{8.9}$$

The greater use of energy leads to an increase not only in temperature but also in treatment cost. Moreover, the increase in energy could accelerate a more complex reaction that could result in the reduction of the treatment capacity (Jiang and Mao 2012).

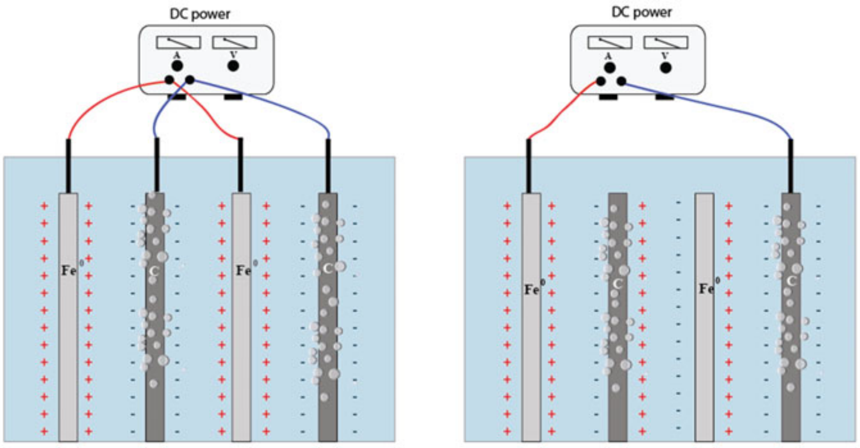
d. *Number of electrodes*

Figure 8.3 presents the same EF design by showing that the number of electrodes added contributes a change in voltage or current as well as removal efficiency (Golder et al. 2007)

Daneshvar et al. (2004) stated that by adding one or more electrodes, the removal efficiency significantly increases. A possible explanation for this might be that, at a high voltage (over standard potential for iron release—0.44 V), a greater number of electrodes mean a greater ‘source’ of Fe^{2+}. Attention should be taken to note that total voltage in the EF reactor is constant among each cell. Another possible explanation for this occurrence is that the addition of electrodes could increase a constant current density, therefore increasing the treatment capacity.

e. *Electrode arrangements*

Following the same EF structure, the electrode arrangements could affect removal efficiency and energy consumption. The pollutant removal efficiency and energy consumption of monopolar and bipolar configurations have been compared in several studies (Daneshvar et al. 2004; Asselin et al. 2008). The results of the aforementioned studies could be summarized to indicate that a monopolar configuration has a lower operating cost; however, in some cases, a higher removal of pollutants could be achieved with the bipolar configuration, possibly due to additional side reactions. This result may be explained by the fact that even though the current in EF is the same, the total voltage in bipolar configuration is double that of a monopolar configuration; thus, the removal efficiency should become higher while energy consumption becomes larger.



Monopolar **Bipolar**

Fig. 8.3 Bench scale of electro-Fenton reactor with aerated monopolar and bipolar arrangements

f. *Fe^{2+} concentration*

Fe^{2+} concentration plays an important role for EF (Plakas and Karabelas 2017). Generally, an increase in Fe^{2+} concentration causes an increase in EF efficiency because Fe^{2+} directly conducts the formation of $HO^{\cdot}$ as indicated in Eq. (8.1). However, the increase in Fe^{2+} concentration also redundantly releases Fe^{3+}, which produces iron sludge during neutral step. An increment of Fe^{3+} also consumes more H_2O_2 as shown in Eq. (8.7) that leads to a reduction in EF efficiency. The optimal Fe^{2+} concentration can vary between wastewaters depending on the organic load, the concentration of H_2O_2, and the presence of scavengers (e.g., inorganic ions to the generation of $HO^{\cdot}$). In an attempt to degrade textile wastewater from a carpet mill in Turkey, Gulkaya et al. (2006) found that with the concentration of Fe^{2+} ranging from 1.1 to 5.5 g/L and the mass ratio of H_2O_2/Fe^{2+} around 95, the COD removal efficiency reached 95%. The author explained that Fe^{2+}, in this case, could play not only the generation of $HO^{\cdot}$ but also a coagulant agent. Chan and Chu (2003) stated that, when Fe^{2+} was higher (227 mg/L), the atrazine could be nearly eliminated from the aqueous solution; the change of H_2O_2/Fe^{2+} had insignificant effects for this treatment.

During EF, while Fe^{2+} concentration is mostly controlled by current density as demonstrated in Eq. (8.9)—type I and II—at a sacrificial iron anode, EF type IV and V could be affected through the Fe^{2+} regeneration by oxidizing Fe^{3+} at a cathode with the same amount of externally supplied Fe^{2+}.

g. *H_2O_2 concentration*

The optimum H_2O_2 is crucially important for achieving high efficiency in the EF process because H_2O_2 directly produces $HO^{\cdot}$ through Eq. (8.1) (Sopaj et al. 2016; Diaw et al. 2017; Gökkuş et al. 2018). The increment of the initial H_2O_2 concentration enhances oxidation during the EF process up to a certain point, at which H_2O_2 begins inhibiting the elimination of pollutants. At a higher H_2O_2 acting as an $HO^{\cdot}$ scavenger, reaction (8.10) becomes more important, and a less reactive $HO_2^{\cdot}$ radical is formed.

$$H_2O_2 + HO^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \tag{8.10}$$

In EF systems type I, III and IV, excluding type II and V, the produced H_2O_2 concentration could be estimated directly from the sparging of oxygen or air through Eq. (8.6). However, many studies show that a significant O_2 had been wasted in an H_2O_2 production process. Therefore, Yu et al. (2014) suggested a current density (CE) equation for producing H_2O_2 from O_2 as follows:

$$\mathrm{CE} = \frac{nFC_{\mathrm{H_2O_2}}V}{\int_0^t I\mathrm{d}t} \times 100\% \tag{8.11}$$

where n is the number of electrons transferred for oxygen reduction to H_2O_2 (normally 2), and CH_2O_2 represents the molar concentration of H_2O_2 (moles per litre).

As indicated in Reaction 8.11, the applied current (or current density) of EF systems significantly affects the produced H_2O_2. Moreover, the cathode material and designed reactor are the most influential factors affecting H_2O_2 production rate (Yu et al. 2014).

h. *Presence of anions*

The key degrading factor of EF is the oxidation capacity of a free radical, particularly $HO^{\cdot}$; any presence of $HO^{\cdot}$ scavengers (mostly anion ions) will reduce the treatment efficiency of EF due to the many interference reactions as follows (Wang and Xu 2012; Asghar et al. 2015):

$$CO_3{}^{2-} + HO^{\cdot} \rightarrow HO^{-} + CO_3{}^{\cdot -} \tag{8.12}$$

$$HCO_3{}^{-} + HO^{\cdot} \rightarrow H_2O_2 + CO_3{}^{\cdot -} \tag{8.13}$$

$$HPO_4{}^{2-} + HO^{\cdot} \rightarrow HO^{-} + HPO_4{}^{\cdot -} \tag{8.14}$$

$$H_2PO_4{}^{-} + HO^{\cdot} \rightarrow HO^{-} + H_2PO_4{}^{\cdot} \tag{8.15}$$

Most anions normally improve solution conductivity or decrease the resistance of a solution that may improve current density as explained by Ohm's Law (Eq. 8.7). Some investigations (Diagne et al. 2007; Zhou et al. 2007; Özcan et al. 2008) noted that the supplement of adequate $SO_4{}^{2-}$ and $NO_3{}^{-}$ ions could improve the degradation of pollutants. However, too much $SO_4{}^{2-}$ and $NO_3{}^{-}$ supplement also decrease the treatment capacity as a reaction to $HO^{\cdot}$ scavengers, which is mentioned below.

$$SO_4{}^{2-} + HO^{\cdot} \rightarrow HO^{-} + SO_4{}^{\cdot -} \tag{8.16}$$

$$NO_3{}^{-} + HO^{\cdot} \rightarrow NO_2{}^{-} + HO_2{}^{\cdot} \tag{8.17}$$

i. *pH of solution*

pH is the critical control factor during homogeneous EF (Gulkaya et al. 2006; Wang et al. 2008). The pH solution in EF has to adjust from ca. 2–4 in order to maintain the EF pollutant removal efficiency (Plakas and Karabelas 2017). This pH adjustment keeps the ferrous ion stable, which reacts with H_2O_2 to form $HO^{\cdot}$ in the solution as described in reaction (8.1) (Barrera-Díaz et al. 2003). The resistance of the solution (Eq. 8.7) is also low and favourable for the EF treatment. Moreover, the production of H_2O_2 in EF types I, III and IV is accelerated at an acidic medium according to reaction (8.6). However, an extremely low pH (≤ 2) enhances H_2

evolution at the cathode as a following reaction, therefore significantly reducing the formation of H_2O_2 (Sun et al. 2015):

$$2H^+ + 2e \rightarrow H_2 \tag{8.18}$$

8.3 Applying Electro-Fenton Process for Wastewater Treatment

In recent years, EF has been applied for the remediation of various wastewaters containing refractory organic matters. The vast majority of the studies may be harvested from the Scopus database (accessed on 29th June, 2018), illustrated in Fig. 8.4:

Figure 8.4 shows that the total number of articles with the key ‘electro-Fenton wastewater’ retrieved from the Scopus database was 502. The studies conducted on EF and its application to wastewater have steeply increased since the first published work in 1996. The analysis of data reveals that nine countries have contributions in EF wastewater research, and the contributions vary from one country to the next. China had the highest research output (156, 31.1%), followed by Spain (82, 16.3%), France (47, 9.4%), Turkey (34, 6.8) and Iran (33, 6.6%). The results also indicate that environmental science was determined to be of the highest interest within research areas, ranking around 62.5% (data not shown). In the environmental science field, degradation of dye compounds, pesticides and pharmaceuticals in wastewaters may be among the most frequently studied areas registered by Scopus. The application of EF for the treatment process is described in further detail below.

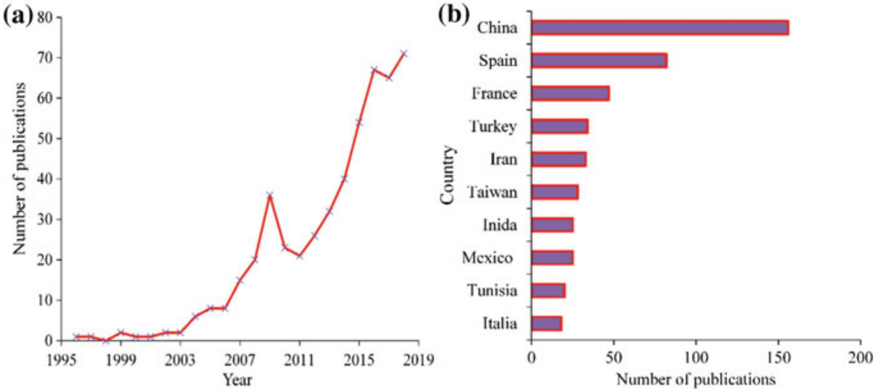


Fig. 8.4 Scopus number of published articles per year (**a**) and country (**b**) by EF with the keywords ‘electro-Fenton wastewater’

8.3.1 Textile Wastewater

With rapid technological developments, the textile industries can be considered one of the most important areas. However, wastewater from this industry represents a significant environmental problem due to the containment of synthetic dyes (especially reactive dyes), which are resistant to the biodegradation process (Gottlieb et al. 2003; Ha 2016).

The reduction of reactive dye content in textile wastewater is of major concern to environmentalists for several reasons. First, the government legislation has become increasingly stringent about the effluent standards. Second, reactive dyes are completely soluble in water and their complex chemical structures contain low-biodegradable groups so that they cannot be readily removed by conventional or biological treatment processes alone. And third, some reactive dyes have the potential to cause cancer or mutations. Without an effective treatment of dyes in wastewater prior to discharge, serious damages to water sources, wildlife and human health can result even at low concentrations (Gottlieb et al. 2003; Malik et al. 2017; Płonka et al. 2017).

Some authors have successfully applied EF for the degradation of this pollutant. Cruz-Rizo et al. (2017) evaluated the efficiency of EF with boron-doped diamond electrodes for the treatment of two refractory dyeing wastewaters from a Mexican textile industry. The continuous flow of oxidation experiments was carried out, resulting in almost 100% TOC reduction for all the dyes at 31 A/m^2 during a 180 min treatment. Özcan and Özcan (2018) analysed the effectiveness of EF for decolouring and degrading naphthol blue black (NBB) in aqueous solutions. NBB was completely converted to intermediate species in a 15 min electrolysis process at 60 mA, but complete degradation took 180 min. The GC-MS analysis shows that at least 6 aliphatic compounds could be identified during the EF process. The author suggested a possible way for the degradation of NBB using EF treatment (Fig. 8.5).

Ren et al. (2016) applied a novel vertical-flow EF reactor for degrading atrazine dye comprised of 10 cell compartments using a PbO_2 anode and a modified graphite felt mesh cathode with a total effective volume of 2 L. After 120 min of electrolysis, the dye had almost converted to intermediate species (around 100%), and the TOC removal efficiency was higher than 60% at pH of 3, voltage of 4.0 V, flow rate of 40 mL/min, Fe^{2+} of 0.4 mM and aeration rate of 80 mL/min. According to the authors, the novel EF system was found to be not only more efficient for degrading atrazine, but also easily controlled in the different concentrations of pollutants compared to the traditional parallel-flow reactor. This could be an ideal treatment performance for practical applications.

Another successful dye mineralization is presented by El-Desoky et al. (2010), who developed a platinum gauze anode (with an area of 3.8 cm^2) and a reticulated vitreous carbon cathode (60 PPI, dimensions of 5 cm × 7 cm, and thickness of 0.9 cm), for the degradation of Levafix blue and red reactive azo dyes in real textile dyeing wastewater. The experiments were conducted in a three-electrode, undivided glass electrochemical reactor containing 250 mL of dye (200 mg/L), and 0.5 mM

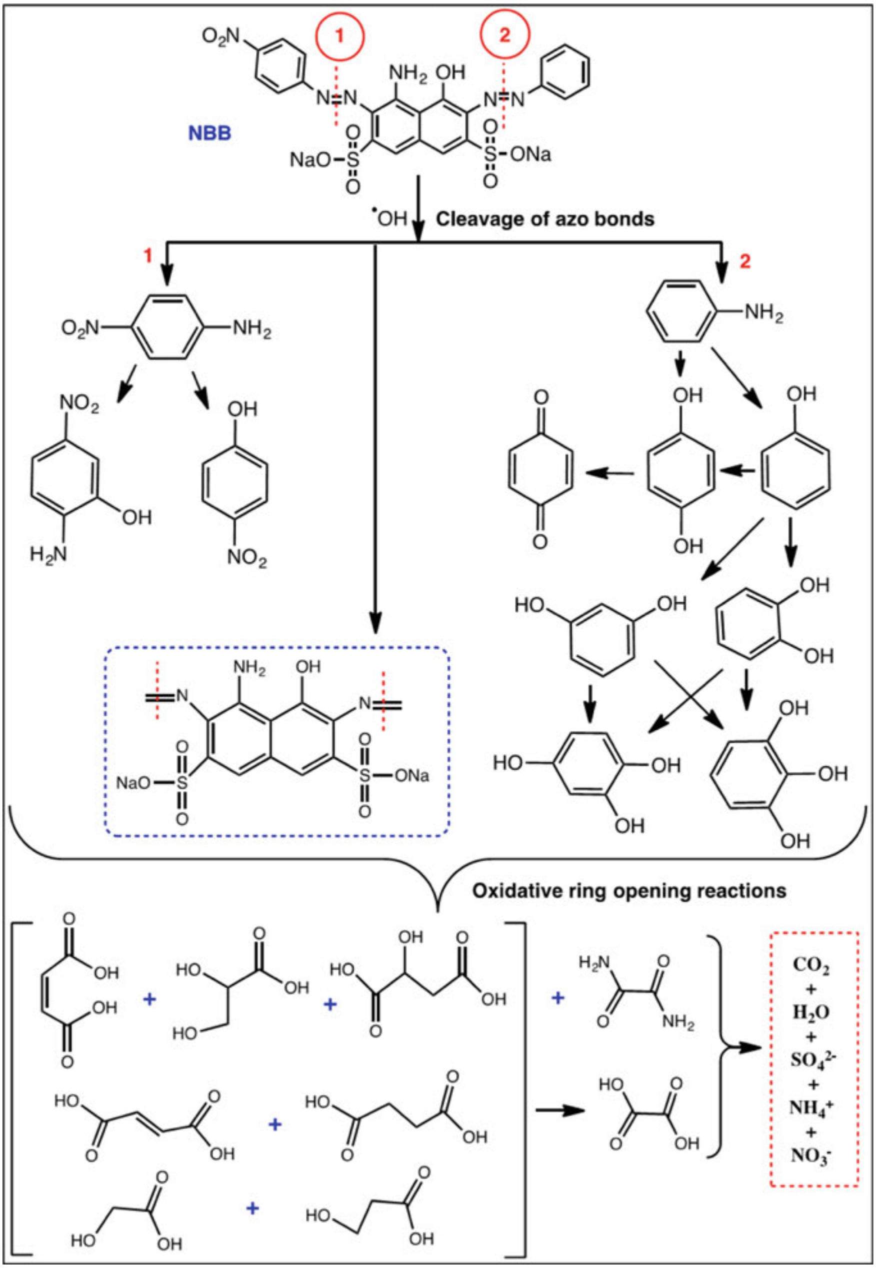


Fig. 8.5 Proposed degradation of naphthol blue black dye by electro-Fenton process (Özcan and Özcan 2018)

of Fe^{2+} at pH 3. At this condition, the dyes almost decomposed (100%) and mineralized about 85–90%. The combination of Fe^{2+} with in situ hydrogen peroxide at a polyacrylonitrile-based activated carbon fibre cloth cathode on the real textile wastewater in Taiwan (COD of 1224 mg/L, TOC of 394.6 mg/L) was investigated by Wang et al. (2010). With a hollow cylindrical structure (diameter of 2.9 cm, height of 7 cm) of a cathode and a platinum wire anode, (oxygen gas rate of 150 mL/min, current density of 3.2 mA/cm^2, Fe^{2+} concentration of 2 mM, and pH of 3), the highest COD removal efficiency reached 75.2%.

8.3.2 Pesticide Production Wastewater

In modern agricultural production, pesticides play an important role in increasing crop yields as well as controlling pests and plant diseases. Pesticides can be classified as insecticides, acaricides, fungicides, herbicides, and plant growth regulators according to their functional characteristics. Many pesticides are utilized in amounts exceeding 50,000 kg/year (Barceló 1993). However, due to the complicated synthesis procedures of pesticide preparation, high equipment requirements, and low raw material utilization rates, nearly 60% of synthetic intermediates are present in the generated wastewater in the form of high-concentration contaminants. Product purification and equipment cleaning can also generate wastewater that contains many synthetic intermediates (Tijani et al. 2014). The intermediates are mostly macromolecular organic compounds with long chains and heterocycles (Deng et al. 2013), and thus the wastewater generated in pesticide production has high COD, toxic substances, complex components and nonbiodegradable substances, all of which usually have directly adverse effects on present living organisms. The wastewater is considered as an adequate treatment before it is released into the environment.

EF has been employed to degrade pesticides from wastewater. Dominguez et al. (2018) reported that by using a boron-doped diamond anode and a carbon felt cathode, EF is a very efficient method for the degradation of Lindane (an organochlorine pesticide) in acidic medium (pH 3). At optimal conditions (400 mA of applied current, 0.05 mM of ferrous ion concentration, 10 mg/L of initial pesticide concentration), Lindane was rapidly degraded within 15 min and reached 80% TOC removal after 4 h of electrolysis. Popescu et al. (2018) compared the pyrimethanil degradation efficiency of taffeta carbon fibre (TCF), unidirectional carbon fibre (UCF) and graphite felt (GF) electrodes as cathodes and boron-doped diamond anodes at two different configurations in the EF process. The authors reported that the best TOC removal efficiency value of 42.4 and 93.1% (at the same conditions, 300 mA using the UCF cathode) was obtained at batch and continuous EF configuration for 120 min of electrolysis, respectively. The author noted that the continuous EF systems could be potentially used for a long treatment time without any operational issues.

Yatmaz and Uzman (2009) reported that EF applied with Fe electrodes and ex situ supplied H_2O_2 is the most efficient method for the degradation of monocrotophos in acidic medium. Monocrotophos was rapidly decomposed within 5 min and the energy consumption of complete removal was 0.834 kWh/kg monocrotophos. Boye et al. (2002) investigated 80% mineralization of herbicide 4-chlorophenoxyacetic acid using EF type III with a Pt anode.

The degradation of herbicide Imazapyr in aqueous medium by EF using a glass frit cathode and a platinum counter anode was studied by Kaichouh et al. (2004). The mineralization of the imazapyr reached over 95% with an Fe^{2+} concentration of 0.5 mM and applied current 100 mA after 120 min of electrolysis. The result is greater compared to conventional Fenton (around 70%) at the same treatment time. With a carbon felt cathode and a platinum anode, Edelahi et al. (2003) had degraded diuron (0.17 mM) completely at only 10 min of electrolysis with COD removal around 93%. The same EF configuration was also investigated by Abdessalem et al. (2008). Although the degradation of 0.05 mM chlortoluron reached only 4 min, the TOC removal efficiency required at least 8 h to obtain 98%. Abdessalem et al. (2010) also conducted a comparative study of a mixture of three pesticides (chlortoluron, carbofuran and bentazon) using the same EF configuration mentioned above. The author stated that the EF process is much less expensive than the photo-Fenton process according to overall treatment cost.

8.3.3 Pharmaceutical Production Wastewater

Various pharmaceutical compounds and their metabolites have been found in the effluents resulting from the different stages of the drug manufacture (Kümmerer 2009; Verlicchi et al. 2012). Most of them are complex organic chemicals such as β-lactam, sulfonamide and aromatic hydrocarbons that are resistant to biological treatment (Ikehata et al. 2006), and therefore, strong oxidation processes in the form of integrated schemes with other physical and biological methods are usually considered for achieving the discharge standards. The EF technology has proved to be effective for the pretreatment of wastewaters generated by this industry. Ganzenko et al. (2018) employed an optimized EF system successfully, using a carbon felt cathode (18.5 cm × 4.5 cm) and a thin film boron-doped diamond anode on niobium substrate (6.0 × 4.0 cm), placed at the centre of the electrochemical cell for significant degradation (over 94%) of cytotoxic drug 5-fluorouracil in an aqueous solution. Experiments were carried out in an undivided glass electrochemical cell (reactor) containing 200 mL of the 0.05 M Na_2SO_4 of pH 3.0, 0.1 mM of the drug and 0.2 mM of $FeSO_4$. The optimized cathode applied current was 300 mA at 6 min, and the final results produced mainly contained inorganic ions (NH_4^+, NO_3^- and F^-) with less than 10% of residual organic carbon. The pretreatment of trimethoprim (TMP) before biological degradation step in aqueous solution and real pharmaceutical effluent using EF was investigated by

Mansour et al. (2015). The mineralization of 58 mg/L (438.5 g/L COD or 125.4 g/L TOC) using an undivided two-electrode Pt/carbon felt cylindrical glass cell of 1 L. The optimal condition treatment was performed using a low Fe^{2+} dose of 0.69 mM, a low current intensity of 466 mA, a pH of 3 and a 2 L/min recirculation flowrate; it has led nearly total removal of TMP after 30 min of electrolysis. At the same conditions, trimethoprim in industrial pharmaceutical effluent almost removed. Although TOC removal was low, the biodegradability of the treated industrial effluent was improved. Overall removal yields were 80 and 89% for 180 and 300 min of EF pretreatment followed by activated sludge process, respectively.

8.4 Conclusion

The homogeneous electro-Fenton process has been applied as a feasible technology for the treatment of widely complex organic pollutants over the last decades. The fundamental differences of EF, such as configuration, effective factors, and applicative trends, have been evaluated and compared. The EF showed it could effectively degrade nonbiodegradable organic matters from wastewaters of industries such as textile and dyeing, pesticides, pharmaceuticals, etc. Many successful cases in the practical elimination of recalcitrant and toxic pollutants suggest the electro-Fenton process to be a promising and effective technology for applications in wastewater treatment. The electro-Fenton process would be more technical and economical to act as a pretreatment step for enhancing the biogradation of wastewater, and then followed by biological treatment processes.

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Chapter 9
Removal of *N*-nitrosodimethylamine for Potable Reuse: Reverse Osmosis Treatment and Monitoring Technologies

Takahiro Fujioka

Abstract For the protection of public health, robust quality assurance and quality control are critical elements in wastewater treatment for potable water reuse. Reverse osmosis (RO) membrane technology is a powerful wastewater treatment process that results in the removal of most contaminants. However, the efficacy of using conventional RO membranes for the removal of *N*-nitrosodimethylamine (NDMA), which is a probable human carcinogen, is often low and highly variable due to NDMA's small molecular size and uncharged characteristics. Moreover, the credibility of RO membranes for NDMA removal is very low due to the lack of technologies for monitoring membrane integrity for continuous assurance. To enhance confidence in water treatment systems for potable reuse, it is important to develop new RO membranes to achieve high removal of NDMA. Additionally, the ability to continuously monitor NDMA concentrations in RO permeate is needed to ensure the safety of recycled water and establish credibility in RO treatment. This chapter provides an overview of recent studies focusing on RO membrane and analytical techniques for the enhanced removal and monitoring of NDMA for potable reuse.

Keywords *N*-nitrosodimethylamine · Reverse osmosis · Membrane

9.1 Introduction

Potable reuse schemes based on the transformation of highly treated wastewater into drinking water sources are increasingly being introduced as a means to provide long-term water security in several countries, including the United States (US) and Australia (Shannon et al. 2008; Lafforgue and Lenouvel 2015; Burgess et al. 2015). One of the major challenges in potable reuse is the removal of trace organic chemicals (TOrCs) that could pose a threat to public health. Because wastewater

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contains a diverse range of TOrCs discharged from households and industrial facilities, their occurrence in recycled water is of great concern (Lampard et al. 2010; Scott et al. 2014; Linge et al. 2012; Debroux et al. 2012). Major TOrCs in wastewater include pharmaceuticals, pesticides, endocrine disrupting compounds, and disinfection byproducts (Luo et al. 2014), and they are often identified at low concentrations ranging from one part per trillion (ng/L) to a few parts per billion (μg/L). Complying with guideline values (ng/L–μg/L levels) is a major challenge in potable reuse, as low TOrC concentrations can be very close to these values, and they can only be accurately quantified using advanced analytical techniques (Lafforgue and Lenouvel 2015).

In recent years, the US potable reuse industry has shifted from indirect potable reuse (IPR) to direct potable reuse (DPR) (Arnold et al. 2012). IPR is based on blending recycled wastewater into natural drinking water sources (e.g., dams and aquifers), such that a "multiple barrier" approach comprising both engineered and natural treatment processes is typically implemented. The components of typical multiple barriers include (a) residential/industrial source control, (b) conventional wastewater treatment, (c) advanced water treatment, (d) environmental buffer and blending, and (e) drinking water treatment (Drewes and Khan 2011). In contrast to IPR, DPR is based on the direct delivery of recycled water with a short retention time for drinking water treatment plants. This technique has the potential to effectively reduce some capital and operating costs; however, DPR is subject to more stringent criteria for recycled water quality (Drewes and Khan 2015; Leverenz et al. 2011). For example, the California State Legislature (US) has recommended improved removal of low molecular weight TOrCs for DPR (CSWRCB 2016).

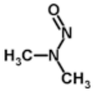
Frequent monitoring of water quality can play a key role in ensuring the enhanced removal of TOrCs. In water reclamation systems, most TOrCs are essentially removed from wastewater by reverse osmosis (RO) treatment: a powerful separation technology that can also remove almost all salts (Drewes and Khan 2011). One challenge in the use of RO treatment is assuring RO membrane integrity for NDMA removal. In addition, despite the high separation capability of RO, some of small and uncharged TOrCs are only partially removed by this technique. One of the most challenging chemicals among the regulated TOrCs include *N*-nitrosodimethlyamine (NDMA, $C_2H_6N_2O$). NDMA is typically identified in RO permeate water at concentrations higher than the target values (Plumlee et al. 2008; Farré et al. 2011; Fujioka et al. 2013; Poussade et al. 2009), including the California regulatory notification level (10 ng/L) (CDPH 2015) and the Australian guideline's level for water recycling (10 ng/L) (NRMMC et al. 2008). To achieve the target NDMA concentration in the final recycled water product, RO treatment is often followed by an ultraviolet (UV)-based advanced oxidation process (UV/AOP) (Plumlee et al. 2008; Poussade et al. 2009). This technique requires a high energy consumption of ~ 1000 mJ/cm^2 to provide a 1.2-log reduction for NDMA (Sharpless et al. 2003), which is far greater than the UV dose required for only disinfection purposes (USEPA 2006). Energy consumption of UV in current AOP may be reduced if greater amounts of NDMA can first be eliminated by RO membranes with high selectivity; thus, such membranes have the potential of making potable reuse more cost-effective. Using high rejection RO membranes along with UV/AOP can also improve the security of recycled water in potable reuse (Werber et al. 2016a). Improved NDMA removal can be continuously ensured only through the introduction of fast and reliable analytical techniques. This chapter provides an overview of potential technologies using RO to enhance NDMA removal as well as those applied to high-frequency monitoring of NDMA in potable reuse.

9.2 Fate of NDMA in Potable Reuse

NDMA ($C_2H_6N_2O$), an *N*-nitrosamine, is small-sized (molecular weight = 74 g/mol), hydrophilic (i.e., log K_{ow} <2), and uncharged in a pH 6–8 solution (Table 9.1). *N*-nitrosamines have the chemical structure $R_1R_2N{-}N{=}O$. NDMA is a disinfection byproduct formed during oxidation or disinfection of biologically treated effluents using strong oxidants such as chlorination, chloramination, ozone, and potassium permanganate (Mitch et al. 2003a). NDMA is often identified in treated wastewater at up to a few hundred parts per trillion (ng/L) levels (Krasner et al. 2009), which is typically higher than the regulatory levels (e.g., 10 ng/L) (Fujioka et al. 2012a). Other *N*-nitrosamines that can be identified in treated wastewater include *N*-nitrosomethylethylamine (NMEA), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosodiethylamine (NDEA), *N*-nitrosopiperidine (NPIP), *N*-nitrosomorpholine (NMOR), *N*-nitrosodipropylamine (NDPA), *N*-nitrosodi-*n*-butylamine (NDBA), and *N*-Nitrosodiphenylamine (NDPhA) (Zhao et al. 2006; Steinle-Darling et al. 2007; Drewes et al. 2006). NDMA is a probable carcinogenic chemical that has been classified by the US Environmental Protection Agency (USEPA 1993). Guideline values for NDMA in drinking water are set at higher concentrations (e.g., 100 ng/L) in the World Health Organization Guidelines (WHO 2011) and Australian Drinking Water Guidelines (NHMRC and NRMMC 2011). Nevertheless, standards for levels of NDMA in potable reuse can be more stringent. For example, California, US has set a public health goal of 3 ng/L for NDMA in drinking water (CDPH 2011), and California’s current notification level for NDMA is 10 ng/L. In fact, the guideline value of 10 ng/L for NDMA has also been established in the Australian Guidelines for Water Recycling intended for potable reuse (NRMMC et al. 2008).

NDMA concentrations in the range of 17–63 ng/L have been reported in raw residential sewage (Sedlak et al. 2005; Middleton et al. 2008; Sedlak and Kavanaugh 2006). NDMA in wastewater is often the result of industrial activities (e.g., the production of rocket fuel, rubber, and cosmetic and toiletry products) (Mitch et al. 2003a; Spiegelhalder and Preussmann 1984). For example, NDMA concentrations at the entrance of wastewater treatment plants can reach over 100 ng/L (Sedlak and Kavanaugh 2006). Additionally, typical wastewater contains high concentrations of NDMA precursors, including dimethylamine (DMA) and tertiary amines (Mitch et al. 2003b; Schreiber and Mitch 2005; Shah and Mitch

Table 9.1 Physicochemical characteristics of NDMA

Name	NDMA
Structure	
Molecular formula	$C_2H_6N_2O$
Molecular weight (Da)	74.1
Molecular volume[1] (cm^3/mol)	75
Minimum projection area[2] ($Å^2$)	20.1
Log *D* at pH 8[1]	0.04
pKa at pH 8[1]	3.5
Distribution at pH 8[1] (%)	0
Dipole moment[3] (Debye)	3.71

[1] Chemicalize (https://chemicalize.com)
[2] Molecular Modeling Pro, Norgwyn Montgomery Software Inc
[3] Milsian 2.1 software

2011) at the ppb (μg/L) levels (Sedlak and Kavanaugh 2006). DMA levels in feces and urine can be identified to be as high as 0.4 and 15.9 mg/L, respectively (Tricker et al. 1992). NDMA precursors can form NDMA through chloramination, which is typically conducted for disinfection purposes before RO membrane treatment (Sgroi et al. 2018). The yield of NDMA formation from DMA is <3% (Mitch et al. 2003a; Schreiber and Mitch 2005). The length of chloramination contact time has a significant impact on NDMA formation, such that Farré et al. (2011) reported that 20–22 h of chloramination contact time led to 170 ± 20 ng/L NDMA concentration, while 1–2 h of chloramination exposure resulted in only 7 ± 2 ng/L NDMA concentration. Although the formation of NDMA can be minimized by optimizing the disinfection process, NDMA levels are typically still higher than 10 ng/L at the time the water has first arrived at the RO process. Thus, in order to comply with the guideline values, additional NDMA needs to be removed using water treatment processes (Plumlee et al. 2008; Munch and Bassett 2004; McDonald et al. 2012a).

NDMA is a highly challenging compound, which complicates water treatment. First, the difficulties associated with analytical determination of NDMA at regulatory concentrations (e.g., 10 ng/L) have resulted in less clarity about the fate of NDMA during water recycling. Another challenge is low NDMA removal by many wastewater treatment processes, including secondary wastewater treatment (Sedlak and Kavanaugh 2006), coagulation (Chung et al. 2009), ultrafiltration (Farré et al. 2011), and granular activated carbon adsorption (Fleming et al. 1996; Soroushian et al. 2004; Schmidt and Brauch 2008). Although RO membrane treatment is a high-level separation technology that achieves sufficient removal of most TOrCs, only partial removal of NDMA (5–80%) has been reported with this technique

(Plumlee et al. 2008; Sedlak and Kavanaugh 2006). In recent potable reuse schemes, NDMA removal has been considered to be reliable only when accomplished through the use of advanced oxidation processes (AOPs) (Leverenz et al. 2011). AOP entails direct photolysis by UV irradiation, which is preceded by the addition of hydrogen peroxide in order to produce a hydroxyl radical: a strong oxidizing reagent.

9.3 Removal of NDMA by RO Treatment

9.3.1 RO Membrane

Most commercial RO membranes currently available for water recycling applications are polyamide-based thin-film composite (TFC) membranes with three layers: an active polyamide skin layer, a polysulfone supporting layer, and a polyether nonwoven fabric backing layer. RO membranes are produced by forming the active polyamide layer on the supporting layer through interfacial polymerization, whereby polyfunctional amine monomers (e.g., meta-phenylenediamine, MPD) react with another solvent solution containing polyfunctional acid chloride monomers (e.g., 1,3,5-tricarboxylic acid, TMC) (Baker 2012). The formed polyamide layer still has a number of unreacted amine and carboxylic functional groups in the polymer chain (Tang et al. 2009). To increase water permeance for a given membrane surface area, recently developed commercial RO membranes have complex “ridge-and-valley” structures and a hollow interior of crumpled nodules throughout the skin layer, which ultimately increase the effective membrane surface area (Fig. 9.1) (Li et al. 2017; Yan et al. 2015; Pacheco et al. 2010). The thicknesses of the skin layer and top film are approximately 200–400 and 30–35 nm, respectively (Fujioka et al. 2018a; Freger 2003). Mechanical support for RO membranes is fundamentally provided by the polyether backing and polysulfone

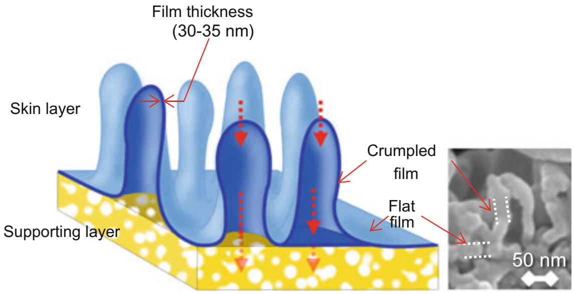


Fig. 9.1 Conceptual image of a thin-film composite RO membrane with a field emission-scanning electron microscope (FE-SEM) cross-sectional image of ESPA2 RO membrane (Reproduced with permission from Fujioka et al. (2018a) Copyright © 2018 Elsevier Ltd.)

supporting layers. The active skin layer acts as a separation layer governing water permeance and separation of solutes. In particular, free-volume holes between cross-linked polymer chains of the active skin layer (0.2–0.3 nm in radius) are expected to govern the permeation of water molecules and solutes (Kim et al. 2005; Wang et al. 2014; Jean et al. 2013).

9.3.2 Rejection by Low-Pressure RO Membranes

NDMA is small in size and is present in an uncharged form at pH 6–8 (Tu et al. 2013; Fujioka et al. 2013b); thus, its rejection of NDMA by RO membranes is typically low and highly variable, as illustrated in Fig. 9.2. Neutral solutes, including NDMA, are primarily rejected through size exclusion, which in membrane separation can be considered as a phenomenon whereby neutral solutes larger than the free-volume hole-size of RO membrane are more likely to be rejected (Fujioka et al. 2012b; Bellona et al. 2004), and their rate of rejection increases according to the size of their molecule (Chen et al. 2011; Fujioka et al. 2013c). Among parameters associated with molecular size, minimum projection area—which is the minimum projected 2D area of the solute—correlates well with rejection (Fujioka et al. 2014a). In other words, the size exclusion mechanism governs the rejection of neutral solutes. Other properties influencing the rejection of TOrCs by RO include electrostatic repulsion and hydrophobic interaction. NDMA is uncharged at the environment pH, which reduces the likelihood of electrostatic repulsion between NDMA and membrane material. NDMA is very hydrophilic (Log *D* = <2, Table 9.1); however, typical commercial RO membranes are

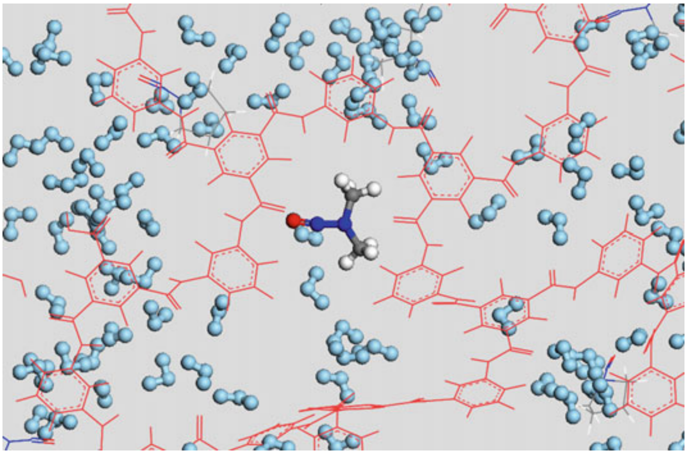


Fig. 9.2 Conceptual image of NDMA and water molecules passing through the RO membrane structure

relatively hydrophobic. Thus, hydrophobic interaction (e.g., adsorption) hardly occurs between these types of solutes and RO membrane (Van der Bruggen et al. 2006). Overall, the principle of size exclusion is likely to govern the rejection of NDMA.

The rejection of NDMA by commercial low-pressure reverse osmosis (LPRO) membranes can vary depending on type of RO membranes. The rejection of *N*-nitrosamines including NDMA by RO membranes has been evaluated extensively at the laboratory scale (Steinle-Darling et al. 2007; Fujioka et al. 2012b; Miyashita et al. 2009; Bellona et al. 2011), such that NDMA rejection by four commercial LPRO membranes (i.e., ESPA2, LFC3, TFC-HR, and 70LW) has been found to range from 37 to 52% (Fujioka et al. 2013b). At full-scale RO treatment plants, the rejection of NDMA varies considerably over a broad range of 4–75%, depending on plant or membrane type (Table 9.2) and other unidentified factors (Fujioka et al. 2013a; Sgroi et al. 2015). NDMA rejection among three RO stages can also vary in many cases. Moreover, a substantial difference in NDMA rejection (10 and 70%) has been reported at the same treatment plant at different sampling occasions (Sedlak and Kavanaugh 2006). It is noteworthy that the RO systems at these plants were operated under similar conditions (system recovery = 85% and average permeate flux = 17–20 L/m^{2}h).

Temperature of the RO feed is one of the potential factors that can cause variation in NDMA rejection. For example, a change in the feed temperature from 20 to 30 °C caused a decrease in NDMA rejection by TFC-HR membranes from 49 to 24% (Fujioka et al. 2012b). On the contrary, changes in solution pH and NDMA concentration in the RO feed can be less important for the variation in NDMA rejection. During a long-term operation, RO system inevitably undergoes membrane fouling, which necessitates periodical chemical cleaning to recover membrane permeability. In general, membrane fouling has a positive impact on NDMA rejection, leading to enhanced removal of NDMA (Fujioka et al. 2013d). Hence, some specific fouling substances in treated wastewater (e.g., fulvic acid or fulvic acid-like substances) are likely to enhance NDMA rejection (Fujioka et al. 2017a). In contrast, chemical cleaning with caustic reagents (e.g., NaOH) or acidic reagents

Table 9.2 NDMA rejection by full-scale RO systems

RO membrane	Location	NDMA rejection (%)	References
TFC-HR	West Basin Water Recycling Plant, USA	28, 56	Sedlak and Kavanaugh (2006), Drewes et al. (2008)
	Scottsdale Water Campus, USA	10, 70	Sedlak and Kavanaugh (2006), Drewes et al. (2008)
	Bundamba Advanced WTP, Australia	11, 14	Farré et al. (2011a, b)
ESPA2	West Basin Water Recycling Plant, USA	34	Drewes et al. (2008), Reardon et al. (2005)
BW30	Torreele Plant, Belgium	50	Krauss et al. (2010)

(e.g., HCl) deteriorates NDMA rejection (Fujioka et al. 2014b). Nevertheless, the impact of caustic cleaning on the separation performance of RO membranes may not be permanent and could be mitigated by a subsequent acidic cleaning step.

9.3.3 High Rejection RO Membranes

Commercial RO membranes used for water recycling applications are typically capable of about 50% NDMA rejection when they are evaluated at the laboratory; however, some RO membranes designated for applications other than water recycling can provide higher NDMA rejection. For example, the ESPAB RO membrane (Hydranautics, CA, USA), which was designed for boron removal in the second pass of seawater desalination applications, provides a remarkably high rejection of NDMA (e.g., 71%) (Fujioka et al. 2013b). Seawater RO membranes also provide high NDMA rejection; however, its permeability can be very low. For example, a newly developed thin-film nanocomposite seawater RO membrane (QuantumFlux SW 75ES, NanoH_2O) fabricated with inorganic nanoparticles showed 61% NDMA rejection (Hofs et al. 2013). NDMA rejection by the seawater RO membranes SWC5 (Hydranautics) and SW30 (Dow Filmtec) can be as high as 82 and 74%, respectively (Fujioka et al. 2013b; Hofs et al. 2013). To date, no commercial RO membranes have been reported that achieved over 90% NDMA rejection. The key structural parameters differentiating NDMA rejection by RO membranes remain unclarified. A recent study (Fujioka et al. 2018a) characterized the skin layer of several RO membranes with different NDMA rejection using positron annihilation lifetime spectroscopy (PALS), field emission-scanning electron microscope (FE-SEM), and atomic force microscopy (AFM). The study reported almost no variation among the RO membranes in terms of their free-volume hole-radius (0.270 nm), effective surface area (200%), and thickness (30 nm).

Other RO skin layer properties may also govern the permeation of NDMA molecules. A number of previous studies investigated the development of the polyamide active skin layer to attain better membrane performance; however, most of this research has focused on anti-fouling properties and water permeability (Kang and Cao 2012). In fact, only a limited number of studies have investigated the improved rejection of small compounds in water, as there has been low demand for separation performance levels higher than those currently available in the desalination industry (e.g., 99% salt removal). Heat treatment techniques have been tested for their efficacy in enhancing NDMA separation by RO membranes (Shintani et al. 2009). Heat treatment can be applied for the modification of commercial RO membrane by immersing RO membranes in high-temperature ultrapure water (Fujioka et al. 2015); it increased NDMA rejection of ESPA2 RO membrane (Hydranautics) from 53 to 62%, while NDMA rejection by two other commercial RO membranes (ESPAB and HYDRA, Hydranautics) was increased by heat treatment from 62 to 79% and from 74 to 88%, respectively (Fujioka et al. 2018b). After heat treatment was applied to a prototype RO membrane, its NDMA rejection

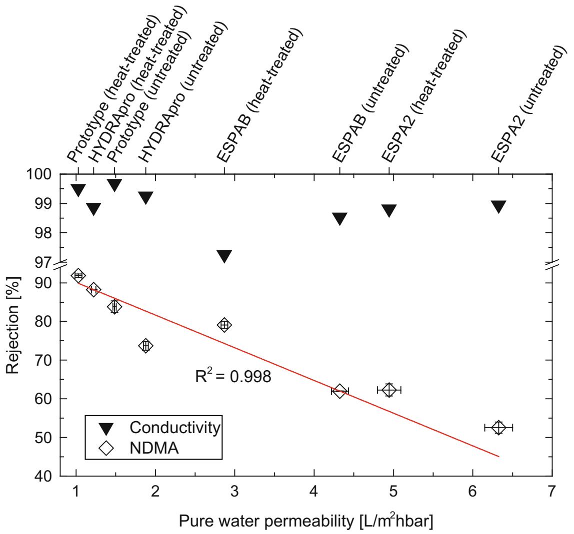


Fig. 9.3 Correlation between NDMA rejection and pure water permeability of eight RO membranes (Reproduced with permission from Fujioka et al. (2018b) Copyright © 2017 Elsevier Ltd.)

reached as high as 92% (Fujioka et al. 2018b). Such studies have identified that heat treatment can enhance the removal of NDMA precursor (e.g., DMA) (Fujioka et al. 2018b) and significantly retard fouling development (Fujioka et al. 2015); however, heat treatment also reduces water permeability, necessitating a linear trade-off between water permeability, and NDMA rejection (Fig. 9.3), as has been commonly reported in the experimental literature (Zhang and Geise 2016; Geise et al. 2011; Bernstein et al. 2011; Werber et al. 2016b). In other words, the transmembrane pressure (TMP) required to achieve a specific permeate flux (e.g., 20 L/m^{2}h) increases according to improved performance in NDMA rejection. Moreover, heat treatment can cause a slight reduction in conductivity rejection, which is probably caused by changes in electrostatic repulsion between NDMA and membrane surface (Fujioka et al. 2018b). Overall, enhanced removal of NDMA by heat treatment can only be achieved at the expense of membrane permeability. Further studies are needed to develop RO membranes with high NDMA selectivity and high water permeability.

9.4 Analytical Techniques for NDMA

9.4.1 Conventional Techniques

The measurement of NDMA concentration in water samples is typically achieved by gas chromatography coupled with different detection techniques; such as, mass spectrometry (GC-MS) (Charrois et al. 2004; Yoon et al. 2011), tandem mass spectrometry (GC-MS/MS) (Munch and Bassett 2004; Llop et al. 2010; Hung et al.

2010), or high resolution mass spectrometry (GC-HRMS) (Ontario 2010; Planas et al. 2008). For example, US EPA Method 521 (Munch and Bassett 2004) has established a reporting detection limit of 1.6 ng/L for NDMA using coconut charcoal solid-phase extraction (SPE), GC-MS/MS, large volume injector, and a chemical ionization (CI) operation mode with CI reagent gas. Other methods include a selective ion storage mode of GC/MS with CI (Pozzi et al. 2011), a sensitive GC-MS/MS technique using electron ionization (McDonald et al. 2012b), and high-field asymmetric waveform ion mobility spectrometry with time-of-flight mass spectrometry (Zhao et al. 2009). Several liquid chromatography (LC)-based systems (e.g., LC-MS/MS or LC-HRMS), along with positive electrospray ionization (ESI), can also be used for NDMA analysis (Plumlee et al. 2008; Zhao et al. 2006; Ripollés et al. 2011; Krauss and Hollender 2008); however, many laboratories have limited routine access to LC-MS/MS or LC-HRMS. Additionally, NDMA analysis can be conducted through high-performance liquid chromatography (HPLC) separation and MS/MS detection (Plumlee et al. 2008).

Because the quantification of low NDMA concentrations at ng/L levels is required by guidelines and regulations, most NDMA methods undergo a pre-concentration step based on a solid-phase extraction (SPE) or liquid-phase extraction (LPE). Most conventional pre-concentration methods are labor-intensive, requiring a large volume (e.g., 200–1000 mL) to make very concentrated extracts (e.g., >1000 fold) through SPE (McDonald et al. 2012a), posing a major challenge. Moreover, these pre-concentration methods typically require the addition of deuterated NDMA (i.e., d_6-NDMA) into the water samples as an internal standard for calibrations and surrogate recovery calculation, which are necessary to compensate for losses of NDMA occurring during sample preparation (i.e., SPE and evaporation). Recent studies have successfully demonstrated the automation of such labor-intensive and time-consuming SPE steps for determining TOrC concentrations in water (Goh et al. 2016; Anumol and Snyder 2015; Ciofi et al. 2013; Rubirola et al. 2017). For example, Goh et al. (2016) reported the successful determination of six estrogens and six glucocorticoids in water using a fully automated online SPE system coupled with LC-MS/MS and ESI. The automated

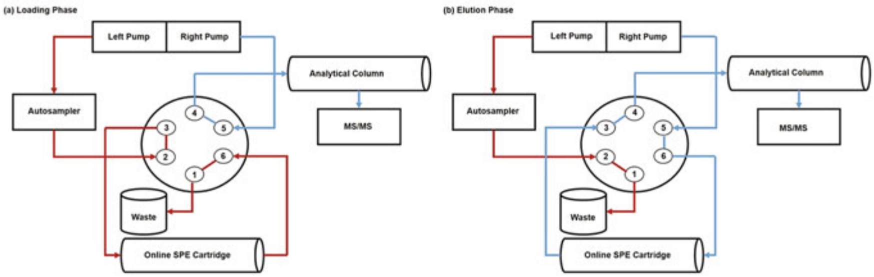


Fig. 9.4 Online SPE-LC–MS/MS configuration of the column compartment valve in the, **a** loading phase, **b** elution phase and LC separation process (Reproduced with permission from Goh et al. (2016) Copyright © 2016 Elsevier Ltd.)

SPE using two two-position six-port valves (Fig. 9.4) is operated with three major steps: (a) loading of sample onto SPE cartridge (position of valve: 6–1); (b) elution of analytes from the SPE cartridge and chromatographic analysis (position of valve: 1–2); and (c) clean-up of SPE cartridge and analytical column, and system re-equilibration.

9.4.2 Emerging Techniques

Kodamatani et al. (2009) recently developed a new analytical method that requires no pre-concentration steps for *N*-nitrosamines (including NDMA), and it is rather based on an HPLC followed by a photochemical reaction (PR): chemiluminescence (CL). This method allows for a direct injection of the aqueous sample (20–200 μL) into HPLC-PR-CL, after which the determination of NDMA concentration is achieved in only 10 min (Fujioka et al. 2016). In the HPLC-PR-CL system, the NDMA in the injected sample is first separated with HPLC, and then NDMA in the eluent undergoes photolysis at the photochemical reactor, where it is ultimately converted into peroxynitrite. Thereafter, the concentration of NDMA is determined on the basis of the photons of light generated at the CL. Quantification of NDMA in wastewater matrix by HPLC-PR-CL can be successfully performed even when water treatment chemicals such as chloramine, hydrogen peroxide, and hypochlorite are present in the water samples. Unlike conventional techniques, HPLC-PR-CL does not require any labor-intensive and time-consuming sample preparation steps. Moreover, conventional analytical methods are incapable of frequent measurements; thus, the fast and reliable HPLC-PR-CL method for NDMA analysis is an important tool in potable water reuse applications to protect public health. A new pretreatment system (anion exchange module, AEM) was recently incorporated into HPLC-PR-CL (Fig. 9.5) to improve the method's detection limit by removing interfering compounds (e.g., nitrate) and converting anions in the eluent to hydroxide ions, which increases eluent pH to the level required by the PR-CR without any chemical additions. The method detection limit of HPLC-AEM-PR-CR has been determined as 0.42 ng/L (Kodamatani et al. 2018).

Researchers recently developed and successfully demonstrated a near real-time NDMA analytical technique that uses the HPLC-PR-CL method to analyze NDMA before and after the pilot-scale RO treatment of an ultrafiltration (UF)-treated wastewater (Fujioka et al. 2017b). Online monitoring of NDMA offers a number of benefits. For example, continuously monitoring NDMA in water after treatment can ensure the quality of recycled water after its exit from DPR plants (Snyder 2014), and the use of such monitoring at the entrance of DPR plants or during water treatment processes can also provide early warning of NDMA spikes and process failures. Additionally, online-monitored NDMA rejection has the potential to become a surrogate indicator for TOrC removal by RO treatment. A recent study (Fujioka et al. 2018c) evaluated the efficacy of online monitoring of NDMA in RO feedwater (UF-treated wastewater) and RO permeate using online NDMA analyzers

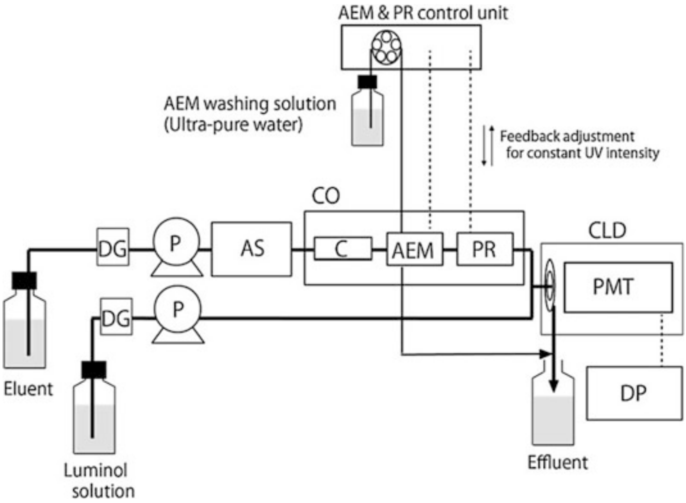


Fig. 9.5 Schematic diagram of the HPLC-AEM-PR-CL system. P: pump; DG: degasser; AS: autosampler; CO: column oven; C: column; AEM: anion exchange module; PR: photochemical reactor; CLD: chemiluminescence detector; PMT: photomultiplier; and DP: data processor (Reproduced with permission from Kodamatani et al. (2018) Copyright © 2018 Elsevier Ltd.)

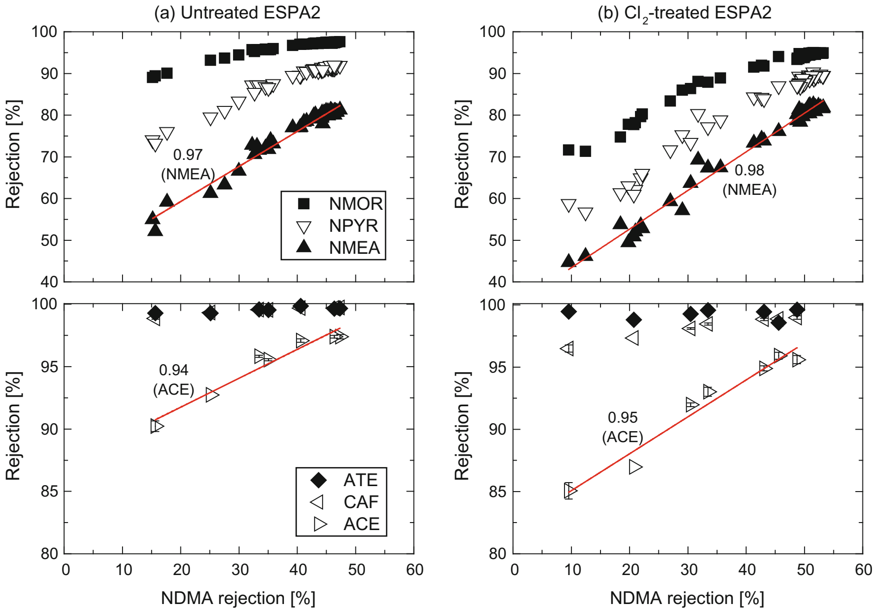


Fig. 9.6 The rejection of TOrCs as a function of NDMA rejection using, **a** untreated, **b** Cl_2-treated ESPA2 RO membranes. ATE: atenolol; CAF: caffeine and ACE: acetaminophen. *R*-squared values are only shown for NMEA and ACE (Reproduced with permission from Fujioka et al. (2018c) Copyright © 2018 Elsevier Ltd.)

(i.e., HPLC-PR-CL) and found variations in the rejection of NDMA and other TOrCs by RO membrane based on changes in operating conditions (permeate flux and feedwater temperature). The researchers identified a linear correlation between NDMA rejection and the rejection of other TOrCs by virgin and chlorine-damaged ESPA2 RO membranes (Fig. 9.6). NDMA is the smallest chemical among TOrCs; therefore, its removal by RO can be a conservative surrogate indicator capable of predicting changes in TOrC removal.

9.5 Conclusions

This chapter reviewed latest studies examining improvements in the removal of NDMA using RO membranes and recently developed online NDMA monitoring techniques for potable reuse. Achieving a high rejection of NDMA using modified RO membranes could enhance the current portfolio of NDMA removal methods in water reuse facilities. However, the RO membranes associated with high NDMA rejection have low water permeability, which requires (a) more energy consumption when operated at a specific permeate flux or (b) more membrane surface areas when operated at a specific pressure. Therefore, further work is needed to develop RO membranes with high selectivity and high permeability. An online monitoring technique for NDMA was recently demonstrated, indicating that continuous monitoring of NDMA in the final product water helps to ensure removal of NDMA prior to the delivery of recycled water. Additionally, online-monitored NDMA data for water before and after RO treatment have the potential to serve as a surrogate indicator of the removal of other TOrCs, which is highly relevant in DPR.

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Chapter 10
Realistic Advancement in Engineered Osmosis for Water Treatment

Ravichandran Rathna, Ekambaram Nakkeeran and Sunita Varjani

Abstract The industrial revolution led to tremendous change in global population and pollution rate. Especially, polluting the available freshwater is creating unexcelled demand for water to meet the global needs. The conventional water reclamation techniques endure energy cost and technical efficiency. Hence, there is a need for sustainable water reclamation technique with low cost, high operation flexibility, performance and maintenance. Forward osmosis or engineered osmosis emerged as the powerful substantial technique suitable for water treatment. This chapter focuses on the advantages, feasibility, challenges and opportunities of engineered osmosis for water treatment. The significant progress of engineered osmosis in the area of water treatment, commercial availability, process configurations and operations are discussed. Further, emanate the potential area of improvement in the near future, integrated designs and other innovative technologies for water treatment by engineered osmosis are also discussed.

Keywords Forward osmosis · Membranes · Module configurations
Draw solutions · Water treatment

10.1 Introduction

Globally, the level of population growth and rising per capita consumption has significantly increased during the past few decades. The growing demands, population, pollution, climatic change, rapid urbanization and industrialization and improper management have enhanced stress on water, ultimately, leading to water scarcity. Water is considered as the elixir for life on the earth. For instance, ancient

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civilization's prosperity and moribund solely depended on the available water sources in the rivers and lakes. Lately, the growing demand for water issue is the most momentous challenge faced in many parts of the world. According to current estimate by the United Nations World Water Development Report (UN-WWDR) 2018, around 1.9 billion population is living in severely water-scarce areas and may rise to nearly 3 billion by 2050 (WWAP 2018). In India, according to NITI Aayog report, nearly 70% of the water has been contaminated and India ranked 120th in the water quality index among 122 countries.

In fact, statistical forecast and prediction report of UN-WWDR 2018 showed that 70% of global water is utilized by agriculture for irrigation purpose while 20% is used by the industries for subsidizing economic growth and augment the living standard. The remaining 10% is exploited for domestic consumption like cooking, drinking and washing. Therefore, the demand for freshwater is increasing with exponentially growing population, rapid industrialization and urbanization, agricultural intensification, increase in water inequality and water mismanagement (Sherbinin et al. 2007). Especially, polluting the available freshwater is creating unexcelled demand for water to meet the global needs. Human activities such as encroachment of fertile lands, deforestation, overgrazing, urbanization and mining activities are the most serious concerns for the declining of existing freshwater sources. These activities eventually lead to global warming and climate change which further aggravate the water stress issues. According to Ismail Serageldin, former World Bank Vice President for Environmental Affairs quoted that 'The wars of the twenty-first century will be fought over water'. Therefore, United Nations (UN) General Assembly on 28 July 2010 conceded The Human Right to Water and Sanitation (HRWS) as universal water rights and further acknowledged that clean, sufficient, safe, acceptable, physically accessible and affordable drinking water and sanitation are essential to the accomplishment of all human rights.

In order to meet the global need for fresh water, researchers, academicians and industries are focused on desalination of seawater since seawater holds 97% of the total water on earth. Desalination technologies have the perspective to disentangle the issues of water scarcity and meet the global freshwater supply/demand. The most widely used technique for desalination is reverse osmosis, whereby high hydraulic pressure is used to separate salts from water through a semi-permeable membrane. However, reverse osmosis system requires high pressure that imposes high energy input cost, besides membrane fouling is another persistent problem in membrane separation that affects the performance of the system (Vrouwenvelder et al. 2008; Peñate and García-Rodríguez 2012). In the past decade, forward osmosis, energy-efficient membrane separation process has gained interest by the researches in the field of wastewater treatment, pharmaceutical and juice processing industries. Forward osmosis is an emerging osmotic pressure-driven membrane technology that overcomes the pressure-driven reverse osmosis process with relatively low fouling tendency which could be reversed. Moreover, this technique is also known as direct osmosis, engineered osmosis or manipulated osmosis that possesses a viable prospect for desalination of seawater; concentrate liquid foods and power generation (Zhao et al. 2012).

Forward osmosis is an osmotic pressure-driven membrane process that allows the solvent from less concentrated solution to high concentrated solution through a semi-permeable membrane. This process separates the water molecules dissolved in the feed solution without phase change. For an ideal forward osmosis, applied pressure difference is zero and the semi-permeable membrane used in the process completely excludes the solutes. The membrane used in forward osmosis is asymmetric in nature, i.e. it consists of two layers, namely, dense active layer and support bound layer. The membrane orientation plays a vital role during the forward osmosis application. Phillip et al. (2010) reported that reverse flux selectivity and the ratio of forward water flux to the reverse solute flux was independent of draw solution concentration and the structure of the membrane support layer, however, affected by the selectivity of the membrane active layer.

The efficiency of desalination process is affected by external concentration polarization and internal concentration polarization. Based on membrane orientation, both the concentration polarization are subdivided into concentrative and dilutive concentration polarization. In case of external concentration polarization, when feed solution faces the membrane active side concentrative external concentration polarization occurs while draw solution faces the membrane active side dilutive external concentration polarization occurs. Similarly, in the case of internal concentration polarization, when draw solution faces the active side of the membrane, concentrative internal concentration polarization occurs while feed solution faces the active side of the membrane dilutive internal concentration polarization occurs. According to McCutcheon and Elimelech (2006, 2007), concentrative external concentration polarization and dilutive internal concentration polarization plays a vital role during desalination process when feed solution is against the active side and draw solution is against porous support side of the membrane.

This chapter intends to provide a valuable insight into water treatment using forward osmosis and different types of membranes used for the process. It also presents comprehensive categories of commercially available membrane modules. This chapter also focuses on the advantages, feasibility, challenges and opportunities of engineered osmosis for water treatment. The significant progress of engineered osmosis in the area of water treatment, commercial availability, process configurations and operations are discussed. Further, emanating the potential area of improvements in near future, integrated designs and other innovative technologies for water treatment by engineered osmosis are also discussed.

10.2 Forward Osmosis

Forward osmosis is an emerging novel water treatment technology and superior to reverse osmosis process with respect to capital cost, energy consumption and membrane fouling. In forward osmosis, water molecules are transported from higher concentration to lower concentration due to osmotic gradient as the driving force through the semi-permeable membrane. Forward osmosis technology operates at insignificant or no hydraulic pressure which ultimately reduces the energy consumption compared to other conventional water treatment methods. Further, it exhibits reversible membrane fouling eventually leading to circumventing the exorbitant cleaning process. Forward osmosis is also considered as a standalone technology that effectively rejects and act as a barrier for most of feed stream contaminants (Coday et al. 2014). In addition, forward osmosis has the prospective to accomplish higher water recovery (Ansari et al. 2018) and flux (McCutcheon and Elimelech 2008) during wastewater treatment. Recently, forward osmosis is applied for treating variety of complex feed streams such as textile wastewater (Han et al. 2016), waste from oil and gas operations (Hickenbottom et al. 2013), swine wastewater (Wu 2018), landfill leachate (Li et al. 2017), municipal wastewater (Wang et al. 2016), radioactive wastewater (Liu et al. 2018) and mining wastewater (Thiruvenkatachari et al. 2015).

The performance of forward osmosis mainly depends on membrane material, membrane module, draw solution and feed type for effective treatment of wastewater.

10.2.1 Types of Membranes

Selection of membrane plays a vital role in the performance and assessment of forward osmosis process. The quintessential forward osmosis membrane shall possess high water flux and solute rejection (feed and draw solutions), negligible membrane fouling, reduced concentration polarization, non-porous membrane, resistance to chemicals, membrane hydrophilicity and higher thermomechanical robustness. Researchers and industrial practitioners are focused on developing a membrane with desirable attributes for its application in numerous fields. Formerly, natural sources like animal intestine and bladders, rubber, ceramic materials, etc., were used as membrane materials for the early forward osmosis research. Hitherto, the development of commercial forward osmosis membranes by Hydration Technologies Inc. in the late 1990s, the commercial reverse osmosis membranes were used. Based on the fabrication material, forward osmosis membranes are classified into cellulosic membrane and composite membrane. Table 10.1 compares the important characteristics of the forward osmosis membranes utilized for water treatment.

10.2.1.1 Cellulosic Membranes

Ever since Schutzenberger, Germany discovered acetate ester of cellulose more than sesquicentennial, cellulose acetate has been a significant material in various applications especially for water treatment. With the advent of phase inversion technique, cellulose acetate in the first instance was used as an osmotic drug delivery system before its use in the desalination process. Cellulosic membranes are commonly

Table 10.1 Important characteristics of forward osmosis membranes used for water treatment

Forward osmosis membranes	Porosity	Water flux (L/m^2 h)	Reverse salt flux	References
Cellulosic membranes				
Cellulose acetate	42.45–56.14%	2.04	98.61%	Shang and Shi (2018)
Cellulose acetate membrane was modified with multi-walled carbon nanotubes	67.18–74.15%	9.1–27.1	0.2239–0.2462 mol NaCl/m^2 h	Jin et al. (2016)
Cellulose triacetate	–	6.0	97.8%	Xiao et al. (2017)
Cellulose triacetate/cellulose acetate (CTA/CA)-based membranes	Porous	10.39	0.084 mol NaCl/m^2h	Nguyen et al. (2013)
Nitrocellulose-based membranes	–	5.6	50.7%	Kocherginsky (2013)
Polyvinyl alcohol modified cellulose acetate	Microporous	8.8	89.9%	Ahn et al. (2015)
Composite membranes				
Polydopamine coated thin-film composite membrane	–	2.2	90–95%	Guo et al. (2018)
Sulfonated polysulfone (SPSU)/poly(vinyl chloride) (PVC) substrate based high-performance thin-film composite	Porous	25.53	89.85%	Zheng et al. (2018)
Thin-film nanocomposite membrane modified with graphene oxide	3.20%	13.2	79.2%	Koo et al. (2018)
Thin-film nanocomposite membrane modified with graphene quantum dots	Porous	102.0	39% Na_2SO	Bi et al. (2018)
Thin-film nanocomposite membrane modified with silver nanocomposite	–	15.2	97.5%	Qiu and He (2018)

synthesized using a dip-coating polymer (acetylated cellulose) by phase inversion technique; hence, known as phase inversion formed cellulosic membrane. Cellulosic membranes are considered as the better renewable resources and have negligible impact to its surrounding environment. Cellulosic materials like cellulose nitrate, cellulose ester, cellulose acetate, cellulose triacetate, and its blended/modified forms are utilized in the process of water treatment. The surface hydrophilicity, porosity, tensile strength, reverse solute flux, internal concentration polarization and fouling are important parameters analysed for its utilization in water treatment process. Cellulose triacetate exhibited better hydrophobicity and reverse solute flux than cellulose acetate. Hydration Technologies Inc. commercialized forward osmosis membranes that presumed to be cellulose triacetate or its derivatives, which exhibited higher water flux and found suitable for water recovery by forward osmosis than commercial reverse osmosis membrane. Further, cellulose triacetate membrane synthesized by immersion precipitation showed higher flux than commercial Hydration Technologies Inc. membranes (Li et al. 2013). Ahn et al. (2015) reported that polyvinyl alcohol modified cellulose acetate membranes exhibited 20% increased water flux than cellulose acetate membrane. Zhang et al. (2011) developed cellulose ester membrane with relatively higher water flux and low internal concentration polarization for treating seawater. In order to improve the forward osmosis process performance, solute rejection and hampers of internal concentration polarization, recently, cellulose acetate membrane was modified with multi-walled carbon nanotubes (Jin et al. 2016). These cellulosic membranes exhibited a significant increase in water flux while treating seawater/saline water, however, it suffers from high internal concentration polarization. In order to overcome internal concentration polarization, further research has to endeavour.

10.2.1.2 Thin-Film Composite Membranes

Thin-film composite membranes are fabricated by in situ interfacial polymerization, developed to enhance the membrane permeability with low solute rejection. Further, thin-film composite membranes are non-porous in nature with a low structural parameter to reduce the internal concentration polarization. Surface porosity, thickness and tortuosity have a significant influence on water flux and internal concentration polarization (Lee et al. 2018a, b; Yip et al. 2010). The unique forge property of the membrane has dominated the commercial forward osmosis market due to its low-cost fabrication and enhanced stability. Thin-film composite polyamide membrane is the standard membrane used for desalination of water with increased water flux, low solute flux and good chemical stability (Yip et al. 2010). Though the water flux and solute rejection of thin-film composite are higher than cellulosic membrane, they are not sufficient enough to meet the current needs. Hence, researchers are using polymer coatings on thin-film composite to functionalize membrane surface and enhance its performance. Guo et al. (2018) developed polydopamine coated thin-film composite membrane that augmented water flux, solute rejection and antifouling performance. Further, mineralized thin-film composite membranes showed higher water flux and phenol rejection in forward osmosis compared to thin-film composite polyamide membrane (Huang et al. 2018). Graphene oxide incorporated thin-film nanocomposite membrane exhibited outstanding water flux and phosphorus rejection than thin-film nanocomposite membrane (Koo et al. 2018). Biofouling is a pitfall for the performance of polymeric membrane especially during desalination and wastewater treatment. In order to improve the membrane fouling resistance and performance, thin-film nanocomposite membrane was modified with zwitterion functionalized with silver nanocomposite (Qiu and He 2018), graphene oxide (Mahdavi and

Rahimi 2018) and graphene quantum dots (Bi et al. 2018) for potential applications in desalination and water treatment.

10.2.1.3 Other Membranes

Recently, hydrogel-based forward osmosis membranes has experienced a resurgence of interest for its low fouling and migration propensity. Qin et al. (2015) developed hydrogel-based nanocomposite forward osmosis membrane for simultaneous separation of oil/water and desalination for shale gas wastewater. When compared with commercially available cellulose triacetate membrane, hydrogel-based nanocomposite forward osmosis membrane exhibited lower membrane fouling and three times the higher water flux with a removal efficiency of >99.9 and >99.7% for oil and multivalent ions. The performance of the hydrogel-based forward osmosis membrane highly depends on the degree of crosslinking layer because it maintains the surface hydrophilicity thereby enhances the strength, antifouling and separation capacity (Qin et al. 2018). In drug delivery, environmentally sensitive hydrogels are used as a smart delivery system that protects the drug compounds from antagonistic environment/interactions. Especially, light-sensitive, pressure-responsive and electro-sensitive hydrogels are widely used in the application of biosepation process (Qiu and Park 2001). Therefore, modifying the chemical structure and incorporation of light-absorbing carbon and graphene moieties on the membrane would have implications on the development of hydrogel-based forward osmosis membrane for water treatment.

10.2.2 Membrane Modules

Membrane module configurations determine the way that the membrane is packed or held for its application. For laboratory-scale research, flat-sheet or tubular membranes are used while plate and frame module is used for large-scale applications. Generally, there are five types of membrane modules used for forward osmosis process, namely, (1) plate and frame, (2) tubular, (3) spiral wound, (4) hollow fibre and (5) hydration bags. Each of these membrane configurations has its own pros and cons during its applications (Fig. 10.1).

10.2.2.1 Plate and Frame Module

Plate and frame module is the simplest and oldest module utilized for packing flat-sheet membrane. In this module, flat-sheet membrane is placed between the frame and support cassette packages. Plate and frame membrane module configuration is also known as stacked membrane modules with a packing density of 100 m^2/m^3. This module is well suited for treating waste streams with apparent

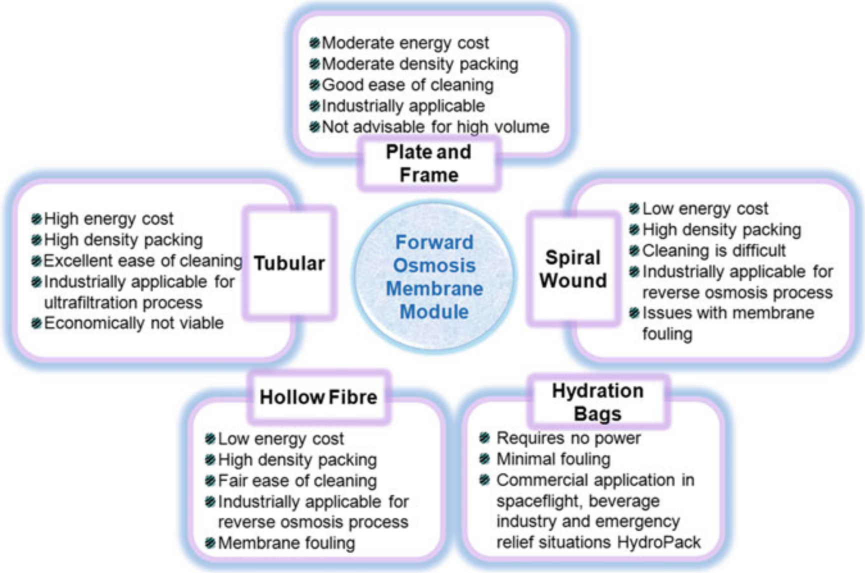

Fig. 10.1 Forward osmosis membrane modules

fouling and viscosities. The main limitations of plate and frame module are (1) low packing density, (2) lack of membrane support, (3) not suitable for high volume streams, (4) monitoring robustness is difficult, (5) rudimentary process parameters and (6) stacked flow distribution (Cath et al. 2006). However, this module exhibits simple flow channel which is suitable for large-scale forward osmosis process.

10.2.2.2 Tubular Module

Tubular membrane module is generally used in ultrafiltration system for water streams with high fouling/viscosity. The packing density of this module is 500 m^2/m^3 and the membrane used is not self-supporting. Though, it possesses higher packing density and simple fabrication than plate and frame module. It is not commercially used for forward osmosis since it endures high internal concentration polarization. In addition, water flux is insignificant and the module is uneconomical for forward osmosis process (Cath et al. 2006). The flow regime for the tubular module is turbulence which limits concentration polarization and fouling during its application.

10.2.2.3 Spiral Wound Module

Spiral wound module configuration is the most common module used industrially for water treatment. The packing density of this module is 600 m^2/m^3 with high membrane area to volume ratio. Spiral wound module has its commercial application in various membrane related applications from ultrafiltration to forward osmosis system (Schwinge et al. 2004). Among the membrane modules, spiral wound module exhibits ease of operation, cleaning and low fabrication cost. Jeon et al. (2018) investigated the accurate model for spiral wound forward osmosis module based on internal and external concentration polarization and reported that transmembrane pressure plays a vital role during the process. Moreover, reversible and irreversible organic foulant plays a crucial role in fouling of cellulose triacetate spiral wound module during desalination and wastewater treatment (Im et al. 2018). Attarde et al. (2016) reported that Spiegler–Kedem model exhibited better suitability than solution diffusion model for design and analysis of large-scale forward osmosis and pressure retarded osmosis applications. Pilot-scale forward osmosis spiral wound cellulose triacetate membrane module showed its suitability for concentrating real municipal wastewater with higher rejection to organic matter and phosphorus, however, exhibited relatively low separation of ammonium (Wang et al. 2016).

10.2.2.4 Hollow Fibre Module

Hollow fibre module is similar to tubular module but it possesses packing density of up to 1600 m^2/m^3. The module uses self-supporting membrane during its application and ideal for high volume water streams. The flow regime for hollow fibre is laminar unlike tubular the mixing is restricted at the membrane surface (Cath et al. 2006). Further, the module suffers from fouling and membrane clogging, hence, its application is restricted to treatment of water streams with a limited concentration of fouling agents. Polyethersulfone hollow fibre forward osmosis membrane fabricated using interfacial polymerization had the potential for seawater desalination with a superior salt flux to water flux ratio (0.094 g/L) than other forward osmosis membranes reported in the literatures (Chou et al. 2010). Wang et al. (2009) demonstrated that *p*-xylylene dichloride modified asymmetric polybenzimidazole nanofiltration hollow fibre membranes could be used in forward osmosis process by adjusting its pore size. Further, internal concentration polarization is the main limiting factor that affects water flux which is influenced by the porous support layer; therefore, further investigation would improve its performance during seawater desalination.

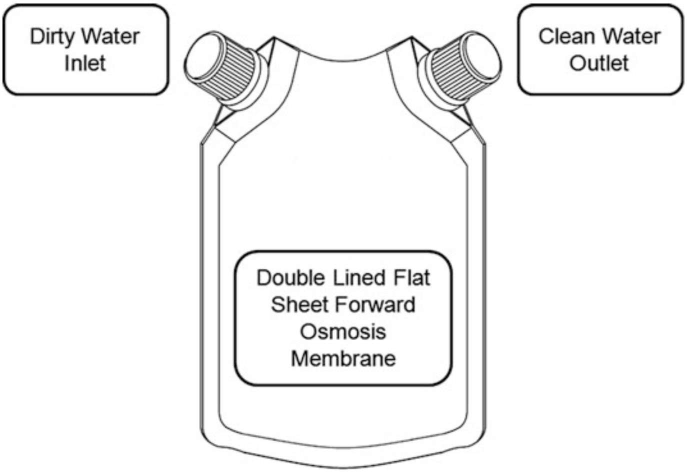

Fig. 10.2 Forward osmosis bags

10.2.2.5 Hydration Bags Module

Hydration bags module are also known as osmotic hydration bags or forward osmosis bags that uses double lined flat-sheet forward osmosis membrane as shown in Fig. 10.2. Recently, NASA Kennedy Space Center, Cape Canaveral, FL, United States and Hydration Technologies Inc. (HTI), Albany, Ontario, Canada developed the forward osmosis bags that converts impure water to pure water through semi-permeable membrane and concentrate the sugar solution. Originally, this module was used to forge sugar/emergency drink from sea and brackish water streams (Nicoll 2013).

10.3 Draw Solutions

The draw solution is the source for driving force in the forward osmosis process. It is also known as osmotic agent/media/engine, driving solution and brine solution. The choice of suitable draw solution is pivotal for the development of forward osmosis technology. The draw solution significantly influences the cost, separation process, accomplishment and the viability of the process. The first and foremost characteristic of draw solution selected for the process should be non-toxic with relatively high osmotic pressure (McCutcheon and Elimelech 2006). Further, it should be economical and easily available with the ease of regeneration and recovery (Cai 2016). The choice of draw solution varies with forward osmosis application and the selection is slightly arduous and intricated. In addition, the volume of draw solution required for the process should also be considered, for instance, the largest desalination capacity in India is 100,000 m^3/day while in Ras Al-Khair in Saudi, it is 9,170,391 m^3/day (largest in the world), hence, the volume of draw solution and ease of regeneration should be contemplated while designing the process. Generally, draw solution is categorized based on the solute nature like volatile compounds (ammonium bicarbonate, sulfur dioxide), organic compounds (glucose, switchable polarity solvents, ethanol), inorganic compounds (sodium chloride, magnesium chloride, ammonium sulfate) and novel synthetic compounds (magnetic nanoparticles, polyelectrolytes of polyacrylic acid sodium, polymer hydrogel). Of all the draw solutions, sodium chloride has been considered as an ideal draw solution for desalination in terms, cost, availability, high osmotic pressure and ease of regeneration. Table 10.2 shows the various draw solutions and their regeneration methods used in water treatment.

The draw solution characteristics such as molecular size, diffusivity and viscosity significantly influence the internal concentration polarization which in turn affects the water flux. For the past decades, researchers focused on identifying a suitable draw solution for the forward osmosis process. Earlier, most of the studies

Table 10.2 Draw solutions and regeneration methods

Draw solutes	Regeneration method	Advantages	Disadvantages
Aluminium sulfate	Precipitation by calcium hydroxide	Energy-efficient	Toxic by-products
Ammonium bicarbonate	Seawater/ brackish water treatment	Low capital cost, Energy-efficient	Poor water quality, complicated procedures, toxic by-products
Ammonium bicarbonate	Thermal separation	Easy and efficient	Energy-intensive, poor water quality
EDTA sodium salts	Nanofiltration	Low operating cost, high salt rejection	Limited only to the divalent salts
Glucose	Seawater desalination	Easy	Energy-intensive
Hydrogels	Magnetic heating	Eco-friendly	Poor recovery rate
Inorganic salts	Reverse osmosis	High water recovery rate, high salt rejection	High operating cost
Magnetic nanoparticles	Ultrafiltration	Low operating cost	Poor salt rejection
Sodium salts	Desalination of brackish water	High water recovery	High capital cost of electrodes
Sucrose	Waste water treatment	Easy	Not pure water
Volatile solutes	Heating/thermal separation	Energy-efficient, easily available	Poor water quality, toxic

were focused on salts, sugar solution and their combination since salt draw solution exhibits higher flux but has high reverse solute diffusion. While in case of sugar as draw solution, shows low reverse solute diffusion with lower water flux. Therefore, its combination exhibited better results (Al-aibi et al. 2016) but still, recovery and ease of regeneration was still an issue. Ou et al. (2013) reported crosslinked poly (*N*-isopropylacrylamide) with sodium acrylate (thermosensitive polyelectrolytes) could be a good candidate for forward osmosis with ease of water recovery and reuse of polyelectrolyte. Recently, researchers have gained attention on smart materials with jeopardized regeneration efficiency like hydrogels and magnetic nanoparticles as draw solution for desalination and wastewater treatment. Zhao et al. (2013) developed thermosensitive multifunctional iron oxide nanoparticles grafted with copolymer poly-(sodium styrene-4-sulfonate)-co-poly (*N*-isopropylacrylamide) for seawater desalination. Recently, South China University of Technology patented a hydrogel capable of desalinating seawater (Fan et al. 2018).

10.4 Applications in Water Treatment

Forward osmosis membrane technology has a wide range of applications in the field of wastewater treatment, water purification, desalination, pharmaceutical industry, food processing and power generation. Commercial implementation of this technology is emanating in the field of water purification, oil and gas industry and pharmaceutical industry. Recently, Aquaporin and Berghof Membranes promulgated a joint developmental agreement to launch forward osmosis products targeted for high-strength industrial wastewater, food and beverage process streams. Figure 10.3 illustrates the challenges and applications of forward osmosis in various fields.

Since 1970, forward osmosis system was proposed for removing salt impregnated in water. However, after the commercialization of forward osmosis membranes, the technology had revivified and laid its impression in wide range of applications. Generally, forward osmosis desalination process involves two main processes namely, osmotic dilution of osmotic agent solution and instigate the separation of fresh water from the diluted osmotic agent solution.

For desalination process, broadly, two types of draw solutions are employed. Initially, Neff initiated volatile compounds as draw solution for desalination in 1964. McCutcheon et al. (2005) developed a novel ammonia-carbon dioxide as draw solution for desalination process that resulted in high water flux and water recovery. Recently, Feng et al. (2018) reported that the performance of ammonium bicarbonate draw solution is significantly influenced by the temperature of feed and draw solution. Trimethylamine-carbon dioxide draw solution is another volatile draw solution that has gained attention as an alternative to ammonia-carbon dioxide with higher viscosity and lower diffusion coefficient for desalination (Xia et al. 2018). However, the challenges with volatile draw solution are incomplete removal of ammonia, scaling, back diffusion and not suitable for drinking water (Cai 2016).

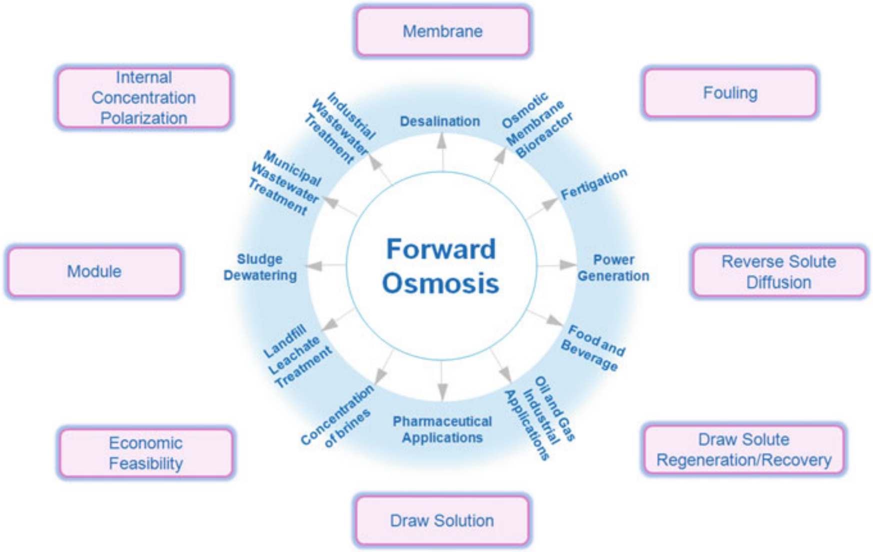

Fig. 10.3 Challenges and applications of forward osmosis

Second, uses of water-soluble salts/particles as draw solution for the generation of fresh water. Achilli et al. (2010) investigated 14 draw solutes such as calcium chloride, calcium nitrate, potassium bromide, potassium chloride, potassium bicarbonate, potassium sulfate, magnesium chloride, magnesium sulfate, sodium chloride, sodium bicarbonate, sodium sulfate, ammonium chloride, ammonium bicarbonate and ammonium sulfate for seawater desalination using flat-sheet cellulose triacetate membrane. Ling and Chung (2011) used super hydrophilic nanoparticles as draw solution for water reuse and desalination process in an integrated forward osmosis—ultrafiltration system, where ultrafiltration system was used to recover the draw solution. Zufia-Rivas et al. (2018) proposed a magnetic nanocomposite with magnetite nanoparticles and sodium polyacrylate as draw solution for polluted continental or wastewaters and the nanoparticles would be regenerated by magnetic decantation. Table 10.3 illustrates the recent applications of forward osmosis in water treatment and desalination application.

Demonstration plant operation of forward osmosis integrated nanofiltration system with magnesium as draw solution produced a suitable quality of water for irrigation purposes (Corzo et al. 2018). Ge et al. (2012) proposed a novel poly (acrylic acid) sodium salt as draw solution for textile industry wastewater treatment. Further, the draw solution was re-concentrated using membrane distillation process. Poly (ethylene glycol) diacrylate coated cellulose acetate membrane exhibited reduced internal concentration polarization, thereby; making forward osmosis as an efficient alternative to reverse osmosis for desalination (Monteiro 2012). Pilot-scale forward osmosis experiments for municipal wastewater treatment using seawater as draw solution exhibited significant improvement in terms of energy requirement

Table 10.3 Recent advances in water treatment and desalination employing forward osmosis

Modern applications	Draw solution	Membrane	Water flux (L/ m^2h)	Water recovery (%)	Draw solution regeneration	References
Acid mine drainage	Sodium chloride	Thin-film composite forward osmosis membrane	5.5–20.5	50	–	Vital et al. (2018)
Brackish water and seawater	Ferric sulfate	Cellulose triacetate membrane	3.75–1.61	–	Chemical precipitation method	Qasim et al. (2017)
Distillery wastewater and melanoidins solution	Magnesium chloride, hexahydrate solution	Aquaporin biomimetic membranes	6.3 and 2.8	70	–	Singh et al. (2018)
Landfill leachate	Sodium chloride	Aquaporin embedded flat-sheet forward osmosis membrane	–	51.5	Reverse osmosis/ electrodialysis	Iskander et al. (2018)
Medical radioactive liquid waste	Sodium chloride	Thin-film composite polyamide forward osmosis membrane	20.4	40	–	Lee et al. (2018a, b)
Oil and gas operations wastewater	Sodium chloride	Cellulose triacetate membrane	2.5–14	80	–	Hickenbottom et al. (2013)
Printed circuit board wastewater	Electroless nickel plating solution	Thin-film composite forward osmosis membrane	39.4	–	–	Gwak et al. (2018)
Seawater	Fertilizer derived draw solution	Cellulose acetate membrane	–	30	Not necessary	Phuntsho et al. (2011)
Sodium chloride in deionized water	Magnesium sulfate	Cellulose acetate membrane	6.8	–	–	Sairam et al. (2011)

and area demand over conventional wastewater treatment (Hey et al. 2018). Xue et al. (2015) proposed a novel strategy to enrich nutrients in municipal wastewater using seawater-driven forward osmosis. Further, municipal wastewater pretreatment with microsieving before subjecting to forward osmosis is considered as a potential technology for protecting the environment from adverse effects (Hey et al. 2017). Cornelissen et al. (2008) demonstrated that reversible and irreversible fouling of thin forward membrane could be eliminated by when the active side of the membrane faces the activated sludge. Lampi and co-authors patented forward osmosis pressurized device and process for generating potable water from seawater, urine, sweat, brackish water and the like (Lampi et al. 2007). Therefore, forward osmosis and its integrated system offers low energy requirement, reduced fouling, high-quality drinking water, draw solution recovery and avoids chemical during the process (Cath et al. 2006; Tan and Ng 2010).

Talaat (2009) demonstrated that 38% of spent dialysis fluid water could be regenerated by forward osmosis employing cellulose triacetate membrane and sodium chloride as draw solution. Forward osmosis has been proposed as a new iteration for microalgal dewatering process (Munshi et al. 2018; Ye et al. 2018). Volpin et al. (2018) investigated that novel fertilizer drawn forward osmosis concept on concentrating human urine where 60% of urine was concentrated for ammonia stripping, and 50% nitrogen and 40% phosphorous (struvite fertilizer) was recovered from urine. Forward osmosis employing ammonium bicarbonate as draw solution (91.6% water recovery) has been proposed as the effective and eco-friendly technique than pressure retarded osmosis (86.6% water recovery) for the treatment of landfill leachate (Li et al. 2017). Microbial fuel cells integrated with anaerobic acidification and forward osmosis produced high-quality effluent and concurrently both bioelectricity recovery and wastewater reclamation (Liu et al. 2017).

Lee et al. (2018a, b) reported that forward osmosis process using sodium chloride as draw solution showed 99.85% rejection rate of natural and radioactive iodine while ultrafiltration and two-pass reverse osmosis hybrid processes showed 99.7% rejection. Liu et al. (2018) compared the removal of Cs(I) from radioactive wastewater by three commercial asymmetric forward osmosis membranes (i.e. cellulose triacetate with a cast nonwoven support, cellulose triacetate embedded with polyester screen support and polyamide-based thin-film composite embedded with polyester screen support) and reported that cellulose triacetate embedded with polyester screen support showed higher Cs(I) retention of 96.24% with a water flux of 33.34 L/m^{2}h employing sodium chloride as draw solution. Zwitterionic surface modified thin-film composite membrane could be used for grey water treatment (Wang et al. 2018).

Integration of forward osmosis with other quality impaired water treatment method exhibited better performance. Forward osmosis coupled with low-pressure reverse osmosis for desalination exhibited better quality of water at low energy and cost with minimal fouling than high-pressure reverse osmosis process (Yangali-Quintanilla et al. 2011). Similarly, Linares et al. (2016) assessed the performance of hybrid forward osmosis—low-pressure reverse osmosis system for seawater desalination and wastewater recovery. Their result showed that the expenses associated with hybrid forward osmosis—low-pressure reverse osmosis system is 16% lower than the conventional reverse osmosis and 17% lower than combined conventional reverse osmosis and membrane bioreactor—reverse osmosis—advanced oxidation process. Thus this hybrid forward osmosis–low-pressure reverse osmosis system is clearly attractive in terms of low fouling and energy-saving.

Cornelissen et al. (2011) developed an osmotic membrane bioreactor coupling the osmotic membrane bioreactor with a reverse osmosis system for treating industrial and municipal wastewater. The developed system exhibited a water flux of 15 L m^2/h at 0.5 M sodium chloride as draw solution that found to be economical than conventional membrane bioreactor coupled reverse osmosis treatment. In osmotic membrane bioreactor based wastewater treatment, removal efficiency of organic compounds with molecular weight less than 266 g/mol is highly based on biological degradability (Alturki et al. 2012). Furthermore, anaerobic osmotic membrane bioreactor potentially recovers both water and energy from low-strength wastewater (Chen et al. 2014, Gu et al. 2015). However, osmotic membrane bioreactor technology is still in its infancy.

10.5 Economic Analysis and Future Prospects

Forward osmosis is an emerging and intriguing technology in the field of water treatment. Compared to other membrane processing, forward osmosis is viable in terms of fouling, scaling, water recovery by high saline concentration, cost and energy consumption scenario. Buckwalter (2017) conducted a study on techno-economic analysis for wastewater treatment and energy recovery using forward osmosis. It was reported that the lifecycle cost of the proposed forward osmosis system was $29.7 million with a specific treatment cost of about $0.35 per cubic metre of treated wastewater. Further, the lifecycle cost of forward osmosis membrane and forward osmosis facility was about $16.4 million and $10 million/million gallons per day of feed solution (Buckwalter 2017). Corzo et al. (2018) reported a comparative simulation study on energy requirements of forward osmosis integrated nanofiltration process and ultrafiltration-integrated reverse osmosis process in a demonstration plant. The study exhibited that the total energy consumption of forward osmosis integrated nanofiltration was 40% higher than ultrafiltration-integrated reverse osmosis process, however, large-scale estimation might be substantially more economical than ultrafiltration-integrated reverse osmosis process. Bench-scale test of fertigation using forward osmosis is still in their infancy and uneconomical. However, the commercial and pilot-scale study of forward osmosis application in wastewater treatment, osmotic dilution of saline water using impaired water and highly saline wastes has the moderate potential for improvement and economically viable (Hancock 2013). Linares et al. (2016) reported that cost and operational expenditures of forward osmosis plant mainly depends on forward osmosis membrane modules, packing density and water permeability. Further research on these areas could reduce the cost and become more economical.

Further development of forward osmosis process for commercially applications, researchers and industrialist are focused on developing novel forward osmosis membranes, minimizing fouling and concentration polarization, identifies novel draw solutions, modelling and designing of module and forward osmosis system. Currently, the groups actively included in forward osmosis process are Oasys Water Inc., Aquaporin Inside^{TM}, NASA, The University of Connecticut in United States, De.Mem Pte Ltd., Berghof Membranes in Netherlands and CSIRO food innovation centre in Australia. Though forward osmosis is more versatile technology, but still it is in cradle stage. Researchers are focussed on developing hybrid forward osmosis membranes, integrating forward osmosis and reverse osmosis systems and discovering novel draw solutions for enhancing the technology in wastewater treatment. Therefore, the future progress in forward osmosis system is to overcome the basic problems on developing a robust membrane with higher water permeability/flux and solute rejection, module configuration to process large volume of sample without fouling and identifying draw solutions that induces high osmotic driving force, zero toxic, compatible with membrane, cost-effective, reliable and ease of regeneration/recycle. This would expedite the applications of forward osmosis in various fields.

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Part III

Biological Wastewater Treatment and Biological Activities

Chapter 11
Recent Developments in Biological Nutrient Removal

R. Yukesh Kannah, M. Gunasekaran, Gopalakrishana Kumar, U. Ushani, Khac-Uan Do and J. Rajesh Banu

Abstract Conventionally, activated sludge process (ASP) is most commonly employed for wastewater treatment. However, the conventional treatment system is inefficient for the removal of biological nutrient to greater extent. Nutrients such as nitrogen (N) and phosphorus (P) has high influence on the receiving water body, cause eutrophication and algal bloom. It leads to reduce of dissolved oxygen (DO) level and in turn high risk to aquatic life. Eutrophication is a major problem in developing countries and is responsible for water pollution. Removal of biological nutrient in the wastewater is an essential task to lead the positive impacts on solving the environmental pollution issues. Developing the biological nutrient removal approach in the wastewater treatment to balance the biogeochemical system of the receiving aquatic environment. Biological nutrient removal is a challenging task and number of operational parameters governs its efficiency. This chapter focusses on recent development in the biological nutrient removal and governing factors of the process.

Keywords Nutrient · Eutrophication · Nitrification · Denitrification PAO

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11.1 Introduction

Water scarcity and shortage of clean water supply threaten developed, developing, and undeveloped countries (Subramaniam 2018). According to the United Nations world population prospects 2017 reports, the global population was expected to be 7.6 billion in 2018, it may be increased to 8.6 billion in 2030. On seeing the population growth rate, the supply of clean water demands high in the upcoming years. In order to minimize the water scarcity, treating wastewater is a beneficial option to save the ground and surface water quality. In worldwide, 80% of wastewater is directly discharged into the global waterway which causes eutrophication and depleting the dissolved oxygen (DO) level. Domestic is the major source of wastewater generation and direct discharge with a high concentration of nutrient (Powley et al. 2016). Domestic wastewater contains a high concentration of inorganic matter such as nitrogen and phosphorus in the dissolved form (Mekonnen and Hoekstra 2018).

In worldwide, the municipal wastewater treatment plant (MWWT) with nutrient removal system was successful in progress, which upgrade the wastewater treatment efficiency, and to control eutrophication issue in the receiving water bodies. Several researchers have suggested physical, chemical, biological, and combined physiochemical methods for nutrient removal (Sen 2015; Bunce et al. 2018). Among these, biological nutrient removal method is effective in removing toxic and harmful compounds in an inexpensive wat (Rajasulochana and Preethy 2016). Biological nutrient removal (BNR) is the process of removing of total nitrogen (TN) and total phosphorus (TP) from wastewater with the help of microorganism. Discharge of wastewater without removal of nutrients cause an adverse effect on the aquatic environment such as excess growth of phytoplankton, reduction in dissolved oxygen (DO) level, odor occurrences and increasing the pollution load.

Most commonly, municipal wastewater contains a high amount of nutrients residues when compared with industrial wastewater. In municipal wastewater stream TN occurs in the dissolved form and the concentration range between 25 and 45 mg/L. TN composed of 60% organic nitrogen and 40% ammonia. Similarly, P is also considered as an essential nutrient that presents in the wastewater. P enters into the environment through sedimentation, rock formation, and degradation process. In the agricultural sector, phosphorus plays a vital role and it acts as fertilizer and feed for crop production (Egle et al. 2016). In municipal wastewater, the concentration of phosphorus varied from 6 to 20 mg/L in the dissolved form.

Many researchers have suggested a cost-effective biological method to degrade the inorganic nitrogen compounds. The following processes are successfully established and executed for biological nutrient removal they are Anoxic/Oxic (AO) (Rajesh Banu et al. 2009a; Do et al. 2012) anaerobic/anoxic/aerobic (A_2/O) (Rajesh Banu et al. 2009b; Uan et al. 2013), Sequencing batch reactor (SBR) (Guo et al. 2007; Yuan et al. 2016), Attached growth (Al-Zreiqat et al. 2018), Modified Ludzack–Ettinger (Liu and Wang 2017), Modified Bardenpho (Emara et al. 2014), Step feed (Guo et al. 2007), University of Cape town (Mannina et al. 2016), Phostrip (Salehi et al. 2018) and Bio-Denitro (Irizar et al. 2004; Tabassum et al.

2018). Developing a proper treatment system for removal of excess nutrients from wastewater will control the environmental issues. Essential nutrient such as N and P is present in wastewater, which has market value when it can be recovered in the form of fertilizer. This chapter provides knowledge about recent updates in biological nutrient removal, different source and composition of nutrient in the wastewater. Meanwhile, the chapter offers information regarding treatment process involved in both biological nitrogen and phosphorus removal.

11.2 Biological Nitrogen Removal

Removal of nitrogen derivatives from treated wastewater is often essential before discharging into the sensitive environment. This will prevent eutrophication on receiving water body and accumulation toxic contamination in the groundwater. Removal of nitrogen can be adopted as fundamental part of treatment system or an additional part to an existing treatment system. Biological nitrogen removal is the process of removing toxic ammonia with the help of enzyme. The toxic nitrogen substances such as ammonia, nitrate, and nitrite are easily biodegradable with the help microorganism. Total nitrogen removal can be achieved by simultaneous biological nitrification and denitrification process. Some example reactors frequently suggested for biological nitrogen removal single sludge system, two sludge system, anoxic/aerobic, step feed anoxic/aerobic, intermittent aeration, postanoxic denitrification and sequencing batch reactor (Metcalf and Eddy 2014). Figure 11.1 show biological nitrogen removal.

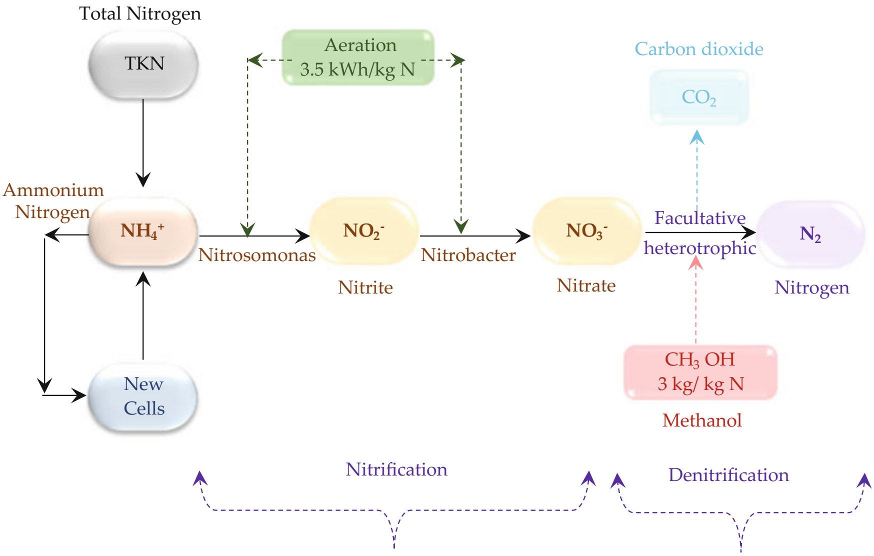

Fig. 11.1 Nitrogen removal pathway

11.2.1 Nitrogen as Pollution Compound

Nitrogen compound frequently occurs in food, air, water, and soil. If the concentration of nitrogen exceeds the limit cause unfavorable health condition to all living organism. Since nitrogen compound management in water and wastewater becomes mandatory due to their toxic effect. In drinking water, present nitrogen residue in the form nitrite and nitrate cause harmful effect to infants and adults. Excess intake of these compounds results in anemia, methemoglobinemia, and cause damage to liver by reducing the content of vitamin A. Especially for infants, excess ingestion of nitrate reduces the oxygen carrying capacity of hemoglobin and leads to death (Garcia-Segura et al. 2018). Wastewater contains varies forms of nitrogen such as organic nitrogen, ammonia nitrogen, nitrite (NO_2^-) and nitrate (NO_3^-). The direct discharge of untreated wastewater into the nearby water bodies results in eutrophication, deplete dissolved oxygen level and toxic to aquatic life (Zhang et al. 2018).

11.2.2 Nitrification and Denitrification Process

Nitrification is the process of converting ammonia into nitrate with the help of aerobic microbes. The biological conversion of ammonium nitrogen to nitrate takes place in two-phase. In the first-phase autotrophic microbe, *Nitrosomonas* convert ammonia into nitrite and in the second phase, *Nitrobacter* converts nitrite into nitrate. Figure 11.1 represents biological nitrification process. The following equation shows the two-phase of ammonia conversion:

$$2\,NH_{4^+} + 3\,O_2 \overset{Nitrosomonas}{\longrightarrow} 2\,NO_{2^-} + 2H_2O\ +\ 4H^+ + \text{New}$$

$$2\,NO_{2^-} + 2O_2 \overset{Nitrobacter}{\longrightarrow} 2NO_{3^-} + \text{New}$$

Denitrification is the process of converting nitrate into nitric oxide, nitrous oxide and nitrogen gas with the help of facultative heterotrophic microbes. Microbes involved in this process consumes nitrate as a final electron acceptor instead of oxygen. During conversion, the additional supply of methanol is required as carbon source. The degradation of carbonaceous organic substrate in this process is same as aerobic but only difference it takes place under strict anaerobic condition. Figure 11.1 represents nitrogen removal pathway. The following equation show the denitrification process.

$$6\,NO_3^- +\ 5\,CH_3OH \underset{heterotrophic}{\overset{Facultative}{\longrightarrow}} 3\,N_2 + 5\,CO_2 +\ 7\,H_2O + 6\,OH^-$$

11.2.3 Factors Influence the Biological Nitrogen Removal

The following factors are an influence on the growth of nitrifying and denitrifying microbes for effective biological nitrogen removal in the wastewater.

11.2.3.1 Dissolved Oxygen (DO)

DO is an essential parameter for the growth of nitrifier in the aerobic basin. For effective nitrogen removal, the maximum DO concentrations maintained in the reactor around 2.0–4.0 mg/L. Presences of DO concentrations less than 0.5 mg/L in anoxic zone will enhance the denitrifier activity.

11.2.3.2 Temperature

Temperature directly impact on the growth of nitrifier and denitrifier in the aerobic and anaerobic basin, respectively. The best temperature for growth of nitrifier was 22–37 °C and similarly for denitrifier was 2–50 °C (Fontenot et al. 2007; Sudarno et al. 2011).

11.2.3.3 pH and Alkalinity

During biological nitrogen removal, the pH and alkalinity of wastewater play an essential role. During the nitrification process, the nitrifier consumes alkalinity and it leads to pH drop. Low alkalinity will affect the growth of nitrifying microbes. Typically, 60 to 100 mg/L of alkalinity need to be maintained in the system for effective nitrification process (Breisha and Winter 2010). The desired alkaline condition in the system can be controlled by adding of the following alkaline agents for example hydrated lime, soda ash, or caustic soda.

11.2.3.4 Food to Microorganism Ratio

The term food to microorganism ratio refers to the amount of biodegradable substrate available for microorganism in the aerobic basin. Most commonly, 0.2–0.4 ratio was followed for activated sludge system (Metcalf and Eddy 2014). For biological nitrogen removal system, it depends on the growth of nitrifier and denitrifier microbes. During the design of *F*/*M* ratio for nitrogen removal, *F* value is based secondary influent BOD concentration. If the nitrogen removal reactors were designed in series with three compartments, then the *M* value may vary from one to another compartment. *M* value for the first compartment is based on reactor volume and solids concentration (microorganism). Similarly, for the second compartment, based on the combined volume of reactor (first and second compartment) and combined solid concentration. The same condition was followed for the third compartment M value.

11.2.3.5 Sludge Retention Time (SRT)

SRT is the essential parameter that influences in biological nitrogen removal. However, SRT is otherwise known as sludge age or mean cell residence time. SRT can express in terms of average time length of microorganism active in the system. If SRT is too low then the system may get affected due to insufficient growth of microorganism. Usually, many treatment systems were designed to remove carbonaceous biological oxygen demand (CBOD) within 2–4 days of SRT. However, the SRT for biological nitrogen removal may vary with respect to the following parameters temperature, reaction size and solid concentration.

11.2.4 Suspended Growth System

In this system, microbes are responsible for nutrient removal and upholding the substrate in suspension. Most of the industrial and municipal wastewater treatments were successfully operated by adopting suspended growth system. In aerobic suspended growth system, the dissolved oxygen level was maintained and it helps the microbes to maintain the substrate in suspension. For high organic biomass concentration, anaerobic suspended growth system was adopted to treat the industrial wastewater followed by removal of nutrients. For the effective removal of nitrogen, the following suspended growth systems were commonly adopted such as Ludzack–Ettinger, Modified Ludzack–Ettinger, aerobic granular activated sludge sequencing batch reactor (Hafez et al. 2010; Ekama 2015; Liu and Wang 2017).

11.2.4.1 Ludzack–Ettinger (LE) Process

In the year 1960–1970s, wastewater engineers had made many attempts to improve the efficiency of conventional activated sludge system for effective nitrogen removal. Ludzack–Ettinger have modified the system by introducing anoxic zone before aeration and clarifier. In this system, the thickened mixed liquor from the bottom of the clarifier was recycled to the influent line. This action could improve the activity of facultative microbes to metabolize the inorganic nitrate. If the recycling performance is get reduced then the rate of denitrification affected, due to insufficient supply of nitrate. Figure 11.2 represents Ludzack–Ettinger (LE) process.

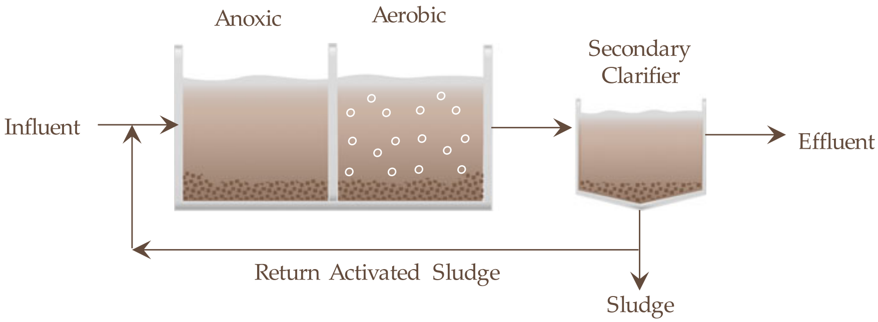

Fig. 11.2 Ludzack–Ettinger (LE) Process (Metcalf and Eddy 2014)

11.2.4.2 Modified Ludzack–Ettinger (MLE) Process

In this process, the original design of Ludzack–Ettinger process was upgraded to target the nitrogen compounds and to improve the removal efficiency. MLE process was similar to LE process, but slight modification was done to enhance the process efficiency. In MLE process, recycling of mixed liquor was between oxic to anoxic zone. The nitrogen removal efficiency was accelerated due to the internal recycling of nitrified wastewater. Excess recycling increases the dissolved oxygen concentration in anoxic zone. DO concentration above 0.5 mg/L in anoxic zone affect denitrification efficiency of the system and subsequent nitrogen removal efficiency (Hocaoglu et al. 2011).

11.2.4.3 Aerobic Granular Activated Sludge Sequencing Batch Reactors

Sequencing batch reactors (SBR) treatment system is opposite to conventional activated sludge process (ASP). SBR has more advantages than ASP, whereas the area required for treatment of wastewater is less for SBR when compared with ASP. In SBR, a single tank involves in four phases of the following process, fill, react, settle and decant. For denitrification, during fill phase mixing is provided in place of aeration. After completion of fill phase, methanol (carbon source) was supplied to enhance the nitrogen removal efficiency. In AGAS-SBR, only three phases are involved namely fill, react and settle.

i. ***Fill/draw***

Due to rapid settling velocity of granules in the reactor, wastewater can be introduced into the reactor at bottom of sludge bed. The concentration of sludge bed becomes denser after settling phase and it creates strict anaerobic environment. This favorable condition will reduce the concentration of nitrate in the wastewater and enhances denitrification process.

ii. ***Aeration***

In this phase, microbes play a vital role in simultaneous biological nutrient removal. This action is possible due to the granular structure; it comprises of both nitrifying and denitrifying microbes. The outer layer of granule contains nitrifying microbes and the inner core contains of denitrifying microbes. High concentration of dissolved oxygen (DO) was maintained in the reactor during aeration. Therefore, the outer layer of granular was closely contacted with DO, which enhances the growth of nitrifying microbes and ends up with nitrification process. The heterotrophic and autotrophic microbes present in the inner core of the granular denitrify the nitrate/nitrite into nitrogen gas.

iii. ***Settling***

In this phase, the granular where settled very faster and it requires short settling time. In addition to this, the idle time of the reactor was neglected. Then the treated wastewater can be easily separated from the granule.

11.2.5 Attached Growth System

In this system, microbes are responsible for converting the organic and inorganic substances. In the attached growth system, microbe forms a layer over surface of packing material and it is termed as biofilm. Recently, researchers have suggested natural and artificial packing material for the suspended growth system. In the nineteenth century, most commonly used attached growth reactor for biological nitrogen removal such as trickling filter and rotating biological contactors. Currently, researchers have developed integrated suspended growth system such as integrated fixed film activated sludge (IFAS) (Ekama 2015), integrated anoxic fixed bed and oxic moving bed biofilm (Gong et al. 2012) and hybrid upflow carrier suspended growth reactor (Le et al. 2018) for effective nitrogen removal.

Advantages

- Operated at high biomass concentration
- No phase separation in nitrogen removal
- Withstand shock loading
- Withstand in fluctuating operational condition.

11.2.5.1 Integrated Fixed Film Activated Sludge (IFAS)

In this system, conventional activated sludge system merged with fixed film media to enhance the nitrogen removal. Fixed film system is commonly employed in the cold regions, for effective oxidization of ammonia in the wastewater. The fixed media retained the biomass in the system for prolonged time and it is not removed

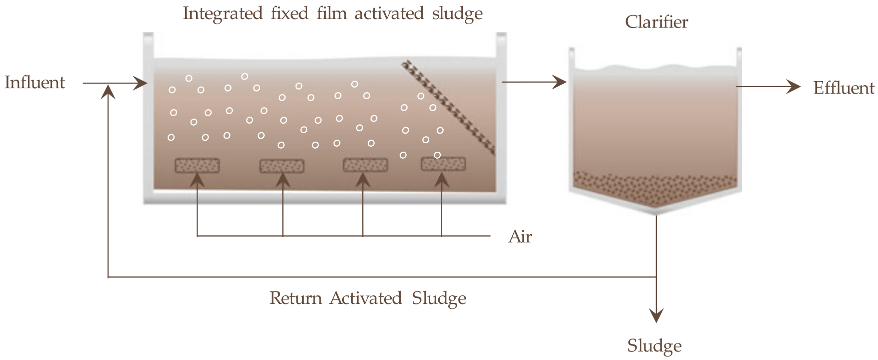

Fig. 11.3 Schematic diagram of integrated fixed-film activated sludge reactor (Ekama 2015)

from the system by conventional sludge waste method. In IFAS, ammonia-oxidizing microbes present on the media carry out effective nitrification than conventional activated sludge system. This could reduce system SRT, as it was based on nitrifier population. The static or moving fixed media, suspended rope or moving bed carrier is introduced to the aerobic reactor. Due to aeration, the nitrifier grows on the surface of fixed media and increases their population density in the aerobic reactor. Figure 11.3 shows the schematic diagram of integrated fixed-film activated sludge reactor.

11.2.5.2 Integrated Anoxic Fixed Bed and Oxic Moving Bed Biofilm

In this system, the conventional A/O reactor incorporated with anoxic fixed bed and oxic moving bed biofilm reactor for effective biological nitrogen removal (Gong et al. 2012). The organics substrate in influent could be employed for anoxic pre-denitrification, which causes more advantage in reduction of heterotrophic biomass production in oxic zones. The reactor was divided into seven-phase, the first two are anoxic phase (fixed bed biofilm) then next four where oxic phase (moving bed biofilm), and the settler placed at last. Heterotrophic biomass was recycled from settler to oxic phase for improving the microbial activity. The DO level was maintained in the range of 2–4 mg/L, in order to uphold the carrier in suspension. In anoxic zone, the DO level is maintained in the range of 0.5–0.7 mg/ L. This could create a favorable environment for denitrifying microbes to oxidize the nitrite/nitrate into nitrogen gas. Figure 11.4 shows the schematic diagram of integrated anoxic fixed bed and oxic moving bed biofilm reactor.

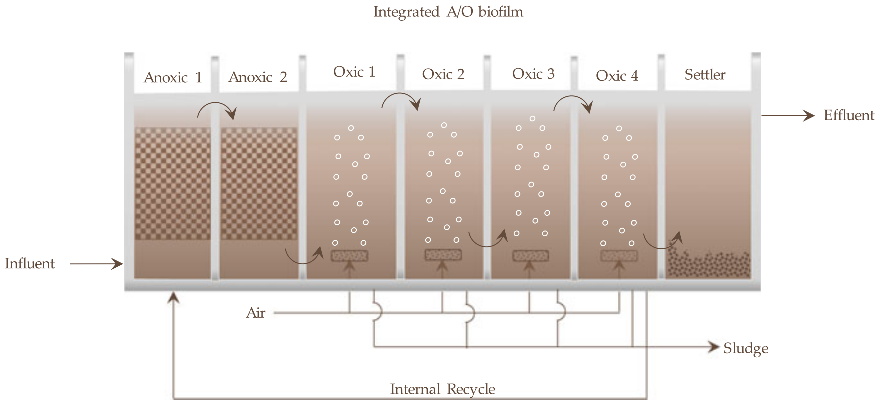

Fig. 11.4 Schematic diagram of integrated anoxic fixed bed and oxic moving bed biofilm reactor (Gong et al. 2012)

11.2.6 *Anammox Process*

Anammox is the process of oxidizing ammonium with the help of microbes under favorable anaerobic condition (Chi et al. 2018). Figure 11.5 show steps involved in anammox process. This process is an eco-friendly and economically feasible to treat nitrate and ammonia enriched wastewater. In this process ammonium oxidizing microbes plays a vital role in conversion of ammonium (NH_4^+) and nitrite (NO_2^-) into nitrogen (N_2) and nitrate (NO_3^-) without additional supply of carbon source under suitable anaerobic condition (Suneethi and Joseph 2011). The growth rate of ammonium oxidizing microbes was more effectively in high concentrated ammonium-rich wastewater with low COD/N ratio at long SRT (Tsushima et al. 2007; Bae et al. 2010; Shen et al. 2012). The following below equation explains the anammox process.

$$NH_{4+} + NO_2 \overset{\textit{Ammonium oxidizing}}{\longrightarrow} N_{2-} + 2H_2O$$

Anammox process has following advantages (1) reducing the oxygen requirement for nitrification (2) ignoring the additional supply of carbon source for denitrification (3) significant reduction in generation of excess sludge (4) achieving higher COD (chemical oxygen demand) removal rate (5) eradicating the release of greenhouse gas (CO_2) during conventional denitrification. It has certain disadvantages (1) adding significant quantity of nitrogen to atmosphere (2) slow growth rate (3) biomass washout. In order to overcome the following issues, many researchers have developed a new process to oxidize ammonia. They are (1) completely autotrophic nitrogen removal over nitrite—CANON (Yue et al. 2018) (2) single reactor system for high activity ammonia removal over nitrite—SHARON (Sri Shalini and Joseph 2018) (3) Deammonification (DEMON) (Gonzalez-Martinez

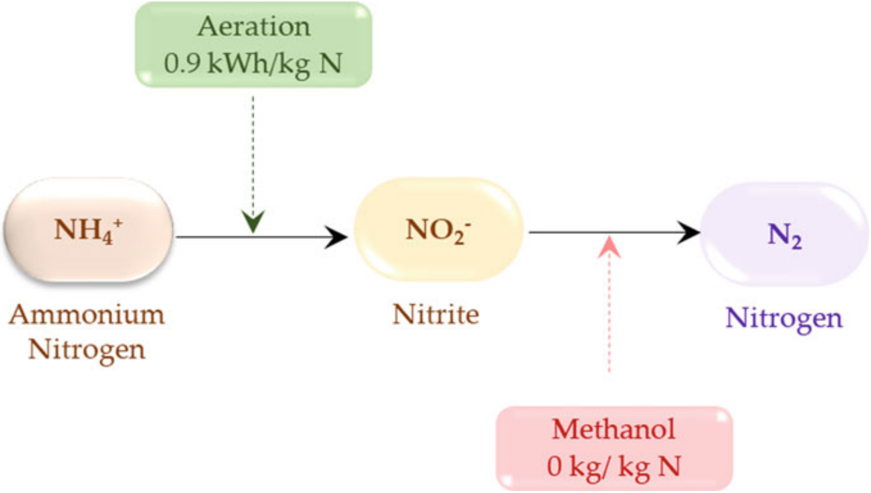

Fig. 11.5 Steps involved in anammox process

et al. 2015), and (4) Oxygen Limited Autotrophic Nitrification/Denitrification—OLAND (Nhu Hien et al. 2017).

Advantages

- Compared with nitrification–denitrification processes a small amount of excess sludge was produced.
- No need of additional supply of carbon source
- Aeration cost saves due to partial ammonia converted to nitrite.

11.3 Biological Phosphorous Removal

Phosphorous exist in different forms in water bodies. Various methods such as chemical precipitation, sedimentation, membrane filtration, and biological methods are implemented to remove phosphorous from water. Among these methods, biological is economically viable (Banu et al. 2008) and produces less sludge when compared with other methods. In the conventional treatment process soluble phosphorous present in the wastewater is getting integrated with microbial biomass. Later it was removed via sludge wasting (Banu et al. 2007). In general, microbes present in activated sludge process (ASP) accounts for uptaking phosphorus in the range of 1.5 to 2.5% of its biomass weight (Raj et al. 2013). In, enhanced biological phosphorus removal (EBPR) processes a group of specialized microbes called phosphorous accumulating organisms (PAO) can accumulate phosphorus into its biomass in the range of 5–12% (Rajesh Banu et al. 2009b). PAO communities consist of *Acinetobacter, Rhodocyclus,* and some coccus shaped bacteria (Bond et al. 1995; Wong et al. 2005). PAO is facultative microorganism and of capable of living in anaerobic and aerobic condition. EBPR process facilitates aerobic and anaerobic conditions for PAO to remove phosphorous from the wastewater.

11.3.1 Factor Influence the Biological Phosphorus Removal

EBPR is an economical process and by which comparatively higher amount of phosphorus removal is possible. The stability and reliability of EBPR were affected by various factors. It includes environmental and operational conditions such as carbon source, COD/P ratio, temperature, pH, cations, dissolved oxygen, solid retention time, and secondary phosphorus release.

11.3.1.1 Carbon Source

The efficiency of EBPR depends on the availability of carbon in the form of readily biodegradable carbonaceous oxygen demand or VFA. The economics of EBPR is mainly influenced by the choice of substrate and cost of the carbon source (Puig et al. 2008). Earlier study reveals that acetate is widely utilized as a carbon sole. Recently, the utilization of many other substrates was performed in EBPR. Table 11.1 list various substrate used as carbon source in EBPR.

11.3.1.2 COD/P Ratio

The influent COD or BOD to total phosphorus ratio (influent COD:P or influent C:P) plays a significant role in phosphorus removal from wastewater. According to Oehmen et al. (2007), the COD:P ratios should be 10–20 mg-COD/mg-P so that PAO tend to dominate the EBPR.

11.3.1.3 Cations

The stability of EBPR mainly depends on cation concentration of the influent wastewater (Schönborn et al. 2001). Water-soluble orthophosphate (PO_4^{3-}) is an

Table 11.1 List various substrate used as carbon source in EBPR

S. No	Process	Substrate used	References
1.	EBPR	Propionate	Oehmen et al. (2007)
2.	A_2O-MBR	Cell lysis	Rajesh Banu et al. (2009b)
3.	AOA	Acetate	Xu et al. (2011)
4.	SBR	Glucose	He et al. (2018)

anion having three negative charges. Phosphorus on its own cannot move across the membrane as it was negatively charged. Its transportation across the microbial membrane need charge neutralization and was facilitated by cations (Mg^{+2}, P^{+}). The charge of orthophosphate is neutralized, when it binds with cations. The neutralized ion can be transported across the cell membrane. Therefore, the presence of these cations increases P removal, while other cations such as calcium are not essential (Esakki Raj et al. 2012).

11.3.1.4 Dissolved Oxygen

Oxygen is required for PAO to metabolize the storage products and uptake of phosphorus. An extreme aeration leads to negatively impact on EBPR process as termination of P-uptake happens due to exhaustion of poly-hydroxy-butyrate (PHB). DO concentrations around 2.5–3.0 mg/L appeared to associate with a plenty of PAOs. Presences of DO greater than 5 mg/L in return and internal recycle line between aerobic to anaerobic and aerobic, anoxic to anaerobic relatively affect EPBR performance (Raj et al. 2013).

11.3.1.5 Solid Retention Time (SRT)

SRT has been specified as one of the most essential factors that affects the performance of EBPR. It was revealed that SRT of 30 days resulted in increases P elimination, reduction of biomass growth and sludge wastage (Lee et al. 2007). SRT above 30 days causes domination of GAO over PAO. This results in a decline of phosphorus removal efficiency in EBPR system (Seviour et al. 2003). Hence, shorter SRT are favorable for PAO in EPBR.

11.3.1.6 Secondary Phosphorus Release

In anaerobic zone the release of phosphorus occur by the uptake of acetate, and it was stored as PHB, which is known as primary Release (Barnard 1984). Yet, phosphorus was also discharged from deposited polyphosphate under anaerobic circumstances when there was an insufficient availability of VFA. The phosphorous discharges during these actions are known as secondary release of phosphorus. The release of secondary phosphorous is much lower than the primary release and it depletes stored PHB. Hence, secondary release must be avoided as much as possible because it unfavorably affects the performance of an EBPR process.

11.4 Combined Biological Nutrient Removal

In combined nutrient removal, both nitrogen and phosphorus removal occurs in a single set of reactor. This kind of arrangement will reduce area requirement as well as energy demand for the process. The process is having an advantage of using single clarifier i.e. responsible for maintaining heterogeneous biomass inside the reactor. Most of the full-scale wastewater treatment systems are based on combined process. Some of the widely used reactor configurations for the combined removal of nutrients are discussed below.

11.4.1 Reactor Configurations

Classical example for biological P removal process is anaerobic/oxic system. It is a suspended growth biological treatment system where the microbes are kept in suspension for treating the wastewater are known as suspended growth system. In suspended growth system microbes has the advantage of getting substrate in radial direction. This leads to greater performance efficiency. Under optimal circumstances, the microbes break down organic matter in the wastewater and reduce pollutant load.

11.4.1.1 In the Anaerobic Zone

PAOs are usually aerobic bacteria and it cannot multiply in anaerobic environment. Anaerobic zone was provided with an adequate source of biodegradable carbonaceous oxygen demand. In anaerobic zone, organic matters are fermented to form volatile fatty acids (VFA). It was utilized by PAO organism under anaerobic condition and was stored in the form of polyhydroxybutyrate (PHB). The formation of PHB need energy and it comes from breakdown of poly-P. This resulted in net rise in the quantity of phosphate across the anaerobic zone. The anaerobic zone in EBPR process act as a conditioning tank, where PAOs are being trained for their work in the consequent aerobic zone (Metcalf and Eddy 2014) for P-uptake.

11.4.1.2 In the Aerobic Zone

In the aerobic zone stored PHB is metabolized, which in turn provides energy and carbon for cell proliferation. PHB metabolism leads to production of glycogen. During this process, luxury uptake of orthophosphate by PAO happens. This leads to the accumulation of phosphate in the form of poly-P inside the PAO and energy discharge by PHB was used to form poly phosphate bond. PHB utilization also enhances cell proliferation. In EBPR process, P removal was achieved by periodical removal of P rich sludge.

11.4.1.3 Anaerobic/Anoxic/Oxic (A_2O) Process

In this process, anaerobic zone earlier to the anoxic and aerobic zone was facilitated. In between the zones mixed liquors are internally recirculated to create favorable conditions for phosphorous and nitrogen removal. In case of phosphorous removal, PAO was cyclically exposed to anoxic and aerobic condition to facilitate the luxury uptake of phosphorous. Internal recycling of nitrified wastewater to anoxic zone facilitates conversion of nitrate to nitrogen. (Rajesh Banu et al. 2009b). Based on A_2O, several other processes have been developed to enhance nutrient removal by rearranging its zones. Numerous combinations and modifications of the A_2O system have been established to meet commercial and regulatory difficulties of wastewater treatment. Figure 11.6 Schematic diagram of Anaerobic/Anoxic/Oxic (A_2O) process.

11.4.1.4 PhoStrip Process

In PhoStrip process, only microorganisms are involved in uptake and release of phosphate the process is also known as sidestream process. The overview of PhoStrip is shown in Fig. 11.7.

During conventional waste activated sludge process. Thickened biomass is reroute to aeration tank from the secondary clarifier but in the PhoStrip process a thickened biomass is rerouted to an additional tank known as stripping thank. In stripper tank, the sludge endures anaerobic detention so that the sludge release dissolved phosphate. The dissolved phosphates are present in supernatant are separated and chemical such as lime is added in order to precipitate phosphate.

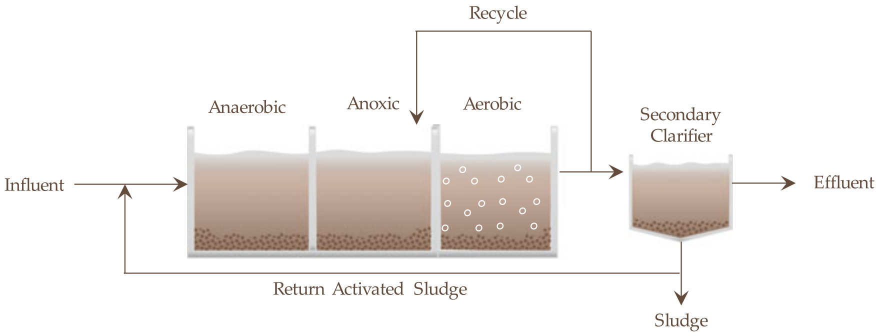

Fig. 11.6 Schematic diagram of Anaerobic/Anoxic/Oxic (A_2O) process (Rajesh Banu et al. 2009b)

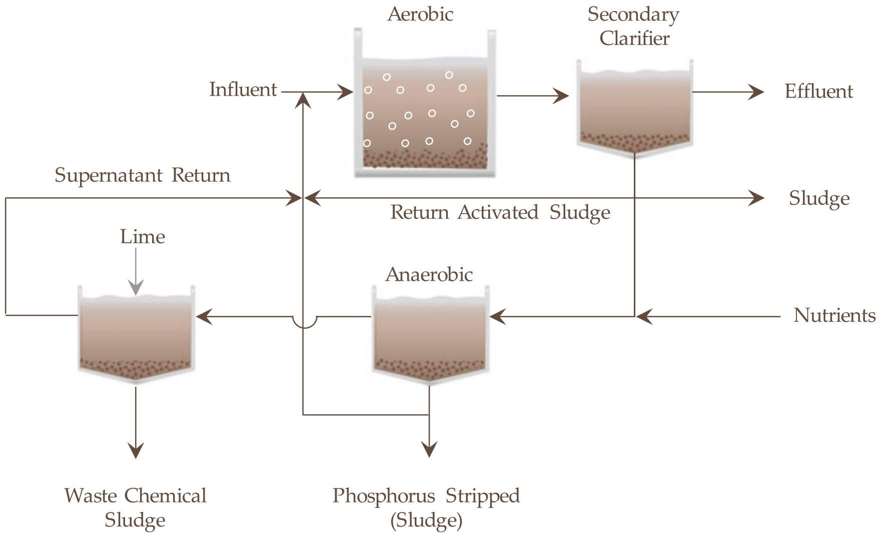

Fig. 11.7 Schematic diagram of Phostrip process (Metcalf and Eddy 2014)

The remaining biomass is recycled back into aerobic zone, where it absorbs dissolved phosphate. This resulted in enhanced removal of phosphate from the influent. More than 75% of phosphorous is removed during PhoStrip process and remaining is removed by biological phosphorous removal (Salehi et al. 2018). It has to be noted that the Phostrip process is unsuitable to treat wastewaters with high nitrogen concentrations.

11.4.1.5 Virginia Initiative Process (UCT-BNR)

It is a modified A_2O process with an addition of interior mixed liquor recycling line between anoxic zone to the anaerobic zone. In UCT process, return activated sludge was recycled into anoxic zone rather than the anaerobic zone. This arrangement reduces the adverse effects of the nitrate recycle to the anaerobic zone. In UCT process, PAOs are specified with the selective benefit of full contact to all accessible organic matter. It is good for both total nitrogen and total phosphorus removal. Figure 11.8 Schematic diagram of Virginia Initiative Process.

11.4.2 Simultaneous Precipitation

Simultaneous precipitation of phosphorus is frequently carried out at aerobic basin of biological nutrient removal system (de Haas et al. 2000). Iron salts are broadly used for this process. Two forms of iron salts ferric and ferrous are commonly used

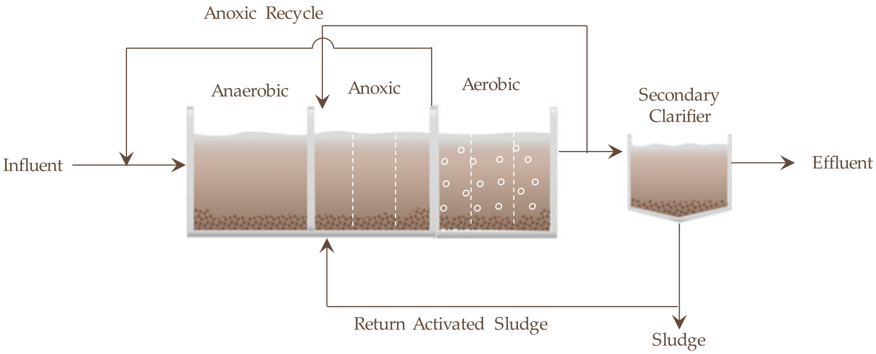

Fig. 11.8 Schematic diagram of Virginia Initiative Process (Metcalf and Eddy 2014)

by the researcher for simultaneous precipitation. Among the iron salts, ferric chloride is utmost frequently utilized for simultaneous precipitation. pH plays major role in precipitation reaction and optimum pH for ferric and ferrous salts were about to 5 and 8 respectively. From the above, it is noted that the iron salts has an advantage over ferric as its optimum pH lies close to wastewater pH.

Alum it is a hydrated form of aluminum sulfate has been widely utilized for simultaneous precipitation (Rajesh Banu et al. 2009a). Removal of phosphorous occurs in two-step between the formation of aluminum hydroxides ($Al(OH)_3$) and aluminum phosphate ($AlPO_4$). In the first step, alum reacts with water to form aluminum hydroxide. In a second step, it form complex with phosphate and precipitate. The above-mentioned reaction are given in the form of equation below.

$$\mathrm{Al}^3 + + 3\mathrm{H_2O} = \mathrm{Al(OH)_3} + 3\mathrm{H}^+$$

$$\mathrm{Al}^{3+} + \mathrm{PO}_4^{3-} = \mathrm{AlPO_4}$$

Though simultaneous precipitation enhances P removal, it affects nitrifier population in BNR. In aerobic basin ammonia oxidation was carried out by a specific group of autotrophic bacteria called as nitrifier. Their nitrification capacity was calculated by the following equation:

$$\mathrm{RN} = \frac{([\mathrm{N{-}NH_4}^+]\ \text{anoxic} - [\mathrm{N{-}NH_4}^+]\ \text{oxic}).(\mathrm{Q} + \mathrm{IR} + \mathrm{ER})}{\text{Volume of volatile suspended solids}}$$

where RN is the specific nitrification rate, expressed in g of $N–NH_4^+$ consumed/g VSS/d. Working on simultaneous precipitation in anoxic/oxic Rajesh Banu et al. (2009a) have reported an inhibition of nitrification rate from 0.049 g $N–NH_4^+$/g VSS/d to 0.38 g $N–NH_4^+$/g VSS/d by alum. In addition, simultaneous precipitation happens to decrease VSS content of sludge if it was added indiscriminately.

The lime-based (calcium derivatives) simultaneous precipitation was also in practice. However, major setback of lime as a simultaneous precipitant was that phosphorus removal happens at pH 9, which was well outside the optimal pH of biological processes. Powdered activated carbon is utilized by researcher in order to remove nutrients from wastewater (Uygur and Kargı 2004). It was used as phosphorus absorbent in three-step anaerobic (An)/anoxic (Ax)/oxic (Ox); the four-step (An/Ox/Ax/Ox), and the five-step (An/Ax/Ox/Ax/Ox). The lowermost discharge nutrient levels were recognized by using the five-step operation which resulted in 75% COD, 44% NH_4–N and 44% PO_4–P eliminations from effluent after 21 h of operation.

Advantages

- Changing of conditions is flexibility
- Ease of operation
- Low investment cost
- Comparatively lesser solids generation
- Enhance settling property of sludge.
- Enhance capillary suction time of sludge.

Disadvantages

- Increased dissolved solids contents on the receiving water
- Increased sludge generation
- Inhibitory effects to nitrification
- Need for pH and alkalinity correction
- Control P concentration in effluent
- Polishes effluent quality
- It prevents sludge bulking.

11.4.3 Phosphorous Recovery from Wastewater

Phosphorous is the most widely used nutrient in agricultural sector. Its requirement in agricultural sector increases day by day, however, the availability of phosphorus ore is limited. In order to overcome this requirement recovery of phosphate from the natural resources such as wastewater will be the best option. According to Yuan et al. (2012), 15–20% of worldwide demand for phosphorus can be fulfilled by recovering P from waste activated biomass. Phosphorus accumulating organism (PAO) plays a major role in biological phosphorous removal. *Accumulibacter phosphatis* a kind of dominating PAO and its population accounts for 5–20% of total population. It is capable of accumulating higher amount of P in the form of orthophosphate. This leads to the formation of P enriched sludge (Desmidt et al. 2015). This kind of sludge can be used for recovery of phosphorus.

Membrane technologies integrated with biological P removal process can be used for P recovery. Examples of such process are osmotic membrane bioreactor (OMBR) (Qiu and Ting 2014) and OMBR coupled with reverse osmosis (Luo et al. 2016). In this process, organics and ammonia are removed biologically. The phosphate-enriched supernatant was subjected to precipitation for its recovery. Integration of nanotechnology with wet oxidation proved to be an efficient technology to recover phosphorus from EPBR sludge. During wet oxidation, disintegration of sewage sludge occurs which leads to liquefaction of phosphorous. Subsequent nanofiltration process helps to separate phosphorus from rest of impurities such as heavy metals and other ions, which can be utilized for the production of fertilizer (Blöcher et al. 2012). Wet extraction is done by means of acids (sulfuric, nitric, and hydrochloric acid) and alkalis (oxides of Na, K and Ca). Above 90% of phosphate, recovery occurs in this process and is widely acceptable because it demands low energy and achieves high phosphorous recovery efficiency (Biswas et al. 2009). The recovered phosphorus products is mainly used for the production of fertilizers.

Struvite ($MgNH_4PO_4 \cdot 6H_2O$) crystallization is frequently used technology for P recovery from sludge produced from EBPR based process. Precovery of about 90% is obtained by struvite crystallization. The precipitates formed were mainly struvite, calcium phosphate and calcite. Anaerobic digestion aid struvite precipitation by releasing PO_4–P and Mg^{2+} from the biomass (Metcalf and Eddy 2014). Metal salt such as Al, Fe can be used to precipitate phosphorous selectively from EBPR sludge. This kind of selective recovery of phosphorous is possible only when phosphorous exist in the form of poly-P or condensed phosphorous. Under such condition, 90% of phosphorous recovery is possible from disintegrated EBPR sludge (Rajesh Banu et al. 2009a).

Phosphorous can also be recovered from ashes, a product of high-temperature incineration process contain good amount of phosphorous. However, the presence of heavy metals concentrate limits its utilization (Petzet and Cornel 2009). European Union developed a method named as SUSAN (Sustainable and safe reuse of municipal sewage sludge for nutrient recovery) to separate heavy metals from ash. In SUSAN, ash was allowed to react with chloride compounds such as magnesium chloride and calcium chloride. The resulting metals chlorides were removed from ash through evaporation at high temperature (850–1000 °C). It removes nearly 90% of heavy metals from ash. Thus, heavy metal devoid ash can be used as an ideal raw material for manufacturing of fertilizers. It also increases the bioavailability of phosphorus in ash from 30 to 50% for fertilizer production.

11.4.4 Sustainable Nutrient Removal in EBPR Process with Sludge Recycle

Sustainable phosphorous removal is possible for a system with low SRT. Under low SRT condition, phosphorus accumulated in the biomass was wasted periodically and it enables the new biomass to uptake phosphorus. However, systems like AAO-MBR and EBPR with sludge recycling runs with high SRT. Under high SRT condition, sludge wastage is minimum and it causes biomass to reach its saturation level for phosphorous intake. This lead to poor performance of phosphorus removal in such systems in long run.

Following case study was carried out by Rajesh Banu et al. (2009b) to achieve sustainable phosphorus removal in A_2O-MBR with sludge recycling system. The operational parameters used for the study are as follows: working volume of the reactor 84 L, flow rate 8.4 L/h, HRT 10 h, sludge recycling 1.5% of Q, Influent TP 5.5 mg/L and TP content of biomass 4.5%. Phosphorus was mass balanced for 100 g (90 days of reactor operation) and details of mass balance were given in Fig. 11.9.

Inlet TP concentration during the study period was calculated by Eq. (11.1)

$$\begin{aligned}\text{Inlet TP (g)} &= Q/\text{day} \ * \ \text{TP influent} \ * \ \text{study period}\\ &= (8.4\,\text{h} \ * \ 24) \times 5.5\,\text{mg/L} \ * \ 90\,\text{days} = 99.8\,\text{g}\end{aligned} \tag{11.1}$$

Effluent TP concentration during the study period was calculated by Eq. (11.2)

$$\begin{aligned}\text{Effluent TP (g)} &= Q/\text{day} \ * \ \text{TP effluent} \ * \ \text{study period}\\ &= (8.4\,\text{h} \ \times \ 24) * 1.1\,\text{mg/L} \ * \ 90\,\text{days} = 20.0\,\text{g}\end{aligned} \tag{11.2}$$

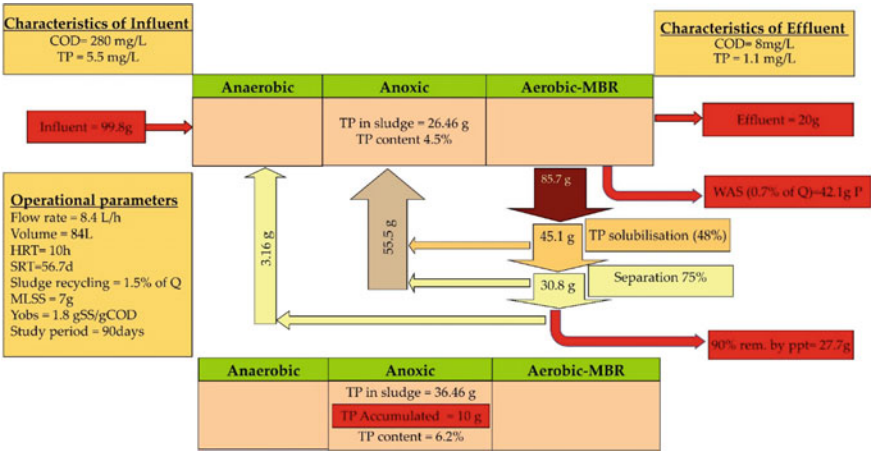

Fig. 11.9 Schematic diagram of TP mass balance

The optimum sludge recycling Q for economical operation of EBPR is 1.5% (Raj et al. 2013).

Total amount of sludge recycled for pretreatment at 1.5% was calculated to be 272.16 L. One liter of sludge consist of 7 g of MLSS (biomass) and total amount of SS was calculated to be (272.16 × 7 g = 20412 g) 20.41 kg SS.

From the total SS, TP subjected to pretreatment was calculated by Eq. (11.3)

$$\begin{aligned} \mathrm{TP}_{\mathrm{pretreatment}} &= \mathrm{SS\ subjected\ to\ pretreatment} \ \times \ \mathrm{TP\ content\ of\ SS}\ (4.5\%) \\ &= \ (20{,}412\ \times\ 0.45) = 85.73\ \mathrm{g} \end{aligned} \tag{11.3}$$

$$\begin{aligned} \mathrm{TP}_{\mathrm{pretreatment}} &= [\mathrm{TP}_{\mathrm{recycled}} + \mathrm{TP}_{\mathrm{removed\ via\ coagulation}}] \\ (85.73\ \mathrm{g}) &= [(58\ \mathrm{g}) + (27.73\ \mathrm{g})] \end{aligned} \tag{11.4}$$

Even though 85.73 g of TP is exposed to pretreatment (thermochemical) only 48% is being solubilized and it was calculated to be (85.73 * 0.45) 41.15 (g). It is well known that only solubilized phosphorus can alone be removed out of the system. Reaming are bound phosphorus (85.73–41.15) 44.58 g and its removal is not possible. Among the solubilized phosphorus, those present in liquid stream can alone be removed through coagulation. In this study, dissolved air flotation (DF) was used to separate solids from liquid and its solid–liquid separation efficiency was 75%. Hence the amount of solubilized phosphorus in liquid stream was calculated to be (41.15 × 0.75) 30.86 g. Lime was used as a coagulant to remove phosphorus from liquid stream and its efficiency was calculated to be 90% (Rajesh Banu et al. 2009a; Do et al. 2013). Total amount of phosphorus removed via sidestream precipitation was estimated to be (30.86 g × 0.9) = 27.7 g.

$$\begin{aligned} \mathrm{TP}_{\mathrm{recycled}} &= [\mathrm{TP}_{\mathrm{bound}} + \mathrm{TP}_{\mathrm{not\ separated\ by\ DF}} + \mathrm{TP}_{\mathrm{not\ rem.\ by\ coagulation}}] \\ &= \ [(44.58\ \mathrm{g}) + (10.26\ \mathrm{g})\ + (3.16\ \mathrm{g})\,] \end{aligned} \tag{11.5}$$

Another and major way of TP escape from the system is through biomass wastage. TP removed through biomass wastage can be calculated from substrate consumed and biomass produced. For substrate consumed following equation is used

$$\begin{aligned} \mathrm{Substrate}_{\mathrm{consumed}} = [(\mathrm{Inf.\ COD}\ - \mathrm{Eff.\ COD})\ \times\ \mathrm{flow\ rate}\ \times\ \mathrm{study\ period}] \\ [(280 - 8)\ \times\ 201.6\ \times\ 90) = 4935.1\,\mathrm{g}] \end{aligned} \tag{11.6}$$

Biomass produced during the treatment has to be wasted to maintain its balance in EBPR. Hence biomass wasted can be calculated using Y_{obs} (0.19 g SS/gCOD) and was calculated to be (4935.1 g × 0.19) = 937.6 g S. Amount of TP removed from the system was calculated from biomass wastage and was estimated to be = (937.6 g SS × 4.5% TP) = 42.1 g.

The mass balance equation for phosphorous in EBRP can be written as

$$\mathrm{TP}_{\mathrm{inf.}} = [\mathrm{TP}_{\mathrm{eff}} + \mathrm{TP}_{\mathrm{Rem.\ Coagulation}} + \mathrm{TP}_{\mathrm{Accumulated}} + {}_{\mathrm{biomass\ wastage}}] \tag{11.7}$$

From the above TP accumulated in the system is calculated by rearranging Eq. 11.7

$$\begin{aligned} \mathrm{TP}_{\mathrm{Accumulated}} &= \mathrm{TP}_{\mathrm{inf.}} - [\mathrm{TP}_{\mathrm{eff}} + \mathrm{TP}_{\mathrm{Rem.\ Coagulation}} + \mathrm{TP}\ \mathrm{TP}_{\mathrm{biomass\ wastage}}] \\ \mathrm{TP}_{\mathrm{Accumulated}} &= 99.8\,\mathrm{g} - [20\,\mathrm{g} + 27.73 + 42.1\,\mathrm{g}] = 10\,\mathrm{g}. \end{aligned} \tag{11.8}$$

The accumulated TP (10 g) raises TP content of the biomass to 6.2%. However, if TP is not removed by side stream (27.7 g), it will accumulate in the system and raise TP content of the biomass to 11%. At this value, biomass attains saturation level and its TP uptake from wastewater decrease leading to poor performance of the system. Hence it can be concluded that side stream removal of phosphorous is mandatory for sustainable removal of phosphorus in systems with higher SRT.

11.5 Conclusion

Excess accumulation of nutrient in the wastewater cause water pollution and create environmental issues. BNR is an essential step before discharging the effluent from treatment plant. However, upgrading the existing treatment plants is recommended to meet the discharge standards and to protect the ground and surface water quality. Numerous integrated technology was developed for BNR to achieve greater nutrient removal. This chapter provides knowledge regarding the recent innovative approaches followed for BNR were discussed. Such as aerobic granular activated sludge sequencing batch reactors, integrated fixed-film activated sludge reactor and integrated anoxic fixed bed and oxic moving bed biofilm reactor. In addition to this, a detailed TP mass balance was also discussed.

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Chapter 12
From Conventional Activated Sludge Process to Membrane-Aerated Biofilm Reactors: Scope, Applications, and Challenges

Deepak Karna and Chettiyappan Visvanathan

Abstract In the midst of increasing global production of domestic wastewater over the years, the treatment capacities did not show promising increments to keep up with it. Traditionally, biological treatment systems such as wetlands, conventional activated sludge (CAS), trickling filter processes, and rotating biological reactors were used to treat these wastewaters. The capital and operation and maintenance (O&M) costs of the process play a critical role in the final system selection. During the past decade, membrane bioreactor (MBR) has progressively replaced these biological wastewater treatment systems. For example, the most advanced form of MBRs called membrane-aerated biofilm reactors (MABRs) could be operated with higher energy efficiency of 70% compared to CAS process. Moreover, even at a low footprint, MBRs could achieve a high volume of treatment in existing area with records of up to 50% extra capacity. Following these MBR systems, the next technological innovation was membrane-aerated biofilm reactor (MABR), which uses the bubbleless aeration through the lumen of fiber membrane. The bubbleless aeration, in fact, assists the smooth growth of microorganisms compared to the bubbled aeration in CAS process which often interferes with the microbial growth in the system. Apart from providing diffused aeration, the membrane also serves as attachment medium for microorganisms that consume organics and nitrogen, thereby purifying the wastewater. Thus, within a single reactor, simultaneous nitrification and denitrification are achieved. The MABRs have been successful in the treatment of variety of pollutants such as landfill leachate, pharmaceutical wastewater, ammonia-rich wastewater, domestic wastewater, and anaerobic digestion liquor. In addition, their applications have flourished for the treatment of high carbon and nitrogen wastewater, volatile organic compounds, and xenobiotic components. However, the major limitation of this process is maintaining optimal biofilm thickness on the membrane surface and scaling-up mechanisms to real scale plants.

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Biofilm, Biological treatment · Microporous membrane

12.1 Overview of Wastewater Treatment

Only a limited number of countries have records on the generation, treatment, and use of domestic wastewater. However, available data shows that about 70% of the generated wastewater is treated in high-income countries, 38% in upper-middle-income countries, 28% in lower-middle-income countries, and approximately 8% in low-income countries (Sato et al. 2013). Globally, 330 billion m^3 of wastewater discharged per year has a potential to irrigate about 15% of all the arable lands (Khalid et al. 2018). Moreover, with the expected increment in future population, the global production of wastewater is also expected to increase significantly (UN World Water Assessment Programme 2017). Thus, there is a serious demand for development and implementation of wastewater treatment systems. The colloidal and particle fraction of the pollutants in the wastewater can be treated utilizing their ability to precipitate, float, or sediment through unit operations such as sedimentation, flotation, flocculation, and filtration. The dissolved organic fractions can be treated using biological treatment processes, and the dissolved inorganic pollutants can be removed by a combination of physical and chemical processes. Considering the O&M cost and the simplicity in the process design, biological treatment processes are often used for domestic wastewater treatment. Biological treatment processes can be classified into aerobic and anaerobic processes based on the wastewater strength. Aerobic processes, which operate with external oxygen supply for the rapid biodegradation of the waste, are often preferred waste treatment approach. The conventional activated sludge process is the common aerobic waste treatment process used in domestic wastewater treatment.

12.2 Conventional Activated Sludge Process

Conventional activated sludge process is the most widely used suspended growth aerobic biological process. In this process, the influent wastewater is mixed with active microorganism in a reactor (aeration tank) and oxygen is supplied for aerobic reactions to occur. The process is carried out in suspension in either a plug flow or a complete mix mode. In the plug flow reactor, the influent is admitted at one end and discharged from the other end without mixing the content, thereby allowing all the particles to stay in the reactor for the same duration. In a complete mix reactor, the whole content is thoroughly mixed together by agitation, and therefore particles stay for different durations in the reactor. Though, theoretically, the efficiency is better in plug flow several practical limitations favor complete mix reactors.

The mixed liquor (wastewater and biomass) is commonly held for a period of 4–8 h in the reactor to complete the reaction. The mixed liquor is then sent to a secondary sedimentation tank to separate the biomass floc from the treated wastewater by gravity settling. This treated wastewater is discharged as the supernatant, while a part of the sludge (return sludge) is recycled back to the reactor by pumping and the rest (waste sludge) is sent to the sludge-handling unit for treatment. The return sludge from the secondary clarifier is admitted into the reactor with the fresh influent to maintain a constant concentration of the active biomass in the reactor. A schematic arrangement of CAS process is shown in Fig. 12.1.

Air is supplied to the process either through diffusers placed underwater or by surface aerators or jet pumps. The air supplies oxygen to the mixed liquor and mixes the content for uniform distribution of the food (organics) and the biomass. In practice, the selection of the aeration system depends on operation and maintenance needs, cost of equipment and appurtenances, and characteristics of the wastewater. It is recommended that for industrial wastewater having heavier solids that may clog the diffusers, surface aerators or jet pumps can be used in order to reduce operation and maintenance needs, while for municipal wastewater, diffused aeration can be used. The efficiency of diffused aeration is much higher than surface aeration, and therefore all pros and cons should be balanced for selection of the proper aeration system.

There are several working variations to the CAS process. The different designs of CAS process are based on several factors like the influent flow rate, organic load, efficiency required, requirement of secondary settling, type of the aeration systems, etc. The other types of CAS process are sequencing batch reactors, tapered aeration, stepped aeration, extended aeration, oxidation ditch, and cyclic activated sludge system (CASS).

Recently, significant development has taken place for sequencing batch reactor (SBR), an activated sludge process in which the aeration and sedimentation are carried out in the same tank, thereby reducing construction cost and land requirement. Essentially, the SBR is a batch process carried out in four consecutive steps: filling, aeration, clarification, and decantation of the supernatant. The wastewater is first filled, then aerated for a fixed time, and then allowed to settle in a quiescent condition. Finally, the supernatant is discharged. The settled sludge containing

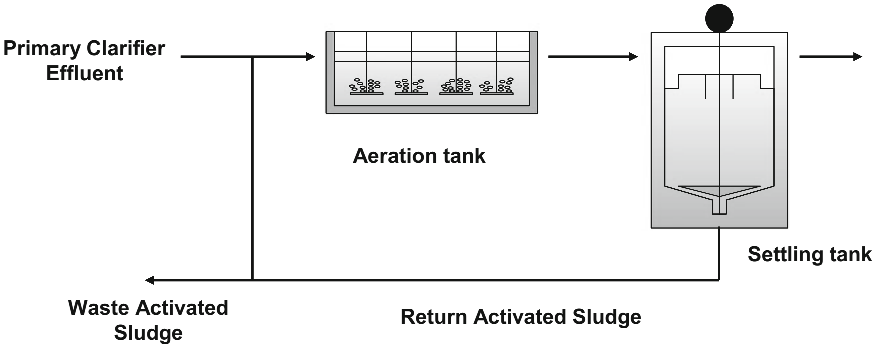

Fig. 12.1 Schematic arrangement of a typical CAS process

active biomass can be used again for the next batch. A part of the settled sludge is wasted periodically to control the biomass concentration. This system eliminates the requirement of a separate sedimentation tank and recycling of sludge. SBR has been found to have a greater capacity of nutrient removal, sludge settling characteristics, and effective removal of scum.

Design criteria of activated sludge process considers kinetic parameters mainly cell yield coefficient and endogenous decay coefficient, and operating parameters like mean cell residence time, food-to-microorganism ratio (F/M), mixed liquor suspended solid (MLSS) concentration, mixed liquor volatile suspended solid (MLVSS) concentration, volumetric loading, detention time, recycling ratio, mixing power, O_2 transfer rate, etc. The efficiency of the activated sludge process is measured in terms of influent and effluent BOD and in general ranges from 75 to 95% depending on the process design and operation.

Other than regular maintenance of the mechanical equipment, pipes, valves, and appurtenances, an operator has to keep a close watch on the operation of the system. Since biological systems are very sensitive to ambient conditions and operating parameters, some changes in the influent wastewater characteristics such as shock loads, presence of toxic chemicals, reduction in nutrients, etc. or operating parameters may produce a shock to the system, reducing efficiency and causing other problems. A very common observation in poorly maintained plants is with sludge settleability. In many cases even for well-operated plants, sludge may not settle or compact properly (sludge bulking). In more problematic cases, sludge may start rising to the top (rising sludge). Improper mixing of the contents of the tank, especially with surface aerators and jet pumps or clogged diffusers (for diffused aeration), can leave some dead areas, encouraging accumulation of scum and anaerobic conditions. Foaming and thick layer of scum formation can occur that may give rise to odor, reduce oxygen transfer rate and efficiency.

12.3 Membrane Bioreactor (MBR)

The membrane bioreactor (MBR) process was introduced to replace the settling tank of the CAS process with membranes. In this modified system, the settling characteristics do not depend on the MLSS concentration in the aeration tank. The MBR systems can be operated with higher MLSS concentration, resulting in very small reactor footprint. Nevertheless, it is still difficult to justify this process due to high cost of membranes, low economic value of high-quality tertiary effluent, and the high rate of membrane fouling.

Three main MBR configurations have been developed in wastewater treatment which are shown in Fig. 12.2a–c. Sidestream membrane (Fig. 12.2a) is mainly for the treatment of industrial wastewater due to its compactness and easy maintenance because of the sidestream position of the membrane relative to the bioreactor. However, to minimize the fouling rate, using the high suspension flow rate recycles throughout the membrane end up in high energy consumption.

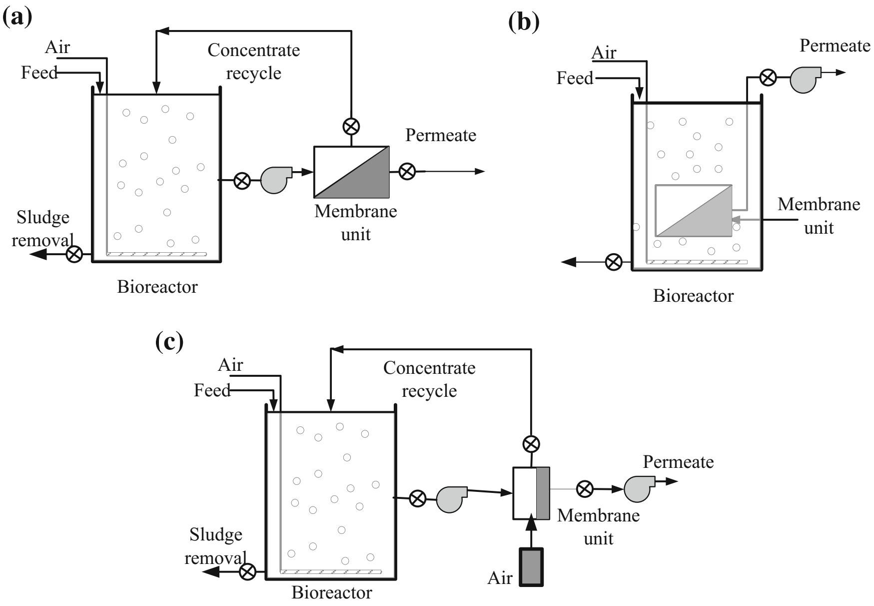

Fig. 12.2 **a** External membrane unit with recirculation pump **b** immersed membrane with suction pump (c) external airlift membrane with suction pump

The second configuration (Fig. 12.2b) is based on the immersion of membrane module directly inside the bioreactor. This module is more extensively used because it functions well under low transmembrane pressure (TMP) and has low energy requirement when air fluid supply is used to achieve turbulence in the reactor. Nevertheless, when some drastic membrane fouling or module clogging occurs, the cleaning protocol results in more complicated maintenance.

To keep the cream from both sidestream system and immersed system (Fig. 12.2c), sidestream system with suspension circulation and local turbulence near membrane surface by air injection at the bottom of the membrane module were introduced. The airlift procedure close to the membrane surface induces a significant turbulence which makes the membranes “half free” packing (moving) and prevention of accumulation of suspended solid inside the membrane even with relatively high membrane packing density.

While early MBRs were operated at solid retention times (SRT) as high as 100 days and mixed liquor suspended solids (MLSS) up to 30 g/L, the recent trend is to use a lower SRT (10–20 days) and lower MLSS concentrations (10–15 mg/L).

Membrane bioreactor process can be considered as a good alternative to CAS process. Comparison between CAS and MBR processes is given in Table 12.1. The main problems in MBR process are membrane fouling, the high cost of membranes, and related facilities. However, MBR process is capable of removing almost 100% of the suspended solids and more than 90% of chemical oxygen demand (COD) resulting in high-quality effluent.

Table 12.1 Comparison of CAS process and MBR process

Conventional activated sludge process (CAS)	Membrane bioreactor (MBR)
Advantages • Low energy consumption as compared to other conventional treatment processes • Low operation and maintenance cost • Relatively longer operational life span	Advantages • Smaller footprint • Shorter start-up time • Less manpower requirement for operation and maintenance • High-quality effluent • No operational problems due to sludge bulking, sludge rising, and *Norcardia* forming • Lower sludge production • High endurance on shock loading
Disadvantages • Large land requirement • Sludge bulking, sludge rising, and *Norcardia* forming • Low endurance on shock loading • Longer start-up period • Low-quality effluent • More man power requirement for operation and maintenance • Higher sludge production	Disadvantages • Membrane fouling • Higher cost for membranes and related facilities • Shorter membrane life span • Need proper pretreatment

12.4 Membrane-Aerated Biofilm Reactors

12.4.1 Layout of MABR

The MABRs are advanced form of “membrane biological reactors” which functions to purify the wastewater through microbes-assisted pollutant degradation processes. In the meantime, the membranes act as a source of diffused (bubbleless) air supply as well as medium for attachment of biofilm. In contrast to the conventional membrane systems, where air/oxygen and substrate are supplied from the same direction, the MABR systems have provision of aeration and substrate supply from opposite directions. Figure 12.3 depicts the comparative substrate and air diffusion process in conventional MBR and MABR system.

In a microscopic view, as described in Fig. 12.4, it can be observed that oxygen is supplied from the lumen of membrane fiber which gets diffused to the outer surface where the microbial spatial distribution occurs.

The inner biofilm layer close to the membrane surface is inhabited by the nitrifying bacteria which require high amount of oxygen for their growth while the bacteria farthest in the biofilm are from the denitrifying group which prefer to grow in anoxic environment. In addition to this, there are a set of heterotrophs which utilize carbon constituents for their growth and development thereby degrading the

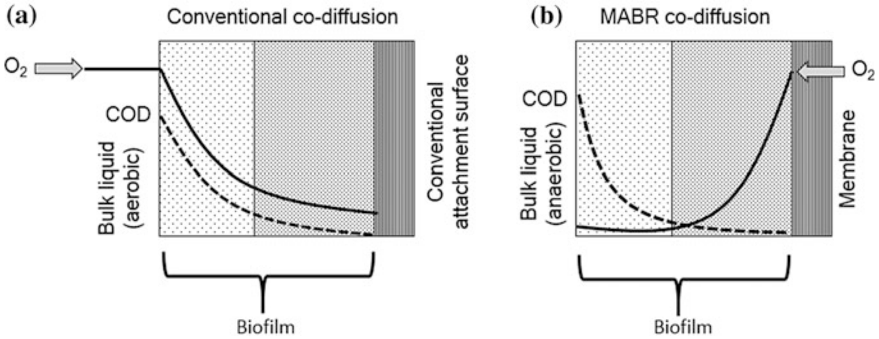

Fig. 12.3 Substrate and aeration supply in **a** Conventional membrane bioreactor systems **b** MABR systems

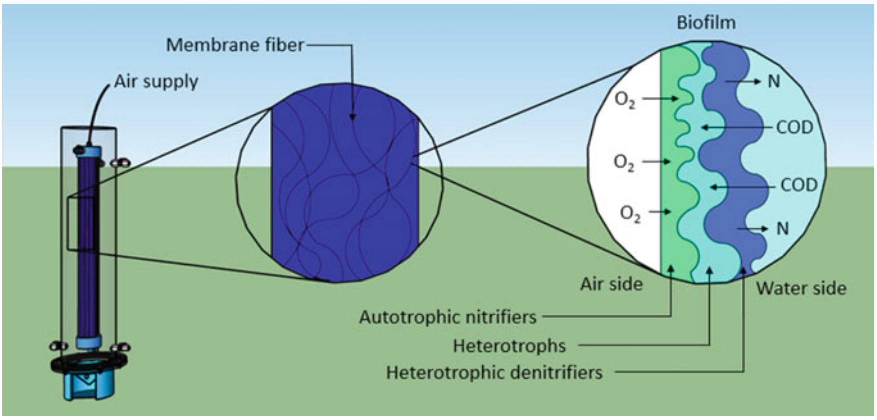

Fig. 12.4 Microbial spatial distribution in biofilm

carbon pollutants. Thus, this distinct set of microbial distribution in the biofilm leads to low footprint as the size of reactor is highly reduced when compared to CAS process.

12.4.2 Characteristic Features of MABR

As discussed earlier, one of the major characteristics of MABR process is the unique distribution pattern of microbes in the biofilm which results from the distribution of potentially limiting substrates, nutrients, and oxygen essential for their growth and development. Such pattern of microbial distribution assists on simultaneous nitrification and denitrification processes occurring on a single reactor vessel.

Another major characteristics associated with MABR system is bubbleless aeration. The conventional activated sludge process has a mechanical aeration which results in the formation of large amount of air bubbles. Such bubbles are responsible for disturbing the microbial growth in sludge produced during treatment process and hence lower the efficiency. It is reported that CAS systems employ 0.27–1.89 kWh/m^3 energy (Hamawand et al. 2017). On the other hand, energy consumption linked to aeration process (thereby being a diffused mechanism) in MABR systems is 0.1–0.2 kWh/m^3, thus indicating 7 times more efficient oxygen transfer than CAS (OxyMem n.d.).

Similarly, the configuration of MABRs enables a small footprint for operation as they are designed in such a way that a large number of membrane fibers are grouped into a single module and a number of modules are arranged in arrays which may also be organized in series so as to treat maximum amount of wastewater. In addition, this process does not require a secondary clarifier which further reduces the footprint.

12.4.3 Operational Configuration

Depending upon the usage and constituent of gas supply, MABR systems can run under two operational modes, viz. dead end and crossflow. The difference in such operational modes mainly impact on the permeability of supplied gas, thereby enabling them to diffuse through membrane surface.

12.4.3.1 Dead-End Configuration

A dead-end configuration of membrane module consists of a sealed end while the other end is used for supply of air into the lumen as shown in Fig. 12.5a. The supplied air is supposed to permeate through the membrane surface without any loss from the ends. Such configuration is suitable for gas supply which is expensive, for example, oxygen, hydrogen, and methane since it supports high gas transfer rate as much as 100%. However, there is one major disadvantage caused by back diffusion of other gases associated with such configuration. The gases produced in bulk liquid such as carbon dioxide and nitrogen may permeate into the membrane and get accumulated inside the lumen thereby reducing the targeted gas transfer from lumen to bulk liquid. Additionally, back diffusion of such gases may replace the desired gas from lumen. The schematic diagram for flow of gases and back-diffusion mechanism in dead-end mode of MABR operation has been presented in Fig. 12.5b.

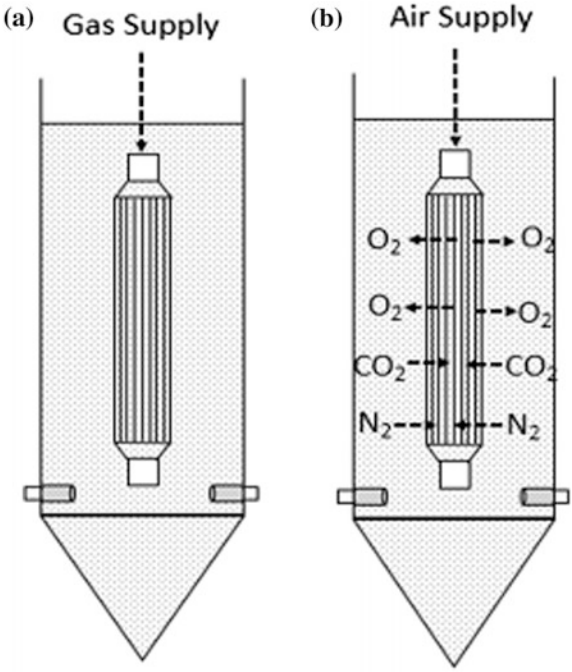

Fig. 12.5 **a** Dead-end mode of MABR operation **b** back-diffusion mechanism

12.4.3.2 Crossflow Configuration

In this mode of operation, both ends of membrane remain open such that the supplied gas from one end can pass through the other end along with a portion of gas permeating through the membrane surface. Such configuration tends to create a nearly stable gas transfer throughout the membrane length in contrast to dead-end mode where the gas transfer is comparatively very limited at the sealed end. In addition to this, it has an advantage of avoiding the back diffusion since the continuous flow of desired gas causes the unwanted gases to expel out from distal end. The schematic diagram of crossflow configuration has been presented in Fig. 12.6a while avoidance of back diffusion is shown in Fig. 12.6b.

A comparative partial pressure of gases in both modes is presented in Fig. 12.7.

Figure 12.7a indicates the partial pressure of individual gases throughout the length of membrane in dead-end mode. It suggests that the proximal end has higher O_2 concentration with high oxygen transfer efficiency while distal end contains higher concentration of N_2 because of back diffusion leading to lower oxygen transfer efficiency. However, as seen in Fig. 12.7b, the crossflow configuration consists of approximately uniform O_2 concentration thereby indicating a higher oxygen transfer efficiency throughout the membrane surface.

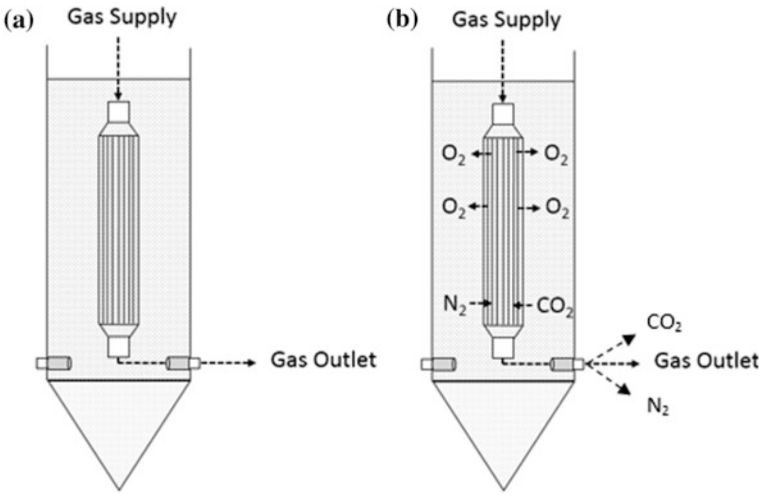

Fig. 12.6 **a** Crossflow mode of MABR operation **b** overcoming back-diffusion mechanism

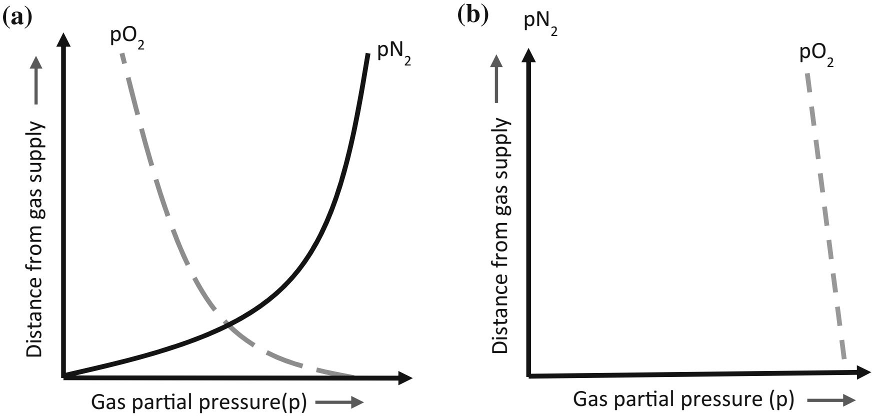

Fig. 12.7 Partial pressure of gases in **a** Dead-end mode **b** crossflow mode of operation

12.4.4 Membrane Fabrication

Different types of membrane modules have been used in membrane bioreactors. Some of the widely used membranes were of flat sheet, tubular, spiral, and hollow fiber configuration. Likewise, membrane processes such as reverse osmosis, ultrafiltration, microfiltration, nanofiltration, etc. also used a variety of polymers such as cellulose acetates, cellulose nitrates, polyacrylonitrile, polyetherimides, polyethersulfones, polyphenylene oxides, etc. creating a required barrier of non-porous, mesoporous, and macroporous surface. However, in MABR systems, the most frequently used membrane modules are of hollow fiber configurations which fall under three groups; microporous, dense (nonporous), or composite.

12.4.4.1 Microporous

The transfer of gases along a microporous membrane is carried out via diffusion through gas-filled pores. In such membranes, the gas transfer coefficient is directly proportional to the porosity of the membranes. Thus, the higher the porosity of the membrane the higher the gas transfer rate. These membranes are mostly prepared from hydrophobic materials such as polyethylene, polypropylene, poly-3-methylbutene-1, poly-4-methylpentene-1, Polyvinylidene difluoride, polytetrafluoroethylene, Polystyrene, and polyetheretherketone among which polyethylene and polypropylene are the most prevalent ones. Besides the advantages of higher gas flux through the membranes, it has a major limitation in operating at higher gas pressures. In other words, the microporous membranes have a low bubble point pressure indicating that with increment in pressure, the aeration results in bubble formation thereby disturbing the microbial growth on the outer membrane surface and causes possible biofilm detachment. Also, (Casey et al. 2000) reported that the deposition of protein and cell debris on the membrane pores may result in hydrophilic pore walls with adequate filling of liquid which makes the membrane unsuitable for long-term operation.

12.4.4.2 Dense (Nonporous)

The nonporous membranes exploit the solution–diffusion mechanism for transfer of gases through the membrane surface. Gases get diffused through the tiny voids that are present in between the membrane polymer chains generated by thermal motion of polymer molecules. As compared to the microporous membranes having a wall thickness of less than 40 μm, the nonporous membranes have a much larger wall thickness, i.e., more than 100 μm. The increased thickness of membrane, on one hand, adds up mechanical strength to the fiber while on the other hand, increases the bubble point pressure. Thus, the membrane system can work up to higher pressures without forming any bubbles. However, the increased thickness may cause a decreased oxygen flux through the membranes resulting from greater diffusional resistance. Mostly, nonporous membranes are prepared from polymers such as polydimethylsiloxane, siliconepolycarbonate, poly-4-methylpentene-1, perfluoroalkyl polymers, ethyl cellulose, polyphenylene oxide, poly-4-vinylpyridine, and polyurethane. Because of higher gas permeability and reduced chemical resistance, the most prominent dense membranes are composed of silicone.

12.4.4.3 Composite

To avoid the major drawbacks of both membranes, a composite membrane has been introduced. It consists of layers of microporous as well as dense membranes. The basic structural configuration of composite membranes is the constitution of two porous membranes (normally made up of polyethylene) separated by a thin layer of dense membrane (composed of polyurethane or polydimethylsiloxane). The advantages such as high mechanical strength, high bubble point of dense membrane, and high gas permeability of microporous membrane are blended into such composite membrane. Thus, this configuration of membranes is the most advanced one used in MABR systems and has been extensively used for both lab-scale and pilot-scale studies.

The mechanisms of gas transfer in each type of membrane configurations are presented in Fig. 12.8.

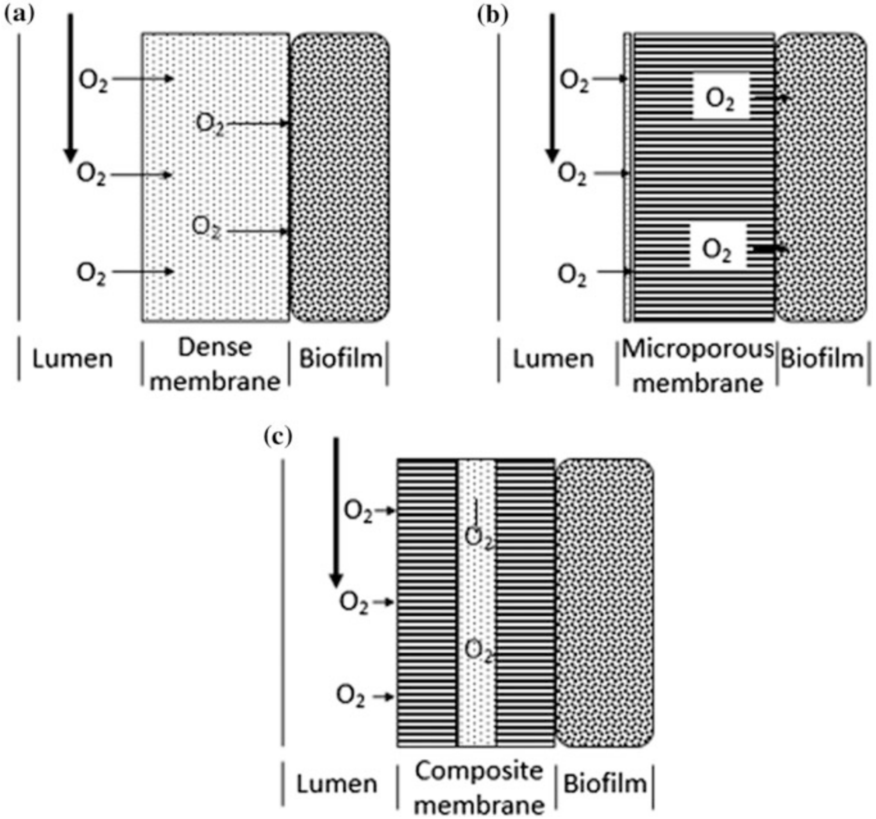

Fig. 12.8 Mechanism of gas transfer in **a** Dense membrane **b** microporous membrane **c** composite membrane

12.4.5 Factors Influencing MABR Performance

Apart from the membrane configuration, there are several other factors that contribute to the MABR system performance. The following section presents the highly influencing factors.

12.4.5.1 Membrane Packing Density

Packing density of a membrane can be defined as the ratio of total surface area of the membrane to the total cross-sectional area of the module (Gunther et al. 2010). Thus, in simple terms, it indicates that, for a given membrane, the higher number of membrane fibers, the higher is the packing density. However, with increasing number of fibers, there is higher probability of fiber confinement which reduces the oxygen flux as well as space for biofilm attachment. A typical membrane module can have a packing density ranging from 7 to 1733 m^2/m^3 (Long 2013). A study by Terada et al. (2006) indicated that ammonia removal rate under steady states was also dependent on specific membrane surface area when assayed for three modules of dimensions 290, 660, and 1190 m^2/m^3.

12.4.5.2 Oxygen Supply Rate (Partial Pressure)

Oxygen supply rate or the partial pressure inside the lumen of membrane also plays a significant role in the performance of MABR. Albeit most of the recent commercial membranes are synthesized to operate at high bubble point pressure (i.e., with ability to withstand high gas pressure), it is always recommended to operate MABR at low pressures but with high oxygen transfer rates. At most times, the practical implementation of MABRs at pilot plants operated under crossflow configuration results in huge amount of gas being unutilized. Thus, a higher oxygen supply rate may cause a huge amount of gas to be lost on one hand and also the detachment of biofilm on outer surface of the membrane on the other hand. In contrast, a lower gas supply may not fulfill the oxygen requirement of biofilm attached. A study by Casey et al. (2000) carried under intra-membrane pressures of 12.5, 25, and 50 kPa indicated that the partial pressure has significant effect on initial biofilm growth rate. Thus, an optimum partial pressure should be maintained for the best MABR performance.

12.4.5.3 Dissolved Oxygen (DO)

A typical MABR system inhabits two types of bacteria, viz. obligate aerobic nitrifiers and anaerobic (anoxic) denitrifiers for simultaneous nitrification and denitrification. In addition to this, there is a large set of heterotrophic bacteria which are targeted to degrade organic compounds. Since each set of microbial community requires a specific DO concentration for their growth and development, an optimal DO inside the reactor needs to be maintained. A typical range of DO for optimal nitrification lies between 0.3 and 4.0 mg/L (Stenstrom and Poduska 2003). Likewise, the optimal DO range for denitrification is recorded as 0.5–1 mg/L (Tan et al. 2013). Thus, it is recommended to adjust the DO concentration of bulk liquid inside reactor in anoxic condition.

12.4.5.4 pH

Biofilm stratification on the membrane surface is significantly sensitive to changes in pH. Different studies indicate different values for nitrification and denitrification processes since it is highly dependent on specific bacterial cluster or microbial community. However, most studies indicate that the optimal pH range for growth of nitrifying bacteria lies in between 6.5 and 8.5 (Prinčič et al. 1998), while that of denitrifying bacteria fall under 7.0–8.0 (Šimek et al. 2002). pH of the bulk liquid is also an indicator of the bacterial activity since a drop in pH may imply higher nitrification while an increased pH may refer to increased denitrification process. Thus, for an optimal MABR performance (i.e., for simultaneous nitrification and denitrification), the pH within reactor must be maintained at neutral.

12.4.5.5 Hydraulic Retention Time (HRT)

Hydraulic retention time refers to the average duration that a compound or pollutant remains in the reactor. Accordingly, it is calculated by the ratio of working volume to the substrate flow rate into the reactor. This parameter plays an important role in determining the operational cost and energy requirements for the system. Apparently, higher HRTs lead to greater investment costs thereby requiring larger working volume and/or decreased flow rate. However, a higher HRT indicates that membrane system acquires more time to react on pollutants thereby increasing efficiency. Most of the lab-scale MABR configurations have been successfully tested with significant microbial growth at HRTs from 1 h to 15 days (Long 2013). According to Hu et al. (2008), HRT less than 8 h showed a decreased TN and ammonia removal. On the other hand, longer HRT may enhance the simultaneous removal of COD and nitrogen but increases the cost of operation. Thus, HRT of 6–12 h has been considered as better range for high COD and nitrogen removals (Semmens et al. 2003).

12.4.5.6 Organic Loading Rate

The concentration of pollutants in the form of organics also plays a vital role in MABR performance. A higher organic load requires a larger microbial population for their treatment while a limited organic substrate may restrict the biological degradation processes. A significant number of microbes indicate higher oxygen requirement inside the reactor. On the other hand, a thicker biofilm may reduce the oxygen permeability of the membrane. Hence, organic load should be suitably maintained as per the reactor configuration (working volume) and specific membrane surface area.

12.4.5.7 Ammonium Loading Rate

The major application of MABR processes has been the removal of organics as well as nitrogen compounds through simultaneous nitrification and denitrification. Thus, an optimal range of ammonium loading is required such that the nitrifiers and denitrifiers can act efficiently for its degradation. The concentration of ammonium loading is also dependent on the type of wastewater. For instance, domestic wastewater contains relatively less ammonium in the range of 30–100 mg/L (Rabah and Darwish 2013), while a landfill leachate has higher ammonium concentration in the range of 500–3000 mg/L (Syron et al. 2013). Similarly, (Brindle et al. 1998) found that almost complete nitrification could be achieved at ammonium loading of 1.2 kg NH_4^+-N/m^3/day, while (Hwang et al. 2009) suggested maximal specific nitrification rate at loading of 3.5 g/N/m^2/day at a DO over 0.5 mg/L. Thus, the studies suggest that when ammonium loading is low, there is high probability of ammonium limitation although significant degradation may occur owing to the population of nitrifying bacteria. On a contrary note, after a threshold ammonium loading concentration, there is a constant maximum nitrification rate and the process is independent of loading rate (Long 2013).

12.4.5.8 COD/N Ratio

Biological nitrogen removal has also been dependent on the ratio of COD to nitrogen. Since nitrification rate is highly dependent on the competition for substrates between autotrophic and heterotrophic microorganisms, a need of optimal COD-to-N ratio is felt so as to maintain ideal removal efficiency (Carrera et al. 2004). For a completely autotrophic nitrogen removal over nitrite (CANON) process, the threshold of COD/N ratio was found to be 1.7 (Zhang et al. 2015), while in MABR process, the bacterial density declined significantly when influent ratio of COD to N decreased below three (Lin et al. 2016). A study by Walter et al. (2005) indicated that high COD-to-N ratio results in considerable decrease in nitrification ratio. This study also suggested that the amount of substrates in the form of COD and nitrogen lead to increased competition between the specific microbes for available oxygen. Different modeling, experimental results, and stoichiometric calculations imply that the optimal COD-to-N ratio falls under 4:1 in MABR systems (LaPara et al. 2006). The effects in removal efficiencies because of variable COD/N ratio may also be accounted by the inhabiting microbial community in biofilm as Lin et al. (2016) found that specific bacterial population and density differed with varied COD-to-N ratio (Table 12.2).

12.4.5.9 Thickness of Biofilm

One of the major influencing factors associated with efficient organics and nitrogen removal in MABR system is the thickness of biofilm. Thickness of biofilm poses substantial limitation in penetration of substrates to the targeted microbial population within the biofilm. Moreover, as the MABR system employs different groups of bacteria, the microbial community growing close to membrane receive highest amount of oxygen and flourish well. This condition leads to increased resistant to diffusive oxygen transport into bulk liquid, thereby limiting oxygen to the overgrowing nitrifiers. Nonetheless, the expanding microbes favor the growth of anoxic denitrifiers inhabiting the rear ends of the biofilm. Thus, it is important to periodically check the microbial population and determine the optimal thickness required for efficient pollutant removal. The optimum biofilm thickness for simultaneous organic and nitrogen removal using MABR was determined as 1600 μm (Terada et al. 2003).

Several methodologies have been put forward to control the thickness of biofilm. The major ones include intermittent high shear and/or gas sparging, mixing, and high tension recirculation (Martin and Nerenberg 2012). This study also suggests that frequent shear stress strips off the thickened biomass and supports the mixing of substrates. Another advantage of short-term air sparging is increment in oxygen supply which promotes nitrification in the reactor system and prevents the acidification of bulk liquid by stripping CO_2 (Stricker et al. 2011). Also, (Pankhania et al. 1999) suggested the use of air scouring with an on mode for 10 s followed

Table 12.2 Typical loading rates used in previous studies

Working volume (L)	Influent concentration		Hydraulic retention time (HRT)	Loading rate (g/m^2-day)		References
	COD (mg/L)	NH_4^+-N (mg/L)		Organic (OLR)	Nitrogen (NLR)	
0.8	30, 60 and 120	30	3 and 6 h	6–24	2.7–5.6	Duvall (2017)
1.63	200	41	12 h	11.6	2.4	Yamagiwa et al. (1994)
60	1000–3000	500–2500	4.5–7.5 days	–	1.4–9.0	Syron et al. (2015)
–	207–410	25.4–56.8	12 h	1.42–3.02	0.20–0.29	Tian et al. (2015a, b)
7.0	274–394	87	6 h	8.4–12.1	2.66	Semmens et al. (2003)

immediately with water flushing for 60 s repeating the process thrice on daily basis for controlling biofilm thickness and to maintain proper membrane cleaning. Likewise, (Brindle et al. 1999), in their study, used wash water flow of 4–6 L/min as well as air flow of 30–40 L/min for a period of 10–15 s for controlling biofilm development.

12.4.6 Modern Use of MABR Systems

MABR systems have been widely used in treatment of different types of wastewater. Their applications have not been limited to treatment of domestic sewage and municipal wastewater but also have been extended to treatment of pharmaceutical wastewater, polluted surface water, synthetic wastewater, high-strength brewery wastewater, landfill leachates, or xenobiotic components. Figure 12.9 summarizes some of the major chemicals that have been successfully treated by MABR processes either in lab-scale models or in pilot plants (Casey et al. 1999).

12.4.6.1 Simultaneous Removal of Organics and Nitrogen

One of the major applications of MABR process is simultaneous and high-rate treatment of organics and nitrogen from wastewater in a single reactor system. An early study made by Yeh and Jenkins (1978) found that 90% BOD removal could be achieved at high organic loadings using pure oxygen fixed film reactor. This initial membrane system clearly outperformed the then prevailing water treatment technologies like conventional activated sludge system and trickling filter system.

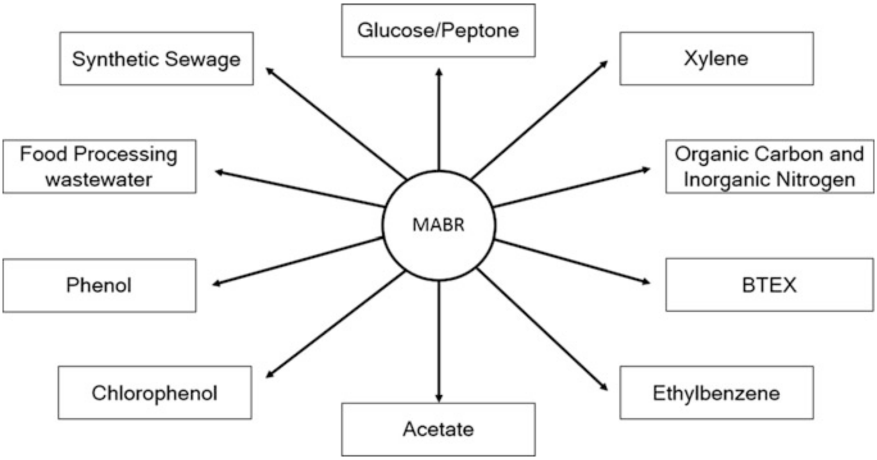

Fig. 12.9 Applications of MABR systems for treatment of different pollutants

With the advancement in membrane types, configuration, and packing density, MABR systems gained more popularity because of its enhanced removal efficiency. Hou et al. (2013) modified the surface of PVDF hollow fiber membranes by coating it with L-3,4-dihydroxyphenylalanine (DOPA) and studied its effect on gas flux and removal performance. The removal efficiency accounted for more than 90, 98.8, and 84.2% for COD, NH_4^+-N, and TN, respectively. Similarly, (Hu et al. 2008) developed carbon-membrane-aerated biofilm reactor and discovered a maximum removal of 86, 94, and 84% in terms of COD, NH_4^+-N, and TN, respectively.

Sabesp: A Case Study

A Brazilian water and waste management company named Sabesp is one of the largest waste management companies providing basic sanitation facilities under all phases of water abstraction, collection, treatment, processing, distribution, and reuse. With increasing crisis resulting from water shortages, stricter legislations were formulated by government and as a consequence, severe necessity was demanded in upgrading the prevalent lagoons to achieve tertiary treatment standards.

Sabesp, OxyMem, and The Dow Chemical Company jointly checked the probability of establishing MABR system in an existing lagoon in Aruja Plant, Sao Paulo. Operated in three reactors serially, with each reactor volume of 9 m^3, the system adjusted high loading rates in first stage, while lowers loading and best effluent quality in third stage. The oxygen transfer across the membrane system was assessed through the mass balance equating the amount of continuous flow of oxygen at inlet and outlet with results suggesting OTR up to 7 gO_2/m^2 d. A four-phase test (start-up, drop-in, biofilm, and optimized biofilm) operated for 200 days indicated achievement of considerable effluent quality. For a loading rate of 2.1 kg COD/m^3 d, the effluent COD concentration was reported less than 100 mg/L. Likewise, effluent NH_4-N concentrations were recorded less than 10 mg/L for influent N loading between 40 and 80 mg/L. In addition to this, the effluent TSS concentration was less than 5 mg/L over the entire trial suggesting that the need of expensive sand filter or membrane filtration could be avoided and reuse of such water could be highly feasible. When assessed for the energy usage, the standard aeration efficiency (SAE) was recorded to be 2.8 kg O_2/kWh which is 7 times higher than that of a typical activated sludge process. Furthermore, with high-efficiency aeration blowers, the numbers for SAE could reach to 14 kg O_2/kWh with energy usage of 0.05 kWh.m^3. Thus, this pilot-scale water treatment plant using MABR on the previously existing lagoon provides an evidence for the takeover of this advanced technology over other conventional treatment processes owing to its financial and technical robustness.

12.4.6.2 Treatment of High-Strength Industrial Wastewater

MABRs have been reported to successfully treat high-strength carbon and nitrogenous wastewater. Brindle et al. (1999) could achieve a removal efficiency of 81% TCOD which accounted for a removal rate of 27 kg TCOD/m^3d when the reactor was operated in plug flow mode. The same study also revealed 80% SSCOD removal in completely mixed conditions. Stricker et al. (2011) used dense hollow fiber membranes for treatment of industrial wastewater having influent COD and TKN values as high as 4700 mg COD/L and 145 mg TKN/L, respectively, and obtained a removal efficiency of 90% COD and 89.3% TKN. Similarly, another study by Hai et al. (2005) carried out for the treatment of synthetic textile industry high-strength wastewater found that TOC removal of 97% while dye removal of 99% could be achieved using hollow fiber membranes operated.

12.4.6.3 Surface Water Treatment

With the increasing use of agricultural pesticides and fertilizers, unregulated discharge of industrial wastes, and unmanaged municipal sewage wastewater, surface water has been severely polluted (Han et al. 2016). The pollutants of surface water mainly comprise carbon and nitrogenous origin. Thus, MABR processes have been sought as a promising technology in removal or degradation of surface water pollutants. A pilot-scale study carried out by Li and Zhang (2017) for treatment of polluted surface water found to have a removal efficiency of 80% for TOC, 92.2% of NH_4^+-N, and 60.3% of TN using MABR process. The study was carried out using PVDF microporous membranes having a specific membrane surface area of 54.1 m^2/m^3 operated in a volume of 470 L and maintained with HRT of 12–48 h. Likewise, another study by Li et al. (2016) suggested a removal efficiency of 86.2% of TN and 76% of TP using MABR process for which the growth of biofilm was enhanced through supplementation of polyhydroxyalkanoates.

12.4.6.4 Treatment of Landfill Leachate

Landfill leachate is the end product of anaerobic digestion of mixed organic and industrial waste, which contains higher proportion of nitrogenous compounds (Christensen et al. 2009). Though attached growth technologies such as moving bed biofilm reactors and rotating biological contractor have been preferred for treatment of landfill leachates, they are expensive. To cope up with such issues, (Syron et al. 2015) analyzed the performance of a pilot-scale MABR system for the treatment of landfill leachate and found highest oxygen transfer rates of 35 gO_2/m^2d. The study also revealed the nitrification of 80–99% for influent ammonium concentrations of 500–2500 mg/L, while COD removal of 80–83% for influent COD concentrations of 1000–3000 mg/L. Thus, the authors provided significant evidence for low-energy options using MABR for efficient leachate treatment.

12.4.6.5 Removal of Xenobiotics from Wastewater

Xenobiotics refer to the chemicals that are not naturally present in the environment and are very poorly degradable. Only limited organic compounds of synthetic origin can be degraded biologically. Thus, any synthetic compounds that can be specifically degraded by certain groups of bacteria can be effectively treated using MABR systems. Since the major player for removal of xenobiotics in an MABR process is microorganism, specific aerobic bacteria can be harnessed in the reactor and be exploited for their natural degradation mechanism. Over recent years, several studies on the degradation of xenobiotics using MBAR have been carried out very efficiently. Heffernan et al. (2009) identified the use of MABR technology exploiting specific biofilm of *Pseudomonas fluorescens* DSM8341 for the treatment of fluoroacetate. Results from this study indicated maximum fluoroacetate removal efficiency of 91.5%. Similarly, (Misiak et al. 2011) used *Pesudomonas knackmussii* B13 strains for the degradation of 4-fluorobenzoate. However, the course of experiment indicated a decrease in specific degradation rate of the compound with time which accounted to the accumulation of fluorine in biofilm. Some of the degradations of major xenobiotics and volatile organic compounds (VOCs) based on MABR systems have been listed in Table 12.3.

12.4.6.6 Treatment of Medical and Pharmaceutical Wastewater

A pharmaceutical industrial wastewater is considered to contain high amount of organics and wide variety of chemical contaminants which are extremely difficult for biological degradation (Enick and Moore 2007). Thus, the treatment process demands rigorous efforts to meet the desired discharge standards. A study by Wei et al. (2012) indicated that the integrated MABR process comprising of hollow fiber membranes with specific membrane surface area of 287 m^2/m^3 achieved considerable removal efficiency of 90% for COD and 98% for NH_4^+-N. The volumetric removal accounted to a maximum of 1311 $gCOD/m^3d$ and 48.2 gNH_4^+-N/m^3d. Another study by Tian et al. (2015a, b) incorporated MABR processes with ozone oxidation and coagulation–flocculation technology for treating pharmaceutical intermediates which resulted in 95% COD and 92% TN removal. The treatment process was facilitated by surface-modified hollow fiber polyethylene membrane having a specific surface area of 50 m^2/m^3 operated in dead-end mode configuration.

12.4.6.7 Treatment of Swine Wastewater

The characteristics of swine wastewater are significantly different from municipal sludge as it contains high amount of total solids diluted with urine and other flush water (Andreadakis 1992). This implies that the treatment method should also be considerably different from that of municipal wastewater treatment process.

Table 12.3 MABR applications in degradation of xenobiotics and VOCs

Pollutant	Configuration	Biofilm seed/source	Removal rates	Reference
Fluorobenzoate	Silicone tubing	*Pseudomonas knackmussii*	1.2 g g^{-1} h^{-1}	Misiak et al. (2011)
1,2 dichloroethane	Single tube extractive membrane bioreactor	*Xanthobacter autotrophicus*	1.36 g C m^{-2} h^{-1}	dos Santos and Livingston (1995)
Acetate	Silicone; Hollow fiber flow-through	*Vibrio natriegens*	–	Casey et al. (2000)
Perchloro-ethylene (PCE)	Silicone; hollow fiber flow-through	Anaerobic seed from lab CSTR and aerobic seed from previously exposed to PCE	0.24 mg L^{-1} h^{-1}	Ohandja and Stuckey (2006)
Toluene	Polysulfone; hollow fiber cartridge	From municipal waste	84%	Parvatiyar et al. (1996)
Benzene, chlorophenol, 2,4-dichloro-toluene	Nonporous silicone membranes, hollow fiber, flow-through	Activated sludge	6800–15,500 gm^{-3} d^{-1}	Kolb and Wilderer (1995)
Acetonitrile (ACN)	Polypropylene hollow fiber, dead end	Adapted activated sludge from pharmaceutical wastewater	21.1 $gACNm^{-2}$ d^{-1}	Li et al. (2009)

Kritsunankul and Wantawin (2008) used a sequencing batch biofilm reactor for the treatment of swine wastewater consisting of low ratios of COD to nitrogen and phosphorous. The study found out a maximum efficiency of 85% in terms of denitrification for the available COD. Likewise, another study by Terada et al. (2003) carried out on non-diluted swine liquid wastewater collected from a process separating excrement and urine, the mean removal efficiency of TOC and N was found to be 96 and 83%, respectively.

Apart from those pollutants mentioned above, some laboratory scale treatment of specific compounds has also been studied using MABR systems. Potvin et al. (2012) analyzed the removal efficiency of tetrabromobisphenol A (TBBPA) in dechlorinated tap water enriched with ammonia using MABR systems. In the study, MABR system provided an average ammonia removal of approximately 83% while TBBPA removal of about 65%. Likewise, (Wang et al. 2012) studied the performance of MABR in removal of an azo dye Acid Orange 7 (AO 7) and its auto-oxidative decolorization product. The results suggested that the microbes *Shewanella* sp. XB efficiently degraded the azo compounds to maximum of 98% while COD removal was recorded as 80%. Another study by Xiao-xiao et al. (2016)

used hydrogen-based membrane aeration biofilm reactor to analyze the removal efficiency of nitrate and perchlorate in simulative groundwater. The results suggested a removal efficiency of more than 95% for each of the targeted pollutants. Similarly, (Şahinkaya et al. 2011) employed oxygen-based membrane biofilm reactor for sulfide oxidation and sulfur recovery using effluents from sulfidogenic anaerobic baffled reactors. More than 98% sulfide oxidation and 75% sulfur conversion could be achieved by the process under optimal sulfide loading and oxygen supply.

12.4.7 Limitations of MABR System

Compared to CAS system, MABR processes impose a significant cost reduction in terms of operation. However, the process is still expensive for wastewater pumping into the reactor as well as supply of pressurized gas into the membrane modules. Another major limitation for MABR process is the poor ability in controlling the thickness of biofilm. With the availability of substrates and oxygen, the microbial community inside the biofilm keeps flourishing and the biofilm thickness is difficult to maintain in optimal condition. Nevertheless, different methods have been developed to avoid the issues, and the research still lacks prominent automated methods for controlling biofilm thickness. Apart from that there still exists possibilities in membrane defects causing process upsets. Though most of the commercially available membranes are supposed to have long-term durability and of high mechanical strength, the precise durability and strength have not been recorded yet. Likewise, any of the membrane fiber rupture in the module may cause air leakage resulting in disturbance of microbial stratum in biofilm. Apart from that biofilms, at sometimes, may become shock sensitive during changes in pH, temperature, or salinity. Poor understanding of scale-up mechanisms for membrane modules for treatment of different types of wastewater also fall under the restrains of MABR studies.

12.4.8 Future Prospects of MABR

The current MABR systems are at the most advanced stage of development with focus on energy savings. A recent data by OxyMem (n.d.) indicates that MABR system can reduce the energy costs to a minimum of 7 times as compared to CAS systems. Apart from that the systems have also been reported to be combined in parallel to other different treatment technologies thereby increasing the efficiency. An effort was made by Tian et al. (2015a, b) to combine MABR systems with ozone oxidation as pretreatment method and improved coagulation–flocculation technology as post-treatment methods for management of pharmaceutical intermediate wastewater. Likewise, (Li et al. 2015) blended MABR with ozone–biological activated carbon process for the treatment of oil field wastewater which resulted in COD removal of 90.6%, TN removal of 78.1%, and oil removal of 87.9%. Thus, because of the low footprint, the future of MABR resides in perfect amalgamation between different wastewater treatment technologies.

Apart from those aforementioned innovations, the technical aspects of MABR system can be enhanced by introduction of high lifetime membranes, development of membranes with low resistance to aeration or having high gas permeability, and membranes with easy attachment of biofilms based on process performance and economic feasibility. In addition to this, the upcoming aspects of MABR exist in understanding the theoretical, biological, and engineering principles behind biofilm structure and stratification development. Likewise, the applications of this system can be expanded to treatment of complex mixtures of constituents in industrial wastewater or leachate, xenobiotic compounds, synthetic intermediates, volatile organic compounds, and composite air pollutants. The future of preferential treatment of such waste depends on the selective seeding of microorganisms inside the reactors. As mentioned in Fig. 12.10, the technical and biological aspects can have significant changes in performance of MABR systems. Hence, the future of MABR needs to focus on perfect blends of biotechnology and engineering principles to enhance performance and broaden applications of this treatment technology.

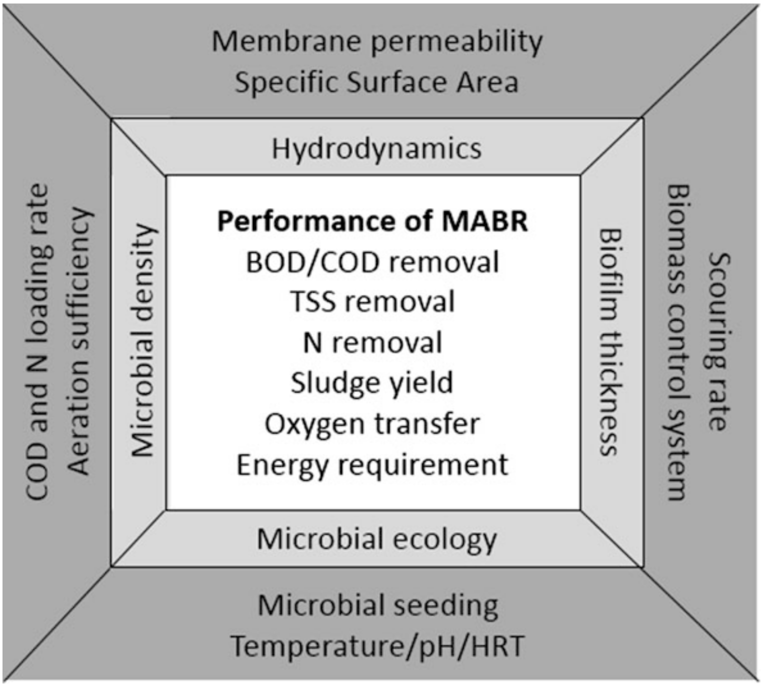

Fig. 12.10 Factors influencing MABR process performance

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Chapter 13
Non-conventional Anaerobic Bioreactors for Sustainable Wastewater Treatment

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Abstract Conventional anaerobic bioreactors have proven to be useful for energy recovery and removing organic pollutants from wastewater. Unfortunately, the application of most conventional anaerobic systems is limited due to their applicability over a narrow range in substrate composition and single type of pollutant removal. The background of the research and development for non-conventional anaerobic bioreactors mainly includes design limitations, technical and economic issues along with environmental impacts from traditional systems. In this connection, the initial approach for developing non-conventional bioreactors included the improvement on existing conventional anaerobic bioreactors with pre- and post-treatment processes. As these improvements only increased the pollutant removal efficiency up to a certain level, research initiatives were carried out to develop non-conventional hybrid systems. These non-conventional bioreactors usually involve a combination of conventional biological system with physical/chemical treatment process to aid the removal of non-biodegradable pollutants. Recently developed non-conventional systems include the modifications in bioreactor designs such as bio-electrochemical systems, multistage bioreactor arrange-

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ments and hybrid anaerobic processes. Performance evaluation of these non-conventional anaerobic systems shows improved product yield and efficient pollutant removal compared to the traditional processes. The key findings from this discussion were listed in the conclusion section along with future insights for this technology.

Keywords Non-conventional · Anaerobic · Bioreactors · Hybrid
Biogas

13.1 Technical Background

Over the last few years, the research initiatives on non-conventional anaerobic bioreactors have been accelerated due to a number of technical limitations and performance issues in the conventional anaerobic systems. Conventional Anaerobic Digestion (AD) processes in wastewater treatment refer to a simple design that involves the removal of common biodegradable pollutants from wastewater using anaerobic microorganisms. Usually, traditional anaerobic processes offer less energy-intensive operation compared to aerobic process, as aeration is not required to supply oxygen for the anaerobic microorganisms. Additionally, it provides with the opportunity to capture methane-containing biogas. Although traditional anaerobic bioreactors offer these two major advantages, generally they suffer from a number of issues like limitations in design modification, limited product revenue, environmental pollution and technical issues in process operation and maintenance.

The following section focuses on the detailed discussion on the technical background behind the development of non-conventional anaerobic bioreactors. For conventional AD process, limitations in design modification and product revenue have been addressed. The discussion was followed by reviewing negative impacts on environment and technical issues present in bioreactor operation and maintenance.

13.1.1 Design Limitations of Conventional Anaerobic Systems

Conventional anaerobic processes are designed to remove common organics and nutrients from wastewater. The design scheme is typically based on the expected removal efficiency of pollutants present in feed wastewater. Treatment processes like activated sludge, adsorption, forward osmosis, advanced oxidation, etc. have already achieved the highest level of optimization and upgradation to remove selected types of pollutants from different wastewater streams. The design and layout of these single types of treatment processes are fixed and options to modify any design aspects are limited. On this topic, traditional anaerobic bioreactors include major design limitations in applying different operating conditions (i.e. separating HRT and SRT, high organic loading rate, improper mixing, etc.), narrow range in product spectrum (only biogas), single type of pollutants removal and limitations in product extraction and purification.

The basic design of conventional anaerobic bioreactors processing wastewater consists of a one-stage activated sludge anaerobic process. The microbes present in the sludge treat the biological wastewater by decomposing the organic material and nutrients from it. The suspended solid sludge provides a limited surface area for contact between the inoculum and substrate. Most anaerobic water treatment processes have different optimal sludge and hydraulic retention times that are easier to operate in multistage anaerobic processes. Apart from the retention time, conventional design processes can only handle a very low loading rate for the organics because of improper mixing and single-stage assembly. At high organic loading, operational issues such as load shock and sludge bilking (excessive growth of filamentous bacteria) can render the reactor's operation unstable (Zhang et al. 2017).

The range of products that can be extracted from this process is also very limited. Each major AD component—VFA, hydrogen and methane—has different operating conditions in terms of temperature, pH, loading rate and retention time. The most recent bioreactor design includes multistage assembly where operating conditions can be varied for different products individually. For example, acetate-type fermentation in VFA production requires a pH range of 5.5–6.0, whereas optimum pH conditions for anaerobic methane production have been reported as being between 6.5 and 8.2 (Mao et al. 2015). Its feasibility is made possible by the multistage anaerobic bioreactor. VFA and methane production requires inhibition of methanogenic microorganisms that consume VFA and biohydrogen. The multistage assembly enables the inhibition of methanogens in the first stage with the optimum operating conditions which can support the growth of methanogens in the second and final stage (Khan et al. 2016). Maintaining different operating conditions for multiple products like VFA–methane or biohydrogen–methane remains a challenge for traditional single-stage designs.

For industrial and domestic wastewater treatment, single-stage activated sludge processes have been utilized for the removal of Chemical Oxygen Demand (COD) and nutrients. This technology has limitations in the form of low COD and nutrient removal, and comparatively long retention times compared to other water treatment technologies. The level of biodegradation is achieved based on the type of microbial population present in the sludge. Therefore, variations in removal efficiencies are generally expected from different single-stage AD processes. Furthermore, traditional design does not employ a physical barrier for sludge retention. For this reason, poor sludge settling and carryover of biological solids are two major limitations evident in AD operations (Zhang et al. 2017).

The range of pollutants present in domestic and industrial wastewater includes additional micro-pollutants that are not easily biodegraded by anaerobic microorganisms present in the reactor. Physical and chemical treatment processes have been integrated with the biological process to achieve complete removal of pollutants from wastewater. A combination of microfiltration with reverse osmosis has been applied for the removal of pharmaceuticals and pesticides, whereas chemical adsorption can serve to remove both biodegradable and non-biodegradable compounds from wastewater (Rodriguez-Mozaz et al. 2015).

Product extraction and purification is another issue to emerge in conventional anaerobic processes. The final product in anaerobic digestion involves methane which does not require any downstream processing; however, the typical methane content in biogas (from AD) only ranges between 40 and 45%. In terms of energy density, the produced biogas is not suitable for industrial and household supply of fuel gas (contains approximately 95–96% of methane). For the production of VFA, solvent extraction method has been extensively applied to extract VFA components from the reactor effluent (Banel and Zygmunt 2011). The cost associated with the extraction process, however, needs a detailed economic assessment on its feasibility before any large-scale industrial application can be considered.

Anaerobic processes designed to produce biohydrogen have a major challenge regarding hydrogen storage. Low density, energy-intensive liquefaction process, hydrogen loss due to boil-off phenomena and metal embrittlement due to hydrogen atom diffusion are potential issues in the biohydrogen storage system (Khan 2017). Bio-electrochemical systems employed to produce methane as a potential solution of the produced biohydrogen can be integrated into a bio-electrochemical system with an AD reactor. It uses the produced biohydrogen as an electron donor to produce methane and carbon dioxide.

13.1.2 Limitations in Product Revenue from Conventional Processes

The success of anaerobic processes in large-scale industrial applications largely depends on the product revenue that can be earned from the products. Current research initiatives on anaerobic process are inclined to optimize the production of methane-containing biogas. Operating conditions, pre-treatment processes as well as different chemical additives have been researched and developed aiming to increase the production of methane from the anaerobic process. Methane as an AD product has certain advantages, for instance, limited downstream processing and easy separation and use. A cost–benefit analysis has been done for different anaerobic processes producing methane as the single product. Results show that the net profits gained from anaerobic processes are always negative, meaning that the expenses exceed the product revenue earned from methane (Khan et al. 2016). For example, membrane processes producing methane-containing biogas from wastewater involve very expensive operations because they involve biogas scouring, low flux, membrane fouling, etc.

So far, research studies on the economic feasibility of anaerobic processes do not include the cost involved for carbon capture and storage. Martínez Arranz (2016) estimated that US \$16/t CO_2 needs to be spent on carbon capture and storage. Yet, no experimental study has been done to economically assess the cost involved to recover dissolved methane from the effluent of anaerobic processes. Therefore, expenses involved in installation and in bioreactor operations are important factors that control the amount of net profit from any anaerobic process. Table 13.1 summarizes the breakdown of energy consumption for two anaerobic membrane bioreactors treating municipal and urban wastewater (Khan et al. 2016).

The contributing factors involving cost and energy consumption provide an idea for future scope of cost reduction. The highest energy consumer has been identified as biogas recycling blower and gas scouring energy consumes about 46% of the total operational cost of current anaerobic bioreactors treating wastewater. An alternative approach to produce Volatile Fatty Acid (VFA) and biohydrogen in this case can curtail the operational cost and improve the net profit gain. The research performed by Kleerebezem et al. (2015) has compared the revenue earned from methane-containing biogas and polyhydroxyalkanoate (a polyester produced through bacterial fermentation, commonly termed as PHA) produced from VFA. For this assessment, wastewater from a cardboard production facility was considered with a capacity of 5000 m^3/day. The following table shows the simplified calculation of product revenue from methane and PHA from cardboard wastewater (Table 13.2).

Some multistage anaerobic processes involve recovering Volatile Fatty Acids (VFA) and biohydrogen along with methane (Nualsri et al. 2016; Xia et al. 2016a, b; Zhong et al. 2015). Generally, for multistage assembly, the initial capital investment is higher compared to the single-stage variant due to reactor vessel installation, multiple membrane modules and electrical equipment. A comparative cost–benefit analysis would be interesting to see whether the added revenue from multiple AD products can exceed the cost associated with initial capital investment, bioreactor operation and maintenance.

Table 13.1 Breakdown of energy requirement for two different conventional AnMBR systems

Conventional bioreactor design	Breakdown in energy requirement	Energy consumption (%)
Submerged AnMBR treating 20,000 m^3 volume municipal wastewater	Gas scouring energy	46.7
	Pumping energy	13.7
	Sludge disposal	7.2
	Chemical consumption	32.5
AnMBR treating (3.2 ± 0.7 m^3/day) sulphate-rich urban wastewater	Biogas recycling blower	73.5
	Sludge feeding pump	14.6
	Stirring power reactor	8.3
	Permeate pump	1.8
	Other consumers	1.8

Table 13.2 Revenue from methane (from biogas) and PHA (from VFA) in a wastewater facility

Process	Anaerobic digestion	PHA production
Parameters	$Y_{CH4/VFA}$ = 0.9 gCOD/ gCOD	$Y_{PHA/VFA}$ = 0.7 gCOD/gCOD $Y_{X/VFA}$ = 0.6 gCOD/gCOD
	COD_{CH4} = 4 gCOD/g	Final COD—PHA content = 80% (f_{PHA} = 0.8)
		COD_{PHA} = 1.67 gCOD/g
Price end product	$€_{CH4}$ = 0.4 €/1000 g	$€_{PHA}$ = 2.0 €/1000 g
Revenue	3.6×10^3 €/day	20.2×10^3 €/day

Modified from Kleerebezem et al. (2015)

13.1.3 Environmental Pollution and Health Issues

Standalone anaerobic digestion processes cannot remove phosphate present in wastewater. The denitrifying microbial group can achieve high removal rates for nitrates. Unfortunately, nitrogen present in other forms and phosphates in general cannot be effectively removed through anaerobic digestion. Different removal techniques such as Iron (III), calcium along with integrated FO processes have been utilized for phosphate recovery in anaerobic wastewater treatment. Since traditional AD processes do not have the provision for design modification or chemical treatment for nutrient removal, nutrient loss is expected in the effluent from an anaerobic bioreactor.

Referring to wastewater treatment, nutrients present in the effluent can potentially explain eutrophication, which is a process whereby an ecosystem is transformed through nutrient enrichment from an external source in waterways (Fagbohungbe et al. 2017). Anaerobic bioreactor effluents rich in phosphorus and nitrogen can be responsible for excessive growth of algae along the surface of a water body and therefore lead plants and other aquatic life experiencing ecological imbalance.

Additional environmental impacts from anaerobic wastewater treatment include global warming, acidification, eutrophication, abiotic depletion, human toxicity and maritime aquatic ecotoxicity (Pretel et al. 2013). These impacts are directly attributed to the removal efficiency of total COD, nitrogen, phosphorus and finally the production rate of methane. The major components of produced biogas from anaerobic wastewater treatment are methane and carbon dioxide, which directly contribute to an anaerobic process's global warming potential.

Dissolved methane present in the anaerobic bioreactor effluent can be discharged into the atmosphere in the form of fugitive emissions. Anaerobic processes operated at low temperature increase the solubility of methane in the liquid phase and the concentration can reach up to 50% in the effluent. The estimated Global Warming Potential (GWP) for methane is 23 times higher compared to CO_2. Therefore, an emission of only 5% can undermine and negate the positive impact of anaerobic

Table 13.3 Useful pre-treatment processes for methane production in anaerobic digestion

Product	Substrate	Pre-treatment (type)	Pre-treatment (process)	Product yield/effects after pre-treatment	References
Methane	Eucalyptus	Mechanical	woodchip	0–14 Lkg^{-1} TS	Nakamura and Mtui (2003)
		Thermal	Woodchip in hot water at 125 °C for 20 min	124 Lkg^{-1} TS	
			Steam explosion to chip at 25 atm, 3 min	194 Lkg^{-1} TS	
		Chemical	Woodchip in 1% NaOH with hot water at 125 °C for 20 min	134 Lkg^{-1} TS	
	Rice, corn, wheat straw switchgrass,	Mechanical	Chopped into 3–5 cm	117–190 Lkg^{-1} VS	Paul and Dutta (2018)
	Green leaves and yard waste	Thermal	Heat in oil bath at 130 ° C and 1 at for 1 h	212 Lkg^{-1} VS	
		Chemical	8% NaOH	472 Lkg^{-1} VS	
		Mechanical + Chemical	Ground to 25 mm at 130 °C with Ammonia	245 Lkg^{-1} VS	
	Rice straw	Chemical	3% NaOH (35 °C and for 48 h)	Energy recovery increased 59.9%	Zhang et al. (2015)
	Maize straw	Chemical	NaOH (4 and 6%) pre-treatment & Fe dosage (50, 200, 1000 and 2000 mg/L)	57 and 56% higher biogas and methane yield, respectively	Khatri et al. (2015)
	Swine manure fibres	Chemical	Aqueous ammonia soaking (Mars et al. 2010)	98% increase of the methane yield	Jurado et al. (2016)
	Waste activated sludge	Biological	Grass *Egeria densa* (*E. d.*)	198.32 ± 2.61 mL/g VS_{added} (18.72 ± 0.14% higher)	Zhen et al. (2015)
	Organic solid waste	Chemical	Ozone dosage (0.05 to 0.5 gO_3/gTS)	37% higher cumulative methane production	Ariunbaatar et al. (2014) and Cesaro and Belgiorno (2013)

(continued)

Table 13.3 (continued)

Product	Substrate	Pre-treatment (type)	Pre-treatment (process)	Product yield/effects after pre-treatment	References
	Solid manure fraction	Biological	Maize silage and grass silage	Methane production increased 5.5 times (from 10 L/kg substrate to 55 L/Kg substrate)	Asam Z-u-Z (2011)
	Maize silage	Mechanical	High pressure (9 Bar)	77% increase of methane content in biogas	Lemmer et al. (2015)
	Household organic waste	Mechanical	Mechanical (shredding) and electroporation pre-treatment of ley crop	3.4 and 9.2% increase in total methane production, respectively	Thorin et al. (2012)
	Swine manure	Biological	Vegetable wastes (50% dw/dw)	an improvement of 3- and 1.4-fold in methane yield	Molinuevo-Salces et al. (2012)
	Pre-treat *Nannochloropsis* LEA, *Nannochloropsis* alga (WA)	Thermal	Thermal pre-treatment (150–170 °C)	40% increase in methane production (to 0.31 L/gVS)	Bohutskyi et al. (2015)

digestion. A relatively new technology of degassing methane can reduce the content of dissolved methane but this is an energy-intensive method (Khan et al. 2016).

Most anaerobic water treatment processes are designed simply to remove the major portion of organic pollutants and common nutrients from wastewater. Emerging pollutants like pharmaceutical waste, antibiotics and non-biodegradable micro-pollutants can be present along with common organic materials and nutrients. Unfortunately, the negative environmental impacts associated with the release of non-degradable pollutants have not yet been identified. For pharmaceutical wastes and antibiotics, trace amounts present in wastewater attack the bacterial cells, and later they develop resistance not only against a single drug but also multiple antibiotics. These groups of multidrug-resistant bacteria develop Antibiotic-Resistant Genes (ARG) due to the long-term presence of these components in wastewater systems. Finally, the development of antibiotic-resistant genes produces antibiotic-resistant bacteria. People affected by these groups of microbes can suffer from serious health issues since most types of drugs/antibiotics cannot be applied as cures (Kumar and Pal 2018).

13.1.4 Issues in Conventional Bioreactor Operation and Maintenance

Technical problems in conventional anaerobic bioreactors can be categorized into operating issues and problems related to the maintenance of bioreactor and its components. The following sections will discuss the issues that are involved in conventional anaerobic bioreactors treating different types of wastewater.

Process inhibition and controlling operating conditions can affect the bioreactor performance, shift microbial activities and to a great extent change the product yield. Anaerobic processes producing methane can be affected by a number of inhibitory compounds that are produced in initial and intermediate stages of a bioreactor's operation. For stable bioreactor operation to occur, controlling the inhibitory compounds can still pose a serious problem. Major inhibitory components include ammonia, volatile fatty acids and sulphide/sulphate.

The nitrogen present in ammonia is an essential nutrient for the anaerobic microorganisms but only beneficial for methane production up to a certain level. Ammonia nitrogen (NH_3 and NH_4^+) is converted from the nitrogen in organic compounds present in the substrate and gradually accumulate in the digester during operation. AD bioreactors having ammonia concentrations between 600 and 800 mg/L (at pH = 7.2–7.5 and mesophilic condition) perform well, whereas other studies reported a value of below 200 mg/L for optimal AD performance. The differences in inhibitory levels are observed due to various types of substrates, operating temperature, pH and period of sludge acclimation. An ammonia concentration between 1500 and 7000 mg/L has been reported as causing digester instability and concurrent decrease in biogas production (Yuan and Zhu 2016). The mechanism in this inhibition involves passive diffusion of free ammonia into microbial cells that results in, first, abnormal cell ectoplasm, and second, an abnormal exchange in sodium–potassium balance. Passive diffusion can lead to a change in pH that affects the stability of the microbial cell. Anaerobic digesters operating in batch mode can be particularly vulnerable to the ammonia inhibition process if the feed solution contains organic nitrogen.

Digester instability is a major problem that can be caused due to the accumulation of VFA in an anaerobic process. AD involves four major steps; these being hydrolysis, acidogenesis, acetogenesis and methanogenesis (Fig. 13.1).

The major components of VFA are acetic, propionic, butyric and valeric acid that are produced in the second and third stages of anaerobic digestion. During the final stage, the methanogens consume the produced VFA much slower than the rate at which VFA is produced. Therefore, a high rate of initial hydrolysis, acidogenesis and acetogenesis can be responsible for possible VFA accumulation in the reactor. VFA accumulation triggers rapid acidification and sharp pH declines in the digester. At pH below 6.5, the growth of methanogens can be affected and at pH below 4.0, a complete inhibition of methanogenic activity can be observed (Mao et al. 2015).

The conventional anaerobic process has the technical limitation of a low organic loading rate so that the reaction rate of the initial three AD stages does exceed the rate of the final stage. Additionally, among different VFA components, only butyric and acetic acids are converted by the methanogens in the final stage. The conversion of propionic acid is not thermodynamically favourable and therefore the possibility of reactor acidification cannot be completely eliminated in traditional single-stage anaerobic systems (Khan et al. 2016). Sulphur is an essential element for methanogenic bacteria and their microbial cells contain more sulphur compared to other anaerobic microbes. In anaerobic digestion, sulphide inhibition can be

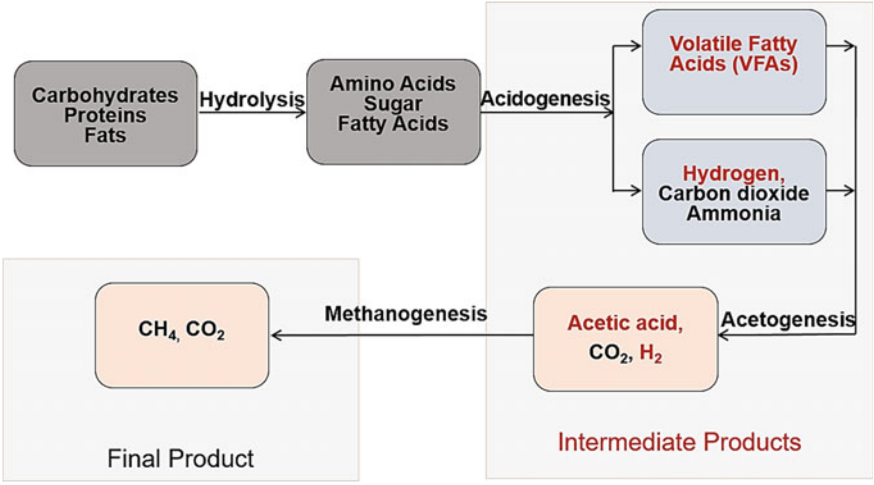

Fig. 13.1 Different steps in the anaerobic process. Khan et al. (2016)

evident if the substrate is rich in sulphur content. Substrates containing sulphate are converted to sulphide by the sulphate-reducing bacteria (SRB). Sulphide inhibition can be constituted through the competition between SRBs and methanogens. Anaerobic digesters having sulphide levels above 100 mg/L or dissociated H_2S levels between 50 and 400 mg/L can cause sulphide inhibition (Yuan and Zhu 2016).

Major operating parameters like temperature, pH and organic loading rate can cause issues in bioreactor operation. A high temperature and loading rate accelerate the initial hydrolysis process and can cause an increase in VFA production. As conventional bioreactors are not designed to extract VFA at the intermediate stage, anaerobic digesters operating at high temperature can be more vulnerable to inhibition due to VFA. Additionally, for full-scale conventional anaerobic digesters, maintaining pH can be a potential challenge where mixing between substrate and inoculum is not uniform. Consequently, a temporary drop in reactor pH can shift the microbial activity, produce inhibitory compounds and decrease methane production.

For conventional anaerobic digesters, foaming can be a serious problem in reactor operation. In the AD process, foaming is referred to as a complex three-phase phenomenon caused by surface-active materials or surfactants present in the substrate as solid or insoluble form. Fatty acids, detergents, soluble proteins and surfactants are responsible for foaming in an AD process. Surfactants can also be present in the digester liquid or in biogas produced in anaerobic bioreactor. For example, industrial wastewater from breweries and dairies are rich in detergents that enter the digester and cause foaming. Foaming creates an operational problem because it creates dispersion of produced biogas in the liquid phase instead of releasing the biogas in the gaseous phase. Finally, an expansion in the digestate volume is observed that reduces the effective digester volume. Effluent spill due to blockage in gas outlet pipe, digester overpressure, damaging digester roof and metabolic shift in the microbial community are some problems associated with foaming (Kougias et al. 2014). Improper operations such as VFA accumulation or adding reagents rich in surfactant content for biogas production can explain the occurrence of foaming in the AD reactor. It can be avoided by adding anti-foaming agents, and also pre-treating the substrate and inoculum to get rid of the surfactant materials.

As wastewater from different sources have a wide range of composition, conventional anaerobic processes suffer from operational issues like process inhibition, abnormal reactor pH and unexpected growth of filamentous bacteria at different operating conditions. Industrial wastewater rich in organic nitrogen and sulphur can cause ammonia and sulphide inhibition, whereas wastewater rich in carbon content or having high temperature can cause inhibition caused by VFA accumulation. The possible technical solutions to eliminate these problems require complex bioreactor assembly with a combination of biological, mechanical and chemical treatment processes.

Along with the issues present in process operations, a few maintenance issues are responsible for limiting the application of anaerobic bioreactors. Some common maintenance issues are as follows: fouling control for membrane bioreactor, cost involved in pre-treating substrates and maintaining process integrity for electrical equipment. In the last few years, membrane technology has gone through a significant level of development in fouling control and cost reduction in membrane fabrication. Membrane bioreactors treating wastewater contain polysaccharides, EPS and organic colloids that are the major contributors to membrane fouling. Additionally, carboxylic acids, proteins and amino acids and dissolved organic carbon can also contribute to membrane fouling significantly. Membrane bioreactors operating at high organic loading rate or shorter hydraulic retention time can have a concentration of these foulants high enough to cause fouling on the membrane surface. Additionally, different types of trace nutrients and dissolved divalent and trivalent ions present in wastewater (Ca^{+2}, Mg^{+2} and Fe^{+3}) can trigger inorganic fouling in the membrane bioreactor (Guo et al. 2012).

Conventional submerged membrane bioreactors operating at Mixed Liquor Suspended Solids (MLSS) higher than 12 g/L have been documented as suffering from severe membrane fouling. For conventional systems, membrane fouling increases the transmembrane pressure followed by a reduction in the permeate flux. Therefore, maintaining a constant flux for the reactor effluent can be a technical challenge due to membrane fouling in anaerobic bioreactors. Recently developed multistage anaerobic bioreactors with mechanical and chemical fouling control processes have reduced the risk of membrane fouling significantly (Guo et al. 2012).

There are several pre-treatment methods for different types of substrates and maintaining different operating conditions can be a technical and economic challenge. The pumps and rotary equipment used for biogas surging, pre-treating substrates, membrane cleaning and product separation have to go through periodic maintenance programmes, which can be an issue when bioreactors are operating in continuous mode. For long-term sustainable operation, maintenance of process equipment used in bioreactors can be a major challenge.

13.2 Improvements of Conventional AD Systems

The major improvements over the conventional anaerobic processes include the addition of pre- and post-treatment processes for efficient pollutant removal and improved energy recovery. Pre-treatment processes that are mechanical, thermal, chemical and biological in character can improve the availability of substrate to the microbes and eventually accelerate the reaction kinetics and pollutant removal through the anaerobic process. The type of pre-treatment processes depends on bioreactor design, type of substrate and product spectrum. Pre-treatment processes along with the main anaerobic process can improve the initial decomposition of the organics as well as selectively inhibiting any particular microbial action(s). Some common mechanical pre-treatment processes include cutting, grinding, mixing, etc. Thermal pre-treatment usually involves processes like explosion of steam to accelerate the initial hydrolysis process. The hydrolysis process can also be assisted by using chemical pre-treatments like acid, alkali and oxidizing agents which are examples of chemical pre-treatment. The biological pre-treatment involves using different types of fungi for producing methane-containing biogas.

13.2.1 Pre-treatment Processes and Additives for Methane Production

Production of methane from anaerobic digestion has achieved considerable improvements through a number of pre-treatment processes and different types of additives. Thermal pre-treatment processes generally have a high temperature that increases the solubility of organic contents in a bioreactor. This method can also accelerate the initial hydrolysis stage of anaerobic digestion. Mechanical pre-treatment like chopping and grinding are effective especially for lignocellulosic biomass and this eventually helps to make the organic content soluble. However, it should be noted that—for methane-containing biogas production—thermal pre-treatment produces phenolic and heterocyclic compounds might to some extent inhibit biogas production.

Ultrasonic pre-treatment is another way of treating organic substrate to improve the biogas yield. When ultrasonic waves propagate through the organic substrate, microbubbles are formed. These bubbles' diameters do reach an unstable shape and eventually collapse. This successive cycle of growth and collapse of microbubbles is termed cavitation, a process that creates high pressure and local heating. The turbulence caused by this phenomenon causes a shear stress in the liquid phase. Both the high temperature and pressure accelerate the reaction rate and help to degrade the organic content present in the substrate (Harris and McCabe 2015). An investigation by Saifuddin and Fazlili (2009) included ultrasound treatment at 20 kHz and 100 W for 10 and 30 min during the treatment of 2% Palm Oil Mill Effluent (POME) in distilled water. Their results included an increase in SCOD from 11 to 29%, and methane production improved by 19%.

Alkaline pre-treatments (with NaOH or ammonia) are effective for avoiding the low pH inhibitory conditions. During anaerobic digestion, a high hydrolysis rate produces long- and short-chain fatty acids that may accumulate inside the reactor. As mentioned already, the final stage of methanation involves consumption of VFA by the methanogens. Since this process is slower compared to the initial hydrolysis, the produced VFA can reduce the pH of the reactor sharply. It has been reported that a pH of less than 6.5 can significantly inhibit the growth of methanogenic archaea (Mao et al. 2015). It is evident that alkaline pre-treatment can be effective for pH maintenance in a neutral zone and benefit the production of methane.

Adding nanoparticles like Co, Ni and Fe in small amounts can significantly improve the production of methane. 1 mg/L Co, 2 mg/L Ni, 20 mg/L Fe and 20 mg/L Fe_3O_4 have been reported to increase the biogas production up to 1.7-fold

(Abdelsalam et al. 2016). This may be explained by the fact that the enzymatic activities are stimulated by the addition of these nanoparticles. For biological pre-treatment, the number of options is narrow compared to mechanical and thermal treatment methods. For example, it has been reported that a ratio of 1:2:1 with carbohydrase: protease: lipase can accelerate the enzymatic solubilization of food waste and produce 350 mL-CH_4/g-soluble COD (Moon et al. 2015).

Pre-treating substrates for biogas production can be considered effective through mechanical, thermal, chemical and biological treatment. However, the full potential of biological and chemical pre-treatment for methane production is still undiscovered. Table 13.3 lists some common pre-treatment methods and additives for the enhancement of biogas production.

13.2.2 Pre-treatment Processes and Additives for VFA and Hydrogen Production

The production of VFA and biohydrogen requires selective inhibition of the methanogenesis process that consumes VFA and biohydrogen produced in the intermediate stage of anaerobic digestion. Unlike methane, very few pre-treatment methods have been developed to improve the production of VFA and biohydrogen.

For VFA, heat and load shock treatment are applied to inhibit methanogenic activity. Heat shock improves the initial rate of hydrolysis, and load shock selectively inhibits the methanogenic activity (Khan et al. 2016). Acid and alkaline pre-treatments are also effective for increasing the production of VFA because methanogens cannot survive outside the 6.5–8.2 range (Mao et al. 2015). Although pre-treatment processes have been clearly evident for VFA production, the separating and purification technology can still be improved. In this regard, adding surfactants/enzymes can be useful for separating the produced VFA from reactor effluent. Mechanical treatment like hydraulic flush has proven to increase the production of VFA. Experiments have confirmed that the degradation of VS actually increased with VFA production (15 and 32%, respectively) when hydraulic flush was applied in buffered leach bed reactors (Cysneiros et al. 2012).

Very few pre-treatment methods have been applied for biohydrogen production along with the application of some chemical additives. Like VFA, biohydrogen is consumed by methanogens during the final stage of anaerobic digestion. Two groups of methanogenic archaea convert VFA and biohydrogen into methane and carbon dioxide. Hydrogen is consumed as an electron donor for the reduction of carbon dioxide by the hydrogenotrophic group (Khan 2017). Therefore, selective inhibition of the hydrogenotrophic group is required for biohydrogen production. Although it is generally expected to apply thermal pre-treatment for biohydrogen production, only a few studies have actually applied the pre-treatment for technical reasons.

Biohydrogen production can suffer a number of inhibitory conditions concerning the treatment process. The intermediate products from pre-treatment can shift or inhibit the microbial activity for biohydrogen production. Consumers of

Table 13.4 Useful pre-treatment processes for VFA and biohydrogen production in anaerobic digestion

Product	Substrate	Pre-treatment (type)	Pre-treatment (process)	Product yield/effects after pre-treatment	References
VFA	Municipal wastewater	Chemical	Sodium dodecylbenzenesulfonate (SDBS) at 0.02 g/g TSS	174 (mg COD/g VSS)	Ji et al. (2010)
	Synthetic wastewater		Sodium dodecyl sulphate (SDS) at 0.1 g/g dry sludge	1143 mg COD/L	Jiang et al. (2007)
	Waste activated sludge (Kadier et al. 2016)		α-Amylase + neuter protease at 0.06 g/g dry sludge	1281 mg COD/L	Luo et al. (2011)
			SDS + α-amylase + neuter protease at SDS = 0.1 g/g dry sludge Enzyme = 0.06 g/g dry sludge	1457 mg COD/L	
	Food waste extract	Mechanical	Oxygen assisted in pre-hydrolysis process to suppress methanogenic activity	97% increase in hydrogen production and 10% increase in VFA production	Sarkar and Venkata Mohan (2017)
	OFMSW	Thermochemical	180 °C, 5 bar, 3 g NaOH/L, inert atmosphere (N_2), 30 min	sCOD increased by 36.7 times	Lee et al. (2014)
		Combined	Hydrogen peroxide (0.66 g/g TS); Microwave = Microwave (2450 MHz), 41 min, heating from room temp. to 85 °C	sCOD increased by 1.67 times	
Biohydrogen	Cassava stillage	Thermal	Heat pre-treatment at 90 °C for 1 h	14 ml H2/gVS (Mesophilic) 69.6 ml H2/gVS (Thermophilic)	Luo et al. (2010)
	Organic fraction of municipal solid waste (OFMSW	Chemical	2.8% Tween 80® (T80) and 1.7 g/L polyethylene glycol (PEG 6000®)	hydrogen yield 116.7 ± 5.2 ml_{H2}/g $Carb._{initial}$	Elsamadony et al. (2015)
	Mixed culture with glucose	Chemical	10.9 mg $FeSO_4$/l	H_2 production 41.6 l/day (1.59 time higher than normal)	(Lee et al. 2009)

(continued)

Table 13.4 (continued)

Product	Substrate	Pre-treatment (type)	Pre-treatment (process)	Product yield/effects after pre-treatment	References
	Brewery wastewater	Thermal + mechanical	magnetic agitation and heat treatment 100 °C per 10 min	Highest H_2 production 1.3 mol H_2 mol^{-1} of carbohydrate	Pachiega (2018)
	Olive mill wastewater	Mechanical	Sonication (1.8 kW, 30 min)	81 ml g^{-1} VS with 50% increase in the yield from non-treated	Rafieenia et al. (2018)
	Cassava wastewater		Ultrasound (50 kHz, 45 min)	200.8 ml g − 1 COD With 149% increase in yield from non-treated substrates	
	Olive mill wastewater	Chemical	Basic pre-treatment by adding calcium carbonate (5 g/L)	Biohydrogen production increased to 1.98 NL/L	Battista et al. (2016)

biohydrogen such as methanogens, propionate producers and bacteria that reduce sulphate and nitrate can curtail the production of biohydrogen. If the pre-treatment process increases the concentration of ammonia and hydrogen, both of them can be a potential threat for the microbes producing hydrogen. Some heat treatment processes accelerate the production of furan, phenol derivatives like furfural, phenol, vanillin as well as alcohol and VFA components like ethanol, acetate, butyrate, propionate, formate, etc.

It has been proven that both groups of by-products inhibit biohydrogen production. Finally, some water treatment facilities concentrate on the wastewater, which in turn increases the concentration of heavy metals like Fe^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cr^{+3}, Cd^{+2} and Pb^{+2}. Concentrations of these metals' ions at or above inhibitory levels can affect the production of biohydrogen significantly (Khan 2017). Regarding different pre-treatment processes, the following methods have indicated improvements in VFA and biohydrogen production. Table 13.4 lists some of those processes.

13.3 Non-conventional Anaerobic Bioreactors

For anaerobic wastewater treatment, bioreactors with different designs and layouts have been employed and improved the removal efficiency of the bioreactor as well as resource recovery from the process. The following section discusses some common bioreactor designs and performance improvements achieved from non-conventional anaerobic bioreactors treating different types of wastewater.

13.3.1 Designs and Layouts

Non-conventional bioreactors have a wide variety of designs and layouts. Multistage anaerobic process, integrated mechanical and chemical separation of pollutants, different packing in fluidized bed reactors, are some common non-conventional designs used in water treatment processes. Some novel bioreactor configurations contain provisions for separate gravity setting, a biohydrogen fermenter and post-treatment facilities for product separation and purification. In other words, multistage bioreactors have been designed to maximize the rate of hydrolysis without compromising the amount of the biogas produced. For example, Bakonyi et al. (2014) used a separate hydrogen fermenter along with a traditional anaerobic digester to improve hydrogen production.

Membrane Technology (MT) can be integrated with different types of anaerobic reactors such as Upflow Anaerobic Sludge Blanket reactors (UASB), Continuous Stirred-Tank Reactor (CSTR), Expanded Granular Sludge Bed (EGSB) and different types of anaerobic biofilm reactors. Membrane technology has been proven useful in removing a range of emerging pollutants including micro-pollutants,

Table 13.5 Designs and layouts of non-conventional anaerobic bioreactors

Design and layout	Operation conditions	Product	References
Two-stage anaerobic submerged membrane bioreactor (CSTR + MT)	Mesophilic condition gas spurging $SGD_m = 1.22$ N $m^3/m^2/h$	Methane yield—0.23 L CH_4/g $COD_{removed}$ Highest VFA—100 mg COD/L	Martinez-Sosa et al. (2011)
Two-stage anaerobic bioreactor with primary settler (UASB + MT)	Temperature—18 ± 2 °C HRT—1 to 3 h (Settler) HRT—11 to 17 h (UASB) Superficial velocity—0.15 to 0.45 m/h Gas sparging $SGD_m = 0.81–1.22$ N $m^3/m^2/h$	Specific methane yield 0.23 Nm^3 CH_4/kg $COD_{removed}$	Gouveia et al. (2015)
Two-stage anaerobic fluidized membrane bioreactor with GAC (AFBR +AFMBR)	Temperature—9 to 30 °C HRT—4.6 to 6.8 h Particle spurging upflow velocity = 75 m/h	Biosolids production averaged at 0.051 g VSS/g COD_R	Shin et al. (2014)
Two-stage anaerobic membrane bioreactor with rotating hollow fibre membrane (CSTR + MT)	Temperature—18.9 ± 3.3 °C HRT—33 h SRT—270 d membrane rotation speed—100 rpm	Specific methane yield—0.012 ± 0.003 L CH4/g MLVSS d with 62.6 ± 1.07% methane in biogas	Ruigómez et al. (2016)
Upflow anaerobic biofilm reactor with polypropylene packing (UFAF)	Temperature—32 to 34 °C pH—6.8 to 7.2 HRT—0.83 to 12.5 d OLR—0.5 to 6.5 kg COD m^3 d^{-1}	CH_4 yield 0.32–0.34 m^3 CH_4 kg^{-1} COD	Ince (1998)
Upflow anaerobic biofilm reactor with PVC ring packing	Temperature—35 °C HRT—2 d OLR—1.44 to 6.29 kg COD m^3 d^{-1}	CH_4 yield 0.32–0.39 m^3 CH_4 kg^{-1} COD COD removal %—98.8	Alves et al. (1998)
Upflow anaerobic biofilm reactor with self-immobilized granules	Temperature—37 °C HRT—0.75 to 5 d OLR—2.22 to 31 kg COD m^3 d^{-1}	CH_4 yield 0.27 m^3 CH_4 kg^{-1} COD	Kundu et al. (2013)
Anaerobic moving bed biofilm reactor (ASBBR) with polyethylene	Temperature—35 °C pH—7.0 HRT—2 to 27.6 d OLR—2 to 28 kg COD m^3 d^{-1}	CH_4 yield 0.341 m^3 CH_4 kg^{-1} COD	Wang et al. (2009)
Hybrid anaerobic digesters with polyethylene packing	Temperature—35, 55 °C HRT—0.5,1 d OLR—1, 2 kg COD m^3 d^{-1}	CH_4 yield 0.03—0.24 m^3 CH_4 kg^{-1} COD	Zielińska et al. (2013)
Hybrid upflow anaerobic sludge blanket reactor (HUASB) with plastic cut rings	pH—6.9 to 7.6 HRT—0.25 d OLR—8 to 20 kg COD m^3 d^{-1}	CH_4 yield 0.25—0.31 m^3 CH_4 kg^{-1} COD	Rajesh Banu et al. (2008)

(continued)

Table 13.5 (continued)

Design and layout	Operation conditions	Product	References
Anaerobic membrane bioreactors with activated carbon (PAC + MBR)	Temperature—35 °C HRT—6 to 24 h SRT—213 days	CH_4 production rate 1.8 ± 0.3 L/d	Xiao et al. (2017)
Upflow anaerobic digester with activated carbon (UAD + PAC/GAC)	Temperature—35 ± 2 °C HRT—5.6 d OLR 2.9 to 12 g COD/L/d	Average methane content in biogas improved to—70.4 ± 4.4%	Xu et al. (2015)
Two-stage anaerobic sequencing batch reactors (ASBR) with magnetic stirring	Temperature—37 °C pH—5.5 COD loading rate—33.75, 50.63, 67.50, 84.38 kg/m^3d	Highest hydrogen content and production rate—33.4% and 1.33 l/d, respectively Highest CH_4 production rate—672.84 ml CH_4/l d	Tangkathitipong et al. (2017)
Forward osmosis MBR with microbial electrolysis cell (AnOMEBR)	Temperature—35 ± 1 °C pH—5.5 COD loading rate—33.75, 50.63, 67.50, 84.38 kg/m^3d	Methane yield 0.281 L/g COD (11.07% higher than conventional FOMBR) 0.537 kJ/d positive energy gain	Zhang et al. (2017)

pharmaceutical compounds, organics and nutrients (Huang and Lee 2015; Krzeminski et al. 2017). Over the past few decades, membrane bioreactors have undergone significant advances in development including fouling control, reduction in energy requirement, cost in membrane fabrication and above all novel configurations. One of the most recent research approaches is the utilization of powdered activated carbon with membrane bioreactors, which has enabled the removal of micro-pollutants and improved the efficiency in removing COD and TOC from the conventional system. This may be due to the fact that organics that cannot be degraded biologically can actually be removed through the adsorption by the powdered activated carbon.

The designs and layouts of novel anaerobic bioreactors for wastewater treatment are diverse and influenced by the type of pollutant removal that the process requires. Table 13.5 summarizes some common designs and layouts of non-conventional anaerobic bioreactors specifically earmarked for wastewater treatment.

Another major type of non-conventional design is integrating Bio-electrochemical Systems (BES) with conventional anaerobic bioreactors. Bio-electrochemical Systems (BES) involve different configurations that can convert chemical energy present in organic matter to electricity or other value-added products. BES systems are beneficial for wastewater treatment in three different ways: (i) they provide an opportunity to treat organic substrates at lower chemical oxygen demand and higher concentration of VFA; (ii) the operation is technically feasible for operating at temperatures below (20 °C); and (iii) they reduce the cost of wastewater treatment since less sludge is produced compared to conventional activated sludge process. Two major variants of BES systems are Microbial Fuel

Cell (MFC) and Microbial Electrolysis Cell (MEC) for recovery of renewable energy from the anaerobic process (Jadhav et al. 2017).

One novel approach for wastewater treatment is to integrate the MFC with anaerobic bioreactors to produce electricity. MEC on the other hand uses a fixed voltage from an external power source to produce biohydrogen and methane. Integrating both MFC and MEC with traditional anaerobic bioreactor has improved biohydrogen and methane production, as well as utilization of organic substrates to a greater extent. MFCs have a potential advantage to recovering by-products like heavy metals and redox chemicals, in which they can be particularly crucial for complex wastewater systems. MEC has both technical and economic advantages in anaerobic process. First, it improves product yield and reduces the cost involved in downstream processing of different AD products. Second, the energy requirement is low (0.6–1 kWh/m^3H_2) compared to the requirement of a conventional electrolysis (4.5–50.6 kWh/m^3 H_2) process. Biohydrogen production from MEC has an overall yield of 8.55 mol H_2/mol-glucose at 0.6 V compared to 4 mol H_2/mol-glucose from dark fermentation (Khan 2017). Since the AD process has a technical limitation in removing phosphates, treating wastewater rich in phosphates (such as swine wastewater, dairy farm wastewater, etc.) can be a problem for anaerobic reactors. Using BES systems can improve phosphate removal efficiency by up to 82% along with the precipitation of struvite ($NH_4MgPO_4 \cdot 6H_2O$) on the cathode's surface. Orthophosphate recovered through this process can be a potential source of fertilizer. Technical feasibility has been proven to recover orthophosphate (600 mg/l) along with the generation of electricity in MFC. Therefore, simultaneous recovery of nitrogen and phosphorus from the anaerobic process can be efficient through the integration of BES (Jadhav et al. 2017).

For example, a single-chamber Microbial Electrolysis Cell (MEC) can be integrated with an Anaerobic Baffled Reactor (ABR) for the production of biohydrogen. MEC in this case uses the effluent from ABR to produce biohydrogen. The MEC–ABR hybrid system achieves 99.0 ± 0.3% COD removal, 1.31 ± 0.04 m^3H_2/m^3d and 2.78 ± 0.11 mL H_2/mg COD hydrogen production rate and yield. Most importantly, the electrical energy recovery is an impressive 138.63 ± 3.11% (Wu et al. 2013). An MEC–AD hybrid system can also be useful for inhibiting the final group of microbes (methanogens) that consume hydrogen and produce methane. A drop in pH from 7.0 to 5.8 in MEC can be an effective strategy to inhibit the growth of methanogens (Kadier et al. 2018). For energy efficiency, an MEC–MFC package can be useful for potential energy recovery as MFC can act as a source of power for MEC. However, the full potential of an integrated BES-anaerobic system is yet to be discovered. Despite the fact that many anaerobic processes have incorporated the BES system, very few studies compared the economic feasibility of a conventional system with a hybrid BES-anaerobic process in wastewater treatment. Till now, BES–AD hybrid systems have been mainly employed to produce biohydrogen from anaerobic digestion. Table 13.6 lists some MEC–MFC packages designed to treat the effluent from upstream processes that offer high energy recovery, effluent removal and improved yield of anaerobic digestion products.

Table 13.6 BES–AD hybrid process

Feedstock	Process design	Operating conditions	Results	References
Synthetic wastewater (Sucrose, NH_4Cl and Na_2HPO_4)	Two-chambered cubic MEC (carbon felt electrodes separated by proton exchange membrane) in the anaerobic process	HRT—3 days Temperature—35 °C Voltage—0.8 V	• Highest COD removal 80.6% at 1.0 V • Highest methane yield 62.8 mL (at 0.8 V)	Ding et al. (2016)
Synthetic wastewater (Sucrose, NH_4Cl and KH_2PO_4)	MEC (felt electrodes, 60 mm × 60 mm)—upflow anaerobic blanket reactor (UASB)	HRT—24 h Temperature—35 ± 1 °C Voltage—1.23 V 30 g $Fe(OH)_3$ (in 280 × 100 × 100 mm UASB)	• Highest CH_4 yield—1.99 ± 0.12 L/d • Highest COD removal 90.7%	Zhang et al. (2013)
Pre-treated food waste extract	MEC (graphite anode and stainless steel cathode, 10 Ω external resistance)—anaerobic digester	Temperature—35 °C Voltage—0.9 V	• Highest Biogas Yield (17.9 m^3/m^3) with 95.8% methane and hydrogen content • 12% more COD removal compared to AD-only • Overall efficiency of AD–MEC exceeded 400%	Hassanein et al. (2017)
A combination of beef extract (0.1 g/L), yeast extract (0.1 g/L), tryptone (0.05 g/L)	MEC (Carbon felt 0.04 m^2 anode connected to titanium wire, 10 Ω external resistance)—AnMBR	Temperature—30 °C Voltage—0.6 V Influent COD—7500 mg/L	• Membrane fouling extended from 60 to 98 h • COD removal increased from 49.4% (conventional AnMBR) to 70.6%	Ding et al. (2018)
Winery wastewater	Pilot-scale continuous flow MEC, with 144 electrode pairs	HRT—1 day Temperature—31 ± 1 °C pH—6.4 ± 0.3 Voltage—0.9 V Conductivity—1.8 ± 0.5 mS/cm	• Maximum current density 7.4 A/m^3 • H_2 recovery 0.07 ± 0.04 L/L/day • Highest biogas production 0.19 ± 0.04 L/L/day with 86 ± 6% CH_4	Cusick et al. (2011)
Cellulose	Two MFCs (each 25 mL) connected in a series to an MEC (72 mL) + dark fermentation reactor	HRT—32 h Temperature—60 °C pH—7.0 (in MEC–MFC) 6.0 (in batch fermenter)	• Highest hydrogen production rate (MEC) of 0.48 m^3 $H_2/m^3/d$ volume) • Highest hydrogen yield of 33.2 mmol H_2/g COD removed	Wang et al. (2011)

(continued)

Table 13.6 (continued)

Feedstock	Process design	Operating conditions	Results	References
Synthetic wastewater	BioH_2-single-chamber MFC Hydrogen-producing bio-fermenter	Temperature—30 °C pH—5.5 M	• Fermentation: 2.85 mol H_2 mol^{-1} glucose • MFC: Maximum energy recovery 559 J/L, COD removal 97%	Sharma and Li (2010)
Vegetable wastewater	MFC—Acidogenic sequencing batch biofilm reactor	Temperature—28 ± 2 °C MFC: (29 ± 2 °C) pH—6.0	• Maximum power density 111.76 mW/m^2 • VFA consumption by MFC: 80% • Hydrogen production rate 2.46 mmol H_2 $h - 1$	Mohanakrishna et al. (2010)
Molasses wastewater	MEC—Ethanol-type batch fed dark fermentation	Temperature—25 °C pH—6.7–7.0 Voltage—0.5–0.8 V	• Hydrogen production rate 1.41 ± 0.08 m^3 H_2 m^{-3} reactor/d at 0.6 V	Lu et al. (2009)
Synthetic media with acetate (100 mM of phosphate buffer)	MEC–MFC coupled system; MEC: two-chamber (450 mL each) MFC: single chamber (350 mL). MFC provides external power for MEC	Temperature—30 °C pH—7.0	• H_2 production rate 14.9 ± 0.4 mL L^{-1} d^{-1} • Maximum H_2 yield 1.60 ± 0.08 mol-H_2 $(mol\text{-}acetate)^{-1}$	Sun et al. (2008)

13.3.2 Performance of Non-conventional Anaerobic Systems

The performance of non-conventional anaerobic bioreactors can be categorized into three major types: (i) improved pollutant removal efficiency, (ii) increased product yield and (iii) reduced energy consumption/ease of operation. Of these three, the removal of soluble organics and nutrients, micro-pollutants, antibiotics and other emerging pollutants has significantly improved due to the integration of membrane technology with the conventional anaerobic digestion process. Specifically, resource recovery and reduction in energy consumption are the primary areas on which research activities have concentrated. Hence, the discussion in this section focuses on improvement of resource recovery and reduction in energy consumption.

For improving the biogas yield different technologies have been applied in anaerobic digestion. One particular approach is to improve the methane content in the produced biogas and another approach can be improving the overall biogas production rate and yield from a specific anaerobic process. Usually, raw biogas contains about 40–45% methane and an additional CO_2 content of 25–55%.

Pressurized anaerobic bioreactors have proven to be useful in enhancing methane content in anaerobic biogas production. A laboratory-scale Auto-generative High-Pressure Digestion (AHPD) (7.5–90.0 bar) experiment with sodium acetate trihydrate increased the methane content in biogas up to 96% in a single-stage reactor system (Lindeboom et al. 2011). Water scrubbing can be applied with two-stage pressurized anaerobic digestion of grass and maize silage hydrolysate in anaerobic acidification reactors. For this operation, a high pressure of 9 bar improved the methane content in the biogas by as much as 87% (Lemmer et al. 2015). A more recent experiment conducted by Merkle et al. (2017) documented an increase of 66–76% methane content when pressure was gradually increased from 1 to 9 bar in a two-phase pressurized UASB reactor.

Another relatively new concept to improve methane content is the aerated methanation reactor where a desorption column of Air/CO_2/N_2 gas stripper is connected to the anaerobic reactor. The desorption column or gas stripper can reduce the amount of dissolved methane in the reactor effluent and improve the methane content in the biogas. However, this technology has certain disadvantages, for instance, a large amount of methane is lost and methane enrichment declines due to O_2 present in the air (Sarker et al. 2018). A sludge anaerobic digester connected to a bubbling desorption column has a maximum enrichment of 87% methane content in produced biogas using municipal sewage sludge at air/sludge flow ratio (m^3/m^3): 0.75–16.0 (Lindberg and Rasmuson 2006). About 8% methane loss was observed at the same experiment with low N_2 concentration at the produced biogas. Another study had an anaerobic design containing CO_2 stripper with compressed nitrogen coupled with semi-continuously mixed and fed reactor. The study used sorghum as substrate and reported an increase in methane content from 71 to 98% when pH rose from 6.7 to 8.4 (Richards et al. 1994).

The hydrogenotrophic methanogens consume biohydrogen produced in the intermediate stage of anaerobic digestion and generate methane. Adding hydrogen supports microbial activity due to the hydrogenotrophic archaea producing methane which contains biogas. Anaerobic digester enriched with hydrogen can improve methane content in the produced biogas. External addition of hydrogen in anaerobic digesters operating in mesophilic and thermophilic conditions can improve the methane content to 89% and 85%, respectively, utilizing cattle manure as substrate (Bassani et al. 2015). Exogenous H_2 addition to anaerobic batch reactors processing maize leaf can improve the methane content to 89%. However, adding H_2 also triggers competition between hydrogenotrophic methanogens (consume hydrogen) and acetotrophic methanogens (consume acetic acid). A microbial shift from the acetotrophic to the hydrogenotrophic group can lead to the phenomenon of VFA accumulating in the anaerobic reactor. A reduction in reactor pH due to VFA accumulation can eventually suppress the production of methane-containing biogas.

Electro-methanogenesis is a process that utilizes Microbial Electrolysis Cells (MECs) where the organic liquid present in the anode transfers the electrons for methanogenesis through decomposition. After decomposition, the donated electrons are consumed to produce hydrogen which results in the production of CO_2 and CH_4. A separate electron transfer process can occur through the electron transfer directly to methanogens. The latter process offers the opportunity to conserve energy compared to the former because the energy required to produce the intermediate H_{2-} is avoided. A recent MEC–AD process using a synthetic medium has resulted in the enrichment of 95% for methane, employing catalysed stainless steel mesh cathode (Sarker et al. 2018).

Production of VFA can improve the performance of anaerobic bioreactors. A full-scale anaerobic process using alkaline fermentation produced VFA from domestic wastewater. The results reported approximately 54% sludge reduction along with an average VFA production of 261.32 mg COD/g VSS. At the same time, the total nitrogen and phosphorus removal efficiencies increased to 73.37 and 89.65%, respectively. Removing VFA from an anaerobic process eliminates the possibility of reactor acidification due to accumulated VFA. In this way, methane production can be improved by maintaining the reactor pH at a neutral range. The findings from this experiment were supported by another study where kitchen wastewater was processed in anaerobic–anoxic–aerobic (A^2/O) at room temperature, i.e. 18–22 °C. The overall VFA yield from this experiment was 63%, and corresponding nitrogen and phosphorus removal efficiencies were 78.2 and 95.2%. The explanation for this improvement was that the presence of propionic and humic acids significantly increased phosphorus uptake and denitrifying phosphorus removal (Zheng et al. 2018).

Biogas spurging is a significantly large energy consumer in the anaerobic digestion process, and it has been effectively employed to control membrane fouling in anaerobic bioreactors. These bioreactors' operation is still very much energy intensive due to the employment of biogas spurging pumps. The MEC-integrated AD system can be a potential solution to this problem. An MEC–AD novel bioreactor can improve COD removal by 12% and furthermore enhance energy efficiency by 400% compared to the conventional anaerobic process (Hassanein et al. 2017). On this topic, some studies have reported an improvement in membrane fouling by increasing the cycle duration from 60 to 98 h (Ding et al. 2018). However, the duration of substrate degradation can be affected by bioaugmentation of the microorganisms in a MEC–AD process.

Improving the performance of non-conventional bioreactors in terms of energy efficiency still requires more research and practical development. Very few economic assessments have been conducted where the revenue earned from anaerobic products with the operating cost of the bioreactor is compared. It has been found that designing a cheap carbon conductive material can improve electron transfer efficiency and eventually improve methane-containing biogas production from anaerobic bioreactors.

13.4 Conclusion and Future Insights

Most of the current research approaches in wastewater treatment involve non-conventional design for anaerobic bioreactor technology for efficient removal of a wide range of pollutants. Addressing the current limitations and technical issues has helped the researchers to work on specific areas that can improve the technical and economic feasibility of the technology for large-scale industrial application. Recent developments in reactor design modification and integration of physical and chemical processes have been proven effective for removing both biodegradable and non-biodegradable pollutants both from different types of wastewater. The following points include some major research initiatives and future insights for anaerobic bioreactor technology in wastewater treatment:

- Most non-conventional systems have been designed so far including the provision of pollutant removal from one specific type of wastewater. Since wastewater from different sources contains a wide range of pollutants with variable concentrations, it is important to design a generic model for a non-conventional anaerobic system which can treat wastewater from different sources.
- For non-conventional anaerobic bioreactors, the production of VFA and biohydrogen from wastewater have already been proven as technically feasible. Economic feasibility has to be assessed for currently established anaerobic systems to encourage the large-scale industrial application.
- Cost associated with carbon capture and storage has not been considered during the assessment of economic feasibility of non-conventional designs. On this issue, what should be considered is biohydrogen being a useful alternative to methane.
- The full potential of BES–AD processes as a major category of non-conventional system is yet to be discovered. The concept of reducing

membrane fouling control using electrochemical systems is still in its early stages and demands more technical and economic assessment.

- Recovering VFA as the main or a co-product with methane can be beneficial in terms of product revenue from multistage non-conventional designs. However, separation and purification technologies for VFA need to be further researched because they are still energy and cost intensive.
- Conventional AD systems are still considered less energy intensive compared to hybrid anaerobic processes using membrane technology. The typical energy requirement for MBR operation ranges from 0.6 to 2.3 KWh (Brepols 2010). As a result, reducing energy consumption can be a potential area of future research for hybrid anaerobic bioreactors using membrane technology.
- Useful pre- and post-treatment processes to aid the production of biogas has improved the performance of conventional anaerobic processes. Findings from these research studies could be utilized to design complex hybrid systems with an improved yield for biogas, VFA or biohydrogen.
- The responses of different microbes and enzymes are still unclear during wastewater treatment process using a non-conventional design with a combination of biological and physical or chemical treatment processes. Pollutants like antibiotics, dissolved metals and pharmaceutical compounds can affect or even inhibit the growth of different anaerobic microbes. A complete understanding of the biological and physicochemical processes is a necessary requirement before treating wastewater from different sources.
- Using the multistage anaerobic process can be a trade-off between high initial cost of installation and an increase in product revenue from multiple products. It is therefore essential to assess this process's economic feasibility to calculate the net profit earned from the anaerobic process.
- It is particularly challenging to improve the energy density of products from non-conventional processes. Treating wastewater with low COD (i.e. domestic or municipal) can be a challenge because the methane, biogas or VFA production rate can be low compared to industrial wastewater that is rich in organic carbon.

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Chapter 14
Advances of Photobioreactors in Wastewater Treatment: Engineering Aspects, Applications and Future Perspectives

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Abstract The photobioreactor is an efficient artificial system in terms of biomass cultivation and removing pollutants. Compared to other conventional technologies, its design and operational processes are superior. Therefore, the photobioreactor specifically targets and tailors for the increasing demand for biomass and stringent pollutants removal standards. Since the early 1950s, there has been a variety of photobioreactor types, and these have been addressing the different technical issues over time and others more recently. As well, diverse applications of the photobioreactor process are becoming more widespread, and this opens for a good opportunity for future sustainable developments. This book chapter discusses advances being made in photobioreactor technology, encompassing: (1) modelling; (2) designs and classifications; (3) applications and (4) future perspectives.

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Keywords Photobioreactors · Algae · Flat plate · Column · Tubular Soft-frame · Green technology

14.1 Introduction

Algae biomass offers numerous benefits, such as feedstock for bioenergy production, biomaterial production, and environmental remediation (Hossain et al. 2015; Bibi et al. 2017; Becker 2007). In recent years, the desire for algae biomass has increased. Nevertheless, the capacity of our natural environment (e.g. ponds, lakes, and oceans) cannot fulfill the required amount of algae biomass. For this reason, man-made algae cultivation systems have been developed to enhance the algae biomass yields required. These are commonly known as open and closed configuration systems (Posten 2012).

Since the 1950s, the closed cultivation system of photobioreactors (PBs) has been explored in the context of environmental remediation. The first documented application was in 1953 for CO_2 sequestration (Torgal et al. 2016). Subsequently, it became recognized as an advanced technology in the wastewater treatment sector and is symbolic of green technology for two critical reasons (Fig. 14.1). First, PBs are robust in configuration and efficient in biomass yield. Artificial environments (e.g. light, temperature, nutrients, and mixing) which support biomass growth can be created. Interestingly, algae growth in PBs is fast, stable and predictable (Singh and Sharma 2012). Second, pollutants are applied as feed for algae cultivation. Consequently, algae in these PBs can consume pollutants accordingly (Kang et al. 2017; Al Ketife et al. 2016). Apart from this, collocation with buildings and its value as a 'green' technology are part of the superior quality of PBs.

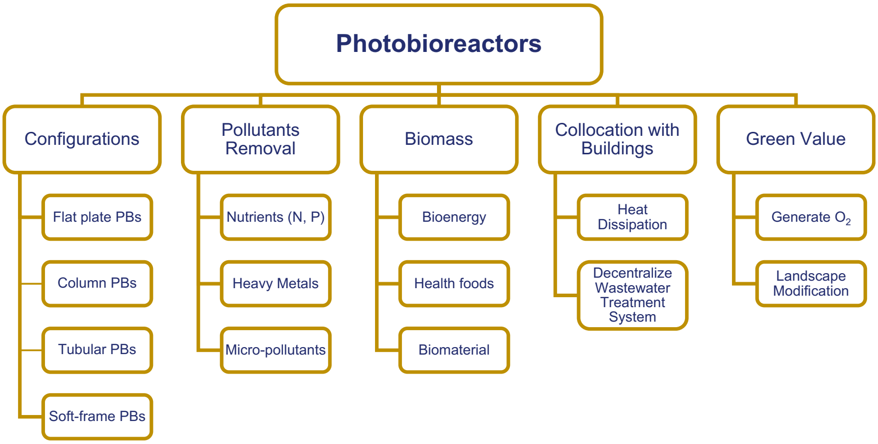

Fig. 14.1 Advanced benefits of PBs technology

Currently, there are many kinds of configured PBs, materials and operation modes. Each type possesses its own advantages and disadvantages, in terms of energy consumption, biomass yield, efficiency in removing pollutants, and upscaling (Yadala and Cremaschi 2014; López et al. 2006; Mirón et al. 1999). The PBs are renovated or upgraded so that efficiencies can be improved or progressed. These renovations have been undertaken as experimental works, coupled with the validation of models and achieved good outcomes. The modelling is conducted using different theories and principles generating specific features so that each single model differs in some way, as well as between models and experimental results. Furthermore, the upscaling and future development of PBs utilizing a more sustainable approach has attracted some concern. Nonetheless, these engineering explorations are what make these PBs an attractive and advanced method of wastewater treatment.

Hence, this chapter focuses on advances in aspects of PB engineering, the emerging applications, and possibilities for the future. Specifically, the modelling applied for estimation purposes of PBs' biomass yield is reported (Sect. 2). The classifications and designs of common types of PBs are described and comparisons made accordingly (Sect. 3). Finally, the applications of PBs in environmental remediation and building collocation are given (Sect. 4), and future perspectives in relation to green technology are discussed (Sect. 5).

14.2 Modelling of Photobioreactors' Engineered Elements

According to literature, modelling in PBs has reached a number of operational parameters. These include the photosynthesis rate, illumination, biomass yield, temperature, hydrodynamic pattern and other sub-parameters. In this section, the two most important parameters are photosynthesis and biomass yield of microalgae and they are described in more detail below (Fig. 14.2).

14.2.1 Microalgae's Photosynthesis Modelling

Theoretically, the photosynthesis process of algae generation O_2 occurs when the O_2 level serves as the indicator for photosynthesis modelling. In this application, the dynamic model of Rubio et al. (2003) was used to estimate photosynthetic O_2 based on some typical factors, for example, photo-adaptation, photo-inhibition, and the illumination effect.

First, the illumination intensity in PBs can be drawn from Lambert–Beer's Law (Eq. 14.1):

$$I = I_{\mathrm{o}} \times \mathrm{e}^{-k \times X \times d} \tag{14.1}$$

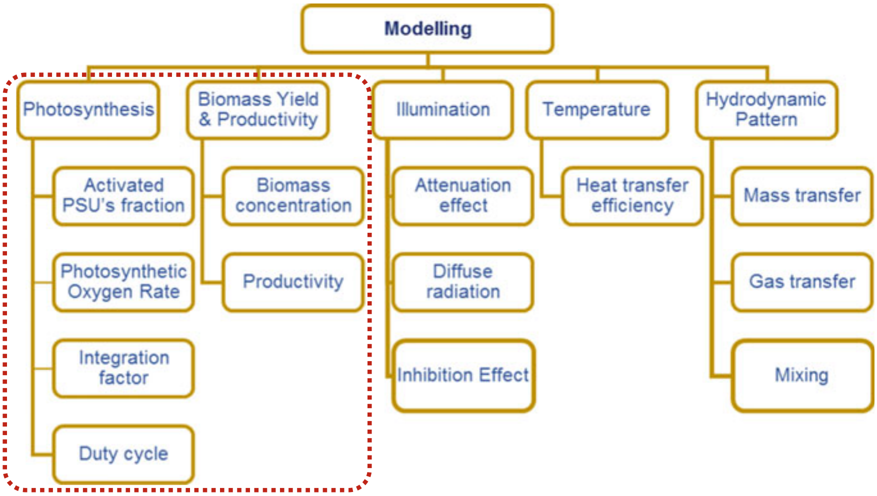

Fig. 14.2 Components of PBs modelling

where

I light intensity at the desired surface (μE/m^2 s)
I_o light intensity at the illuminated surface (μE/m^2 s)
k attenuation constant of the culture at concentration X
d distance from the irradiated surface (m).

Based on the achieved light intensity, the photosynthesis model is a function of the square-wave light regime, represented by I_o, φ and v, as follows:

$$\frac{dX}{dt} = \frac{\beta \times I(T)}{\alpha \times \vartheta} \times \left[(1 - X) - \frac{\alpha}{I}\frac{X}{k + X}\right] \tag{14.2}$$

where

X the fraction of activated photosynthesis unit (PSU) as in Rubio et al. (2003)
T the dimensionless time, $T = \frac{t_c}{t}$
T_c cycle time
α light-saturation constant
β characteristic frequency
κ saturation constant for the rate-controlling enzymatic reactions.

Thus, the photosynthetic oxygen rate (P_{O_2}) is calculated as below:

$$P_{O_2} = (P_{O_2})_{\max} \times \int_0^{\emptyset} (1 - X)\,dT \tag{14.3}$$

where

P_{O_2}	photosynthetic oxygen rate (mg O_2 cell^{-1} s^{-1})
$P_{O_2\,\max}$	maximum photosynthetic oxygen rate (mg O_2 cell^{-1} s^{-1}).

According to García-Camacho et al. (2012), the light saturation, characteristic frequency and saturation constant are calculated as in the following way:

$$\alpha = \frac{r_m}{k_a \times a}$$

$$\beta = \frac{r_m}{a}$$

$$k = \frac{K_s}{a}$$

where

r_m	maximum disappearance rate of activated PSU due to photochemical quenching (PSU cell^{-1} s^{-1})
k_a	kinetic coefficient (m^2 PSU^{-1})
a	total concentration of PSUs (PSUs·cell^{-1})
K_s	constant of Michaelis–Menten model.

In the case where the model parameters ($P_{O_2\,\max}$, α, β and κ) are identified, P_{O_2} is achieved by integrating Eq. 14.3 once a pseudo-stationary $X(\tau)$ cycle is done. The values of X at the beginning and the end of the cycle are similar, therefore making this calculation feasible.

If the required parameters are unknown, then they need to be estimated. The loops of those parameters are conducted utilizing the experimental conditions until the discrepancy of modelling and experiments are acceptable (Brindley et al. 2016). Furthermore, estimating those variables can be done through the photosynthesis–irradiance (P–I) curve, applying continuous light and nonlinear regression model as demonstrated in Eq. 14.4 (Rubio et al. 2003).

$$\frac{P_{O_2}}{P_{O_2\,\max}} = \frac{I}{2\alpha}\left[\left(1 + k + \frac{\alpha}{I}\right) - \sqrt{\left(1 - k - \frac{\alpha}{I}\right)^2 + 4k}\right] \tag{14.4}$$

Since the photosynthetic dynamic is determined, it can be applied to design PBs and operate them properly. A comparison of the modelling work and experimental results confirms an acceptable deviation of 10%. These outcomes are applied to calculate the integration factor (T) (Eq. 14.5), ranging from 0 to 1, and illustrating the response of algae culture and light intensity.

$$T = \frac{P_{\text{model}} \times (I_o) - \Phi \times P_{\text{cont}} \times I_{\text{o}}}{P_{\text{cont}} \times (\Phi \cdot I_o) - \Phi \cdot P_{\text{cont}} \times I_{\text{o}}} \tag{14.5}$$

where

P_{cont} the productivity calculated using Eq. 14.4 for continuous light.
Φ ranges from 0.4 (diluted culture) to 0.05 (concentrated culture).

On the other hand, the duty cycle (φ) which serves to quantify irradiance absorption efficiency can be estimated as Eq. 14.6. The value of duty cycle (φ) must be low enough to satisfy $I_{\text{o}} \times \varphi < \alpha$ to maintain the proper illumination received by algae (Brindley et al. 2016).

$$\varphi = \frac{I_{\text{av}}}{I_{\text{o}}} = \frac{\left(1 - \exp\left(-C_{\text{b}} k_{\text{opt}} L\right)\right)}{C_{\text{a}} k_{\text{opt}}} \tag{14.6}$$

where

C_{b} biomass concentration (g m^{-3}),
L light path of the device (m) (e.g. depth of a raceway or thickness of a flat panel)
k_{opt} the extinction coefficient, given by the Lambert–Beer law (m^2 g^{-1})
C_{a} areal biomass concentration (g m^{-2}).

14.2.2 *Prediction of Microalgae's Biomass Concentration and Productivity*

The estimation of biomass concentration can be done via the mass balance (Eq. 14.7) as written below (Pruvost et al. 2011):

$$\frac{\mathrm{d}X}{\mathrm{d}t} = r(t) + \frac{1}{t}(X_{\text{in}} - X) = r(t) + D(X_{\text{in}} - X) \tag{14.7}$$

where

$r(t)$ mean volumetric production or nutrient consumption rate in the system (mg/L.h)
t residence time (h)
D dilution rate
X_{in} initial biomass concentration (mg/L).

Since the biomass concentration is known, the productivity is calculated as equation below (Yadala and Cremaschi 2014):

$$P = \frac{X}{V} \tag{14.8}$$

where

V volume of the reactor (L).

14.3 Photobioreactors' Classifications and Designs

Generally, PBs are classified based on their configurations, including flat plate, column, tubular, and soft-frame (Fig. 14.3). In addition, the hybrid systems which are combinations of other technologies, such as membrane are recognized. However, it is not discussed in this section due to being hybrid and not original. Concerning the PBs' classification, any differences emerging from configurations offer certain levels of significance in terms of biomass yield, operating conditions, energy and saving of materials. So far, the most important operating parameters indicated were illumination pattern, temperature and mass transfer.

Regarding the illumination pattern, sunlight is the commonly used source, but artificial light, for instance, fluorescent and LED are becoming more widespread for their ability to extend the illumination period. The advised illumination intensity for algae is from 33 to 400 $\mu E/m^2$ s, while the over-illumination results in photo-inhabitation and damaged algae cells accordingly (Singh and Singh 2015). The phenomenon of illumination attenuation is also recorded due to the mutual shading effect on algae cells, distance from the illumination source to algae cells, orientation, climate conditions and obstruction of PB materials (Hu and Sato 2017).

Temperature is another key operating factor determining the PBs' efficacy. The appropriate temperature conditions the reproduction of algae. The optimal temperature range is reported from 15 to 30 °C (Singh and Singh 2015; Pires et al. 2017). Most of the researches have used room temperatures ranging from 20 to 25 °C, while the outdoor temperature varies seasonally and from day to night time. A low temperature curtails the algae biomass yield; therefore, this technology is preferable in tropical conditions and in the temperate zones where temperature and illumination are sufficient. In this regard, PBs can control temperature and illumination efficiently whereas in open systems this is not very successful. In the literature, there are several methods to control temperature such as applying dark sheets for shading, spraying water, submersing PBs in water and heat exchanger application (Ugwu and Aoyagi 2008; Prakash et al. 1997; Wang et al. 2012). Each method is known for its efficiency and ongoing costs.

Hydrodynamic pattern is the main reason PBs operate efficiently as it determines the mass transfer and homogenous environment. Typically, the application of CO_2

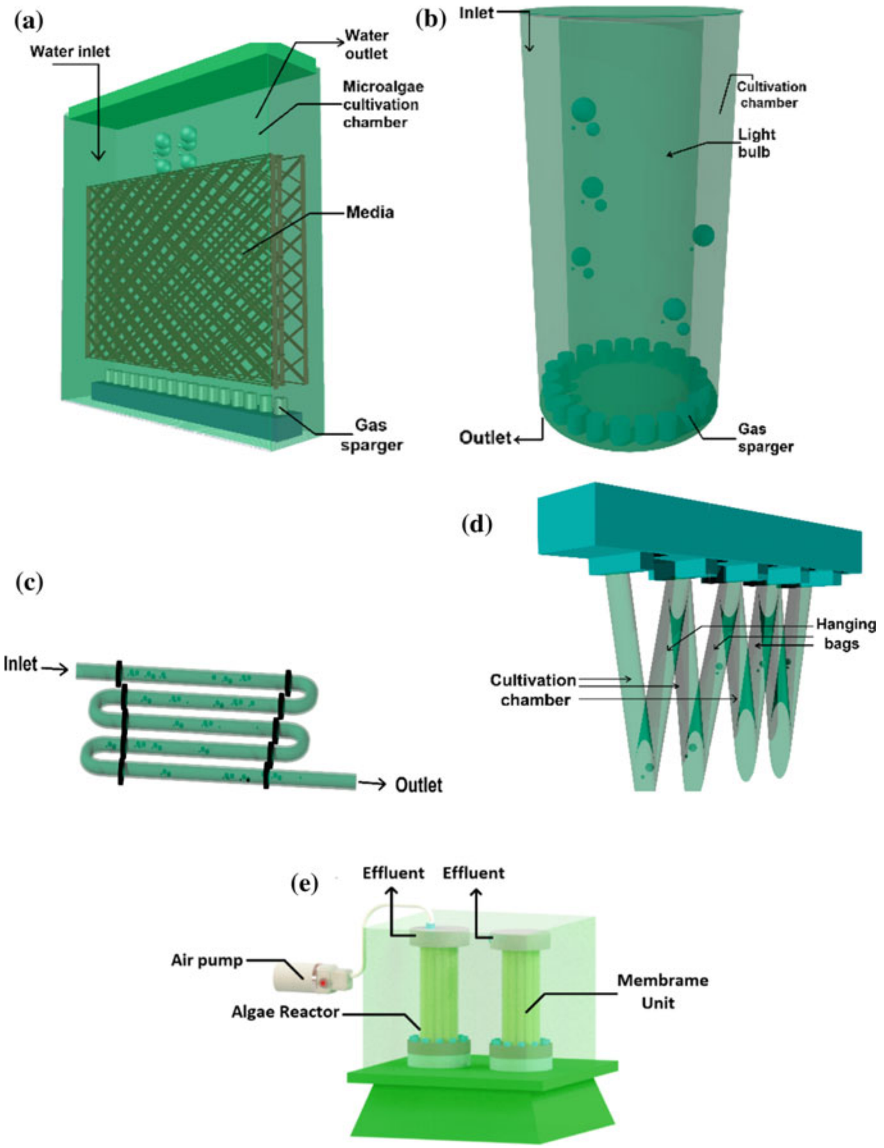

Fig. 14.3 Common types of PBs **a** flat plate, **b** column, **c** tubular, **d** soft-frame and **e** hybrid (Vo Hoang Nhat et al. 2018)

gas for algae cultivation is applied for adequate mixing of the bulk liquid. Furthermore, it ensures the consistency of pH, DO, nutrient supply and illumination received by each algae cell. Over-mixing is observed with damage done to algae cells, and for this reason it is advised that the mixing rate be from 20 to 50 cm/s

(Posten 2009). Regarding the turbulence level, it is preferred that the Reynolds number be higher than 2300 (Shariff and Chakraborty 2017).

14.3.1 Flat Plate Photobioreactors

Flat plate PBs consist of flat surface plates in a transparent reactor. This promotes algae development through the attached growing process. The flat plate PBs possess a considerable illuminated surface:volume ratio (Jung et al. 2014; Sun et al. 2016) which is easily fabricated and adapted to any light paths. Other important features of flat plate PB are its modest mechanical usage and energy consumption, estimated at 50 W/m^3 (Sierra et al. 2008; Guo et al. 2015). Furthermore, the high mass transfer characteristic ($K\mathit{la} = 0.007\ s^{-1}$) is reported since biomass clogging, sedimentation and leakage are eliminated (Huang et al. 2017).

Amongst the factors determining flat plate PBs, temperature and illumination are considered to be the most critical. The proper conditions maximize the biomass yield, and the efficacy in removing pollutants. The effects of temperature and illumination not only depend on the design of PBs and their operation but are also influenced by the local geographical environment.

Illumination

The PBs' orientation affects biomass yield thanks to the more illumination received. In this case, Slegers et al. (2011) proved that the north-south panel orientations generated 50% higher biomass yield than east-west orientation, regardless of algae species and the employed latitudes. This strategy was highly efficient in large-scale PBs plants, comprising a number of flat plate PBs, however, the influence of orientation on single flat plate PB was insignificant, being only 5%. When comparing certain countries' biomass productivity, Algeria was observed to have 25% more than the Netherlands. Furthermore, algae species were in harmony with different light paths, for example *Phaeodactylum Tricornutum* prefers a longer light path, while *Thalassiosira Pseudonana*'s growth substantially corresponded to the short path. Similarly, Sierra et al. (2008) observed a two-fold higher illumination of vertical flat plate PB than the horizontal one in winter time. However, it was 65% less in summer time where both the PBs were north-south oriented. In the east-west orientation, the vertical PB received illumination that was more than 17% in winter time and less than 3% in summer time compared to horizontal PB. Apart from the weather conditions, latitude affected the PBs' working performance, as did the orientation.

Temperature

Temperature is always a critical parameter determining PBs' efficiency. Through temperature, heat is provided for algae growth. Hence, temperature and heat optimization in PBs are conducted via the heat exchangers regulated by the internal fluid circulation, PBs culture and the surrounding environment. According to Sierra et al. (2008), the heat transfer efficiency of the internal fluid circulation was ultimately higher than the efficacy of PBs' culture and surrounding environment, being reported as 505 and 37 W/m^2 K. Regarding internal heat transfer, water fluid and air sparging contributed to some extent. The overall heat transfer calculations referring to Reynolds number (Eq. 14.9) or heat balance (Eq. 14.10) were given as

$$H = 4.32 \ * \ Re^{0.71} \tag{14.9}$$

$$m_{\text{water}} \cdot C_{\text{water}} \cdot (T_{\text{outlet}} - T_{\text{inlet}}) = H \cdot A \cdot \frac{(T_{\text{culture}} - T_{\text{inlet}}) - (T_{\text{culture}} - T_{\text{outlet}})}{\ln\left(\frac{T_{\text{culture}} - T_{\text{inlet}}}{T_{\text{culture}} - T_{\text{outlet}}}\right)} \tag{14.10}$$

where

m_{water}	mass flow rate of the cold fluid (kg/h)
C_{water}	mass heat capacity of the cold fluid (J/kg °C)
$T_{\text{inlet,outlet}}$	temperature of influent and effluent (°C)
T_{culture}	temperature of culture (°C)
A	surface area of heat exchanger (m^2)
H	overall heat exchange efficiency (W/m^2 °C)
Re	Reynold number.

The contribution of internal fluid circulation, air sparging and exchange of PBs culture and environment were 60, 36 and 4%, respectively, to the overall heat transfer in the flat plate PBs.

Orientation and configuration also determine the temperature level. For example, the vertical flat plate PBs received 20% more algae photosynthesis activity compared to the horizontal one (Qiang et al. 1998). This was due to the dispersed radiation obtained by the vertical configuration while the horizontal one received direct radiation. The dispersed radiation was more applicable to algae growth (Acién et al. 1997, 1998).

Scale Up

With reference to scaling up, the following steps are suggested. From Eq. 14.8, the real biomass productivity P_r is calculated considering the volume-to-surface ratio of the flat plate PBs system:

$$P_r = P \times \frac{V}{S_t} \tag{14.11}$$

where

P_r	real biomass productivity (g L^{-1} d^{-1})
V and S_t	volume (m^3) and total surface area (m^2) of flat panels PBs. The V/S ratio is from 40 to 70 L/m^2.

Number of modules:

$$n = \frac{S_{\mathrm{t}}}{S} \tag{14.12}$$

where

S surface area of each flat plate PB (typically H = 1.5 m, L = 2.5 m).

14.3.2 Column Photobioreactors

Column PBs are constructed with a vertical column configuration. For the suspended process, the culture is aerated for mixing and CO_2 is supplied. This type of PB has sufficient gas–liquid mass transfer, biomass yield and light/dark cycle control features (Hu and Sato 2017; Sierra et al. 2008; Pham et al. 2017; Janoska et al. 2017; Jiménez-González et al. 2017). The configuration of column PBs is simple in that they are designed by connecting modules and/or combined with other techniques, especially the membrane process (Chang et al. 2016).

There are two subcategories of column PBs encompassing airlift and bubble column configurations. As such, airlift PBs achieve mixing and mass transfer by injecting air into the compartment, which conditions the hydrodynamic circulation via the downcomer compartment. The mixing in the airlift PBs is completed without any decline in the growth of the algae consortium, thanks to the reduction of shear force to the fluid. In bubble columns, the hydrodynamics and mass transfer are dependent on the size of bubbles and how they are introduced into the fluid from the sparger. In this case, Chiu et al. (2009) reported that algae cultivated in airlift PBs were observed to have a higher specific growth rate (0.226 d^{-1}) compared to bubble columns PBs (0.180 d^{-1}).

Illumination

Apart from outdoor sunlight, an artificial light source such as LED is increasingly applied in PBs. Although LED’s price is still currently expensive, it has been falling steadily. On the other hand, the energy consumption and life expectancy of LED are superior compared to that of a traditional light source. The application of LED light in PBs is limited to only a few studies and laboratory-scale PBs with volumes smaller than 5L (Glemser et al. 2016). Thus, López-Rosales et al. (López-Rosales et al. 2016) employed LED in a pilot-scale bubble column PB (60L). There was a direct correlation between light availability and algae growth. The maximum specific growth rate of algae and daily irradiance were observed to have a linear relationship. Furthermore, the daily mean absorbed volumetric photon flux ($F_{\mathrm{vol}}(t)$) was reported to be absorbed by culture.

$$I_{\mathrm{av}}(t) = \frac{2I_{\mathrm{o}}(t)}{R^2\pi} \int_{o}^{\pi} \mathrm{e}^{-k(t)(r-\cos\Phi+\sqrt{R^2-r^2\sin\Phi}} \, r\mathrm{d}r\mathrm{d}\Phi \tag{14.13}$$

$$F_{\mathrm{vol}}(t) = I_{\mathrm{av}}(t)k(t) \tag{14.14}$$

where

$F_{\mathrm{vol}}(t)$	the photon flux absorbed in the entire culture volume (μE m^{-3} s^{-1}).

The advised illumination irradiance is from 200 to 1500 μE m^{-2} s^{-1}. Consequently, any over-illumination beyond this range may cause photo-inhibition as the light/dark cycle is important in the illumination of PBs. Lengthening the lighting period for up to 24 h can enhance the algae's photosynthesis activity, though this requires excessive energy consumption. Other applications operate those PBs with light/dark cycle of 12:12 or even apply an artificial light source immediately after sunset. During the night, the dark zone in PBs is formed due to the self-shading effect of algae cells. The volume fraction of the dark zone is calculated below as follows:

$$\gamma_{\mathrm{C}} = (r_{\mathrm{C}}/R)^2 \tag{14.15}$$

where

r_{C}	local radial from central line
R	internal radius of the bubble column.

Temperature

The concept of temperature effect and control in column PBs is similar to other types of PBs. Temperature is essential in providing heat for algae growth and therefore, heat balance in bubble column PBs should always be considered in the design and operation process. Given that most PBs are located outdoors, the heat balance must include the effect of sunlight and local weather. Consequently, the heat exchanger is established in the bubble column PBs, and calculated using the formula below:

$$A_{\mathrm{exchanger}} = \frac{Q_{\mathrm{rad}} \times a_{\mathrm{rad}}}{U \times (T_{\mathrm{culture}} - T_{\mathrm{water})}} \tag{14.16}$$

where

$A_{\mathrm{exchanger}}$	area of heat exchanger
Q_{rad}	solar radiation received
A_{rad}	thermal absorptivity
T_{culture} and T_{water}	temperature of culture and cooling water.

Scale Up

The scaling up of column PBs requires a consideration of illumination, bubble size, mass and heat transfer. In practice, the superficial gas velocity is employed from 1 to 2.8 cm/s which enhances bubble passage frequency from 25 to 62%. Furthermore, the bubble chord length and bubble velocity distributions are observed to be wider at higher superficial gas velocities. The bubble chord length varies from 0.164 to 0.221 cm while the bubble rise velocity is recorded from 64 to 107 cm/s (Ojha and Al-Dahhan 2018). However, the microbubble of 500 μm is preferred because it can increase mass transfer and photo-bioreaction (Zhao et al. 2018). The following steps are applied to the scaling up of bubble column PBs:

Fanning Friction factor

$$C_\mathrm{f} = 0.0791 \times Re^{-0.25} \tag{14.17}$$

Liquid velocity

$$U_\mathrm{L} = 2\left[\frac{g \times d_\mathrm{B}}{1.8}\right]^{0.5} \tag{14.18}$$

where

g gravitational acceleration (m/s^2)
d_b bubble diameter (m).

Volume of bubble column

$$V = \frac{Q_\mathrm{L} \times \left([\mathrm{O_2}]_\mathrm{in} - [\mathrm{O_2}]_\mathrm{out}\right)}{K_\mathrm{L} \times a_\mathrm{L}\left([\mathrm{O_2}]_\mathrm{sat} - [\mathrm{O_2}]\right)(1 - \varepsilon)} \tag{14.19}$$

where

Q_L	liquid flow rate entering bubble column (m/s)
$[\mathrm{O_2}]_\mathrm{in}$ and $[\mathrm{O_2}]_\mathrm{out}$	oxygen concentration in the inlet and outlet (mg/L)
$[\mathrm{O_2}]_\mathrm{sat}$ and $[\mathrm{O_2}]$	driving force for the transport of oxygen from liquid to gas phase (mg/L)
$K_\mathrm{L}a_\mathrm{L}$	volumetric mass transfer efficiency
ε	gas holdup.

Minimum diameter of the bubble column

$$D = \sqrt{\frac{4 \times Q_\mathrm{L}}{\pi \times U_\mathrm{b}}} \tag{14.20}$$

where

U_b bubble rise velocity (m/s).

14.3.3 Tubular Photobioreactors

Tubular configuration is another common type of PBs which has been widely mentioned in the literature (Kayahan et al. 2017; Henrard et al. 2011; Gómez-Pérez et al. 2015). The tubular PBs' design is diverse and includes bent, horizontal, vertical and spiral shapes. They are established in forms of arrays/layers being next to each other. A U-shaped connector is employed to combine all the single units while the mixing is conducted by central pumps or airlift systems. In other words, tubular PBs are modified column PBs and function by extending the hydraulic retention time. The design and operation of tubular PBs is more complicated and excessive energy consumption has been reported. Similar to column PBs, light source illumination in tubular PBs can be either sunlight or artificial light. The emerging trend is that laboratory-scale tubular PBs prefer artificial light while the pilot- and full-scale tubular PBs are conducted with sunlight or both. Regarding oxygen concentration, the horizontal tubular PBs are observed as having high DO concentration which is detrimental to algae growth and therefore needs to be removed. The maximum diameter and length of tubular PBs should be 0.1 and 80 m, respectively, to obtain the optimal fluid velocity of 0.3–0.5 m/s (Molina et al. 2000).

Air Mixing and Mass Transfer

Mixing is an indispensable design and operating parameter in tubular PBs. It aims to enhance the gas–liquid mass transfer efficiency and control algae in a proper light/dark cycle. In this case, baffles are installed to stimulate mixing, which also conditions the diffusion of gasses (Ugwu and Aoyagi 2008). It is well-known that energy consumption is a challenge in tubular PBs, and the application of static mixing even uses more energy. Thus, the twisted fluid tubular PBs is considered to be a novel design and one that saves energy. Swirl mixing is an option to reduce flow velocity but the mixing conditions are still efficient. Furthermore, a benefit of augmenting the biomass productivity is observed since the light/dark cycles are improved. The fluid velocity in twisted tubular PBs is 0.35 m/s compared to the traditional PBs of 0.5 m/s and 38% of energy is saved (Gómez-Pérez et al. 2017). In the case of flow velocity, this can reduce to 0.2 m/s and subsequently the energy consumption saved amounts to as much as 77%.

The mass transfer of gasses, O_2 and CO_2 in air and liquid are considered where, first CO_2 is supplied as an inorganic source for algae assimilation, and second O_2 is produced through the photosynthesis process. For achieving equilibrium concentration of these gasses, this can be referred to as the Henry law as documented below:

$$[\mathrm{O_2}]^* = H_{\mathrm{O_2}} \times P_{\mathrm{O_2}} = H_{\mathrm{O_2}} \times (P_{\mathrm{t}} - P_{\mathrm{v}}) \times \frac{F_{\mathrm{O_2}}}{F_{\mathrm{CO_2}} + F_{\mathrm{O_2}}} \tag{14.21}$$

$$[\mathrm{CO_2}]^* = H_{\mathrm{CO_2}} \times P_{\mathrm{CO_2}} = H_{\mathrm{CO_2}} \times (P_{\mathrm{t}} - P_{\mathrm{v}}) \times \frac{F_{\mathrm{CO_2}}}{F_{\mathrm{CO_2}} + F_{\mathrm{O_2}}} \tag{14.22}$$

where

H_{O_2} and H_{CO_2}	Henry constant of oxygen and carbon dioxide
P_{O_2} and P_{CO_2}	partial pressure of oxygen and carbon dioxide in gas phase
P_t	total pressure
P_v	water vapour pressure.

Scaling Up

The scaling up of tubular PBs includes the corresponding scaling of the mixing system and solar receiver (or algae cultured module). As for the algae cultured modules, the size of the tube diameter is scaled up correspondingly. Although in practice, the length of tubular PBs is limited to a certain range, the scaling of the reactor's diameter has to consider changes in light/dark volume and cycle. Thus, the biomass productivity of this system declines unless the light/dark cycle is maintained properly. The frequency of the light/dark cycle is optimized at 1 s^{-1} (Molina et al. 2000), which is of such a standard for any scaling design. This designed light/dark cycle of two scales must be the same and can be calculated as below.

Thus, the frequency v is

$$v = \frac{1}{t_f + t_d} \tag{14.23}$$

where

ν	cycle frequency
t_f, t_d	light and dark period (s).

The correlation of light/dark interchange velocity at large-scale (U_{RL}) and the small-scale (U_{RS}) may be calculated on the scale factor f (Molina et al. 2000), as below:

$$U_{RL} = f \alpha U_{RS} \tag{14.24}$$

The factor f is the ratio of the tube diameters at both the larger and smaller scales. The parameter α is retrieved from the φ values at the two scales:

$$\alpha = 1 - \varphi L1 - \varphi S \tag{14.25}$$

$$\varphi = \frac{V_f}{V_f + V_d} \tag{14.26}$$

where

V_f	illuminated volume of period t_f
V_d	dark volume of period t_d.

14.3.4 Soft-Frame Photobioreactors

Soft-frame is the new trend in PB design in terms of materials, flexibility, mobility and saving space. Unlike other traditional PBs that employ hard materials and non-movables, the soft-frame PBs can be divided into small modules and are more mobile. Furthermore, these bags are made of ethylene vinyl acetate/ low-density polyethylene (EVA/LDPE), polyethylene (PE) and polytetrafluoroethylene (PTFE), which are foldable and replaceable. Thus, the PBs require less space, have a larger working volume and can be rotated towards light sources. However, research into the applications of soft-frame PBs is currently limited. Soft-frame PBs are able to integrate with other traditional PBs. As such, a vertical flat panel PB containing a plastic bag between two iron frames has been utilized (Rodolfi et al. 2009). This bag is then replaced when excessive fouling and contamination occur. The aeration is undertaken via a PVC plastic tube drilled with minute holes (approximately 1 mm).

14.4 Materials

There are a number of materials used for PBs soft-frame fabrication. For example, Hamano et al. (2017) cultivated algae on cellulosic/PTFE membrane sheets, and then applied this to PBs soft-frame. There was no requirement for mixing the PBs once the nutrient was supplied by capillary mechanism, and subsequently energy consumption was minimized. Unfortunately, the high cost of PTFE material restricts the commercialization of this technology. The amount of energy utilization is also substantially curtailed in EVA/LDPE PBs (Jones et al. 2017). In addition to this, the surface aeration and rocking platform mixing methods replaced the sparging system. The power input processed was at 57.6–903.3 W/m^3 with no significant influence being exerted on algae growth. In large-scale operations, Chemodanov et al. (2017) integrated PE PBs into building design. However, the growth rates fluctuated widely which entailed further clarification. On the other hand, Pagliolico et al. (2017) tested a number of materials for PBs soft-frame and for the design of static screens for windows in buildings (Table 14.1). Amongst these types, the disposable ice bag achieved a maximum specific growth rate ranging from 0.009 to 0.006 h^{-1}.

Scale Up

Nonetheless, this brand new technology does not to date have scaling-up guidelines. The relevant research done on soft-frame PB at the pilot and industrial-scale levels is fragmented. According to previous studies, there are some particular examples of upscaling soft-frame PB. For example, a polyethylene sleeve with the length, thickness and width of 100 m, 200 μm and 0.4 m has been devised. It has a total volume of 40.4 L per bag (Chemodanov et al. 2017). The system's total volume is 3400 L arranged in four floors of the building. The mixing was done through the bottom of the bags and water was exchanged from the top. Similarly,

Table 14.1 The application of materials in soft-frame PBs (Pagliolico et al. 2017)

	Bag size (mm)	Culture volume (ml)	Wall thick (mm)	Cubicle size (mm)	Culture volume (ml)	Max thick (mm)	Surface area/ volume (mm^{-1})	Aeration rate (vvm)
Disposable ice bag: Nine circular cubicles with square packing	150 × 150	120	0.05	45	13	17.5	0.12 × 2	–
Aerated disposable ice bag: Nine circular cubicles with square packing	150 × 150	120	0.05	45	13	17.5	0.12 × 2	0.4
Three rectangular cubicles arranged in three horizontal lines	150 × 150	120	0.125	35 × 135	40	19.5	0.09 × 2	–
10 circular cubicles with hexagonal packing	300 × 240	250	0.1	65	25	18.5	0.13 × 2	–
10 aerated circular cubicles with hexagonal packing	300 × 240	250	0.1	65	25	18.5	0.13 × 2	0.2

Chen et al. (Chen et al. 2013) cultivated algae in a 5L plastic bag illuminated with tungsten filament lamps. Abomohra et al. (Abomohra et al. 2014) cultivated *S. obliquus* in plastic (polyethylene) bags of 2 m length, 20 cm width and 0.2 mm thickness plastic bags.

Soft-frame PBs are a very promising invention and have much potential for industrial-scale production. Their limitations, however, include inadequate illumination, and the cost and longevity of materials. Furthermore, insufficient mixing is another problem due to the formation of a dead zone inside. In the PBs commercial market, the go-to-market products are currently for either hanging or floating options, such as Algasol Technology (AlgaSol Renewable 2018). This product offers a price range from US$2.175 to 3.125/item, assuming that the surface area ranges from 10 to 250 m^2 (AlgaSol Renewable 2018).

14.4.1 Comparisons of PBs' Configurations

The configurations of PBs are diverse and there are variations in biomass yield efficiencies. The design and operation of these PBs are based on a number of parameters, such as algae species, local geographical conditions and reactor personnel's operating skills. Comparisons of PBs are somewhat relative. As such, Yadala and Cremaschi (2014) compared the designs of tubular, column and flat plate PBs via the modelling approach. Consequently, the horizontal tubular PB proved to be the best design with minimum cost. Furthermore, the ideal diameter and length of this horizontal reactor should be 0.05 and 15.12 m, respectively. The best combination ascertained was the tubular PBs, *P. tricornutum* species located in Hyderabad (India), where the irradiance variation was minimal and avoided damage to the algae biomass. However, this requires more research to validate previous results and outcomes obtained.

One example undertaken by López et al. (2006) provided a comparison study of tubular and bubble column PBs in outdoor conditions. The tubular PBs achieved an illumination 2.5 times stronger than bubble column PBs, made possible due to their higher illuminated surface and horizontal configuration. The reported biomass yield and productivity of the tubular PBs were 7 g/L and 0.55 g/L d, respectively, whereas bubble column PBs were 0.41 g/L and 0.12 g/L d, respectively. However, although energy balance details are required for further comparison, this scenario has not yet been documented. Conversely, Mirón et al. (1999) argued that bubble column PBs are more prominent compared to the horizontal tubular PBs in both experimental and engineering analysis. Here, the authors explained that the bubble column experienced less photo-inhibition, and sufficient illumination was maintained in the low light intensity scenario. The parameters for scaling of the bubble column were established without technical difficulties. According to Mirón et al. (1999), the horizontal tubular PBs are impractical in large-scale industrial and commercial applications. The advantages and disadvantages of these PBs' configurations are summarized in Table 14.2.

Table 14.2 Main advantages and disadvantages of flat plate, column, tubular and soft-frame PBs

PB types	Advantage	Disadvantage
Flat plate PBs	High illumination surface area	Space dominance
	Appropriate to outdoor cultivation	Consist of photo-inhibition effect
	Sufficient biomass yield	Dark zone problem
	Modular configuration	High construction and energy costs
Column PBs	Efficient mass transfer	Inner illumination preferable
	High mixing efficiency	Modest surface to volume ratio
	Compact system	High mixing cost
	Greater gas hold ups	Illumination efficiency reduce while scaling up
	Best exposure to light/dark cycles	
	Easy to scale up	
	Less fouling problem	
Tubular PBs	High illumination surface area	More modules needed to increase scale
	Easy to construct and maintain	Fouling problem
	Efficient mass transfer	Over-heating
	Low power consumption	High operation cost
Soft-frame PBs	Flexible	Easily damaged materials
	Foldable	Insufficient mixing due to dead zone
	Replaceable	Possibility of leakage
	Small foot-print	High material costs

Biomass yield is reported to have wide variations in terms of both biomass concentration and productivity. Flat plate PBs are observed as having the largest biomass concentration (7.5–96.4 g/L), followed by column PBs with internal illumination (19.78 g/L). The other types of PB that achieve biomass concentration of around 4 g/L are listed in Table 14.3. Ozkan et al. (Ozkan et al. 2012) discovered that the high biomass yield was unprecedentedly high compared to the common biomass yield in flat plate PBs of 2 g/L. Unfortunately, there was no clear explanation for this outcome. However, the productivity was comparatively lower than the open pond, tubular and other flat plate PBs. This was recorded as 0.71 g/m^2 d while the other technologies ranged from 11 to 27 g/m^2 d. There were three reasons for this result: (i) the low reproduction rate of applied algae; (ii) insufficient illumination; and (iii) mass transfer in the system. Likewise, Hu and Sato (2017) achieved a biomass yield of 19.78 g/L through internal illumination. The authors agreed that the effect of reactor size and algae species were obvious considerations. A challenge here is to accurately compare the performance of PBs' configuration. What must also be considered here is the impact of other factors, for example, specific algae strains, geographical conditions, operation efficiency, energy consumption and cost analysis.

Table 14.3 Performance of types of PBs in certain operating conditions

No.	Configuration	Type of PB	Algae species	Light irradiance (μmol/m^2. s^1)	Light–dark cycle (h:h)	Light source	Biomass concentration (g/L)	Biomass productivity	References
1	Flat plate in PBs	Flat plate	*Botryococcus braunii*	100	24:0	Fluorescent	96.4	0.71 g/m^2	Ozkan et al. (2012)
2	Flat plate gas-lift PBs	Flat plate	*Scenedesmus ovalternus*	1300	24:0	LED	7.5	0.11/d 25.0 ± 0.5 g/m^2 d	Koller et al. (2017)
3	Flat-panel airlift PBs	Flat plate	*Chlamydomonas reinhardtii*	1500	24:0	LED	4.5	29–54 g/m^2.d	de Mooij et al. (2016)
4	Foam-bed PBs	Column	*Chlorella sorokiniana*	334 ± 16	–	LED	4.7	0.10/h	Janoska et al. (2017)
5	Closed PBs	Column	Green algae (genus *Chlorella* and *Stigeoclonium*) and cyanobacteria (cf. *Oscillatoria*)	204	12:12	Metal halide	0.49–0.84	0.039–0.084 g/L d	Arias et al. (2017)
6	X-shape PBs	Column	*Chlamydomonas reinhardtii*	100	11:13	LED	1.359 ± 0.007	–	Pham et al. (2017)
7	Water-circulating column PBs	Column	*Chlorella* mutant *PY-ZU1*	40 ± 2 klx	24:0	–	–	112.6 mg/L d	Yang et al. (2016)
8	Vertical multi-column airlift PBs	Column	*Chlorella pyrenoidosa*	672	–	Solar light	1.3–1.56	–	Huang et al. (2016)
9	Internal illumination PBs	Column	*Dunaliella tertiolecta*	250, 420 and 1000	Continuous or flash	LED	19.78	10.18 g/L d	Hu and Sato (2017)

(continued)

Table 14.3 (continued)

No.	Configuration	Type of PB	Algae species	Light irradiance (μmol/m^2. s^1)	Light–dark cycle (h:h)	Light source	Biomass concentration (g/L)	Biomass productivity	References
10	Ion-exchange membrane PBs	Column	*Chlorella vulgaris*	110	–	Fluorescent	4.24, 3.13 and 2.04	0.30 ± 0.04, 0.23 ± 0.01 and 0.17 ± 0.01 g/L d	Chang et al. (2016)
11	BIOCOIL PBs	Tubular	*Chlorella sorokiniana*	100	12:12	White fluorescent	0.9–1	0.52/d	Concas et al. (2016)
12	Horizontal PBs	Tubular	*Arthrospira platensis*	70	–	Fluorescent	7.11 ± 0.53	0.86 ± 0.03 g/L d	da Silva et al. (2016)
13	Horizontal and vertical tubular PBs	Tubular	*Phaeodactylum tricornutum* *Thalassiosira pseudonana*	50–700 W/m^2	Natural light cycle	Sunlight	0.2–12	1.4–3.29/d	Slegers et al. (2013)
14	Combined-light PBs	Tubular	*Nannochloropsis salina*	500	24:0	LED	7.2	0.888/d	Iluz and Abu-Ghosh (2016)
15	Macroalgae PBs	Soft-frame	*Cladophora* sp., *Ulva compressa* and *Ulva rigida*	238–348	Varied	Solar	–	–	Chemodanov et al. (2017)
16	Biofilm-based PBs	Soft-frame	*Pseudochoricystis ellipsoidea*	300–340	12:12 and 24:0	LED	–	8–10 g/m^2 d	Hamano et al. (2017)

14.5 Applications of Photobioreactors

It is essential that PBs can be applied in a diverse range of contexts, for example, environmental remediation, pharmaceutical and healthcare, biomaterials and energy. The algae biomass cultivated in PBs can consume pollutants in culture and these contaminants (nutrients, micropollutants, heavy metals) are removed accordingly. The received biomass can also be applied to either producing bioenergy or pigment extraction as required by the pharmaceutical industry. In recent years, algae have been employed in the biomaterials sector which extends to chemistry, biotechnology and construction industries. In this section, the advances made in PBs with specific reference to environmental remediation and building collocation are the focus.

14.5.1 Environmental Remediation

As previously mentioned, the efficiency of PBs depends on many factors with the main one being the reactors' configurations are precise. Consequently, any applications of PBs in environmental remediation are heavily dependent on these configurations (Table 14.4). These are explained in more detail below.

Flat Plate Photobioreactors

A modification type of flat plate known as the twin-layer PBs was developed by Shi et al. (2014), including the glass mesh supported by a nylon membrane that was attached to each other. This flat plate PB removed 70–99% of N and P, respectively, these amounts being three and two times, higher than the open pond system of Boelee et al. (2014). The concentrations of N and P in the effluent were below 1.3 and 1 mg/L, respectively, and met the discharge standard of the European Water Framework Directive. Furthermore, the N and P concentrations in the influent were noticeably large, being 5000 and 450 mg/L, respectively. Previously, this system proved its nutrient removal efficiencies in municipal and synthetic wastewater, having removed more than 90% of the pollutants within 9 days. In another study, the maximum N and P uptake rates were 1.0 and 0.13 g/m^2 d, respectively (Boelee et al. 2011). This finding which used the traditional biofilm reactor was actually poorer than the twin-layer PBs' efficacies.

Flat plate PBs are useful for remediating air pollution and one such example is CO_2 removal. Martín-Girela et al. (2017) enhanced CO_2 adsorption up to 0.125 μmol CO_2/μmol photons in flat plate PBs. The flash light was operated in this PB and resulted in sevenfold higher photosynthetic activity than when utilizing continuous light.

Column Photobioreactors

Pollutants are removed by both bubble column and airlift configurations in these PBs with a number of targeted pollutants. In a laboratory-scale PB, Lee et al. (2015)

Table 14.4 The removal of contaminants by PBs

No.	Configuration	Type of PB	Wastewater source	Algae species	Removal efficiency (%)					References
					TN	TP	COD	PPCPs and organic	Others	
1	Twin-layer PBs	Flat plate	Municipal wastewater	*Halochlorella rubescens*	70–99%		–	–	–	Shi et al. (2014)
2	Plastic sheet PBs	Flat plate	Municipal wastewater	Various	Uptake 1.0 g/ m^2 d	Uptake 0.13 g/ m^2 d	–	–	–	Boelee et al. (2011)
3	Lab-scale PBs	Column	Synthetic wastewater	Algae and bacteria consortium	60.4–70.5	93.2–96.4	95.5–96.7	–	–	Zhang et al. (2018)
4	Batch PBs	Column	Municipal wastewater after anaerobic digestion	*Coelastrum microporum*	35–88	43–89	59–80	–	–	Lee et al. (2015)
5	Airlift PBs	Column	Bio-industrial wastewater	*Chlorella sorokiniana*	100	100	86.84	–	–	Podevin et al. (2017)
6	Bubble Column PBs	Column	Synthetic wastewater	*C. vulgaris*	60–99	100	–	–	–	Al Ketife et al. (2016)
7	Full-scale Tubular PBs	Tubular	Olive washing water	*Sphaeropleales*	–	–	85.86 ± 1.24%	94.84 ± 0.55%	–	Maza-Márquez et al. (2017)
8	Horizontal PBs	Tubular	*Arthrospira platensis*	70	n.d	Fluorescent	7.11 ± 0.53	0.86 ± 0.03 g/L. d-	da Silva et al. (2016)	
9	Batch PBs	Soft-frame	Toilet wastewater	*Trametes versicolor*	80	80	80	48	–	Hom-Diaz et al. (2017)
10	Full-scale horizontal tubular PBs	Soft-frame	Agricultural run-off	*Pediastrum* sp., *Chlorella* sp., *Scenedesmus* sp., and the cyanobacteria *Gloeothece* sp	n.d	n.d	n.d	73% tonalide 68% galaxolide 61% anti-inflammatory compounds	n.d	García-Galán et al. (2018)

noted that carbon uptake benefited from longer operation in the dark, although N and P utilization were favoured in light conditions. Overall, COD, TN and TP were removed at 59–80%, 35–88% and 43–89%, respectively. Furthermore, microalgae growth was disturbed by nitrifying bacteria. Thus, when the nitrifying process slowed down, algae could grow faster and more chlorophyll pigment was produced (Krustok et al. 2016). Zhang et al. (2018) enhanced the efficiency in removing nutrients via the algae and bacteria consortium. The maximum COD, TN and TP removal efficiencies were 96.7, 70.5 and 96.4%, respectively, and these amounts corresponded to the influent concentrations of 1200, 200 and 16 mg/L. The granulation activity of bacteria was enhanced by green algae and proved able to resist temperature fluctuations. In another study, it was found that the different nutrient ratio levels conditioned the development of the microorganism and algae consortium (Arias et al. 2017). For example, the total inorganic N/inorganic P (21 mg N/L and 2 mg P/L) resulted in the excessive growth of cyanobacteria over a period lasting 234 days.

Similar to flat plate PBs, the column PBs proved their use in removing CO_2 wherein CO_2 emission gas from industry were reused for mixing in the reactors. Typically, Chen et al. (2012) employed power plant fuel gas to cultivate algae, finding that the uptake rate of *Spirulina platensis* could be 2234 kg CO_2 per year. This was equivalent to 74 ton/ha. year. Furthermore, *Chlorella vulgaris* consumed 80% CO_2 in airlift PBs, wherein the influent and effluent CO_2 concentrations were 20,000 and 4700 ppm (Sadeghizadeh et al. 2017). Jacob-Lopes et al. (2009) developed operational manuals to remove CO_2 in bubble column and airlift PBs. Here, the small-scale system complied with the air circulation whereas the industrial scale preferred the two-stage sequential operation. The removal efficiency and loading were reported at 52.5% and 12.217 g carbon/m^3 reactor d, respectively, when the inlet CO_2 concentration was 15%.

With reference to heavy metal, the complete removal of Cu (II) was reported by Arun et al. (2017). Nevertheless, this may actually hinder the nitrate uptake rate, resulting in the decrease of biomass yield. Specifically, the maximum biomass yield was 5.628 ± 0.05 g/L without Cu (II) in the monoculture, although it fell to 2.51 ± 0.01 g/L due to interference by the Cu (II) concentration of 30 mg/L. Markou et al. (2015) quantified the heavy metals biosorption rate as lasting from 15 to 30 min, and it reached equilibrium within 30–60 min in a laboratory-scale bubble column PB. It also emerged that the living carbohydrate-enriched biomass of *Arthrospira platensis* eliminated more than 30% of Cu^{2+} and Ni^{2+} compared to the dry carbohydrate-enriched one. The higher intracellular biosorption of living algae in comparison to the dry biomass was the only reason for this. Different algae species also performed differently in the bubble column PBs. The dry biomass of *C. vulgaris* was more distinctive than *A. platensis* (Ferreira et al. 2011). For instance, the equilibrium biosorption values of *C. vulgaris*, removing 0.499, 0.634 and 0.664 mmol/g from Ni^{2+}, Pb^{2+} and Zn^{2+}, respectively. Conversely, the amounts were 0.354, 0.495 and 0.508 mmol/g, respectively, in the case of *A. platensis*.

Tubular Photobioreactors

Studies on tubular PBs for removing pollutants are limited because most of the focus has been on optimizing biomass yield and operating conditions. Anbalagan et al. (2017) reported that N and P removal efficiencies were 91 ± 2% and 95 ± 4%, respectively, in a tubular PB operating at a steady-state condition. Furthermore, this reactor could eliminate CO_2 and toluene at 76 ± 7 and 89 ± 5%, respectively. This outcome was achieved at a liquid/gas ratio of 15 regardless of the hydraulic retention time or dilution rate. The concentrations of CO_2 and toluene were significantly high at 24% and 498 mg/m^3. Similarly, Binnal and Babu (2017) reported that the CO_2 fixation rate was 273.66 mg/L d in tubular PBs under N starvation conditions.

Treating wastewater of fishery farms, Michels et al. (2014) discovered that N and P were initially removed at 49.4 and 99%, respectively. At this stage, the N and P concentrations were 41.3 and 4.96 mg/L. When an additional phosphorus source of 10 mg/L was applied, the N and P removal efficiencies surged to 95.7 and 99.7%, respectively. According to these researchers, the ratio of N:P in the medium was an important issue and it should be close to the Redfield ratio (16:1). In a long-term assessment (168 days) for treating effluent in an urban wastewater treatment plant, the N and P removal efficiencies were 89.7 and 86.7%, respectively. These were higher than the results concerning high removal rates of an algae pond which were 65.1 and 58.7%, respectively (Arbib et al. 2013).

Currently, pharmaceutical and personal care products (PPCPs) are targets of PB treatment. Although such remediation is limited it is envisaged that there will be an increase in treatment in the near future. Kang et al. (2017) studied the performance of periphyton PBs when treating PPCPs. As such, Bisphenol A was removed in amounts varying from 72 to 86.4% while hydrochlorothiazide, ibuprofen, carbamazepine and gemfibrozil were moderately treated from 6.45 to 48.7%. It was concluded that the microbial community contributed more to PPCPs' removal than microalgae biomass. In the tubular PBs the periodic and low irradiance illumination influenced the efficacy of removing PPCPs.

Soft-Frame Photobioreactors

Soft-frame PB is a new technology but information on its ability to remove pollutants is rare. Hom-Diaz et al. (2017) reported that more than 80% of $N\text{-}NH_4^+$, TP and COD from toilet wastewater were eliminated in plastic bag PBs. Furthermore, 48% of PPCPs were removed in these PBs. The major documented outcomes were sufficient hydraulic retention time (HRT) (8 days during period I and 12 days during period II) and microbial activity.

14.5.2 Building Collocation Applications

Previously, PBs in large- and industrial-scale scenarios were established in open space areas. However, integrating PBs and buildings is now developing as an innovative approach. The remarkable applications of this collocation are heat

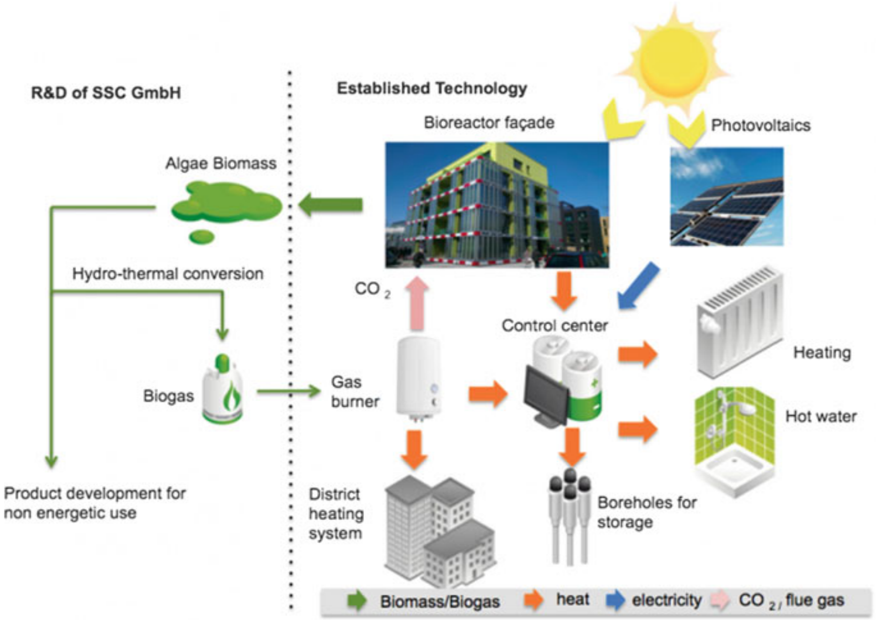

Fig. 14.4 PBs and building collocation concept (Torgal et al. 2016)

dissipation, pollutants remediation and green structure as illustrated in Fig. 14.4 (Torgal et al. 2016). With reference to the remediation of pollutants, the following benefits are offered:

(1) Pollutants (e.g., CO_2, nutrients) can be employed as food for algae cultivation
(2) Centralized treatment and operation, thus saving in transportation fees
(3) Revenue from extracting pigments from algae
(4) Heat supply for the building.

It is likely that the preference is for flat plate PBs being collocated in buildings due to their flexibility, modular and high surface area. This advantage allows flat plate PBs constructed as windows or walls on buildings. It should be noted here that the configuration of tubular and bubble column PBs does not please this requirement. The only alternative for tubular and bubble column PBs is to be located on rooftops, however, these PBs may consume additional space. Flat plate PBs furthermore do not require extensive energy for mixing and this makes them a promising option for remediation.

The worlds' first PBs collocation building was constructed in Hamburg (Germany) in 2013 (Real Green Heat 2013). This building can supply heat for residents throughout the year. The redundant heat is stored by geothermal boreholes, and subsequently it is released by PBs. These approaches should be further developed to ensure that 'green' and environmentally friendly values are introduced into urban lifestyles whilst contaminants are treated and reduced.

14.5.3 Case Studies

In this scenario, Zamalloa et al. (2013) installed a flat plate PB on the rooftop of a building and examined its efficiency in removing pollutants (Fig. 14.5). Domestic wastewater was first treated utilizing the chemical biological process (A-stage). Subsequently, the effluent was fed to the above-mentioned PB for further treatment (I-Stage). The flat plate PB included twin polycarbonate sheets of 10 mm thickness connected to a PVC pipe at the bottom for homogenous bulk liquid distribution. The total area of the PB was 0.5 m^2 with a working volume of 5 L. It was oriented in a north-south direction with an inclination of 30°. The HRT of 24 h was designed to operate this PB and sunlight was the major light source. The system's overall efficiencies in removing COD, TN and TP were 74, 82 and 67%, respectively. This system possessed the advantage of simple design and low cost, in which the total capital and operational costs were estimated to be only 0.5 €/m^3 wastewater.

14.6 Future Perspective

Through laboratory and pilot-scale research the efficiency of PBs in wastewater treatment is a promising development with many practical outcomes. However, industrial-scale PBs still face many challenges. Currently, there are a number of pioneer companies involved in PB technologies. However, the high cost of biomass harvesting, biofuel production and energy consumption for mixing are the main obstructions in making it more acceptable (Judd et al. 2017). Thus, the collocation of PBs and buildings for the purposes of cutting costs is the right option for the

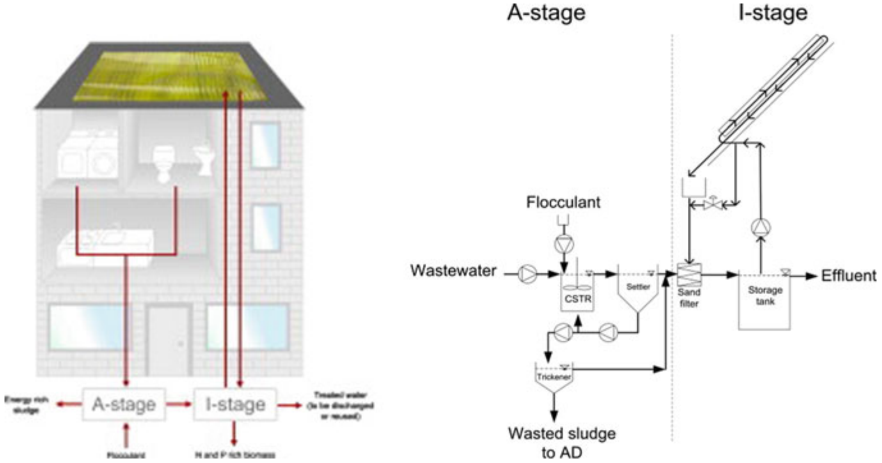

Fig. 14.5 Flat plat PBs installment in building and pollutant removal concept (Zamalloa et al. 2013)

future. It has been considered in diverse types of buildings such as apartments, exhibition centres and transportation systems (The 2011 International Algae Competition 2018).

The development of PBs has been strongly supported by modelling because the experimental process is difficult to conduct in a large-scale context. It is suggested that the modelling approaches be applied if there are more than six considered variables. However, there are modest or specifically accepted guidelines for designing and constructing PBs. This process is still very much in the 'trial and error' stage. In a few other places, the design manuals for upscaling of the flat plate and tubular PBs have been proposed (Slegers et al. 2011, 2013). Furthermore, Fuente et al. (2017) established illumination modelling that can be upscaled. The upscaling of PBs is promising as an environmentally and energy friendly strategy. It is one where there is much scientific interest in its development and subsequent widespread acceptance (The 2011 International Algae Competition 2018; Öncel et al. 2016).

In economic terms, the average cost of closed vertical PBs is estimated at €30 and this corresponds to an area of 500 m^2 (Torgal et al. 2016). The details of this PB type are illustrated in Table 14.5. The return on investment from installing PBs will reportedly be realized after approximately between 9 and 13 years. However, if a bio-fertilizer is added this will shorten to 7 years as it generates more economic return. There are some options to curtail the cost burden. For example, having a sunlight source can reduce the expense to US$307 per 0.5 kg dry cell. Total production costs should then diminish when employing larger reactors (US$121 per 0.5 kg dry cell in 200 L reactor compared to US$197 per 0.5 kg dry cell in 17 L unit). On the other hand, it has been documented that the reuse of a spent medium saved a modest US$8 per 0.5 kg dry cell (Issarapayup et al. 2011). These methods did cause a decline in the growth of algae. Thus, it is unlikely that stand-alone PBs can currently meet the requirements of economic and renewable energy targets, but it does so in terms of the wastewater treatment process.

Table 14.5 Cost analysis of PBs based on the scale factors and functions

PBs cost—closed vertical type	PBs area (m^2)					
		100	200	500	1000	5000
Bio-fertilizer and irrigation	Total cost (€)	6695.5	8535.9	11,296.4	15,897.3	52,704.5
	Cost per m^2 (€)	67	42.7	22.6	15.9	10.5
Heat generation	Total cost (€)	9060.5	11,373.9	14,843.9	20,627.3	66,894.5
	Cost per m^2 (€)	90.6	56.9	29.7	20.6	13.4
Electricity and heat generation	Total cost (€)	10,060.5	12,573.9	16,343.9	22,627.3	77,894.5
	Cost per m^2 (€)	100.6	62.9	32.7	22.6	15.6

14.7 Conclusion

Generally, PBs are an advanced technology offering many benefits and especially since pollutants are removed and biomass is harvested concurrently. This wastewater treatment system has been making great strides in terms of design and application in recent years. The design is becoming more flexible and durable while the applications are increasingly consumer-friendly through the collocation with infrastructure such as buildings. Some limitations are evident in that PBs encompass high energy consumption and technical constraints in upscaling, especially at the industrial-scale level. However, its advances in and contributions to wastewater treatment have been indicated. Clearly, it is a high promising candidate for wastewater treatment in terms of green technology and helping humanity to protect the natural environment.

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Chapter 15
Microbial Community in Anaerobic Digestion System: Progression in Microbial Ecology

Luong N. Nguyen, Anh Q. Nguyen and Long D. Nghiem

Abstract Anaerobic digestion (AD) is a biochemical process that involves four microorganism groups, namely, hydrolyzers, acidogens, acetogens, and methanogens. These groups function in syntrophy and have intra-dependent metabolic pathways. Changes in one group (e.g., over-/underexpressed population and function) can alter this chain of anaerobic process and consequently AD performance. With recent progress in culture-independent techniques, an array of previously unknown and uncultured microorganisms has been recently uncovered in the AD process. Discoveries on the diversity and structure of the AD microbial community can provide new information on digester stability and performance (e.g., biogas production). This chapter provided a critical analysis of the current knowledge on the AD microbial community, focusing on the factors affecting microbial community and the relationship between microbial community and AD performance. Gaining a better understanding of microbial ecology could be the key for greater AD efficiency and biogas production capacity.

Keywords Anaerobic digestion (AD) · Microbial community · Microbial ecology Core microbiome

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15.1 Introduction

Anaerobic digestion (AD) has long been used in wastewater treatment plants (WWTPs) to stabilize sewage sludge prior to beneficial reuse or disposal. Recently, there has been a growing emphasis among the water industries and municipalities to achieve sustainability goals by shifting from a sole focus on wastewater treatment to include energy generation and resource recovery. The AD process has then played a vital role in this paradigm shift. The AD process converts sludge into biogas, which mostly contains methane, carbon dioxide, and a nutrient-rich slurry called digestate. Other organic wastes such as food waste, dairy processing waste, agricultural reject, and others have been brought into the AD process (Nghiem et al. 2017). These organic wastes supplement AD with carbon and nutrients and consequently boost biogas production. With this anaerobic co-digestion (AcoD) approach, WWTPs can produce biogas which can be used to produce electricity to offset their energy consumption. AcoD has an additional benefit of reducing the amount of organic waste that is otherwise bound to landfills. Although AD is a mature technology, maintaining a stable and high-performance digester is still a challenging exercise. This is mainly due to the complexity of microorganisms that are involved in the AD process. These microorganisms maintain a syntrophic relationship and depend on each other for their survival and growth (Carballa et al. 2015; Regueiro et al. 2015; Ortseifen et al. 2016; Ju et al. 2017).

A fundamental step to characterize the AD microbial community is the taxonomic and phylogenetic classification of DNA sequence—biomarker of microorganism. The last few decades have seen a revolution in molecular techniques to investigate the small-subunit rRNA sequence (16S rRNA) from simple polymerase chain reaction (PCR) to high-throughput sequencing such as next generation sequencing (NGS). The development of culture-independent techniques has uncovered an abundant array of previously unknown and uncultured microorganisms. Due to these technical advances, the number of investigations on microbial community in the AD process underwent an impressive increase in scientific publications (Carballa et al. 2015; Razaviarani and Buchanan 2014; Gagliano et al. 2015a; Li et al. 2015). NGS has made large advancements in the understanding of the underlying driving force—the microbiome—in AD process. For example, the AD microbial community could be characterized in terms of taxonomic profile and composition. Understanding the connection between microbial community and AD performance can provide intuitive information for optimization of the AD process. This chapter, therefore, provides a state-of-the-art review on the AD microbial community, including the factors affecting microbial diversity and structure and the relationship between microbial community and digester performance.

15.2 Microbial Community—The Driving Force in AD Process

There are four phases in the AD process each is facilitated by a distinctive group of microorganisms (Fig. 15.1). There is also a syntrophic relationship among the very diverse functions of these microorganisms in growth conditions, physiology, metabolic activities, and stress tolerance. The performance of AD is dependent on this complex syntrophic relationship. For example, the main product of the acetogens is acetate, which is also a major carbon and energy source for the methanogens (Fig. 15.1). Corresponding to the four phases in Fig. 15.1, the AD microorganisms are categorized into four groups, namely, hydrolyzers, acidogens, acetogens, and methanogens mainly based on their specific functions in the AD process. These groups of microorganisms are taxonomically divided in the domain of bacteria (hydrolyzers, acidogens, and acetogens) and archaea (methanogens). From the domain, the AD microorganisms are arranged in successive levels of biological classification in the taxonomic hierarchy with the following order: kingdom, phylum, class, order, family, genus, and species. The following section provides a detailed description of each phase in the AD process focusing on different groups of microorganisms and their ecology.

15.2.1 Hydrolyzers

Anaerobic hydrolytic bacteria are widely distributed in various ecosystems such as soils, sewage, rumen of animals, compost, and AD sludge. Hydrolytic bacteria (Phase 1) are the first to react to convert complex organic matter (i.e., carbohydrates, proteins, and lipids) into low molecular weight compounds such as sugar,

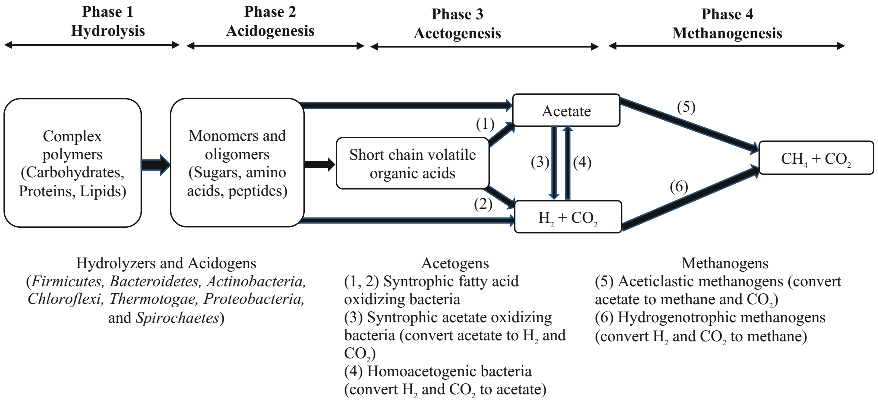

Fig. 15.1 Schematic representation of four phases in the AD process with associated group of microorganisms

amino acids, and peptides (Fig. 15.1). These intermediates serve as food for the next groups of microorganisms in the process chain. Without the initial step by the hydrolytic bacteria, the AD process cannot occur naturally. A functionally stable AD, therefore, contains a healthy portion of hydrolytic bacteria.

Hydrolytic bacteria can be found in a number of different phyla such as *Chloroflexi*, *Thermotogae*, *Firmicutes*, *Bacteroidetes*, *Proteobacteria*, and *Spirochaetes*. *Firmicutes* and *Bacteroidetes* are the two most dominant phyla in AD (Fig. 15.2). The abundance of hydrolytic bacteria in AD depends on factors such as type of inoculum, operating temperature, cell retention time (CRT), and substrate characteristics. The abundance of major phylum in the AD process is presented in Fig. 15.2.

As a unique feature of the hydrolytic bacteria, they produce cellulosome, a special multienzyme complex that enables them to secrete different hydrolases such as glucanases, hemicellulases, chitinases, and lihanases. These enzymes enable hydrolytic bacteria to break down a variety of complex organic wastes. Cellulosome was first discovered in 1983 from the *Clostridium thermocellum* in thermophilic AD (Lamed et al. 1983). Since then the role of cellulosome and its presence in the many hydrolytic bacteria were discovered. The cellulosome bridges the connection between bacteria, enzyme, and substrates. It has been demonstrated that the hydrolytic bacteria cannot produce enzymes without cellulosome. The presence of these enzymes has made hydrolytic bacteria important in AD of various organic wastes.

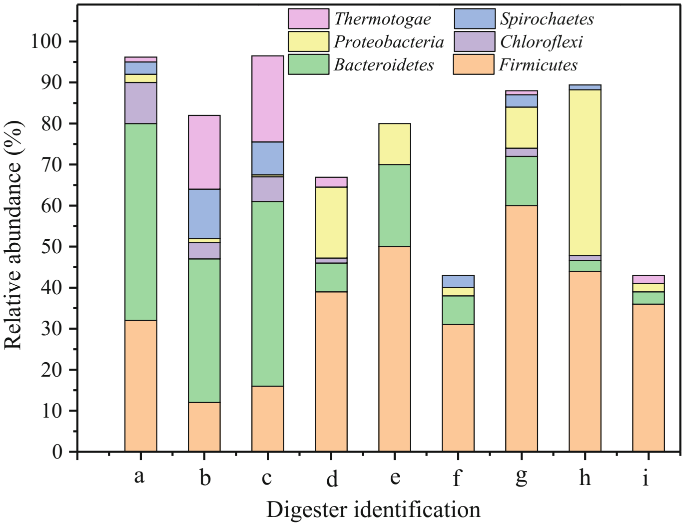

Fig. 15.2 Relative abundance of major phylum in the AD process. Data were extracted from most recent studies, which used high-throughput sequencing technologies to detect their abundance. The digester identification indicates the source of data [a, b, and c] (Guo et al. 2014), [d] (Hanreich et al. 2013), [e] (Li et al. 2013), [f] (Ortseifen et al. 2016), [g] (Rademacher et al. 2012) and [h and i] (Wu and He 2013)

15.2.2 Acidogens

In Phase 2, acidogenic bacteria use the products of hydrolyzers—sugars, amino acids, and peptides—as electron acceptors to generate fermentation products such as formic acid, acetic acid, propionic acid, butyric acid, pentatonic acid, alcohols, CO_2, and H_2 (Fig. 15.1). Acetate, CO_2, and H_2 can be used directly by the methanogens (in Phase 4), while other higher organic acids are subsequently transferred to acetic acids and H_2 by the acetogenic bacteria (Phase 3).

Acidogenic bacteria include facultative and obligate microorganisms. The former can live in both aerobic and anaerobic conditions while the latter is strictly anaerobic. Species of acidogenic bacteria can be found in phyla *Firmicutes*, *Bacteroidetes*, *Proteobacteria*, and *Actinobacteria*. A few species have been isolated from AD such as *Clostridium* (*Firmicutes*), *Peptococcus* (*Firmicutes*), *Bifidobacterium* (*Actinobacteria*), *Desulfovibrio* (*Proteobacteria*), *Corynebacterium* (*Actinobacteria*), *Bacillus* (*Firmicutes*), *Pseudomonas* (*Proteobacteria*), and *Desulfobacter* (*Proteobacteria*) (Shiratori et al. 2006; Nanninga and Gottschal 1987). These species are especially abundant during high fermentation period, confirming their roles at this phase.

A number of abiotic factors can influence the population of acidogenic bacteria such as digester design, temperature, CRT, and substrate characteristics. Out of these, substrate characteristics (i.e., composition and concentration) are considered to exert the greatest influence. For example, *Desulfovibrio* spp., a sulfate-reducing acidogen, was significantly enriched during AD of high sulfate-containing substrate (Nanninga and Gottschal 1987). Also, *Clostridium* sp., a cellulosic waste degrading bacterium, was found to be dominant in high cellulose substrate (Izquierdo et al. 2010).

15.2.3 Acetogens

Acetogenesis is the third phase of the AD process. In this phase, organic acids such as propionic, butyric, and pentatonic acid are metabolized into acetic acid and H_2 by acetogenic microbes (Fig. 15.1). A number of acetogens belong to the genus *Syntrophomonas* (e.g., *Syntrophobacter wolinii* and *Syntrophomonas wolfei*), which are syntrophic fatty-acid oxidizing microbes. The H_2 production in this process inhibits acetogenic metabolism. The hydrogen partial pressure should be very low so that the thermodynamic conditions become favorable for conversion of volatile fatty acids (VFAs) to acetate (Fig. 15.3). The activity of hydrogenotrophic methanogens is extremely critical to maintain low hydrogen partial pressure in AD (Cazier et al. 2015; Amani et al. 2010). Failure to maintain this interaction is detrimental to the overall AD performance, resulting in VFA accumulation in the system. The success of the acetogenesis determines the biogas production efficiency because 70% of methane is produced through acetate reduction.

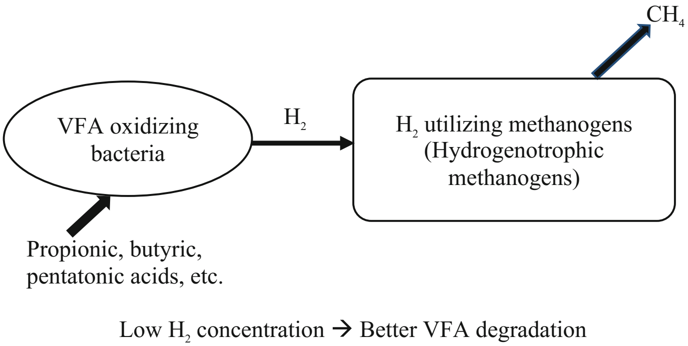

Fig. 15.3 Schematic diagram illustrates the syntrophic acetogenesis

Syntrophic acetate oxidizing (SAO) bacteria can be seen as a stabilizer in the AD process. They play an important role in maintaining the AD stability especially when the system undergoes environmental fluctuations. For example, aceticlastic methanogens, which contribute more than 70% of methane production, are sensitive to high ammonia concentrations, VFAs, heavy metals, and sulfide. Under such conditions, SAO can adapt to dominantly convert acetate to H_2 and CO_2, which are then used by the hydrogenotrophic methanogens for methane production (Sun et al. 2014). This decreases the accumulation of acetate and raises the pH of the digester to support the aceticlastic methanogens. Acetate oxidization by syntrophs has a low conversion rate, and thus altering the operating conditions to support syntrophic growth is necessary. A few SAO microbes are detected from both mesophilic and thermophilic AD. These include *Pseudothermotoga lettingae*, *Thermacetogenium phaeum*, *Syntrophaceticus schinkii*, and some in the phylum of *Spirochaetes* (Westerholm et al. 2010; Hattori et al. 2000; Lee et al. 2015).

Non-syntrophic acetogens are also present in the AD process in the form of homoacetogenic bacteria. This group can utilize H_2 and CO_2 to produce acetate. This reaction is thermodynamically favorable and does not require the presence of methanogens. An example of microbes in this group is the *Clostridium aceticum* that was isolated and characterized as obligately anaerobic (Braun et al. 1981). However, this pathway is less favorable in the AD process and the homoacetogenic bacteria are often outcompeted by hydrogenotrophic methanogens for H_2. To date, the homoacetogenic bacteria have not been elucidated in detail.

15.2.4 Methanogens

The methanogens belong to the archaea domain that is capable of producing methane gas. They are ubiquitously present in anaerobic environment and play important role in the global carbon cycle (Kouzuma et al. 2017). In the AD process, the methanogens are critical for biogas production. So far, researchers have found 65 methanogenic species and grouped them in five orders: *Methanobacteriales*, *Methanococcales*, *Methanomicrobiales*, *Methanosarcinales*, and *Methanopyrales* (Nielsen et al. 2007; Wang et al. 2018). These species are extremely sensitive to oxygen and are registered as slow-growing microbes as they restrict to a limited number of organic compounds for carbon and energy sources (Holmes and Smith 2016).

Based on substrate utilization, methanogens can be sub-divided into three groups: Methylotrophic methanogens that utilize methyl and other one-carbon compounds; Hydrogenotrophic methanogens that utilize CO_2 and H_2; and Aceticlastic methanogens that utilize acetate (Fig. 15.1). Among these archaea, aceticlastic methanogens are responsible for the majority of methane production in AD. This is consistent with the high abundance of the genera such as *Methanosaeta* and *Methanosarcina* (Fig. 15.4) in most of the AD processes. The genus of *Methanosaeta* is strictly aceticlastic methanogens. Chen and He (2015) reported the robustness of *Methanosaeta* genus at high levels of acetate in AD (44 mM). On the other hand, the genus *Methanosarcina* has versatile metabolic pathways and is

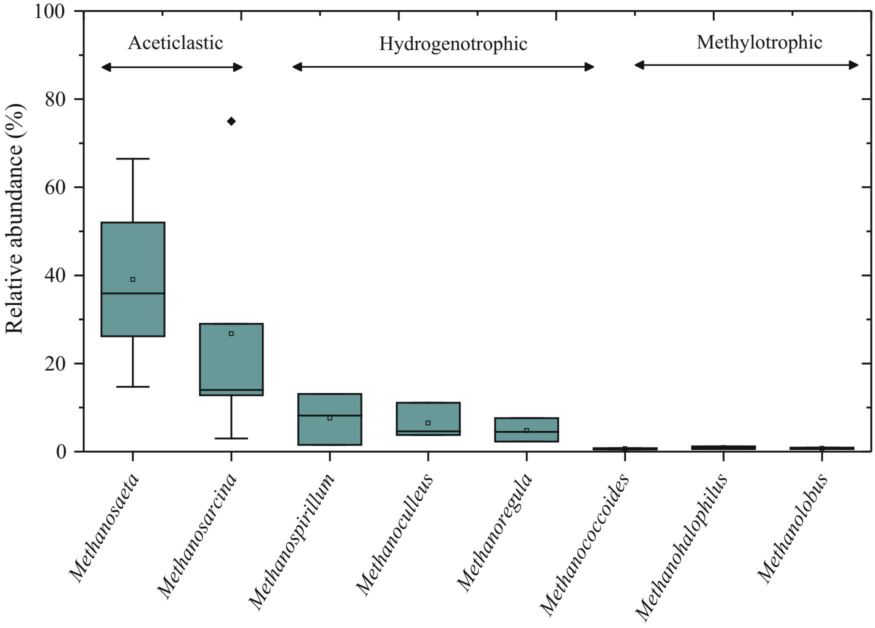

Fig. 15.4 Relative abundance of major methanogen genera. Data were extracted from most recent study that used high-throughput sequencing technology to detect their abundance. The relative abundance was calculated against the total archaea (Chen and He 2015; Guo et al. 2015; Rivière et al. 2009; Jang et al. 2015). The whiskers of the box represent the minimum and maximum values. The bottom and top of the box are the first and third quartiles, respectively, and the line inside the box denotes the median. The solid diamond represents the outliers

relatively tolerant to perturbations (e.g., low pH and high VFAs) (Venkiteshwaran et al. 2017). Compared to aceticlastic methanogens, hydrogenotrophic methanogens occur in AD at lower relative abundance (Fig. 15.4). However, the hydrogenotrophic methanogens are typically tolerant than aceticlastic methanogens under harsh conditions. It has been observed that the methanogenic community shifted from aceticlastic to hydrogenotrophic dominant under perturbed conditions (Lerm et al. 2012; Vanwonterghem et al. 2014). The presence of hydrogenotrophic methanogens, although at relative low abundance, is essential to keep the hydrogen partial pressure low and thus support the acetogenesis of VFAs.

AD is a biochemically complex process driven by syntrophic microorganisms. The performance and stability of an AD rely on its microbiome composition and the interactions among microbial groups. Previous studies have demonstrated that variations in the abiotic factors (i.e., digester design and operation) affect the digester performance outcomes but underestimate the change in the microbial community and its relation to the digester performance. In this era of next generation sequencing technologies, it is envisaged that the microbial community profile of many types of AD will be revealed. Detailed connections between microbial community profiles and digester performance can then provide new insights for engineers to better control the AD process. A research roadmap is proposed in Fig. 15.5 to integrate digester microbial community with understanding digester performance and optimization.

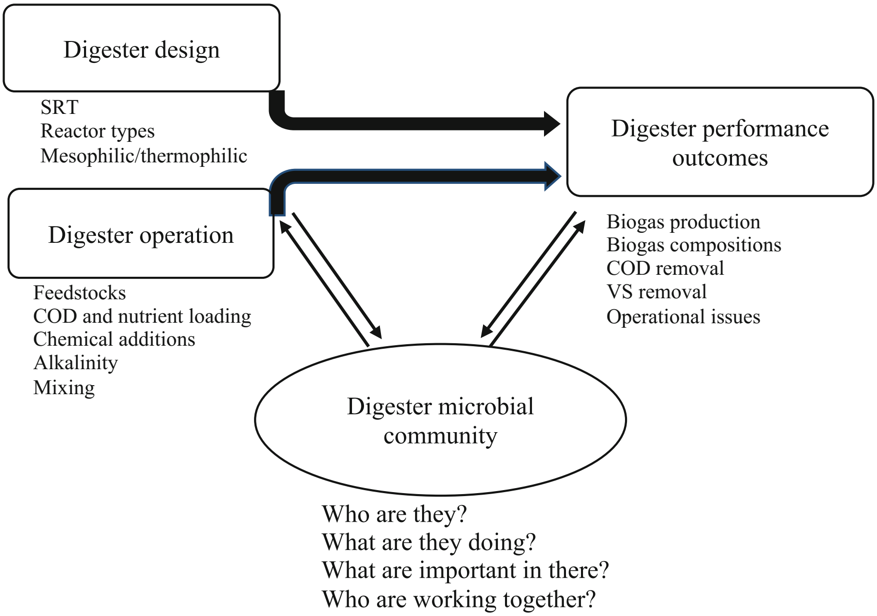

Fig. 15.5 Integrated digester microbial community into the understanding digester performance and control

15.3 Factors Influencing the Microbial Community in AD

The community diversity including richness (i.e., how many species are in a community) and evenness (i.e., how close in numbers each species in a community is) are described using alpha diversity indices. The alpha diversity indices include Observed species, Chao 1, Simpson, and Shannon. Observed species and Chao 1 are used to describe community richness and Simpson and Shannon are used to describe community evenness. The community structure includes the composition and abundance of species at different taxonomical levels (i.e., phylogenetic structure). It is often reflected by the distribution of individuals among species in a community. The differences between communities are measured by the beta diversity. Computational ecology method such as principal coordinate analysis (PCoA), principal components analysis (PCA), and nonmetric multidimensional scaling (NMDS) are used to profile the community structure and to estimate the distance among communities (e.g., dissimilarity). The following sub-sections provide detailed description on the influence of abiotic factors (e.g., temperature, OLR, CRT, and substrate characteristics) and biotic factor (e.g., inoculum source) on the AD microbial community (i.e., diversity and structure).

15.3.1 Temperatures

Mesophilic (30–40 °C) and thermophilic (50–60 °C) are the two common operating conditions in AD. Each condition presents specific advantages and the selection between them is mainly due to a number of factors. Thermophilic AD offers high metabolic rates, high biogas yields, and deactivation of pathogen due to higher operating temperature but its effluent contains high concentration of VFAs especially propionic acid. Mesophilic AD can maintain high organic loading rates but has lower metabolic rate compared to thermophilic AD (Labatut et al. 2014). Generally, thermophilic AD is more susceptible to environmental perturbations than mesophilic AD because the latter has lower community diversity (Moset et al. 2015; Gagliano et al. 2015b; Niu et al. 2015; Shaw et al. 2017). Low diversity of thermophilic AD is consistently reported in literature. For example, Shannon index of thermophilic AD has been reported lower than that of mesophilic AD (6.14 vs. 4.99) (Moset et al. 2015). A twofold decrease in microbial diversity and evenness has been observed when the operating temperature of AD was changed from 37 to 55 °C (Gagliano et al. 2015b). A negative correlation between temperature and all microbial diversity indices has been reported (Lee et al. 2017). The archaeal community of thermophilic AD is also less diverse than that of the mesophilic AD (Niu et al. 2015). An elevated temperature induces a selective pressure on the community resulting in the enrichment of tolerant strains and decrease in diversity. On the other hand, mesophilic AD is relatively resilient to sudden changes in operating conditions. For example, it has been observed that mesophilic AD has shown resistance to total ammonia nitrogen inhibition of up to 1.6 g/L, whereas thermophilic AD has failed at half dose (Niu et al. 2015). Aceticlastic methanogens has shown extreme sensitivity to sulfide inhibition (e.g., 50% inhibition at 8–17 mg/L), while hydrogenotrophic methanogens were favored (Pender et al. 2004). Generally, a community with high diversity has greater capacity to maintain its stability under perturbances. For this reason, a relative higher diversity and evenness in the mesophilic AD leads to stable performance.

Phylogenic analyses revealed the difference in microbial community structure of mesophilic and thermophilic AD. Clustering analysis (i.e., principal coordinates analysis (PcoA)) revealed a clear separation between mesophilic and thermophilic communities (Carballa et al. 2011), suggesting the different evolution pathways of the community in each condition (Fig. 15.6). Kirkegaard et al. (2017) demonstrated a clear distinction between mesophilic and thermophilic AD communities after surveying 32 full-scale AD in 20 WWTPs in Denmark over a 6-year period. The major phyla were shifted from *Bacteroidetes*, *Proteobacteria,* and *Chloroflexi* to *Firmicutes* and *Synergistetes* dominant in thermophilic AD (Jang et al. 2016). The predominance of the phylum *Firmicutes* was because of their capability to produce diverse enzymes performing hydrolysis, acidogenesis, and acetogenesis. Hydrolytic and fermentative bacteria grow more rapidly at higher temperature and could cause the imbalance between the bacterial and methanogens community's population in thermophilic AD. In thermophilic AD, *Thermotogae* (>60%) was the dominant phylum while *Bacteroidetes* (>47%) was highly expressed in mesophilic AD (Guo et al. 2014). The observed results could be due to the phenotype of *Thermotogae* phylum that can thrive at high temperature.

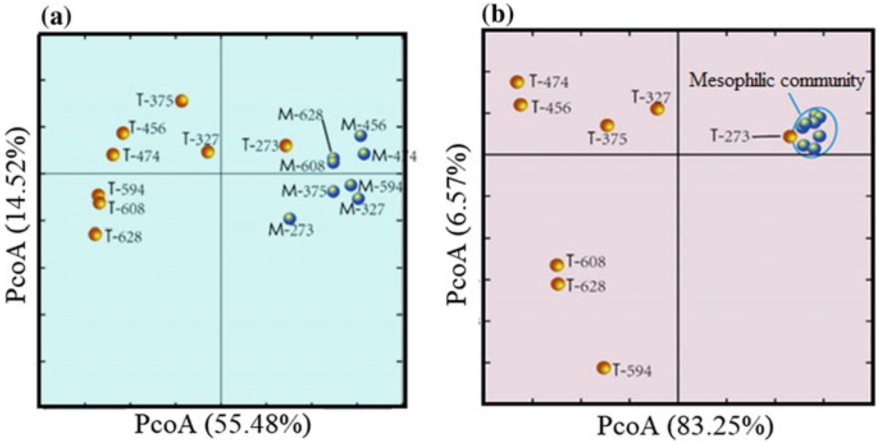

Fig. 15.6 An example of the PcoA plot of **a** archaeal and **b** bacterial communities, indicating the different microbial community structures in mesophilic and thermophilic AD. The data are from Ghasimi et al. (2015)

Different operating temperatures also induced the development of distinct methanogenic community. Mesophilic AD was dominated by the families of *Methanotrichaceae*, *Methanocorpusculaceae*, *Methanoregulaceae,* and *Methanomassiliicoccaceae*, whereas *Methanobacteriaceae* and *Methanomicrobiaceae* were prominent in thermophilic AD (Shaw et al. 2017). This also suggested that the aceticlastic methanogens are dominant in mesophilic AD and hydrogenotrophic methanogens are preferable in thermophilic AD (Ghasimi et al. 2015). Shaw et al. (2017) detected the well-known association between the hydrogen-producing bacteria such as *Ruminococcaceae* and *Prevotellaceae* and hydrogenotrophic methanogens *Methanomicrobiaceae* in thermophilic AD. The shift of methanogenic community from aceticlastic to hydrogenotrophic methanogens at high temperature is currently unclear and future research is required. Overall, temperature is one of the most significant factors determining the microbial community diversity and structure.

15.3.2 Organic Loading Rate

Organic loading rate (OLR) can have a profound impact on the microbial community diversity and structure. Microbial community diversity often decreases under high OLR (Jang et al. 2016; Kundu et al. 2013). Aceticlastic and hydrogenotrophic methanogens are especially affected under this condition. For instance, the underrepresentation of aceticlastic and hydrogenotrophic methanogens was observed under the increase of OLR from 2.22 to 6 kg COD/m^{3}d in both mesophilic and thermophilic AD (Kundu et al. 2013). On the other hand, the phylum *Firmicutes* is often overexpressed under high OLR. For example, the population of *Firmicutes* increased from 4 to 48.4% when OLR changed from 2.7 to 7.2 kg COD/m^{3}d. Two- and threefold increase in the abundance of *Firmicutes* was observed in AD of glycerol, fat oil, and grease with high OLR (Ferguson et al. 2016). The phylum *Firmicutes* were significantly enriched when OLR is increased from 2.74 to 4.12 kg VS/m^{3}d (Sun et al. 2017). Bacteria of phylum *Firmicutes* are capable of degrading VFAs to acetic acid. Under a high OLR, VFA productions are accelerated which would favor the growth and reproduction of *Firmicutes*. Accordingly, it has been indicated that the increase of *Firmicutes* was correlated with deterioration in methane production, suggesting that the *Firmicutes* abundance could be an indicator of process overloading and fluctuated performance.

After the phylum *Firmicutes*, *Bacteroidetes* is the second most enriched under increased OLRs. *Bacteroidetes* spp. is mainly involved in hydrolysis and acidogenesis in AD. An elevated OLR provides substrates for growth. Prevalence of *Bacteroidetes* was observed in AD of macroalgae biomass associated with high protein content due to OLR increase (Sun et al. 2017). The profound abundance of *Bacteroidetes* could lead to the high production of VFAs in the digester (Regueiro et al. 2015).

Phyla such as *Proteobacteria*, *Synergistetes*, *Spirochaetes*, *Chloroflexi*, *Thermotogae*, *Actinobacteria,* and *Planctomycetes* show variable patterns in response to the OLR changes. OLR increase could suspend the growth of *Proteobacteria* and *Chloroflexi* phylum from 23.8 to 5.4% and 14.5 to 2.5%, respectively (Chen et al. 2014). The abundance of *Proteobacteria* increased from 6.7 to 14.5% when there is an increase in OLR from 1.37 to 2.74 kg VS/m^{3}d but dropped to 1.9% at OLR of 4.12 kg VS/m^{3}d (Sun et al. 2017). Similarly, *Synergistetes* was significantly suspended at 300% increase in OLR. The varied reaction of different phyla to change in OLRs reflects the wide array of microorganisms in AD with different tolerance levels to environmental pressures.

Methanogenic community shows different degrees of disturbances by OLR stress. *Methanosarcina* increased from 2.9 to 22% under overloading condition, whereas *Methanosaeta* decreased by approximately 50% (Fig. 15.7) (Razaviarani and Buchanan 2014). Also, the methanogenic community shifted from *Thermoplasmata* (24.4%), *Thermoprotei* (18.0%), and *Methanobacteria* (30.8%) to *Thermoplasmata* (70.4%) and *Methanomicrobia* (16.8%) (Chen et al. 2014) at high OLR. Lerm et al. (Lerm et al. 2012) revealed the enrichment of hydrogenotrophic methanogens (*Methanospirillum hungatei* and *Methanoculleus receptaculi*) under high OLR. However, in some cases, a stable methanogenic community has been reported. High-solid AD of municipal sewage sludge under OLR range of 3.4–5.0 g VS/Ld does not affect methanogenic community and methane yield (Gómez et al. 2011). It is suggested that there exists a critical level of OLR increase. Overall,

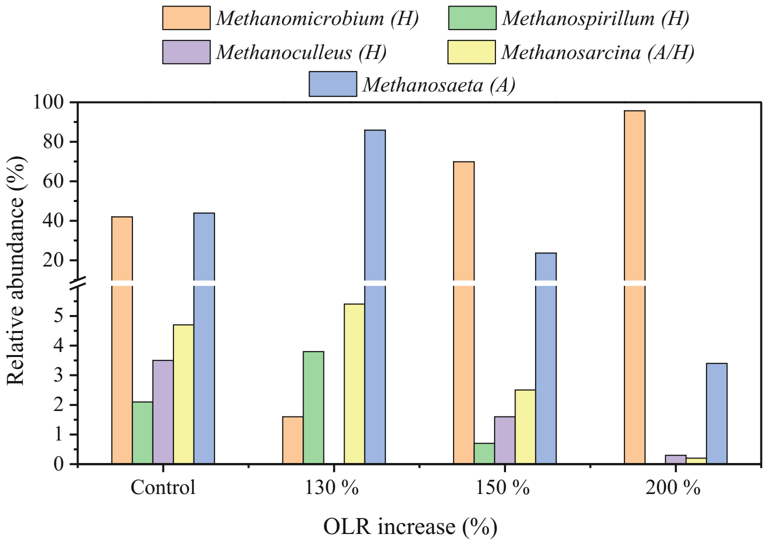

Fig. 15.7 Dynamic changes of methanogenic genera abundance under the different OLR increase (%). The data were extracted from Razaviarani and Buchanan (2015). The letters in the parentheses H and A indicate the hydrogenotrophic and aceticlastic methanogens, respectively. The relative abundance of each taxon was calculated against the total methanogenic population

maintaining the OLR of AD is highly recommended to ensure the stability of microbial community and system performance. In case of changing OLRs (i.e., addition new substrates and co-digestion), detailed evaluations on the maximum OLR at which the resilience of AD community could be maintained are required.

15.3.3 Cell Retention Time

CRT is an important operational parameter (Appels et al. 2008). Determination of approximate CRT has an important value on operational points. Overly long CRT could reduce the digester capacity while too short CRT could decrease the treatment efficiency because of biomass washout (Amani et al. 2010; Vanwonterghem et al. 2015).

Low CRT could result in the reduction of microbial community diversity in AD. However, no report on the change of community diversities could be retrieved from the literature at this stage. A few studies reported the shifts in the microbial community structure under different CRTs. The population of phylum *Bacteroidetes* was significantly enriched from 12.5 to 22% when CRT was decreased from 20 to 5 days (Lee et al. 2011). The enrichment of *Bacteroidetes* is consistent with the increase in OLR as lower CRT means higher OLR into the digester. This observation further reconfirms that there is favorable growth of phylum *Bacteroidetes* under high substrate levels. Meanwhile, loss of the bacteria in the phylum *Chloroflexi* occurred when CRT was decreased from 20 to 4 and 5 days. The *Chloroflexi* sp. is capable of degrading persistent organic compounds but they need longer time for the degradation.

In comparison to the bacterial community, methanogenic community is profoundly affected by low CRT due to its slow growth rate. CRT of below 5 days is insufficient for a stable digestion due to the accumulation of VFAs and washout of methanogens (Appels et al. 2008). Accumulation of propionate was observed in a digester operating at CRT of 8 days due to the washout of syntrophic propionate oxidizers (Vanwonterghem et al. 2015). Similarly, the *Archaea* gene copies significantly decreased under short CRT, indicating the washout of methanogens (Lee et al. 2011). It is recommended that CRT cutoff should be above 10 days (Ju et al. 2017; Appels et al. 2008) for a stable performance. This value is subject to change depending on substrate complexity.

15.3.4 Substrate Characteristics

In recent years, concern about climate change and energy security has renewed the interest in AD as a platform for renewable energy production for organic wastes (Nghiem et al. 2017). Arrays of organic wastes have used the AD process for biogas production enhancement. Although the benefits of AD of organic wastes have been well documented, little is known about the effect of different substrates on AD microbial community. Thanks to the development of high-throughput sequencing technology, more studies have focused on revealing the microbial community diversity and structure in AD. This section provides a summary of such studies performed within the last 5 years on some of the most common substrates.

Lipid-rich substrates. Lipid-rich substrates are from various sources such as dairy industry, food processing industry, slaughterhouses, restaurant oil trap, and vegetable oil/fat refineries. The anaerobic hydrolysis of lipids produces mainly long-chain fatty acids (LCFA). Although this process occurs rapidly, the subsequent step of LCFA oxidation via β-oxidation process is slow. Due to the mismatch between LCFA production and consumption, AD of lipid-rich substrates influences the microbial community, specifically the methanogens.

Co-digestion of lipid-rich substrates such as fat oil and grease with sewage sludge (SS) increased both bacterial and archaeal richness (Yang et al. 2016; Ziels et al. 2016). Adding 10% (VS) of fat, oil, and grease (FOG) into the digestion of SS increased the community richness from 6.2 to 8.5 (Simpson index) (Amha et al. 2017). Bacterial community structure reacts faster than the methanogenic community does in response to the addition of fat, oil, and grease. For example, the population of bacteria involved in the hydrolysis and acidification was higher in the AcoD of fat, oil, and grease compared to the mono-digestion of SS (Fig. 15.8). The complementarity between two substrates results in the better nutrient balance and provides the greater opportunity for microbial growth over the mono-digestion. The phylum *Firmicutes* was enriched in the AcoD of fat, oil, and grease and SS from 22.9 up to 56.5, 32.6, and 10.4% with fat, oil, and grease addition increase of 1, 2, and 3 g VS, respectively. Fatty-acid oxidizing bacteria *Syntrophomonas* was significantly enriched within the bacteria community from 3 to 14% after FOG addition (Fig. 15.8a) (Ziels et al. 2016).

Significant changes in the methanogenic community were observed in the AcoD of fat, oil, and grease. Hydrogenotrophic *Methanospirillum* was enriched from 1.3 to 34% (Fig. 15.8a). Another strictly aceticlastic methanogen, *Methanosaeta*, was also out dominated in the fat, oil, and grease co-digestion (Ziels et al. 2016). The enhancement of these genera was positively correlated with biogas production, suggesting their roles in the AD of fat, oil, and grease. The Bray–Curtis dissimilarity values between the control and fat, oil, and grease digester were significantly different, suggesting the shift of the community (Fig. 15.8b). Similarly, Yang et al. (2016) demonstrated the dominance of *Methanosaeta*—a genus of *Methanosarcinales* order—in AcoD of fat, oil, and grease and SS. The abundance was positively correlated with the biogas production in the redundancy analysis (RDA).

Changes in the microbial community were found to be similar in the AD of pig/cattle slaughterhouse wastes. The enrichment of fatty-acid oxidizing bacteria such as *Syntrophomonas* sp., *Coprothermobacter* sp., and *Anaerobaculum* sp. occurred under digestion of pig/cattle slaughterhouse wasters (Palatsi et al. 2011). Palatsi

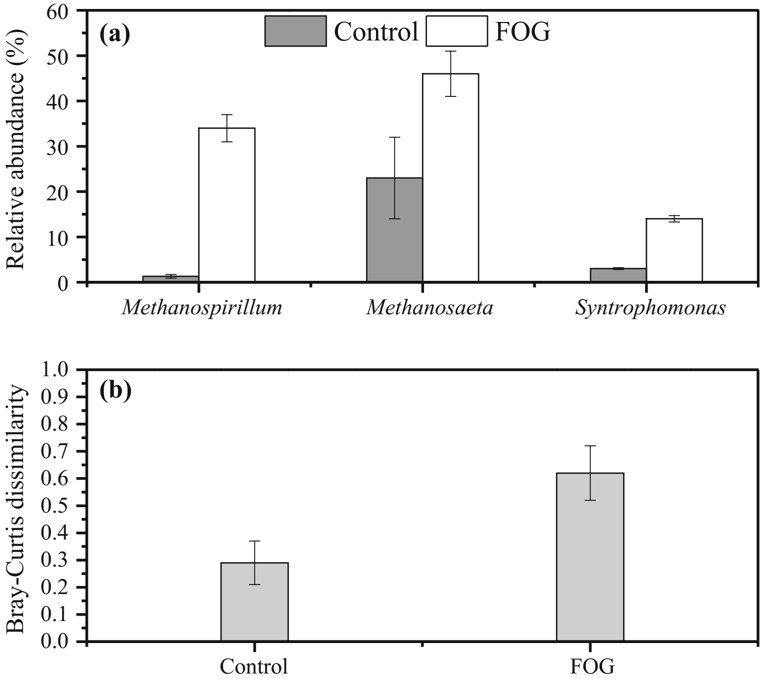

Fig. 15.8 The relative abundance of three major genera, which showed significant enriched under FOG digestion (**a**). The Bray–Curtis dissimilarity indicated the shift of methanogenic community under FOG co-digestion (**b**). Data were extracted from **a** and **b** Ziels et al. (2016)

et al. (2011) demonstrated the syntrophy between the *Syntrophomonas* and *Methanosarcina* in the digester feeding with high lipids content wastes.

Carbon-rich substrates. Addition of carbon-rich and nutrient-rich substrates in AcoD has demonstrated increased biogas production due to their complementary effects (Nghiem et al. 2017; Wickham et al. 2018). The addition of carbon-rich substrates also affects the digester community. AcoD of food waste strongly affects the microbial community diversity and structure. A gradual decline in community richness and evenness was observed upon a stepwise increase of food waste (Xu et al. 2017). Shannon index decreased from 9.42 in control to 5.21 in digester with 57% food waste addition (OLR %) together with the disappearance of 3787 Observed species. Addition of food waste induced profoundly the growth of substrate-favorable groups in the digester. The microbial community diversity and evenness decreased with food waste addition and the degree of decrease was proportional with the increased food waste ratio (Jang et al. 2016).

Two bacterial phyla, *Firmicutes* and *Actinobacteria,* showed the most distinctive change under the addition of food waste. The phylum *Firmicutes* outcompeted others with an increase of abundance from 14.5 to 56.5% at 40% food waste addition (OLR %), but their abundance decreased to 10.4% when added food waste at 57%. On the other hand, *Actinobacteria* population gradually increased with the increase of FW addition. Their population peaked at 56%. The results suggest that bacteria of phylum *Actinobacteria* are favorable to high organic loading stress. In another study of AcoD food waste and waste activated sludge, the phylum *Bacteroidetes* increased significantly from 10.6% (control) to 39.8, 46.3 and 45.8% with food waste addition of 25, 50, and 75% (VS ratio), respectively (Jang et al. 2016). It was suggested that the substrate characteristics and mixing ratio were highly related to the development of various phyla in different studies.

Adding food waste caused the dominant population of the methanogenic community to shift from *Methanosarcina* to *Methanosaeta*. The abundance of *Methanosaeta* increased from 3.7 to 36.1%, indicating their tolerance under high OLR. Of note, the bacterial community was affected more by excessive food waste addition in comparison to the methanogenic community. This suggested the high tolerance of methanogenic community to high food waste levels, but the reasons behind this remain unclear (Xu et al. 2017).

Lignocellulose-rich substrates. Plant-based or “lignocellulosic” substrates such as grass silage, pulp and paper mills wastes, hay, bagasse, and agricultural residues are considered the most abundant raw materials for biogas production in the AD process (Anwar et al. 2014; Shrestha et al. 2017). Lignocellulose is a matrix of biopolymers including cellulose, hemicellulose, and lignin. The AD of lignocellulose-rich substrates is limited mainly due to the complex chemical structure (Shrestha et al. 2017). Cellulose is a crystalline microfibril that is insoluble and difficult to degrade. The microfibrils are attached to hemicellulose, which is a polymer of various sugars. Lignin is crosslinked with cellulose and hemicellulose providing a rigid structural support to the biopolymer matrix. To achieve the desired performance, the AD of lignocellulosic substrates often required pretreatment and co-digestion.

Only a few reports on the microbial community in the AD of lignocellulosic substrate are available. The microbial community is less diverse in the AD of lignocellulosic substrates probably due to the substrate recalcitrant that limits the growth of many microorganisms. The community in the AD treatment of xylose, xylan, and cellulose was less diverse than that of the AD treatment of food waste (Wilkins et al. 2015). The phylogenetic structure of the AD process treatment of lignocellulosic substrates mainly contains the phyla *Firmicutes* and *Bacteroidetes* (Azman et al. 2015). The phylum *Firmicutes* accounted for 97% of the total in AD of waste papers (Tsavkelova et al. 2018). The population of phyla *Firmicutes* and *Bacteroidetes* was above 65% in four different digesters treatment of corn stover (Liu et al. 2018). These observations suggest the role of bacteria in the phyla of *Firmicutes* and *Bacteroidetes* in the hydrolysis of lignocellulosic substrates.

15.3.5 Inoculum Sources

The effect of inoculum sources on the AD process has been demonstrated in a number of studies (Gu et al. 2014; Ventorino et al. 2018; Han et al. 2016; Liu et al. 2017). Gu et al. (2014) compared six different inocula including digested dairy manure, digested swine manure, digested chicken manure, digested municipal sludge, and anaerobic granular sludge. All the inocula were used in the batch digester treatment of rice straw with the same inoculum-to-substrate ratio of 1:1 (VS content). Digested dairy manure was found to be the best inoculum among six different inocula. Liu et al. (2017) observed significant differences in methane production when compared to three inocula (digested municipal sludge, digested stillage, and digested manure) in a biomethane potential test with inoculum and substrate (cellulose) ratio of 4:1 VS content.

Inoculum is microbial source for the AD process. The AD microbial community resembles their respective source of inoculum. Han et al. (2016) used four inocula from stillage, manure, paper milling, and wastewater sludge digesters. All the inocula were used for the digestion of cellulose. The results indicated similar compositions of inoculum and digester microbial community. However, the microbial community diversity decreased in the digester in comparison to the inoculum. On the other hand, De Vrieze et al. (2015a) observed that the digester community has higher richness than inoculum community. The reason is probably due to the variation in the substrates in different studies.

Liu et al. (2017) observed the effect of inoculum only at the initial state (one cell retention time). Over time, the digester performance and digester community were comparable among four different inocula sources. The authors suggested that under a long operation period, substrate characteristics and operation condition driven the digester performance and community structure rather than the inoculum sources. De Vrieze et al. (2015a) also observed that the microbial community evolved toward a similar composition in five digesters initially inoculated with five different inocula.

The effect of inoculum source on the digester community resilience has also been reported (De Vrieze et al. 2015a). De Vrieze et al. (2015a) investigated the resilience of digester inoculated with five different inocula under stress conditions (i.e., high total ammonia nitrogen). The inocula included digested potato waste (I), digested mix maize, lipid and fruit waste (II), digested mix maize and manure (III), digested municipal sludge (IV), and a mixture of abovementioned inocula (V). The results indicated that the effects of total ammonia nitrogen were inoculum dependent. The digesters inoculated with I and II maintained their methane production function, whereas methane production deteriorated in the digester with inocula III, IV, and V at the maximum total ammonia nitrogen tested. This observation is because microbes in inoculum I and II have higher level of adaptation to total ammonia nitrogen. The results suggested that the use of selected or enriched inoculum for typical substrates or operating conditions could enhance process stability.

15.4 Connecting Microbial Community to AD Performance

15.4.1 Microbial Community Diversity and AD Performance

Microbial community diversity indices (i.e., richness and evenness) could probably indicate process performance. A more richness and evenness community indicates the presence of more species that could enhance community resilience toward perturbations (Wittebolle et al. 2009; McCann 2000; Regueiro et al. 2012). On the other hand, less diverse community is susceptible to changes probably due to the high level of specialization (Regueiro et al. 2012). However, to date, the linkage between community diversity and AD performance remains unclear. Indeed, the extent influence of microbial community diversity on AD performance has not been determined. So far, results in the literature are still inconsistent. Venkiteshwaran et al. (2017) showed no correlation between digester performance (i.e., CH_4 production), community richness, and evenness. Similarly, Li et al. (2015) compared the community diversity at stable and deteriorated stages and showed no differences in diversity indices between two stages. Their results suggested that diversity indices were not sensitive for process status indication. This limitation is probably because the diversity indices are statistical data to describe the community diversity without consideration of its compositions (Li et al. 2015; Dearman et al. 2006). No correlation between Shannon index (i.e., evenness) and methane yields has been reported (Fig. 15.9) (Jang et al. 2016; Xu et al. 2017). On the other hand, some studies have claimed that the microbial community evenness relates with the digester function (Lee et al. 2017; Carballa et al. 2011). Carballa et al. (2011) demonstrated that the digester with higher evenness in the bacterial community achieved a higher biogas production. Lee et al. (2017) observed a positive correlation between bacterial evenness and COD removal. Wittebolle et al. (2009) reported that the initial community richness and evenness were the key factors to preserve the community function under perturbation conditions, although this study was not done with the AD process. Due to the inconsistency, richness and evenness index need to be carefully considered as process indicators. More data from the future studies, especially on those that use high-throughput sequencing technologies, are needed to unmask potential trends. It is also suggested that future studies should focus on the methanogenic community given that it has lower diversity in comparison to bacterial community. Until then, the finding of the community diversity and digester performance relationship can be used to indicate proactive AD performance.

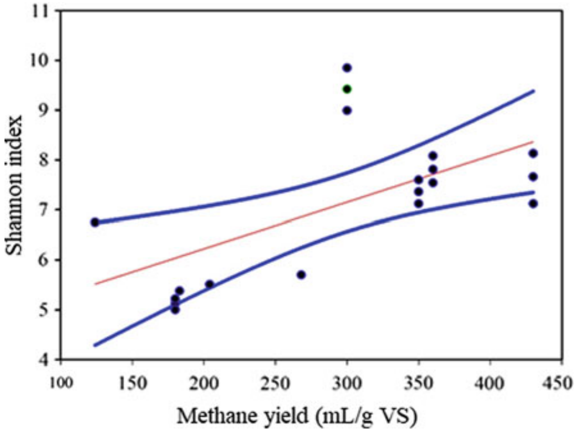

Fig. 15.9 A linear regression analysis of Shannon index and methane yield with ±95% confidence intervals. The data retrieved from Jang et al. (2016) and Xu et al. (2017). The plot (R^2 = 0.37) indicates diversity index that cannot be used to predict digester performance. The red line and the space between two blue curves are the linear regression and the boundary of ±95% confidence intervals, respectively

15.4.2 Microbial Community Structure and AD Performance

Information on the relationship between AD microbial community structure and its function has gained much attention recently as they can be applied to potentially engineered AD with superior functions (Werner et al. 2011) or to indicate process stability (de Jonge et al. 2017).

The AD microbial community naturally shows degrees of variation at constant operating conditions. In other words, there is a degree of variation in community population in a functionally stable community. Variation (i.e., presence and/or variation of specific organisms) due to changes in environmental variables must be larger than naturally occurring changes. Previous sections in this chapter have defined a list of genera that showed significant variation under changes in environmental variables. These include phyla of *Firmicutes*, *Bacteroidetes,* and *Actinobacteria* (hydrolytic and fermentative bacteria), *Syntrophomonas* and *Synergistetes* (acetogenic and syntrophic acetate oxidizing) and *Methanosaeta*, and *Methanoculleus* (methanogens). Consequently, a few studies have reported the linkage between microbial community structure and AD performance.

Analyzing the microbial community compositions at stable and deteriorative stage, Li et al. (2015) revealed the correlation between microbial community structure and process stability. Syntrophic fatty oxidizing and acid producing bacteria outcompeted other bacteria at the deteriorative stage. The mismatch between acid production and consumption were accounted for system deterioration. Regueiro et al. (2012) observed that hydrolytic and methanogenic activities linked with the high abundance of *Bacteroidetes* and *Archaea*. Lignocellulose-degrading microorganism population was correlated with biogas production in the AcoD of food waste and wheat straw (Shi et al. 2018). Yang et al. (2016) provided the details positive correlations between the *Methanosaeta* and biogas production. The hydrogenotrophic *Methanobacteriales* correlated with biogas production in 29 full-scale digester studies, confirming their role in maintenance of digester function (De Vrieze et al. 2015b). Negative correlation between community structure and AD performance has also been reported. High level of VFAs led to the reduction of syntrophic acetogenic bacteria (Peng et al. 2018). Ziels et al. (2016) suggested to track the syntrophic LCFA-degrading bacteria abundance to regulate the loading rate of fat, oil, and grease into the AD. Understanding the linkages between community structure and AD performance provide estimation of thresholds at which the function and resilience of the AD process are maintained.

15.5 Summary and Future Outlook

This chapter reviews recent literature to provide new insights into microbial ecology in the AD process. The information include microbial community driven the AD process, factors influencing the microbial community diversity and structure, and the linkages between microbial community and AD performance. The available studies suggest that the community diversity and structure are different among digesters. This may be due to the greater variety of abiotic factors such as temperature, OLR, CRT, substrate characteristics, and in biotic factor such as inoculum sources among digesters. Despite these variations, some common observations from this chapter are the following:

(i) Bacteria in the phyla of *Firmicutes*, *Actinobacteria*, and *Bacteroidetes* dominate the AD microbial community.
(ii) The population of bacteria in the phyla of *Firmicutes*, *Actinobacteria*, and *Bacteroidetes* varies profoundly when the AD process experiences a changing condition.
(iii) Altering the operating conditions (e.g., increased OLR and adding co-substrates) positively affects the microbial community diversity and structure beyond a threshold.
(iv) The methanogenic community is more susceptible to environmental variables in comparison to the bacterial community. The reason is mainly due to the higher diversity and functional redundancy of the bacterial community.

Understanding the connection between microbial community and AD performance can provide intuitive information for optimization of the AD process. Future interactions between microbial ecologists and environmental engineers in combination with the availability of new methods to characterize microbial community could offer opportunities to integrate microbial community and performance into a unified picture. This information could be used to design, maintain, and operate a more efficient AD.

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Chapter 16
Emissions of Volatile Organic Compounds from Solid Wastes and Leachate at a Municipal Solid Waste Dumpsite in Thailand

Chart Chiemchaisri, Wilai Chiemchaisri and Maneerat Boocha

Abstract In this study, volatile organic compounds (VOCs) contamination in solid wastes disposed at a municipal solid waste dumpsite in Thailand was investigated. Due to poor upstream segregation, several volatile organic compounds such as benzene, toluene, ethylbenzene, and trichloroethylene were detected in yard wastes, food wastes, plastic wastes, and foam wastes components. Their concentrations were found varied from 1 to 5 mg/kg of solid wastes, being highest in fresh wastes and reduced according to the age of wastes (between 2 and 7 years) and waste locations (upper and lower parts in the waste pile). Field measurement was used to assess the fate of emission of those compounds from solid waste dumping area (7.4 ha). It was found that benzene was the most emitted compound from the waste pile to the atmosphere whereas trichloroethylene was majorly drained out with leachate form and subsequently emitted to the atmosphere from leachate holding pond. The rising temperature in the waste pile from normal temperature of 40–80 °C during daytime increased the emission of VOCs from the wastes by four folds. Their emissions could be significantly reduced by the provision of cover material and heat management.

Keywords Cover soil · Landfill gas emission · Municipal solid wastes
Open dump · VOCs

16.1 Introduction

More than 60% of municipal solid wastes collected in Thailand in the 2000s are still disposed in an unsanitary way (AIT 2004). As a consequence, it creates environmental quality deterioration such as bad smell, disease outbreak, leachate

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contamination to surface and groundwater bodies as well as harmful gas emissions. The biodegradation of organic matter in solid wastes arises from human activities at solid waste disposal sites also contribute to the release of greenhouse gases such as methane and carbon dioxide. In Thailand, it was estimated that about 115.4 Gg of methane was released from solid waste disposal sites to the atmosphere per year (Chiemchaisri et al. 2007). Globally, about 16–20 Tg of this greenhouse gas was emitted from waste disposal activities (Bogner and Matthews 2003). Additionally, other gases such as volatile organic compounds (VOCs) which contaminated in several domestic and industrial products and waste components are potentially harmful to human and the environment even though they are present at lower concentration. VOCs are organic chemicals that have a high vapor pressure at ambient temperature. They are also characterized by their low water solubility. The most common VOCs found in landfill gas are benzene, toluene, ethylbenzene, and xylenes so-called BTEX compounds. Nevertheless, VOC species can include other compounds such as chlorinated methane, ethane, ethylene, fluorinated hydrocarbons, and aromatic hydrocarbons (Scheutz et al. 2004). Many of them are classified as carcinogenic substances such as benzene, formaldehyde acetaldehyde, etc.

The contamination of VOCs in municipal solid wastes (MSW) can be found in various household hazardous wastes. These wastes, which include household cleaners, automotive product, home maintenance products, and lawn and garden products, can contain many synthetic organic compounds that are toxic, carcinogenic, or otherwise hazardous (Reinhart 1993). When disposed of in landfills, the constituents of solid wastes can be released into landfill leachate and landfill gas. The emissions of VOCs from solid waste landfills varied considerably. Table 16.1 summarizes observed BTEX concentrations in the atmosphere of landfill sites in some selected countries. Among them, the VOC contamination at landfills in Thailand was found at relatively high level. Eklund et al. (1998) estimated global emissions of 13,000 ton of non-methane organic compounds (NMOCs) from solid waste disposal in landfills. The concern of VOC contamination in solid waste and their impact have been increasing at international level. In the US, USEPA has regulated the operation of municipal landfills through Resource Conservation and Recovery Act resulting in about a sharp decrease in VOC emission from the diversion of hazardous wastes from municipal solid wastes. In other means, the implementation of technologies which can be used for reducing VOC emission include adsorption, absorption (scrubbing), thermal/catalytic oxidation and

Table 16.1 BTEX concentrations (μg/m^3) reported in atmospheric landfills

Compounds	China	Hong Kong	Korea	Turkey	Thailand
Benzene	1.2–167.0	7.3–73.0	0.16–115.0	5.6–3138	55–5656
Toluene	1.7–202.0	12.0–113.0	0.16–6218	23.4–10,234	10–4362
Ethylbenzene	0.1–52.0	1.8–24.0	1.78–3100	4.9–3717	28–4997
Xylene	0.3–169.0	6.2–45.7	0.17–4166	7.9–7464	53–4845

Source Na roi-et et al. (2017)

biological treatments could also be helpful. Nevertheless, those VOC mitigation measures are still rarely implemented in developing countries due to the financial constraint.

This chapter presents information from a case study of field investigation of VOC contaminations and their emissions from a solid waste dumpsite. To quantify VOC emissions, major VOC species and their concentrations in landfill gas and leachate emitted from open waste disposal area were analyzed and their emission rates were estimated. The level of VOC contamination in various solid waste components was determined so that the fate of their release as gaseous and leachate emissions could be quantified. Furthermore, the effect of solid waste disposal conditions and environmental factors, i.e., moisture content, temperature and age of solid wastes, on VOC emission was also examined.

16.2 Investigation of VOC Emission from Solid Waste Dumping Area

The study was conducted at a solid waste disposal site located in central flat terrain region of Thailand. The site receives 800–100 ton of municipal solid wastes daily since early 1980s. It has a total area of more than 10 ha in which the disposed wastes at the site were accumulated up to more than 1 million cubic meters. Within the waste disposal area, solid waste dumping piles were formed at about 15–20 m depth including the height of about 10 m above ground and 5–10 m below the original ground level. During the raining period, leachate collected from the waste disposal area is gravitationally drained into open channel constructed surrounding the waste disposal area and pumped into a large storage pond of 9560 m^3 volume. That leachate stored in the pond was kept for evaporation during the dry season.

In order to determine VOC emissions from the waste disposal site, gas and leachate samples were collected and analyzed for VOC concentrations using gas chromatography-mass spectrophotometry (GC-MS). Once the major VOC species detected in those samples were determined and their concentrations were then monitored for quantification of their emissions following the methodology described in the literature (Chiemchaisri et al. 2010). Figure 16.1 shows the cross-sectional profile of the solid waste disposal site and underlying soil conditions. The gas concentration profile within the waste pile was determined by collecting gas samples at different depths (0.5, 1.0, and 1.5 m). Leachate samples were also collected from the leachate storage pond and analyzed for their chemical characteristics and VOC concentrations (APHA 1998). Leachate quantity was estimated using Visual Hydrologic Evaluation of Landfill Performance (HELP) software (Waterloo Hydrogeologic Inc.).

Total potential emissions of VOCs from disposed solid wastes were determined by extraction of VOCs in the solid waste samples collected at different depths of 0.5

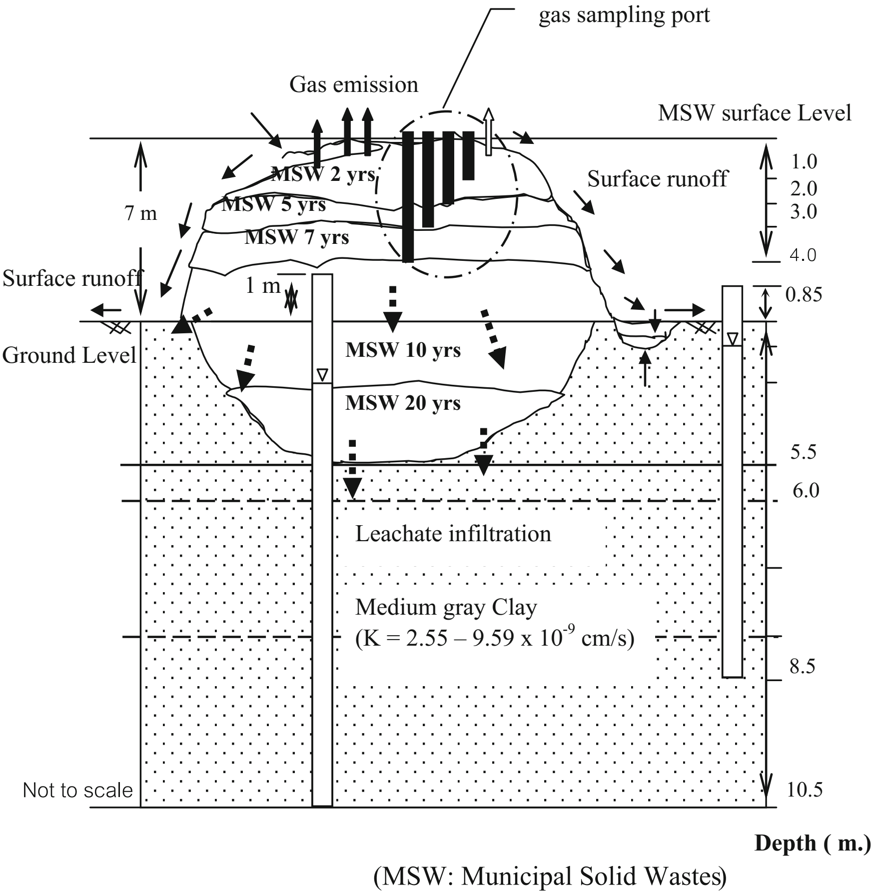

Fig. 16.1 Cross-sectional profile of solid waste dump site and underlying soil condition

and 1.0 m from the waste disposal area. The analyses were performed using purge and trap methods, USEPA SW 846 Method 5035 (USEPA 1996).

The estimation of diffusive VOC emissions was calculated based on their concentration gradients along the depth in the waste pile. The one-dimensional diffusion gas transport equation (Tchobanoglous et al. 1993) presented in the Eq. (16.1) is used.

$$NA = -\frac{D_z \mathrm{d}CA}{\mathrm{d}z} \tag{16.1}$$

where

N_A	Diffusive gas emission rate (g/cm^2 s)
D_z	Vertical gas diffusive coefficient (cm^2/s)
dC_A/dz	Gas concentration gradient (g/cm^3/cm)

Meanwhile, VOC emission from leachate pond was estimated using two-film theory. The mass transfer to water to gas phase are calculated using mass transfer coefficient as described in the Eq. (16.2).

$$N_{\mathrm{VOC},i} = K_{\mathrm{OL},i} C_{\mathrm{L},i} \tag{16.2}$$

where

$N_{\mathrm{VOC},i}$	Evaporation rate of VOC from pond (g/m^2 s)
$C_{\mathrm{L},i}$	VOC concentration in leachate storage pond (g/m^3)
$K_{\mathrm{OL},i}$	Overall mass transfer coefficient of VOC (m/s)

The empirical expressions proposed by Bunyakan et al. (2001) was used to determine the overall mass transfer coefficient of VOCs from an open pond.

In order to determine the contamination of VOCs in solid wastes disposed at the disposal site under various conditions, VOCs were extracted from different waste components, i.e., food wastes, paper, plastic, foam, and yard wastes using open loop stripping (OLS) technique. Furthermore, the waste samples obtained from different disposal conditions, e.g., wet and dry conditions (surface and submerged condition in the waste pile) and different disposal ages (2, 5, and 7 years) were subjected to VOC extraction under medium and high-temperature exposure (40 and 80 °C).

16.3 Characteristics of Solid Wastes and Leachate at Dumpsite

The characteristics of fresh and disposed solid waste samples under different conditions, i.e., disposal ages of 2, 5, 7, 10, and 20 years were determined. The fresh solid waste samples contain food and plastic wastes as their major components whereas plastic bags were mostly found in aged wastes. In Thailand, it is commonly practiced that the leftover food wastes are placed into plastic bag before being discarded into the waste bin. Due to their nonbiodegradable characteristics, plastic bags became the predominant waste components after long-term disposal in dumpsite. The waste density was found varied with disposal ages and depth in waste pile due to compaction from waste settlement. Moreover, moisture content was also increasing with depths, being lowest (3%) at the surface and highest (55%) inside the waste pile.

The monitoring of leachate characteristics which performed regularly twice a year suggest the following results; pH 7.8–9.0, BOD 160–365 mg/L, COD 1280–4640 mg/L, TKN 218–418 mg/L, PO_4^{3-} 0.11–0.33 mg/L, TDS

11,000–12,820 mg/L. The BOD/COD ratio of 0.08 in those leachate samples suggest highly stabilized condition. Substantial biodegradation of highly or moderately biodegradable organic substances would be expected within the waste pile where leachate would be retained over a long period. Nevertheless, their characteristics could not meet the effluent standard specified by the Ministry of Natural Resources and Environment, Thailand (BOD < 20 mg/l, COD < 120 mg/L) and their further treatment in biological/chemical units would be required. For this purpose, an advanced leachate treatment system utilizing chemical coagulation, sand filtration, microfiltration, and reverse osmosis has been demonstrated at the same solid waste disposal site to reduce most pollutants including toxic organic compounds (phenolic compounds and phthalic acid esters) in the landfill leachate to a biosafety level (Theepharaksapan et al. 2011). Meanwhile, all heavy metals examined (Pb, Ni, Cd, Cu, Fe, Mn) in leachate samples were at low levels and well below the standard limits.

16.4 VOC Contamination and Emissions

16.4.1 VOC Contaminations in Solid Wastes

The extent of VOC contamination in municipal solid wastes disposed at the dumpsite was quantified. Major physical components in solid waste samples obtained from different conditions were classified into food wastes, paper, plastic, foam, and yard wastes. VOC extraction of each component was performed at different temperatures of 40 and 80 °C. These extraction temperatures were set according to the fact that the temperature of wastes at the surface was varied between 40 and 50 °C whereas they were found to be 73–80 °C at the mid-depth of the waste pile during daytime.

The contamination of TCE was found highest in fresh waste sample at 15.94 mg/kg. Toluene and benzene were also detected at significant level of 6.46 and 0.47 mg/kg, respectively. The emission of VOC was increased when the temperature rose from 40 to 80 °C. The waste components contributing to higher emissions of VOC were plastic and yard wastes. Meanwhile, the mixed waste sample was also found contaminating high TCE and toluene. Due to poor waste segregation, cross-contamination of VOC took place in a mixture of different waste components. It is anticipated that plastic wastes contribute to significant level of these VOC contaminations. Urase et al. (2008) reported the plastic materials, e.g., polystyrene instant noodle cup released the highest amount of VOCs and estimated the total release of VOCs of 40 mg from 1 kg of noodle cup at 80 °C.

For aged wastes of 2 and 5 years old, toluene contamination was found highest followed by TCE and benzene at 2.56–6.90, 2.29–6.88, and 0.14–1.64 mg/kg. The VOCs were found contaminated in all waste components, i.e., plastic, paper, and foam. In 7 years old wastes, TCE, toluene, and *o*-xylene were the major VOCs

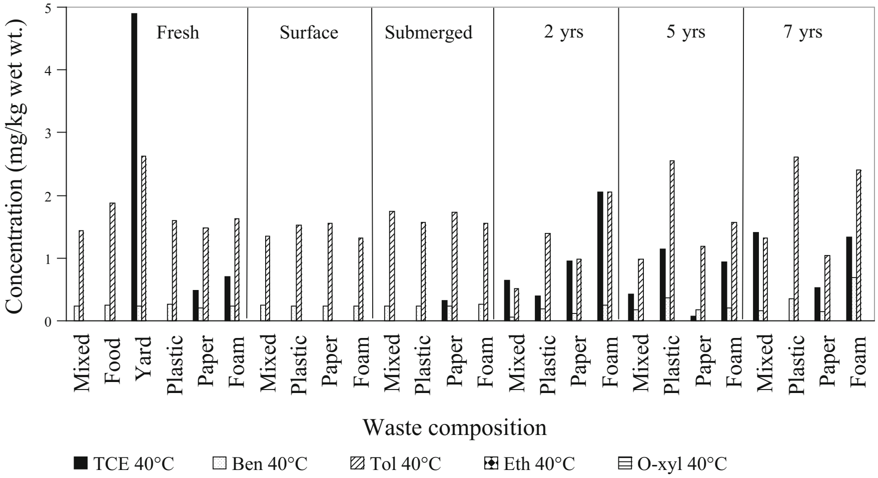

Fig. 16.2 VOC concentration contaminated in solid wastes under different disposal conditions

detected at 5.13, 3.20, and 2.41 mg/kg. There was not much difference between the contaminations of VOCs in solid wastes of different ages (Fig. 16.2).

For the same waste age (2 years old), the contamination of VOC in solid wastes at the surface of the waste pile was found lower than those in submerged wastes at mid-depth of waste pile. Toluene, TCE, and *o*-xylene contaminations were 1.69, 0.96, and 1.64 mg/kg at the surface and 4.30, 9.85 and 1.72 mg/kg at mid-depth of waste pile, respectively. Figure 16.3 shows VOC concentration found contaminated in solid waste samples of different ages and disposal conditions (at 40 °C extraction temperature). From the results, it was found that the rising of temperature in the waste pile from 40 °C (average temperature) to 80 °C (maximum temperature detected within waste pile during daytime) increased the emission of VOCs from the wastes by about four folds. Zou et al. (2003) also reported that VOC emissions from a Chinese landfill in summer were a 1–2 order of magnitude higher than those in the winter period.

16.4.2 VOC Concentrations in Gas and Leachate Emitting from the Dumpsite

The analyses of VOC in gas samples suggest that benzene, toluene, *m*/*p*-xylene, *o*-xylene were predominant in the samples (Table 16.2). Among them, toluene was detected at highest concentrations followed by *m*/*p*-xylene. Their concentrations were found increasing with sampling depth from surface. For leachate samples, the most frequently found VOCs were benzene, toluene, ethylbenzene, *o*-xylene at 50–100%. The concentrations of TCE and toluene were found higher than other VOC

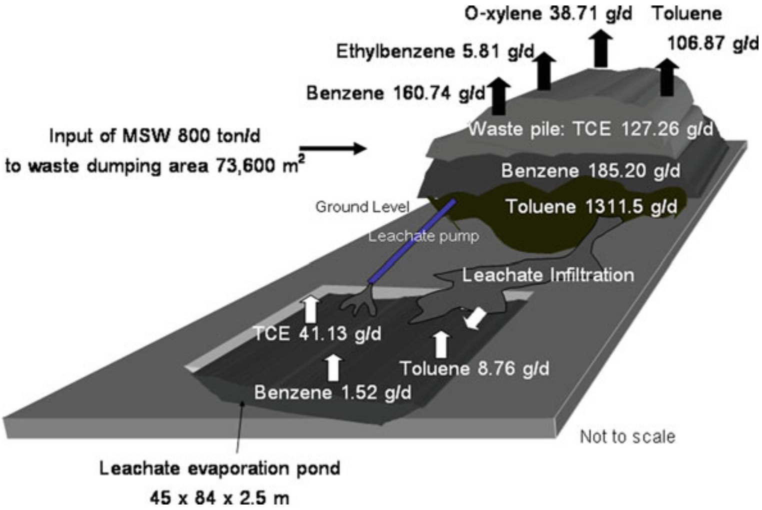

Fig. 16.3 Fate and rate of VOC emission from the solid waste open dump site

compounds. Meanwhile, ethylbenzene was not detected in both gas and leachate samples. Tong et al. (2008) studied volatilization behavior of BTEX compounds on different underlying materials and reported that volatility speed of BTEX compounds was benzene > toluene > mixture of BTEX compounds > ethylbenzene. Their volatility speed from water was faster than sand and soil. The underlying materials acted on volatilization of VOCs were mainly through increasing volatility area and influence on the available of pore during the volatilization.

16.4.3 VOC Emission Rate from Solid Waste Dumpsite

The emission rates of VOC (BTEX and TCE) from the waste pile to the atmosphere is presented in Table 16.3. From the analyses of VOC concentrations in gas

Table 16.2 VOC concentrations in gas and leachate samples at waste disposal area

Compounds	Gas (μg/m^3) @ depth from surface			Leachate (mg/L)
	0.5 m	1.0 m	1.5 m	
Benzene	250	301	703	0.38
Toluene	337	4112	25,979	1.35
m/p xylene	51	147	1712	0.19
o-Xylene	31	217	768	ND
Trichloroethylene	ND	ND	128	6.32

ND Not detected

samples obtained from the waste pile at different depths, highest concentrations of benzene, toluene, *o*-xylene, and ethylbenzene were detected at 4 m depth at 16,500, 13,100, 4500, and 500 μg/m^3, respectively. The diffusive surface emission rates of benzene, toluene, *o*-xylene, and ethylbenzene were then estimated at 21.84×10^{-4}, 14.52×10^{-4}, 5.26×10^{-4}, and 0.79×10^{-4} g/m^2 d, respectively. In leachate storage pond, the concentration of TCE was found highest at 6.31 mg/L followed by toluene, benzene at 1.35 and 0.38 mg/L whereas ethylbenzene and *o*-xylene concentrations were not detected. The estimation of VOC emission from open leachate storage pond was 7.21 g/m^2 d for TCE, 0.53 g/m^2 d for benzene and 2.08 g/m^2 d for toluene, respectively. Bunyakan et al. (2006) also demonstrated that the emission of VOCs from water surface depends on wind speed and water depth. Nevertheless, the condition of deep storage pond (2.5 m) and low wind speed (<2.4 m/s) would not have a significant impact on accelerating VOC volatilization at the studied dumpsite.

The determinations of total VOC (BTEX and TCE) emission through direct gaseous diffusion from the waste pile and evaporative emission rates from the leachate storage pond are presented in Table 16.3. For the basis of this calculation, actual waste disposal area (73,600 m^2) with constant fresh wastes input (800 ton/day) and leachate production were assumed. The VOC emissions were evaluated at different temperatures between 40 and 80 °C, the actual variable temperature detected in the waste pile at the site. The quantity of leachate from the whole dumping area was estimated at 6.51 m^3/d.

From the investigation, TCE was found only emitting from leachate pond through evaporation at a rate of 41.1 g/d. This emission accounted for 32.3% of total TCE released from the wastes during the laboratory extraction (127.3 g/d at 40 °C). For TCE, there was no significant direct gaseous emission observed. Its behavior was much different from that of benzene where direct emission to the atmosphere from the waste pile was the predominated emission pathway (86.8%). Meanwhile, the emissions of ethylbenzene and *o*-xylene were found to be similar to that of benzene. The elevated temperature (to 80 °C) in the waste pile increased their emission rates from the site significantly se compounds were emitted from the waste only at high temperature. Figure 16.3 demonstrates the emission of major VOCs from the studied site.

Table 16.3 Determination of VOC in solid wastes and their emissions

VOCs	VOCs in solid wastes (g/d)		Direct gaseous emission		Diffusive emission through leachate	
	40 °C	80 °C	g/d	%	g/d	%
TCE	127.3	550.1	0.0	0.0	41.1	32.3
Benzene	185.2	595.3	160.7	86.8	1.5	0.8
Toluene	1311.5	2902.6	85.4	6.5	8.8	0.7
Ethylbenzene	ND	9.2	5.8	63.3	0.0	0
o-Xylene	ND	38.8	38.7	99.7	0.0	0

16.5 Mitigation of VOC Emission from Solid Waste Dumpsite

In order to reduce those VOC emissions from the dumpsite, mitigation of direct emission of BTEX compounds and TCE contamination in leachate should be minimized. Most simple method for reducing the emissions would be the provision of natural cover materials over the waste dumping area. Chiemchaisri et al. (2010) have demonstrated that the use of sandy loam or clay cover soil could reduce the BTEX emissions from waste dumping by 60–99%. Adsorption of BTEX compounds by soil particle was the main mechanism for reducing their emissions during which moisture content played an important role in regulating their adsorption capacity. Scheutz et al. (2004) also revealed that the reduction of VOC emissions through final cover soil could be due to their biodegradation occurred in parallel with methane oxidation reaction. Ortiz et al. (2003) also demonstrated the use of natural materials such as peat and tree bark for eliminating BTEX compounds in biofilter with 85% removal efficiencies at empty bed residence time of 60 s.

The provision of cover material would also help to reduce leachate quantity significantly. Thus, the release of TCE together with leachate could be minimized. The collection of leachate drained from the waste disposal area and provision of proper natural treatment method would also help to eliminate the remaining VOCs effectively (Thörneby et al. 2006).

On the other hand, it was recommended that appropriate heat management in landfill sites is an important countermeasure to avoid unusual high emission of VOCs because the heat generated by the biodegradation of organic solid wastes may promote the release of VOCs especially in the case of sites that receive biodegradable and plastic waste materials (Urase et al. 2008).

16.6 Conclusions

VOC contamination in municipal solid wastes at a solid waste disposal site in Thailand was investigated. BTEX (benzene, toluene, ethylbenzene, and xylene) compounds were the major VOCs among which toluene concentration was found highest in both gas and leachate samples. For benzene, ethylbenzene, and *o*-xylene, direct emission to the atmosphere from the waste pile was the major emission route whereas TCE was found mainly emitting from the surface of the leachate storage pond. The provision of appropriate cover material to reduce their emissions are recommended together with appropriate heat management in the waste disposal site.

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Chapter 17
The Role of Microbes in Chromium Bioremediation of Tannery Effluent

Pratishtha Gupta, Rupa Rani, Avantika Chandra, Sunita Varjani and Vipin Kumar

Abstract Leather-based industries utilize nearly 90% of chromium-containing tanning agents for converting raw skin/hides into leather. Apart from chromium, different metals such as iron, aluminum, zircon, and titanium are also used for various tanning applications. Tannery wastewater is highly complex and contains high amount of inorganic, organic, and dissolved solids including chlorides and sulfates. The chromium present in the effluent can have adverse effects on the environment. Hence, the treatment of effluent before releasing it into the environment becomes an important issue. Bioremediation is a recent technique for treatment and disposal of industrial wastewater. This approach is advantageous as compared to conventional treatment methods which are costly, time-consuming, and generate toxic end products. Bioremediation is the potential, cost-effective, and environmental-friendly technique that uses several microbes in treatment of wastewater, soil, and sediments. Hence, this chapter focuses on the role of microbes in chromium remediation from tannery effluent. This chapter will also focus on the various mechanisms such as biosorption, bioaccumulation, and microbial reduction of chromium by microbial cells.

Keywords Leather · Heavy metals · Biosorption · Bioaccumulation
Microbial reduction

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17.1 Introduction

Chromium is widely used in different industrial purposes such as leather tanning, electroplating, paints and pigment synthesis, metallurgy, and petroleum products synthesis. Of the various oxidation states, Cr (III) and Cr (VI) are predominantly present in the environment (Kimbrough et al. 2010). Cr (III) is an essential trace metal but forms strong complexes with oxygen. Cr (VI) is the most toxic, carcinogenic, and mutagenic in nature. It causes skin irritation, respiratory problems, and eye diseases in humans (Cefalu and Hu 2004).

Tanning is one of the oldest and fast expanding industries in India. The effluent released from tanning process contains large amount of inorganic and organic compounds specifically rich in chromates and sulfates (Durai and Rajasimman 2011). The maximum tolerance limit for chromium in drinking water and inland surface water is fixed at 0.05 and 0.1 mg/L (WHO 2004), respectively, whereas chromium in industrial discharge ranges from 0.1 to 400 mg/L. Therefore, treatment of effluent for pollution abatement becomes necessary.

Conventional methods such as reverse osmosis, precipitation, adsorption, ion exchange, and filtration used in treatment of wastewater streams are costly and environment harming methods requiring high energy and large amount of chemicals (Malik 2004). Biological approaches in contrast to conventional methods are environmentally sustainable, cost-effective, and cheap. The use of microbes and microbial-associated processes in remediation of chromium from wastewater streams is gaining insight in present time (Mani and Kumar 2014). The present chapter deals with the comprehensive assessment on the potential of microbes in remediation of chromium from tannery effluent. In this chapter, different microbial-associated processes such as biosorption, bioaccumulation, and microbial reduction in remediation of chromium are described.

17.2 Chromium Toxicity to the Environment

Chromium is 17th most abundant element in the Earth's mantle. It is widely used in different industries such as electroplating, tanning of leather hides, alloying, textile, ceramics, and pigments (Bhalerao and Sharma 2015). Among the various oxidation states of Cr, the most stable and common forms are Cr (III) and Cr (VI). Trivalent form of Cr is less toxic, insoluble in water, has low mobility, and is mainly bound to organic matter in soils (Shadreck and Mugadza 2013). Cr (VI) mainly exists as CrO_4^{2-} and CrO_3 is the toxic, highly soluble form of Cr and can cross the membrane of living organisms. At high oxygen or Mn concentration, Cr (III) can be oxidized to Cr (VI) (Fig. 17.1).

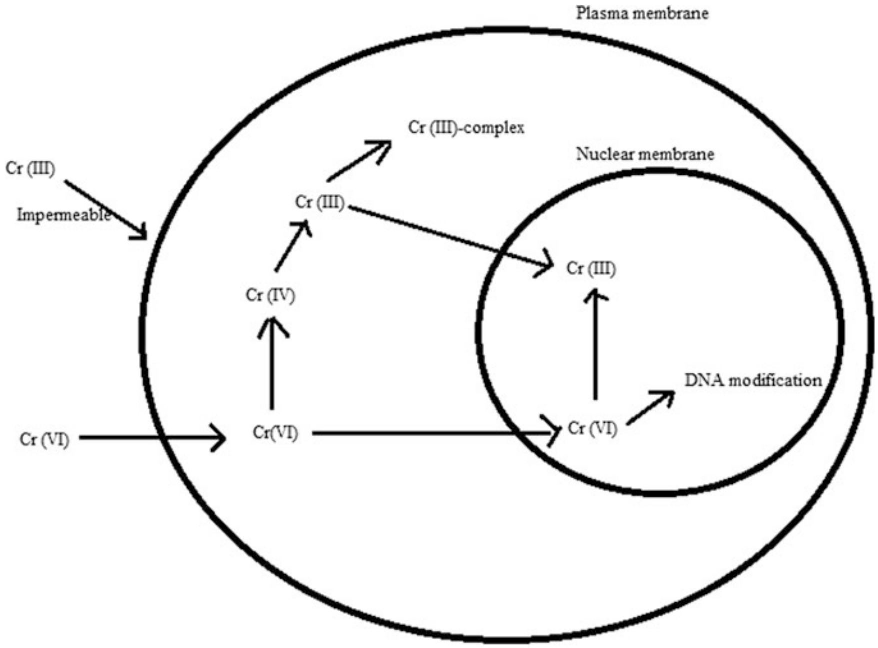

Fig. 17.1 Mechanism of Cr (VI) toxicity and mutagenicity. Adopted and modified from Narayani and Shetty (2012)

17.3 Chromium Biosorption by Microbes

Biosorption is defined as the use of cheap, environmental friendly, and abundant biosorbents in removal of pollutants from wastewater, especially nonbiodegradable metals (Park et al. 2008). Common biosorbents are nonliving bacteria, algae, yeast, fungi, weeds, and agricultural wastes (Joutey et al. 2015). The use of microbes as biosorbents not only absorbs metal from the effluent but also converts highly toxic form of metal into less toxic through oxidation–reduction reaction mechanism. Several studies have shown the use of different chromate resistant bacteria to remove chromium from industrial effluent such as *Pseudomonas fluorescens* (Bopp and Ehrlich 1988), *Enterobacter cloacae* (Komori et al. 1990), and *Acinetobacter* sp. (Srivastava and Thakur 2007).

17.4 Mechanism of Biosorption

There are four different chromium biosorption mechanisms (Saha and Orvig 2010) as follows:

(i) **Anionic adsorption**: In this, the negatively charged chromium species bind to the positively charged group present on the surface of the biosorbent. This method of biosorption is pH dependent. At low pH chromium adsorption increases while it decreases with reduction in pH of the medium.
(ii) **Adsorption-coupled reaction**: In this mechanism, the biomass completely reduced the Cr (VI) into Cr (III) in the presence of an acid. Then, the Cr (III) is adsorbed by the biomass.
(iii) **Anionic and cationic adsorption**: In this mechanism, a part of Cr (VI) is reduced to Cr (III). A part of Cr (VI) as anion and Cr (III) as cation is adsorbed by the biomass.
(iv) **Reduction and anionic adsorption mechanism**: In this mechanism, a part of Cr (VI) is reduced to Cr (III) and usually Cr (VI) is adsorbed by the biosorbent while Cr (III) remains in the solution (Table 17.1).

17.5 Chromium Bioaccumulation

Trivalent form of chromium is practically impermeable to the biological membranes. However, in aqueous solutions, Cr (III) readily form complex with biologically relevant ligand molecules. These complexes are taken up by the cells (Ksheminska et al. 2005). Cr (VI) exists as CrO_4^{2-} in aqueous solutions. This form of Cr (VI) is structurally similar to other anions such as SO_4^{2-}. Cr (VI) enters the cells through two major mechanisms: facilitated transport through a non-selective anion channel and sulfate transporters. Inside the cells, Cr (VI) is rapidly reduced to Cr (III), and therefore the concentration of Cr (VI) will never be equal on both sides of a plasma membrane. Reduction capacity of the cells is the main power by which Cr (VI) is bioaccumulated (Joutey et al. 2015).

Table 17.1 Chromium biosorption by microbial strains from tannery effluent

Bacterial strains	Cr (VI) removal	Reference
Bacillus circulans	48%	Khanafari et al. (2008)
Cyanobacteria	93–99.5%	Pandi et al. (2009)
Bacillus sp.	97–98%	Lalith and Mohan (2017)
Staphylococcus sp.	92–93%	Lalith and Mohan (2017)
Bacillus circulans	34.5 mg Cr/g dry weight	Srinath et al. (2002)
Bacillus megaterium	32.0 mg Cr/g dry weight	Srinath et al. (2002)
Bacillus sp. QC1-2	99%	Campos et al. (1995)

17.6 Chromium Reduction by Microbes

(i) **Aerobic reduction**

Under aerobic conditions, the bacterial Cr (VI) reduction occurs in two or three step processes. Initially, Cr (VI) is reduced to short-lived Cr (V) and Cr (IV) before final conversion to stable end product, Cr (III). However, it is not clear whether the reduction of Cr (VI) to Cr (III) is a spontaneous process or enzyme mediated. The common electron donors in Cr (VI) reduction process are NADH and NADPH. The enzyme chromate reductases reduced Cr (VI) to intermediate Cr (V) and to final product Cr (III) via electron shuttle. Several researchers have reported chromate reductases activity in cell-free extracts during aerobic Cr (VI) reduction.

(ii) **Anaerobic reduction**

Under anaerobic conditions, both soluble and membrane-bound enzymes catalyze the process of Cr (VI) reduction (Cheung and Gu 2007). In this reaction, Cr (VI) serves as a terminal electron acceptor in the respiratory chain, while carbohydrates, proteins, fats, hydrogen, and NAD(P)H serves as an electron donor. The Cr (VI) reduction potential of anaerobes is associated with their electron transfer system catalyzing the electron shuttle along with respiratory chain.

(iii) **Enzyme-mediated Cr (VI) reduction**

Extracellular Cr (VI) reduction

The extracellular enzymes are produced by bacteria and are exported into the media to reduce the Cr (VI). Several studies have reported the role of extracellular chromate reductase produced by bacteria in Cr (VI) remediation. The extracellular chromate reductase produced by *Pseudomonas putida* in Cr (VI) reduction is reported by Priester et al. (2006). Rath et al. (2014) reported the production of extracellular chromate reductases by *Bacillus amyloliquefaciens* isolated from chromite mine environment. Wang et al. (1991) reported that the bacteria with membrane-bound reductases can also reduce Cr (VI) to Cr (III) by extracellular processes.

Intracellular Cr (VI) reduction

The intracellular Cr (VI) reduction mediated by enzymes involves the cytoplasmic soluble chromate enzymes. The intracellular process involves the use of electron donors such as NADH and NADPH. Polti et al. (2011) have reported the intracellular Cr (VI) reduction by *Streptomyces* sp. MC1 isolated from sugarcane. Several strains were reported for intracellular chromate reductase production such as *Bacillus subtilis*, *Rhodobacter sphaeroides*, *Pseudomonas aeruginosa*, *Pseudomonas* sp. CRB5, and *E. coli* ATCC 33456 (Fig. 17.2; Table 17.2).

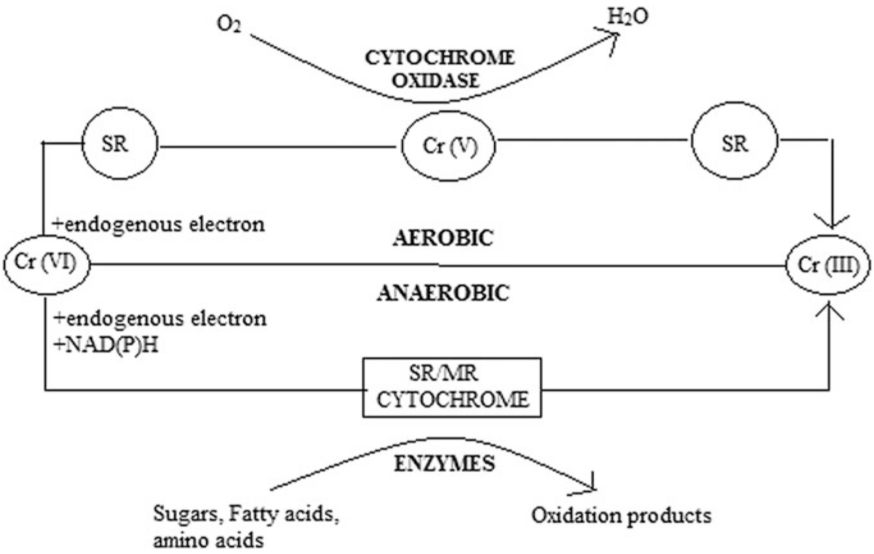

Fig. 17.2 Mechanism of aerobic and anaerobic chromium (VI) reduction. Adopted and modified from Joutey et al. (2015)

Table 17.2 Case study of microbial-mediated Cr (VI) reduction from tannery effluent

Strain	Cr (VI) reduction	Reference
Pseudomonas aeruginosa	94% in 48 h	Munawaroh et al. (2017)
Cellulosimicrobium sp.	98.6%	Naeem et al. (2013)
Pseudomonas sp.	64.4% in 72 h	Farag and Zaki (2010)
Staphylococcus aureus *Pedicococcus pentosaceus*	90% in 5 h 90% in 10 h	Ilias et al. (2011)
O. intermedium	97.1%	Batool et al. (2012)
Pseudomonas aeruginosa	57.7%	Ganguli and Tripathi (1999)

17.7 Case Study on the Role of Microbial Consortium in Chromium Remediation from Tannery Effluent

The biosorption potential of *Spirulina, Oscillatoria,* and *Synechocystis,* individually and as a consortium from a segregated stream, viz. exhausts chrome liquor (ECL) and synthetic BCS solution to remove chromium was studied by (Shashirekha et al. 2011). The species studied was found to be effective in removing chromium and reducing sulfates, BOD, COD, etc. The results of the experiment depict that consortium was better in terms of performance when compared to individual treatment or conventional treatment methods for leather and other industrial wastewater containing chromium.

The chromium remediation potential of *Saccharomyces cerevisiae, P. aeruginosa*, and *B. subtilis* was studied by Benazir et al. (2010) in consortia and in immobilized forms. Initially, the chromium content of effluent reported was 770 mg/L but after remediation, it reduced to 5.2–5.7 mg/L. The maximum remediation ability was observed for *S. cerevisiae—P. aeruginosa* consortia, followed by immobilized beads of *S. cerevisiae* and *S. cerevisiae—B. subtilis* consortia.

Bhattacharya et al. (2015) studied the efficiency of bacterial consortium in simultaneous removal of phenol and Cr (VI) from tannery effluent. Application of bacterial consortia resulted in 78% removal of chromium from initial 16 mg/L Cr (VI) concentration at 96 h of treatment. From the study, it was concluded that the mentioned consortia could be efficiently used in chromium (VI) removal from tannery effluent.

Pinon-Castillo et al. (2010) concluded that the bacterial consortium significantly removed Cr (VI) from industrial wastewater after 15 days of incubation. The dominated genera in bacterial consortium from T-RFLP 16sRNA gene sequencing were *Pseudomonas*/*Stenotrophomonas* or *Enterobacter/Halomonas.*

Chakraborty et al. (2016) prepared two consortia: Consortia I by mixing all isolates showing high Cr (VI) reduction potential and consortia II by mixing all synergistic isolates. Each consortium was tested for Cr (VI) reduction potential. The consortium I and consortium II reduce nearly 2500 and 3000 µg Cr (VI)/g dry cell biomass in 60 and 84 h, respectively.

Shukla et al. (2012) prepared a cyanobacteria mat comprising a consortium of *Chlorella* sp., *Phormidium* sp., and *Oscillatoria* sp. to remove hexavalent chromium. The adsorption experiment using different chromium concentrations 2–110, 15–30, and 300 ppm at pH 5.5–6.2 was carried out in batches. 96% reduction in metal concentration was found within 210 min of treatment.

17.8 Conclusion

The present chapter reveals the potential of microbial mechanisms in chromium remediation from tannery wastewater streams. The use of biological methods for wastewater treatment is better as compared to conventional methods in terms of cost and sustainability. Several researchers revealed the application of microbial consortium in removal of chromium from wastewater streams is far better in terms of efficiency when compared with individual strain treatment. However, the application of microbial consortia in remediation of chromium from polluted wastewater streams needs more extensive research to be undertaken. Moreover, the applications of consortia in field applications for treatment of highly contaminated tannery effluent need to be studied.

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Chapter 18
Biofouling Detection on Reverse Osmosis Membranes

Cervinia V. Manalo and Wataru Nishijima

Abstract Reverse osmosis (RO) membrane technology is considered to be the premier process used for the purpose of seawater and brackish water desalination and water treatment of municipal and industrial wastewater for water reclamation and reuse. Membrane biofouling is a significant challenge in RO processes due to the interference of biofilm formed on the membrane surface on membrane performance. Thus, diverse areas of research are geared towards the understanding, prevention, and control of biofouling. Diagnosis of biofouling is difficult since no single microbial assay on the source water can accurately predict biofouling during the RO process. Biofouling evaluation methods of fouled membranes and collected biofoulants from the treatment processes are counterproductive when biofouling prevention is warranted. It is therefore important for the detection tests to be predictive enough taking into consideration the water quality characteristics of the source feed water, the properties of the RO membrane used for the water treatment, and the hydrodynamic properties during the RO process. This chapter provides an overview of biofouling tests most commonly used for detection of biofouling in the source feed water, and in the foulants and fouled membranes. It has a brief section on the use of flow cell units that can simulate hydrodynamic conditions in the RO plant with the ability to predict biofouling.

Keywords Biofouling · Detection · Reverse osmosis membrane

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18.1 Reverse Osmosis Membrane Technology and Biofouling

18.1.1 The Global Water Demand and the Role of RO Membrane Technology

Water is a very essential part of human life: for consumption and daily living use as well as for non-potable services like recreation, agriculture, and industrial applications. Due to the differences in seasons and location, freshwater distribution and availability through the natural water cycle like precipitation and runoff are very irregular worldwide, resulting in significant variations in per capita water availability between countries and with some countries experiencing absolute scarcity of fresh water (WWAP 2015). The availability, demand, and use of water have also suffered huge impacts due to climate change, socioeconomic development, and population growth (Arnell 2004; Alcamo et al. 2007; Vörösmarty et al. 2010). Aside from population growth and urbanization, food and energy security policies, as well as macro-economic processes, i.e. globalization in trade and changing consumption patterns have influenced the global water demand. And due to the expected growing demand from major sectors such as domestic use, manufacturing, and thermal electricity, the demand is projected to increase by 55% by the year 2050 (WWAP 2015).

Research studies and recent technologies are geared towards the management of existing water resources as well as the development of alternative ones such as water reclamation, recycling, water reuse, desalination of seawater and inland saline aquifers, and others (Miller 2006; Shannon et al. 2008). On a global scale, desalination, despite the limits posed due to energy concerns associated with the technology, has great development potential due to the following reasons (Ghaffour et al. 2013): firstly, large cities lacking fresh water sources are located along the coastal regions and thus these areas have ready access to seawater. And then secondly, desalination has a secure and unlimited source of water supply since feed water supply is unaffected by climatic conditions. Desalination can be categorized based on the mechanism of separation: (1) thermal processes (multi-stage flash, multiple effect distillation, vapor compression distillation) and (2) membrane-based processes [electrodialysis, nanofiltration (NF), reverse osmosis (RO)] (Greenlee et al. 2009). Compared to the thermal-based processes, membrane desalination is increasing due to substantial improvements and innovations towards reducing the costs of desalinated water compared to other water resources, mainly in the RO process (Ghaffour et al. 2013), with a reported 55% growth rate per year in desalination capacity (Global Water Intelligence (GWI/IDA DesalData) 2013). As of 2015, there are about 18,426 desalination plants worldwide and 150 countries practicing desalination (IDA (International Desalination Association) 2015). The four major membrane suppliers, DOW, Hydranautics, Toray, and Toyobo are responsible for some of the state-of-the-art seawater reverse osmosis (SWRO) large-scale desalination plants which are found in Perth in Australia, Llobregat in

Spain, Tuas in Singapore, and Fukuoka in Japan, respectively (Lee et al. 2011). Compared to conventional thermal desalination, the RO membrane system does not suffer from corrosion, has the ability to use low-grade heat, and has been shown to reduce energy consumption owing to the efficient energy recovery systems and the development of more robust membranes (Shannon et al. 2008). Usage of the RO process has evolved, originally for the desalination of seawater and brackish water (Greenlee et al. 2009; Afonso et al. 2004; Fritzmann et al. 2007; Khan et al. 2014) to the treatment of different water types containing varying inorganic and organic contaminants (Ang et al. 2011; Malaeb and Ayoub 2011), and more specifically in the treatment of municipal and industrial wastewater (Khan et al. 2014; Ang et al. 2011; Ridgway et al. 1983; Wilf and Alt 2000; Bódalo-Santoyo et al. 2003). In the past, wastewater treatment is focused on pollution abatement, but in the last two decades, there is an increased amount of municipal wastewater recovered for reuse (Levine and Asano 2004). Global interests and efforts are also made in utilizing reclaimed wastewater for both potable and non-potable purposes (Levine and Asano 2004; Toze 2006). Although conventional treatment can produce water to meet existing regulations, information about its effectiveness to control harmful trace contaminants are limited such that advanced treatment technologies such as membrane bioreactors, microfiltration (MF), ultrafiltration (UF), NF, and RO proved to be more effective for wastewater reuse (Levine and Asano 2004). The RO membrane process plays a vital part in this goal due to its higher rejection of impurities (Fig. 18.1). It essentially produces clean water only at a lower cost compared to other membrane-based technology (Pandey et al. 2012). The presence of large-scale commercial RO membrane plants is proof of the use and capability of the RO technology for wastewater reclamation purposes. These 6 large-scale plants are found in West Basin and Orange County in California, Kranji, Bedok, and Ulu in Singapore, and in Sulabaiya, Kuwait (Bartels 2006). The range and scope of studies in RO membrane technology encompass the whole process, from its

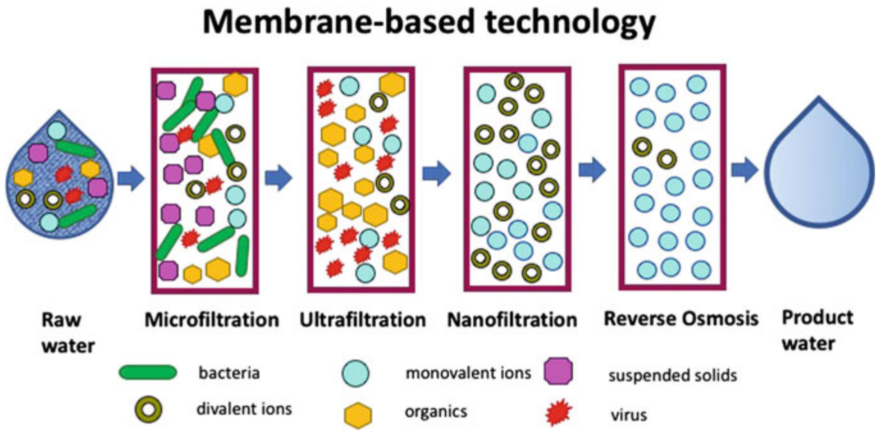

Fig. 18.1 Clean water production of the RO process

application to treating various types of water until post-treatment of the clean water, despite the challenges posed during operation (Greenlee et al. 2009; Malaeb and Ayoub 2011). For both desalination and water reclamation and reuse, the application of RO membranes faces a significant challenge because of membrane performance decline due to membrane fouling.

18.1.2 Membrane Biofouling and RO Membrane Performance

Major challenges in RO desalination include relatively low recovery for seawater desalination thereby producing large volumes of concentrated brine, fairly low removal of low-molecular-weight contaminants, specifically, boron in seawater, and membrane fouling (Shannon et al. 2008). Membrane fouling is the accumulation of unwanted substances on the membrane surface and remains a critical issue to the desalination industry worldwide since it decreases the performance efficiency of the RO process. The main types of membrane fouling are crystalline fouling/scaling, organic fouling, particulate and colloidal fouling, and microbiological fouling or biofouling, which are categorized based on the materials responsible for the fouling (Flemming 1997), such as sparingly soluble inorganic compounds, dissolved and macromolecular organic substances, suspended and colloidal particles, and microorganisms, respectively (Pandey et al. 2012). Membrane fouling is a complex and dynamic process involving various steps in the development of the fouling layer. During organic, inorganic, and colloidal fouling, a rapid initial step involves foulant-membrane interactions and then a gradual long term-step involving foulant–foulant interactions (Tang et al. 2009). Biofouling, on the other hand, involves conditioning, cell attachment, cell growth, and then cell dispersion (Khan et al. 2013a).

Microorganisms are found everywhere in the environment and can grow to create biofilms in the presence of nutrients and under favorable conditions. However, its adverse effect on the RO process is determined by the extent to which biofilm grows and proliferates (Flemming 2002). All nutrients in the water, inactive bacterial biomass after disinfection, biofilm fragments, and dead cells can serve as potential energy sources to the remaining microorganisms when disinfection has been incomplete resulting in biomass production and biofilm formation (Baker and Dudley 1998; Mansouri et al. 2010). These substances should be completely removed or at the very least kept to a minimum, making the pretreatment of the RO feed water an important part in the RO process.

Biofouling refers to the deposition and growth of biofilms to the point that the presence of biofilms on the membrane systems leads to performance decline (Flemming 1997). A biofilm is a complex assembly of sessile microbial communities permanently attached to the membrane due to the presence of self-produced extracellular polymeric substances (EPS), which are mainly polysaccharides and proteins (Flemming and Wingender 2010). For membrane systems like the RO system, the biofilms interfere in the separation process and give rise to enhanced concentration polarization, increased hydraulic resistance, decreased membrane permeability, and decreased salt rejection, but in terms of process efficiency, permeate flux decline and the decrease in salt rejection are considered to be the main concerns (Matin et al. 2011). The kinetics of the flux decline usually shows an initial rapid decline typically correlated with the early attachment and growth of microorganisms on the membrane surface and a slow decline (plateau) phase whereby an equilibrium condition between biofilm growth and EPS production and biofilm loss is taking place (Flemming and Geesey 1991). Rather than a result of changes in the inherent properties of the membrane, the flux decline is most likely a consequence of the biofilm acting as a transport barrier leading to increased hydraulic resistance against water transport (Matin et al. 2011). Studies related to fouling mechanisms have reported that bacterial cells and EPS play major roles in the flux decline (Herzberg and Elimelech 2007; Chong et al. 2008). An increase in the transmembrane pressure (TMP) is a result of a hindered back diffusion of salts, elevating the osmotic pressure on the membrane surface due to the presence of biofilm, resulting in permeate flux decline (Herzberg and Elimelech 2007; Chong et al. 2008; Herzberg et al. 2009). The associated EPS surrounding the biofilm, on the other hand, increases the hydraulic resistance to permeate flow (Herzberg and Elimelech 2007; Herzberg et al. 2009), contributing to the decline in flux.

A similar mechanism has been reported to be responsible for the decrease in salt rejection, wherein EPS and biofilm have significant contributions (Matin et al. 2011; Herzberg and Elimelech 2007). The presence of bacterial cells in the EPS matrix hinders the back diffusion of salts thereby increasing the salt concentration near the membrane surface (Herzberg and Elimelech 2007). This phenomenon results in an enhanced solute transport through the membrane due to the increased solute concentration in the boundary layer (Matin et al. 2011), leading to a decrease in salt rejection. In addition, adverse effects of biofilm growth on boron rejection were attributed to both an increase in hydraulic resistance to permeate flow due to the bacterial EPS and a biofilm-enhanced osmotic pressure near the membrane surface (Huertas et al. 2008).

18.2 Methods for Biofouling Detection

Biofouling, unlike the other types of membrane fouling that can generally be controlled by reducing the foulant concentration, is difficult to manage and control by simple reduction of microorganisms in the source feed water (Vrouwenvelder et al. 2008). Thus, biofouling can only be prevented and controlled with the proper selection of anti-fouling strategies (Pandey et al. 2012). A vital part in designing cost-effective strategies is biofouling detection. Since biofouling is a consequence of a severe biofilm formation in the membrane units resulting in membrane performance decline, specifically operational problems during the RO process, a mixture of methods of quantification of biofilm amount and the associated operational problem encountered, such as pressure drop, flux decline, or salt rejection, are determined to have a reasonable diagnosis of biofouling. This section describes various methods of detecting biofilm amount in the source water, in foulants, and in fouled membranes. Biofouling detection units employing hydrodynamic conditions simulating real filtration conditions in the RO process is also briefly presented.

18.2.1 Water Quality Parameters of RO Feed

Regardless of the fouling type, evaluation of the quality of the feed water is essential in determining the proper pretreatment and RO design for water treatment. Research studies have shown that the differences in fouling layer composition are influenced by the quality of the source water (Khan et al. 2013b, 2014). Different source waters treated by the RO process can be roughly categorized based on two fundamental water quality parameters (DOW 2010), total dissolved solids (TDS) content, which can be referred to as salinity, and the organic load in terms of total organic carbon (TOC). Brackish water has medium TOC content with medium to high salinity and seawater has low to high TOC and high salinity, while municipal wastewater has a high organic load with medium salinity. Silt density index (SDI) is a water quality parameter used to describe the fouling potential of water and is regarded as an important feed water quality guideline for pretreatment and RO system design (Teng et al. 2003; Mosset et al. 2008). It is the most common indicator used in practice and the feed SDI should be consistently <5 or <3, depending on the RO system design, as recommended by membrane manufacturers (DOW 2010). It measures the rate at which a 0.45 μm membrane filter is plugged when the water is passed through the membrane filter at a constant applied gauge pressure (DOW 2010). However, SDI is not always reliable and accurate and its sensitivity to other factors such as pH, membrane characteristics, and turbidity of water poses a huge drawback in its use as a fouling index (Mosset et al. 2008; Alhadidi et al. 2012; Rachman et al. 2013). It also has limited capability in measuring fouling potential due to other foulants such as colloidal deposition and organic adsorption (Choi et al. 2009). Studies have also shown that despite the SDI values of feed water within limits prescribed by membrane suppliers, biofilm formation and biofouling were not prevented (Schneider et al. 2005; Huang et al. 2013), confirming the need of additional or other water quality parameters to predict biofouling or at the very least, indicate biofouling potential. Thus, as a measure of biofouling potential, quantification of organic matter, biomass of microorganisms, and substances promoting bacterial adhesion and growth are also determined.

The starting point of biofilm growth is the rapid accumulation of organics (humic substances and polysaccharides) on the membrane surface (Subramani et al. 2009), which are also accompanied by bacterial cell adhesion and cell adsorption (Khan et al. 2013a). In the second stage of adhesion, the adhesion process is strengthened by loosely bound organisms when EPS are released (Dunne 2002).

Thus, feed water quality parameters for biofouling propensity include the determination of organics in the feed water. The usual tests for determination of organics are TOC content and dissolved organic carbon (DOC) content. The organic carbon in the water sample is oxidized to carbon dioxide, by combustion in an oxidizing gas or by UV-promoted or heat-catalyzed chemical oxidation, and the carbon dioxide released from the oxidized sample is detected by a conductivity detector or a nondispersive infrared detector (Potter and Wimsatt 2005). These tests are used to determine the water quality of feed water in order to evaluate pretreatment efficiency, establish operating conditions, and maintain the quality of discharged effluents (Khan et al. 2013a, b, 2014; Schneider et al. 2005; Huang et al. 2013; Norberg et al. 2007; Xu et al. 2010; Zhao et al. 2010; Jeong et al. 2013a; Miyoshi et al. 2016). Based on membrane manufacturers, pretreatment should be considered when TOC exceeds 3 mg/L (DOW 2010). UV254, like TOC and DOC, is a bulk parameter used to determine organic amounts in feed water (Khan et al. 2013b; Huang et al. 2013; Norberg et al. 2007; Zhao et al. 2010). It is mainly used to quantify the aromatic compounds and unsaturated bonds in a compound that strongly absorb UV radiation and is related to the humic component of the organic matter (Choi et al. 2009; Norberg et al. 2007; Sim et al. 2018). For this determination, the water sample is passed through a 0.45 μm filter, transferred to a quartz cell, and then analyzed using a spectrophotometer to measure the UV absorbance at 254 nm (Potter and Wimsatt 2005). Most recently, it has been used as a monitoring and control parameter for organic micropollutants in wastewater (Altmann et al. 2016). However, monitoring the changes in bulk parameters like TOC, DOC, and UV254 is not suitable for the evaluation of the changes in the concentration of specific organic components (Miyoshi et al. 2016) that will be helpful in assessing the cause of biofouling in the RO units.

Fluorescence measurements given as 3D excitation-emission matrices (EEMs) have found favor in the analysis of dissolved organic matter based on characteristic regions of excitation-emission wavelength corresponding to distinct organic components (Chen et al. 2003) and have been used to characterize different water systems (Miyoshi et al. 2016; Hudson et al. 2007; Henderson et al. 2009; Pype et al. 2013; Carstea et al. 2016). A study showed the capability of F-EEM coupled with fluorescence regional technique in assessing RO membrane integrity by analyzing feed and permeate samples from pressure vessels, complete stages, and RO trains of two full-scale plants (Pype et al. 2013). Another advanced method of characterizing humic, non-humic, and other fractions of organic compounds based on molecular size is through the use of the liquid chromatography-organic carbon detector (LC-OCD) or size exclusion chromatography-organic carbon detector (SEC-OCD) (Huber et al. 2011; Chen et al. 2016). It has been extensively used for determining the efficiency of pretreatments for water treatment through analysis of raw and treated water (Miyoshi et al. 2016; Jeong et al. 2012, 2016; Kimura and Oki 2017; Monnot et al. 2017). Although these methods are promising, they are mainly used in research studies and are not used online or on-site (Sim et al. 2018) but permeate water samples can be collected in strategic locations to evaluate the performance of the RO units (Pype et al. 2013).

Commonly used biological tests for quantifying microorganisms in the feed water are heterotrophic plate count (HPC) (Reasoner and Geldreich 1985) and total direct cell count (TDC) (Hobbie et al. 1977). HPC is determined by culturing the microorganisms from the sample water in an appropriate nutrient medium to develop colonies, which are then counted and reported as the number of colony-forming units (CFU) as a measure of culturable microorganisms (Reasoner and Geldreich 1985). Direct count methods are preferred instead of culture techniques because they are much faster by simply counting the stained microorganisms directly under a microscope (DOW 2010). TDC requires filtration of the water sample through a membrane filter and the microorganisms retained on the filter are stained with a dye, usually acridine orange, and then observed and counted under an epifluorescence microscope (Hobbie et al. 1977). As expected, feed water with low and high concentrations of bacterial content based on these tests showed low and high biomass concentrations, respectively after membrane autopsies (Vrouwenvelder and Van der Kooij 2001). Biomass can also be determined by measuring adenosine triphosphate (ATP), a biomolecule found in all cells, whether plant or animal (Holm-Hansen and Booth 1966). The accumulation of ATP on the surface of glass rings in an online operated biofilm monitor is determined as a function of time and is reported as the biofilm formation rate (BFR) (Vrouwenvelder and Van der Kooij 2001). ATP concentrations are obtained by an enzymatic reaction using the luciferine-luciferase assay (Holm-Hansen and Booth 1966). The amount of light produced is determined by a luminometer and the ATP concentration is derived from the linear relationship between light production and reference ATP concentrations (Vrouwenvelder et al. 2008). Studies have shown a good correlation between ATP and the biomass content in feed water (Vrouwenvelder et al. 2003; Veza et al. 2008). Thus, ATP is considered as a suitable water quality parameter for biofouling potential. However, HPC and ATP values were found to be correlated in water only when organic loads are low, but not when organic loads are high (Veza et al. 2008). Furthermore, even low concentrations of biodegradable components could still lead to biofouling based on assimilable organic carbon (AOC) test and BFR test (Vrouwenvelder and Van der Kooij 2001). And although lessening bacterial concentration in the feed water is the primary countermeasure to avoid biofouling, it has been reported that biofouling reduction was largely dependent on decreasing the concentrations of AOC (Schneider et al. 2005). This indicates that despite being direct methods for bacterial content, tests like HPC and TDC are not suitable as biofouling parameters. In addition, HPC values are generally a small fraction of the total number of cells present, as little as 1–10% or less than TDC values (DOW 2010), an extreme underestimation when considering a single assay as a measure of biofouling potential.

Thus, biofouling potential of water has also been determined through quantification of substances that promote bacterial adhesion and growth. Microorganisms are surrounded by self-produced EPS, which are composed of polysaccharides, proteins, DNAs, nucleic acids, and other biopolymers rendering the structure and architecture of biofilms (Flemming and Wingender 2010). Therefore, these substances are crucial in initial bacterial adhesion and attachment, and biofilm growth.

As previously mentioned, according to several studies, EPS and biofilms are instrumental to the decline in permeate flux and salt rejection (Matin et al. 2011; Herzberg and Elimelech 2007; Chong et al. 2008). Feed and permeate waters are usually analyzed for EPS components, typically polysaccharides and proteins, to characterize the components of the water samples associated with biofilm formation as well as to ascertain their removal or production during pretreatment or during the RO process itself (Chong et al. 2008; Herzberg et al. 2009; Zhao et al. 2010; Jeong et al. 2012; Lee et al. 2010; Baek et al. 2011). Polysaccharide content is usually analyzed by the phenol-sulfuric acid method wherein carbohydrates in the sample are stained yellow–orange when treated with phenol and sulfuric acid, which later can then be spectrophotometrically measured, and the concentrations are determined using a carbohydrate standard like glucose (DuBois et al. 1956). Protein concentrations can be determined through various means but are typically determined through the traditional dye-based absorbance measurements like Bicinchoninic acid (BCA) assay (Chong et al. 2008; Jeong et al. 2012) or the Lowry (Alkaline Copper Reduction) Assay (Herzberg et al. 2009; Lee et al. 2010). As a subclass of EPS, transparent exopolymer particles (TEPs) are individual, free-floating particles and have been found to be an important agent in biofilm formation and knowledge and understanding of their dynamics in seawater, surface water, and wastewater would be beneficial in pretreatment and fouling/biofouling control strategies (Miyoshi et al. 2016; Berman et al. 2011; Meng et al. 2013; Bar-Zeev et al. 2015). Similar to the polysaccharides and protein measurements, TEP concentrations are determined through dye-absorbance measurements. The water sample is filtered through a polycarbonate filter and the accumulated TEP on the filter is stained with the Alcian blue dye, which is subsequently eluted with sulfuric acid and the absorbance of the resulting solution measured spectrophotometrically with xanthan gum as the calibration standard used to quantify TEP (Passow and Alldredge 1995). Although the quantitative analysis of each component is relatively straightforward, an important aspect of characterizing EPS is the extraction of the component from the biofilm. A good extraction method should keep the characteristics of the component intact, should not cause cell lysis, and should be able to collect all EPS components (Nielsen and Jahn 1999). AOC is the fraction of the TOC used by microorganisms that result in an increased biomass concentration (Hobbie et al. 1977) and is used to evaluate bacterial regrowth potential (BRP) (Van der Kooij 1992) in the feed water of the RO unit (Jeong et al. 2012, 2013a; Vrouwenvelder and Van der Kooij 2001; Dixon et al. 2012a, b). High amounts of AOC may also cause severe biofouling, especially when there is a high bacterial load in the feed water (Schneider et al. 2005). The principle of the AOC test is based on the measurement of the growth of an inoculum in a water sample until the stationary phase, with the assumption that the growing bacteria have assimilated all of the AOC in the water (Van der Kooij 1992). The net growth of the bacteria is measured by various methods and then converted to an AOC or AOC-equivalent concentration (Van der Kooij 1992). It has been shown that AOC values in seawater were strongly correlated to RO biofouling in a full-scale plant, showing its predictive capability for biofouling (Weinrich et al. 2016). However, since the test is not yet standardized for seawater, in one study, the organism used for the inoculum was isolated first from the fouled RO membrane in the experimental site (Carstea et al. 2016) Thus, existing AOC tests are continuously developed and improved to increase its sensitivity, decrease the turnaround time to have a faster analysis, and make it applicable to highly saline marine water samples (Jeong et al. 2013b). These water quality tests are still lacking in terms of reliable predictive capabilities for biofouling (Sim et al. 2018) since low values of AOC, ATP, and BFR do not essentially signify the absence of biofouling (Vrouwenvelder et al. 2008). Table 18.1 shows a summary of the advantages and disadvantages offered by the detection methods discussed in this section and some methods used for the extracted foulant. Unless otherwise specified, the methods are applicable for both seawater desalination and wastewater reclamation.

18.2.2 Analysis of Foulants and Fouled Membranes

Significant studies have been done on the analysis of foulants and fouled membranes during membrane autopsies in order to establish that biofouling was the cause in the decline of membrane performance. Foulants are detached from membranes, membrane coupons, and spacers, and the collected foulant subjected to tests for bacterial counts or organic content. Plate counts, TDC, EPS concentration, and ATP analyses of foulants are the most typical means of assessing biomass of foulants. Aside from the additional procedure for extraction of the analytes from the foulant, these tests when applied in the characterization of the biofilm extracted from the foulant material offer the same general advantages and disadvantages as when they are used for water quality characterization (Table 18.1). However, additional information gathered by several investigations will be discussed to show these tests' suitability as biofouling detection methods. Evaluation of EPS on extracted foulants and directly on fouled membranes give information on the biofilm morphology, description of the fouling layers, and most importantly give insights into the biofouling mechanism (Ridgway et al. 1983; Herzberg and Elimelech 2007; Chong et al. 2008; Herzberg et al. 2009; Khan et al. 2013b; Jeong et al. 2012, 2013a; Lee et al. 2010; Baek et al. 2011; Suwarno et al. 2012; Alzahrani et al. 2013; Chen et al. 2013; Kwan et al. 2015). Comparison of EPS in feed solutions and in foulants also showed the preferential adsorption/accumulation of polysaccharide on the membrane surface when forming the fouling layer (Herzberg et al. 2009). ATP analysis of foulants, on the other hand, showed differences in fouling layers extracted from membranes elements from a seawater RO (SWRO) plant and a wastewater RO (WWRO) plant. It was found that generally, lead elements have greater biomass concentration than terminal modules and that the lead elements of the WWRO plant have more developed and mature biofilms than the lead elements of the SWRO plant (Khan et al. 2014). Evaluation of ATP concentration in foulants also showed that higher ATP content leads to higher fouling load, signifying biofilm development as the RO operation progresses (Khan

Table 18.1 Advantages and disadvantages of detection methods used for water quality characterization and extracted foulant material

Water quality parameters	Pros	Cons
TOC and DOC	Provides quantitative information; can be used online	No predictive capability for biofouling; gives bulk assessment only of organic compounds
UV_{254}	Provides an estimate quantity of humic component of organic matter; can be used online	No predictive capability for biofouling; gives bulk assessment only of a specific set of organic compounds
F-EEM	Provides qualitative assessment of specific organic compounds	No predictive capability for biofouling; cannot be used online; cannot provide quantitative information; expensive instrumentation
LC-OCD	Provides quantitative information of specific organic compounds	No predictive capability for biofouling; cannot be used online; expensive instrumentation
HPC	Requires no expensive equipment; gives biofouling potential	No predictive capability for biofouling; cannot be used online; gives only the number of culturable microorganisms in water sample; laborious; time-consuming
TDC	Provides total bacterial count; faster than culture techniques; gives biofouling potential	No predictive capability for biofouling; cannot be used online; no viability information provided
ATP; BFR as ATP	Provides concentration of active biomass in water; gives biofouling potential	No predictive capability for biofouling; cannot be used online; time-consuming and requires skilled personnel
EPS and TEP	Provides quantitative information of EPS components (polysaccharide, proteins) and insights into biofilm mechanism; gives biofouling potential	No predictive capability for biofouling; cannot be used online; extraction and sample preparation procedures are time-consuming
AOC	Provides bacterial regrowth potential of water sample; gives biofouling potential; reported the predictive capability for biofouling	Cannot be used online; modification needed to fit highly saline samples; microbial content may not be representative of the sample since known organism for inoculation should be used for reproducible results; time-consuming and laborious

et al. 2013a). ATP was also reported to be a better parameter for biomass concentration than TDC and HPC since ATP values are less scattered upon analysis of biofilm in lead elements from membrane installations (Vrouwenvelder et al. 2008).

The membranes, on the other hand, whether virgin or fouled membranes are usually analyzed for surface characteristics and the observed characteristics correlated to biofilm structure, adhesion, attachment, and growth, as well as biofouling kinetics and mechanism, which then can give insight on designing proper biofouling control strategies (Khan et al. 2010, 2011, 2013a, b, 2014; Herzberg and Elimelech 2007; Herzberg et al. 2009; Norberg et al. 2007; Xu et al. 2010; Jeong et al. 2013a; Lee et al. 2010; Baek et al. 2011; Alzahrani et al. 2013; Subramani and Hoek 2008, 2010). Table 18.2 shows a summary of the advantages and disadvantages of the membrane characterization methods discussed in this section. Hydrophilic/hydrophobic properties are usually determined by measuring contact angles, usually through the sessile drop method using a goniometer (Subramani et al. 2009; Norberg et al. 2007; Xu et al. 2010; Zhao et al. 2010; Jeong et al. 2013a; Lee et al. 2010; Baek et al. 2011; Subramani and Hoek 2008, 2010; Khan et al. 2010, 2011). Multiple probe liquid contact angle measurements were also used to describe membrane surface energies for bacterial cells and membranes (Subramani and Hoek 2008, 2010). A higher contact angle usually represents a higher hydrophobicity of the membrane surface (Jeong et al. 2013a). Studies showed that more hydrophobic membrane surfaces are more favorable to initial bacterial adhesion and attachment, have higher cell deposition rates and hence, have the greater amount of accumulated bacterial cells (Norberg et al. 2007; Xu et al. 2010; Jeong et al. 2013a; Lee et al. 2010; Subramani and Hoek 2008, 2010; Khan et al. 2011). It has also been reported that the exposure to cleaning agents altered membrane surface characteristics, and that only sodium hypochlorite effectively broke the adhesive bonds between bacterial EPS and membrane surfaces, essentially cleaning the membrane (Subramani and Hoek 2010). The typical method used to evaluate membrane surface topography is atomic force microscopy (AFM) and results are usually associated with surface roughness (Khan et al. 2013a; Subramani et al. 2009; Norberg et al. 2007; Xu et al. 2010; Zhao et al. 2010; Jeong et al. 2013a; Lee et al. 2010; Baek et al. 2011; Alzahrani et al. 2013; Subramani and Hoek 2008, 2010; Khan et al. 2010, 2011). A rough membrane surface, in the case of virgin membranes, is assumed to have a greater potential to foul and vice versa (Tang et al. 2011). This assumption has been clearly demonstrated in numerous studies, which showed that the rougher RO surfaces were more prone to bacterial cell and EPS attachment, had higher microbial deposition rates and had a greater accumulation of biofoulants resulting in thicker biofilms (Khan et al. 2013a; Norberg et al. 2007; Zhao et al. 2010; Jeong et al. 2013a; Lee et al. 2010; Baek et al. 2011; Subramani and Hoek 2008, 2010; Khan et al. 2010, 2011). It was reported that organic layers forming on the RO membrane resulted in a rougher surface and had greater bacterial adhesion (Subramani et al. 2009). AFM measurements were also used to provide qualitative and quantitative information on foulant-membrane and foulant-foulant interactions. Herzberg and co-workers (Herzberg et al. 2009) showed an increase in the adhesion forces between a carboxylated-modified latex particle and membranes fouled with EPS upon additions of calcium ions, suggesting the influence of other substances in the biofouling of RO membranes.

Epifluorescence microscopy is the typical method used for determining TDC in water samples (Hobbie et al. 1977) but it can also be used for the analysis of extracted foulants from biofilms to give TDC (Vrouwenvelder et al. 2008). Owing to the emergence of a variety of fluorochromes, applications of fluorescence microscopy in biofilm studies have extended beyond total bacterial count. When

Table 18.2 Advantages and disadvantages of membrane characterization methods

Membrane analysis	Pros	Cons
Contact angle measurement	Gives insights into the relationship between hydrophobic/hydrophilic character of the membrane and biofilm formation; can be used to describe membrane surface energies for bacteria and membranes	Cannot be done online; no predictive capability for biofouling
AFM	Provides membrane surface topography; gives insights into the relationship between surface roughness of the membrane and biofilm formation; gives insight into adhesion forces between membrane-foulant and foulant-foulant interactions	Cannot be done online; no predictive capability for biofouling
Epifluorescence microscopy	Provides bacterial counts, viability, and 2D distribution of bacteria in the biofilm	Cannot be done online; limited to the analysis of thin biofilms
CLSM	Provides 3D structure of biofilms, quantitative information of bacterial structure and components	Cannot be done online; slow scanning of the laser; restricted availability of fluorescence filters; not suited for very thick and opaque biofilms

coupled with a specific fluorescent staining dye, epifluorescence microscopy can provide not only total bacterial counts, but also bacterial activity, viability, and 2D distribution of bacteria (Vrouwenvelder et al. 2008; Lee et al. 2010; Subramani and Hoek 2010; Wolf et al. 2002). The disadvantage of epifluorescence microscopy is its limited application to thin biofilms only (McFeters et al. 1995). Confocal laser scanning microscopy (CLSM) coupled with fluorescence dye staining, on the other hand, can provide 3D spatial arrangement within the biofilms, characterize bacterial groups or strains in the biofilm, and is an important tool in assessing the structure-function relationships in biofilms (Wolf et al. 2002). Similar to epifluorescence microscopy, CLSM measurements were used to provide TDC and viability information from extracted foulants (Jeong et al. 2012, 2013a). Because CLSM can analyze thicker biofilms than epifluorescence microscopy, with a suitable imaging software, cut pieces of fouled membranes or membrane coupons can be analyzed for biofilm amount, components, and viability, as well as biofilm characteristics such as thickness, biovolumes, and percentage coverage, and can give insights into biofilm formation and mechanism (Khan et al. 2013a; Herzberg et al. 2009; Vrouwenvelder et al. 2008; Huang et al. 2013; Lee et al. 2010; Berman et al. 2011; Chen et al. 2013). Using the biofilm characteristics obtained by CLSM measurements, it was revealed that an abrupt rise in TMP coincides with biofilm formation (Chen et al. 2013), indicating performance decline due to biofouling. Limitations of the CLSM technique include the restricted number of available fluorescent filter combinations in contrast to epifluorescence microscopy and is relatively time-consuming due to the slow scanning of the laser for the production of high-quality images (Wolf et al. 2002). And though it can analyze thicker biofilms than epifluorescence microscopy, it is not suited for the analysis of very thick and opaque biofilms (McFeters et al. 1995).

It has been shown that the biofilm morphology and accumulation of biofoulants are dependent on membrane surface properties (Khan et al. 2010, 2011; Subramani and Hoek 2010) and it is established that bacterial cell and membrane surface interactions play a significant role in initial bacterial adhesion and thus biofilm formation (Habimana et al. 2014). With this in mind, biofouling potential tests incorporating the properties of the RO membrane used and the water quality of the feed water are more reliable methods for determining biofouling propensity than a single water quality index (Manalo et al. 2016). NF and RO membranes analyzed by fluorescence microscopy showed accelerated growth rate and formation of viable cells within a period of only 5–10 h, suggesting this as the critical time period for biofilm growth and development (Lutskiy et al. 2015). This signifies that the assessment of the susceptibility of membranes to biofilm formation can be done at a significantly shorter period of time. Fluorescence intensity using the microplate reader as a measure of biofilm formed on the RO membrane surface after soaking cut pieces of the membrane in secondary effluent water, which was enhanced with microorganisms and glucose for accelerated biofilm formation, proved to be a reliable biofouling potential method that incorporates fouling tendencies of both feed water and the RO membrane (Manalo et al. 2016). These studies show that surface membrane analysis of biofilm content like fluorescence analytical methods can be utilized as an indicator of biofouling potential of both RO membranes and feed water. However, as much as these tests can be used as biofouling potential methods, the inclusion of RO system performance analyses in detecting biofouling will give the greater advantage of predicting biofouling in a smaller scale but at an earlier time, such that biofouling in the RO plants can be mitigated or controlled.

18.2.3 Fouling Simulators and Canary Cells

Biofouling potential methods mentioned in the previous sections are not predictive enough to ascertain that biofouling event during the RO process will occur. Using flow cells is very important in biofouling studies since they can simulate hydrodynamic conditions used in real RO plants, and thereby mimic the fouling events. Specifically applied for biofouling studies, a flow cell unit with a transparent window for microscopic viewing of fouling in real-time was developed [Fig. 18.2; (Subramani and Hoek 2008)]. Images taken by a camera are later translated into percentage of coverage of cells deposited on the membrane surface and results showed that cell deposition rate was influenced by permeate flux, membrane

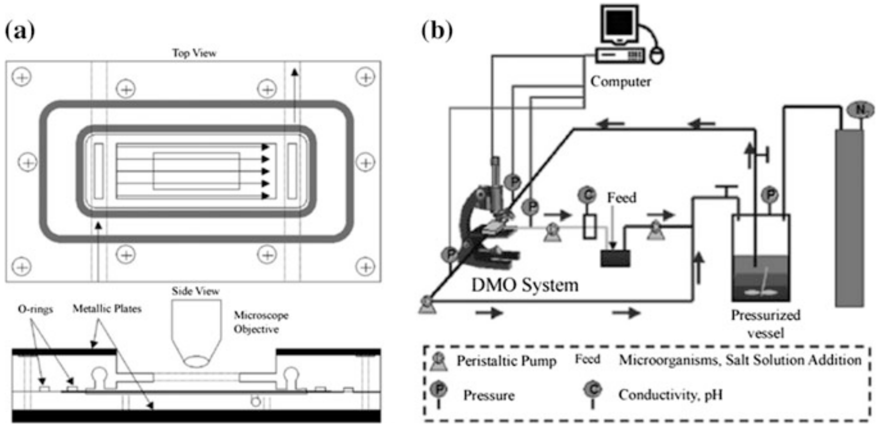

Fig. 18.2 **a** Direct observation module made from two polycarbonate plates with a 2-mm thick glass window and **b** flow system operating at applied pressures up to 300 psi. The module is placed on the fixed stage of a microscope equipped with a 10× objective and 4× CCD camera to obtain real-time observations during the experiment through a transparent window on the top plate of the module (Subramani and Hoek 2008)

resistance, concentration polarization, and membrane surface characteristics such as roughness and hydrophobicity (Subramani and Hoek 2008). It was further improved by incorporating into the high-pressure membrane flow cell an optical microscope with fluorescence imaging as an external monitoring device for detecting biofouling development and cleaning [Fig. 18.3; (Huang et al. 2010)]. The new optical membrane module proves the importance of flow cells that are able to simulate practical seawater desalination operating conditions for the evaluation of the influence of these operating parameters on bacterial adhesion and removal in small-scale laboratory studies (Huang et al. 2010).

Biofouling detection, while the RO filtration is in operation, is vital to avoid shutting down the process due to irreversible fouling, which in the end, sacrifices the membrane element for an autopsy. Because indicators of fouling while the RO process is ongoing are operational parameters such as flux decline due to increase in TMP, worsening product quality, usually determined as a decrease in salt rejection, and pressure drop across the module, flow cell devices that can monitor the fouling state of the membranes as well as the performance of the membrane unit are in great need (Fig. 18.4). The flow cell devices, when combined with non-invasive methods for fouling detection has the ability to gather information and monitor the fouling state of a filtration process in real-time. These devices, which should be placed in strategic locations, can be used to determine when membrane cleaning is already warranted by the RO process, thereby saving the membrane systems from irreversible fouling and costly membrane replacement. Costs are also minimized when membrane cleaning is applied at the onset of fouling and not at the later stages, where optimum membrane performance can no longer be restored. These fouling

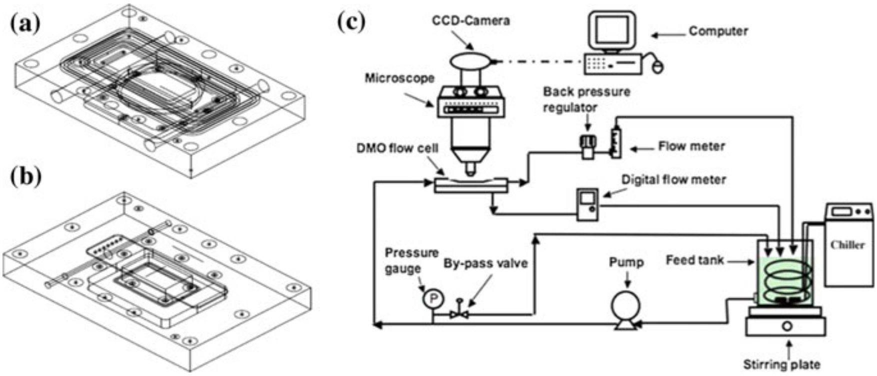

Fig. 18.3 The improved high-pressure optical module made of (**a**) stainless steel top plate with an optical window and (**b**) stainless steel bottom plate, and (**c**) a schematic diagram of the optical membrane module integrated with pressure, flow, and microscopic observation components. The module withstands pressures up to 1200 psi while allowing high transmission of UV and visible light (Huang et al. 2010)

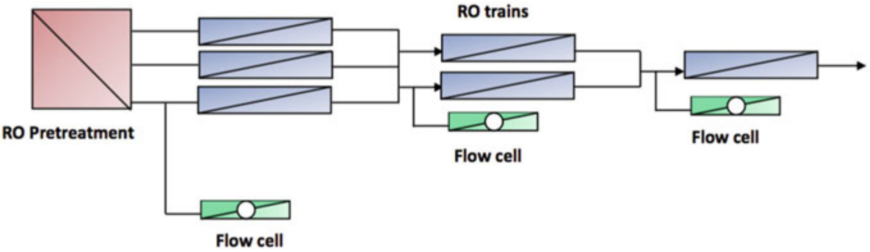

Fig. 18.4 Incorporation of flow cells in the RO process

detection devices can be directly employed within the module unit (in situ) or on small cell units attached as a side-stream (ex situ) (Sim et al. 2018).

An example of this device has been developed more than 10 years ago, the membrane fouling simulator (MFS, Fig. 18.5), wherein fouling was monitored by changes in the pressure drop, as well as visual, microscopic, and non-destructive observations through a transparent window (Vrouwenvelder et al. 2006). Sections of the membrane, feed and permeate spacers from the MFS and membrane modules were analyzed to evaluate the accumulated fouling layers. The transparent window allowed in situ visual and microscopic observations during the operation of the MFS and with a digital camera, images were captured showing the effect of a nutrient (acetate) on the accumulation of foulant material on the membrane [Fig. 18.6; (Vrouwenvelder et al. 2006)]. A recent study using the MFS units for comparing two RO systems operated in parallel employing different water types

Fig. 18.5 The developed membrane fouling simulator, MFS (external dimensions of 0.07 m 0.30 m × 0.04 m) with a transparent window. The MFS was operated at a pressure of 100 kPa (~14.5 psi) under crossflow and no permeation conditions (Vrouwenvelder et al. 2006)

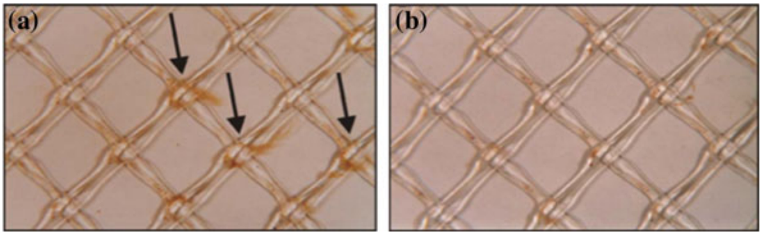

Fig. 18.6 Visual in situ observations of the membrane and feed spacer in the MFS during operation through the transparent window (**a**) with 0.100 mg acetate-C/L and (**b**) without acetate dosage (after a run time of 6 days). The flow direction is from left to right. The original scale is 10.7 mm × 6.2 mm. Black arrows indicate darker colored material in the feed spacer crossings in MFS with added nutrient (Vrouwenvelder et al. 2006)

showed that biofouling trends in the MFS are similar to those as the spiral wound modules (SWM) in the RO system (Massons-Gassol et al. 2017), signifying the capability of the MFS unit as a biofouling indicator. Incorporation of non-invasive techniques into the MFS makes it a more lucrative tool for monitoring biofouling during operation. The optical coherence tomography, a relatively new and advanced monitoring technique was incorporated into the MFS to characterize the biomass in situ and non-destructively in UF membranes (Fortunato et al. 2017), in NF membranes (Fortunato and Leiknes 2017), and in RO membranes (West et al. 2016). However, since the MFS operates at a low pressure and usually without a permeation flux, it only gives a partial simulation of the conditions in the RO plant (Sim et al. 2018).

The canary cell, a side-stream RO flow cell, that simulates the SWM typically applied in RO plants was recently developed [Fig. 18.7; (Sim et al. 2015)]. It offers non-invasive monitoring of high-pressure colloidal fouling and cleaning and because of a dimensionless correlation curve for the cell and the SWM, it can function as an early warning device for fouling (Sim et al. 2015). Although it is primarily developed as a colloidal fouling monitor, it was reported to be capable of in situ, in real-time, and non-destructive monitoring of growth of biofilm using ultrasonic

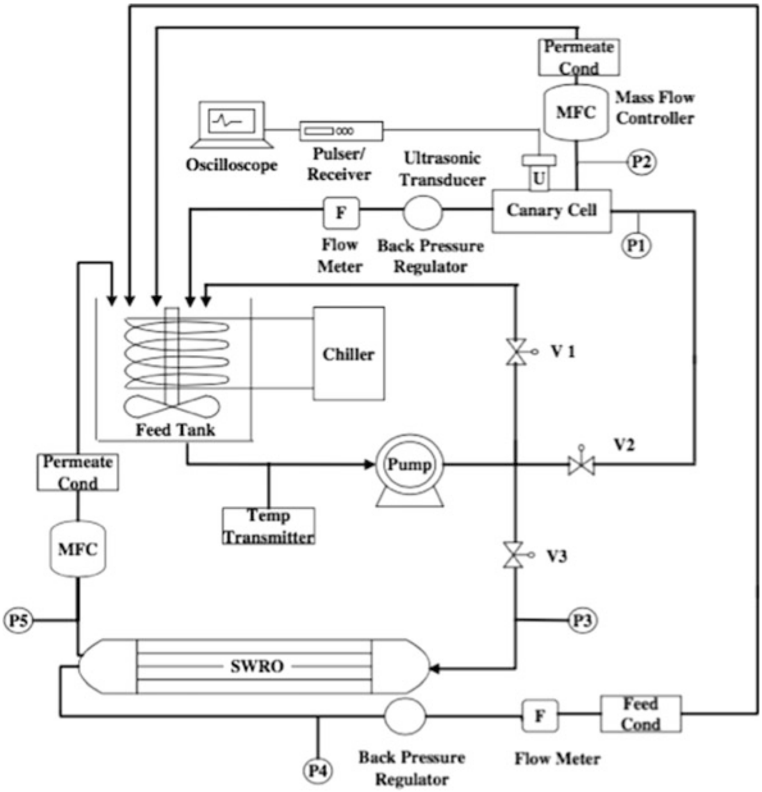

Fig. 18.7 Schematic diagram of the spiral wound module (SWM) and the canary cell with ultrasonic time domain reflectometry (UTDR). The canary cell was operated at similar crossflow velocities as the SWM under constant flux. The feed was delivered from a continuously stirred tank kept at 30° with cooling water from a chiller. The permeate fluxes for the SWM and the canary cell were held constant by two separate mass flow controllers (MFC). TMP was measured using pressure transducers and salt concentration of the feed and permeate for both SWM and canary cell was determined using a conductivity meter. The UTDR system consisted of a transducer, externally mounted on the cell, a digitizer, and a pulse-receiver (Sim et al. 2015)

time-domain reflectometry (UTDR) by periodic dosing of silica (Sim et al. 2015). UTDR uses sound waves to locate biofilm on the membrane surface and based on the transmission and reflection of an ultrasonic waveform traveling through a particular media, for example, the biofilm, information on the physical characteristics of the biofilm can be gathered (Mairal et al. 2000). Other methods for monitoring the fouling state of the membrane for all fouling types have been reviewed and their strengths and capabilities presented by Sim and co-workers (Sim et al. 2018). They have highlighted the importance of fouling indices and monitoring techniques that can be incorporated into the RO process for a better knowledge of the fouling state of the membrane, even when the operation is ongoing.

18.3 Summary

There is no single assay for biofilm amount or membrane performance indicator that can accurately predict biofouling. Existing water quality parameters and surface membrane analysis can be used as biofouling potential tests but the incorporation of the hydrodynamic conditions happening in the RO plant is essential for a method to be able to predict biofouling. As a preventive measure, preempting the biofouling event enables the RO plant to take countermeasures to avoid irreversible biofouling, which once it has occurred necessitates costly membrane replacement instead of the less expensive membrane cleaning. The advantage of fouling simulators and canary cells cannot be ignored since these units give the fouling scenarios for the RO process and can serve as a warning in advance of the fouling event. It is evident that there is still a need for developing biofouling detection methods that are specific and function as sensitive indices for biofouling, are non-destructive and can provide results readily and timely.

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Part IV

Advanced Materials and Technologies for Future Water and Wastewater Treatment

Chapter 19
Applications of Nanotechnology and Biotechnology for Sustainable Water and Wastewater Treatment

Adhena Ayaliew Werkneh and Eldon R. Rene

Abstract Nowadays, water pollution and freshwater scarcity have become a serious problem worldwide, causing concerns to both public health and the environment. To reduce these challenges, various treatment technologies have been adopted. Among these technologies, nanotechnology- and biotechnology-based techniques are usually applied separately for water (domestic purposes) and wastewater (reuse) treatment. This chapter focuses on new and emerging nano- and biotechnologies for the sustainable removal of pollution causing constituents during water and wastewater treatment. Besides, the toxicological and safety aspects of different nanotechnologies and their current and future perspectives are discussed.

Keywords Water and wastewater treatment · Nanomaterials · Microbes
Nanotoxicity · Microbial toxicity

19.1 Introduction

Environmental pollution together with global warming is one of the foremost global challenges of the twenty-first century (Rodgers 2006; Soler and Sánchez 2014; Pino et al. 2017). Besides, access to freshwater in many developing countries is affecting millions of families worldwide, and it is still a threatening issue that needs to be resolved very soon (Qu et al. 2013; Thines et al. 2017). The extensive industrial development, rapid population growth, and climate change contributes largely to the deterioration of the physicochemical and biological characteristics of the

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available water resources (Cundy et al. 2008; Chong et al. 2010; Zeng et al. 2011; Xu et al. 2012). From the industrial sectors and due to the lack of improved water supply and sanitation systems, high quantities of pollutants are discharged into the environment every day. Increasing concentrations of toxic pollutants including heavy metals, organic and inorganic pollutants, and other complex compounds are being discharged alongside the huge volume of wastewater (Xu et al. 2012) that may have devastating effects on the environment and public health (Yue et al. 2015). Therefore, there is an urgent need to remove these pollutants from wastewater before the final discharge of the treated water into the natural environment.

The conventional water treatment technologies (Fu and Wang 2011) used for the remediation of water pollutants are the activated carbon-based adsorption (Srivastava et al. 2011; Zamboulis et al. 2011), membrane filtration (Ersahin et al. 2012), ion exchange (Gode and Pehlivan 2006; Xing et al. 2007; Motsi et al. 2009; Ostroski et al. 2009; Taffarel and Rubio 2009), coagulation and flocculation (Zhang et al. 2003), reverse osmosis (Bodalo-Santoyo et al. 2003), flotation and extraction (Rykowska et al. 2008), electrochemical treatment (Lu and Astruc 2018), advanced oxidation processes, and biosorption (Esser-Kahn et al. 2008; Kavamura and Esposito 2010; Dave et al. 2010) that are presently being employed in several industrial situations (Thines et al. 2017). However, most of the conventional treatment technologies have certain drawbacks in terms of its operational methods, energy requirements, processing efficiency, and economic benefits thereby reducing their large-scale and long-term applicability. From a sustainability point of view, the use of microbes and nanomaterials for the removal of pollutants has received tremendous attention from the research community.

Nanomaterials are very small in size, i.e., approximately 1–100 nm, and shows unique characteristic that enables them to be used in innovative applications (Qu et al. 2013; Werkneh et al. 2018a, b) such as in the area of wastewater treatment and others. They exhibit high surface area-to-volume ratio, which is very significant to produce “highly reactive surface area than the bulk counterparts” (Bethi and Sonawane 2018). Nano-oxides (silver, gold, iron, and titanium) are common nanomaterials which have been employed so far for the remediation of pollutants in contaminated water and soil environments (Panácek et al. 2006; Chopra 2007; Rai et al. 2009; Aditya et al. 2013; Poulose et al. 2014; Bethi and Sonawane 2018).

The ever-growing field of environmental biotechnology offers to solve complex environmental problems in the ecosystem and the natural environment. According to the International Society of Environmental Biotechnology (ISEB), environmental biotechnology is defined as an “environment that helps to promote the development, use and regulation of biological systems for the remediation of contaminated land, air and water environments that works efficiently to sustain an environment friendly society” (ISEB 2018). Several microorganisms have been investigated for the treatment and elimination of toxic pollutants present in complex environmental systems. The microorganisms not only help to break down the persistent organic pollutants into innocuous end products, but they also help to control, detect, and monitor water pollution (Girotti et al. 2008; Kumar et al. 2015).

Nanotechnology offers several advantages because of their unique physicochemical characteristics such as large specific surface area, higher reactivity, and small size. From an environmental biotechnology perspective, the use of various microbial communities provides versatile application terms of addressing the sustainability issues such as their environmental friendliness and low cost for large-scale industrial operations. In this chapter, the technological advancements of nano- and biotechnologies for the sustainable treatment of water and wastewater will be addressed. The applications of various nanomaterials for disinfection and microbial control, adsorption and catalytic oxidation, and sensing and environmental monitoring issues have also been discussed. With respect to microbial biotechnology, their advantages and disadvantages in bioremediation and biotransformation of contaminants as well as the toxicological aspects are also explained.

19.2 Sustainable Water and Wastewater Treatment Technologies

19.2.1 Nanotechnology Perspective

With the development of nanotechnology, its application in water and wastewater treatment is becoming increasingly popular (Bethi et al. 2016; Kunduru et al. 2017; Zhang et al. 2016). Freshwater contamination by heavy metals, organic and inorganic compounds, and other microorganisms are a topic of important concern in both developing and developed countries. In this section, the disinfection and microbial control, catalytic oxidation, and other applications of nanomaterials will be addressed.

19.2.1.1 Nanomaterials for the Disinfection of Pathogenic Microbes

Disinfection is the critical step in the water purification process to avoid the burden of water-borne diseases. In the water treatment industry, the use of conventional disinfectants (i.e., ozone and chlorine as the disinfectant) possess the formation of toxic “disinfection by-products” (DBPs) (Bethi et al. 2016), which are also called the halogenated disinfection by-products, bromate, carcinogenic nitrosamines, etc. The use of UV disinfection is an emerging alternative for oxidative disinfection, i.e., disinfectants that produce a minimal DBPs when compared to other conventional disinfectants. However, this technology also requires high dosage for the effective removal of certain viruses such as adenoviruses. Therefore, the drawback of conventional disinfectants urges the development of alternative approaches that can improve the robustness of pathogenic removal while avoiding the formation of DBP (Qu et al. 2013). Table 19.1 shows the potential of various nanomaterials and their disinfectant mechanisms.

Table 19.1 Antimicrobial mechanisms of nanomaterials for the destruction of pathogens

Nanomaterial	Antimicrobial mechanisms	References
Nano-silver	– Releasing of toxic metal ion (e.g., Ag^+) to kill the pathogenic microorganisms	Rai et al. (2009)
Nano-TiO_2	– Generating ROS, e.g., TiO_2	Hebeish et al. (2013)
Chitosan nanoparticles	– Destruction of cell membrane through direct contact (e.g., chitosan nanoparticles)	Higazy et al. (2010)
Nano-ZnO	– Releasing of –*zinc ions, production of H_2O_2 and membrane damage	Qu et al. (2013)
Carbon nanomaterials	– Oxidative stress, membrane damage	Martynková and Valášková (2014)

Note ROS reactive oxygen species; *NP* nanoparticles

From a practical viewpoint, an ideal disinfectant should possess the following requirements (Zhang et al. 2016; Bethi et al. 2016): (i) no formation of harmful disinfectant by-products; (ii) disinfection within a short time; (iii) formation of a broad antimicrobial spectrum; (iv) easy operation and low energy cost; (v) low toxicity to the environment and health of living organisms; (vi) must not to be corrosive and easy to store; and (vi) the sludge after treatment should be safe for final disposal. Recently, various nanomaterials have lower propensity to form DBPs, while they exhibit the antimicrobial characteristics without strong oxidation process. These include nano-silver (Rai et al. 2009), chitosan nanoparticles (Higazy et al. 2010), photocatalytic titanium dioxide, TiO_2 (Hebeish et al. 2013), and carbon-based nanomaterials (Martynková and Valášková 2014). The nanomaterials have the capacity to kill pathogenic microorganisms by releasing toxic metal ions.

19.2.1.2 (Photo)Catalytic Applications of Nanomaterials

Photocatalysis is an advanced oxidation process that can be applied for the removal of pathogenic microorganisms and trace contaminants from water. In this process, the biodegradability nature of hazardous and nonhazardous impurities is enhanced. Nanocatalysis includes the following steps (Reddy et al. 2016): (i) diffusion of the pollutant, (ii) adsorption onto the surface of the catalyst, (iii) reaction occurring on the surface of the catalyst, (iv) desorption of the product(s) from the surface of the catalyst, and (v) diffusion of the product from the surface. Photocatalysis is also used as a polishing step for the treatment of recalcitrant organic compounds. The main barrier is the slow kinetics due to the limited light influence and photocatalytic activity. However, many recent research works have focused on enhancing the photocatalytic reaction kinetics and the range of photoactivity (Max Lu 2018; Thines et al. 2017).

Most of the conventional waste treatment technologies create secondary pollutant at the end of the process for which further treatment is required. To overcome such challenges, researchers have developed the advanced oxidation processes

(AOPs) as an alternative for the complete degradation, i.e., the mineralization of the organic pollutants to innocuous end products (Altin 2008; Arslan-Alaton et al. 2010; Eskelinen et al. 2010; Kurniawan et al. 2006; Martínez-Huitle and Brillas 2009; Matta et al. 2007; Muñoz et al. 2006; Santhosh et al. 2016; Stasinakis 2008). Photocatalysis has received special attention because of its potential application in environmental remediation. For the treatment of wastewater, photocatalysis is a promising technology because it offers high efficiency/oxidation rates and reduces the pollutant to the simplest nontoxic forms (Bethi and Sonawane 2018).

The photocatalytic mechanisms for the degradation of organic pollutants involve two stages of oxidation (Eqs. 19.1–19.4) and reduction (Eqs. 19.6–19.10) reactions on the surface of the photocatalyst (Bethi and Sonawane 2018):

$$\text{Photocatalyst} + hv \rightarrow h^{+} + e^{-} \tag{19.1}$$

Oxidation reactions:

$$h^{+} + e^{-} \rightarrow \text{heat} \tag{19.2}$$

$$h^{+} + \mathrm{H_2O} \rightarrow \mathrm{H}^{+} + \mathrm{OH}^{*} \tag{19.3}$$

$$2h^{+} + 2\mathrm{H_2O} \rightarrow 2\mathrm{H}^{+} + \mathrm{H_2O_2} \tag{19.4}$$

$$\mathrm{H_2O_2} \rightarrow \mathrm{HO}^{*} + \mathrm{OH}^{*} \tag{19.5}$$

Reduction reactions:

$$e^{-} + \mathrm{O_2} \rightarrow {}^{*}\mathrm{O_2}^{-} \tag{19.6}$$

$${}^{*}\mathrm{O_2}^{-} + \mathrm{H}^{+} \rightarrow \mathrm{HO_2}^{*} \tag{19.7}$$

$${}^{*}\mathrm{O_2}^{-} + \mathrm{HO_2}^{*} + \mathrm{H}^{+} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \tag{19.8}$$

$$\mathrm{H_2O_2} \rightarrow \mathrm{HO}^{*} + {}^{*}\mathrm{OH} \tag{19.9}$$

$$\text{Organic pollutants} + \mathrm{OH}^{*} \rightarrow \text{degradation products} \tag{19.10}$$

Numerous studies have been performed by researchers where photocatalysts were applied to treat water pollutants under the illumination of ultraviolet and visible lights at the laboratory scale (Moon et al. 2003; Parra et al. 2003; Yu et al. 2005; Peng et al. 2006; Venkatachalam et al. 2007; Min et al. 2007; Chang et al. 2009; Geng et al. 2009; Yue et al. 2015; Bethi and Sonawane 2018). The performance of photocatalytic technology has been replaced by the nano-sized photocatalysts. Examples include the following: the mesostructured titanium oxide (m-TiO_2) nanoparticles produced by doping with sulfur (Liu et al. 2009; Tian et al. 2009), carbon (Vu et al. 2012), boron (Li et al. 2008a, b), iodine (Su et al. 2009), fluorine (Jiang et al. 2008), nitrogen (Wang et al. 2012), iron (Yu et al. 2010), silver (Suwanchawalit et al. 2012), manganese

(Shao 2008) and cobalt (Kuljanin-Jakovljevic et al. 2009). Such modified TiO_2 nanoparticles have shown excellent photocatalytic activity for the degradation of a wide range of organic pollutants (Bethi and Sonawane 2018).

19.2.1.3 Applications of Nanomaterials as Adsorbent

The adsorption process is the most widely used polishing step for water and wastewater in order to remove the inorganic and organic contaminants. The conventional adsorbents have drawbacks such as low sorption capacity, lack of selectivity, limited surface area/active sites and short adsorption–regeneration cycle, i.e., short life span, which reduces the cost-effectiveness of the adsorbents. The adsorbents such as activated carbon (granular and powdered forms), ion exchange resin, and inorganic materials such as activated alumina and zeolite are well known in the field of environmental and chemical engineering. These conventional adsorbents are extensively used for removing pollutants from water and wastewater streams (Crini et al. 2018). However, the high cost associated with the production of these materials and their long-term use has always posed several operational challenges for large-scale operations. In the line of adsorption-based research, the development of nonconventional adsorbents is emerging because of the possibility to remove aqueous pollutants not only efficiently but also at a low cost. Besides, some of the nonconventional adsorbents are prepared from industrial by-products and agricultural residues that help to close the waste to products supply chain and promote circular economy.

Nanomaterial-based adsorbents such as carbon nanotubes (CNTs), metal, and metal oxides possess large specific area, yield fast kinetics and specific affinity to different contaminants, and offer high reactivity. Their adsorption efficiency toward a certain type of contaminant is higher than the conventional adsorbents such as activated carbon (Bethi and Sonawane 2018; Jun et al. 2018; Li et al. 2003; Rao et al. 2007; Singh and Susan 2018; Yang et al. 2008). Metal oxide-based nanomaterials also offer exceptional advantages for the removal of heavy metals because of the good adsorption and catalysis properties in the presence of light or a heat source. Examples include low-cost adsorbents of aluminum oxide, titanium dioxide, and iron oxides (Deliyanni et al. 2003; Lu et al. 2006; Mayo et al. 2007). In addition, the polymer dendrimers are also very effective for removing both heavy metals and organic pollutants, where the nano-adsorbents are present in the form of powder or as porous granules (Bethi and Sonawane 2018).

The removal of textile dyes by conventional processes is challenging when compared with other industrial wastewaters. However, the polymeric hydrogels have shown to be promising for the adsorption of organic and inorganic pollutants including dyes (Paulino et al. 2006; Li et al. 2008a, b; Li 2010; Suarez-Parra et al. 2003), phenolic compounds (El-Hamshary et al. 2007), ammonia (Zheng and Wang 2009), heavy metals (Gad 2008), etc. In this regard, the adsorption mechanism of organic pollutants by hydrogel[1] follows physical adsorption, ion exchange and/or chemisorption mechanisms (Bethi and Sonawane 2018). Table 19.2 shows the application of nanomaterials as adsorbent for the removal of various types of pollutants from both water and wastewater. In addition, environmental nanomaterials have been also used for sensing and monitoring water and wastewater characteristics. The major difficulties in water and wastewater treatment are the lack of fast pathogen detection sensors and the extremely low concentration of toxic micropollutants in water bodies (Zhang et al. 2016). The innovative in situ detection sensors with higher selectivity, sensitivity, and fast response are recommended specifically under emergency situations (during water-related accidents). Nanomaterials such as graphene, noble metals (Au and Ag), quantum dots, and carbon nanotubes possess significant characteristics such as unique magnetic or optical and electrochemical characteristics, where their incorporation into sensors could concentrate trace pollutants for detection (Qu et al. 2013).

Nanoparticles have promising reuse applications in sensors and medical diagnostic kits, environmental monitoring, and in several industries such as electronics, fine chemical, energy, and cosmetics (Abdullaeva 2017). With respect to the application of nanoparticles in the field of environmental engineering, nanoparticles have reuse applications in drinking water treatment, adsorption of toxic metals, and other pollutants from water, inactivation of pathogens, and the transformation of toxic materials into less toxic compounds. The nanoparticles that have reuse applications are first recovered through the biomineralization process using various types of microbes. For example, the conversion of selenium oxyanions (selenite and selenite) present in wastewater to selenium nanoparticles has widespread applications in semiconductor manufacturing, fertilizer industry, as well as for the removal of heavy metals from wastewater (Staicu et al. 2015).

19.2.2 Environmental Biotechnology Perspectives

Environmental biotechnology deals with the application of biological processes to protect and restore the environment from pollution causing constituents through the suitable use of biotechnology, alone or in combination with other technologies (Pachiega et al. 2018). Research and innovation in environmental biotechnology are crucial in developing scientific solutions for preventing, mitigating, and reversing environmental destruction with the support of microorganisms, i.e., the biocatalyst. The following are the key applications of environmental biotechnology from a waste management viewpoint.

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[1] Hydrogel* is a “three-dimensional cross-linked polymer network” that consists of the hydrophilic functional groups –OH and –COOH where they make the hydrogel hydrophilic, and the penetration of water into the hydrogel is done by a simple diffusion mechanism.

Table 19.2 Nanomaterial-based adsorbents for the removal of selected wastewater pollutants

No.	Pollutants	Nano-adsorbent	Surface area (m^2/g)	Optimum conditions	AC (mg/g)	RE (%)	References
1	Congo red	Magnetic $Fe_2O_4^-$ graphene nanocomposite	33.6	298 K, 10 mg/L initial conc., 10 mg/25 mL of adsorbent dose	118.2	N/A	Yao et al. (2012)
2	Malachite green	Reduced graphene	931	303.15 K, pH 3.7	476.2	95%	Gupta and Khatri (2017)
3	Methyl orange	Functionalized CNTs loaded TiO_2	N/A	298 K, pH 6.5 at 30 min and 5 mg/L of conc.	42.85	100%	Ahmad et al. (2017)
4	Methylene blue	Graphene oxide/Fe_3O_4	118.2	298 K, 10 mg/L of conc., 10 mg/25 mL of adsorbent dose	45.3	N/A	Yao et al. (2012)
5	Methyl violet	Graphene oxide sponge	N/A	298 K, pH 6.0, 100 mg/L conc.	467	98.8%	Liu et al. (2011)
6	4-chloro phenol	Nano-graphene oxide (NGO)	N/A	75 mg/L of conc., and flow rate of 1 mL/min	145.2	N/A	Eslami et al. (2016)
7	Phenol	Nitrogen-doped carbon nanotube	102	298 K, pH 7.0, and 0.6 mmol/L of initial conc.	0.16 mmol/g	N/A	Diaz-Flores et al. (2009)
8	p-nitro phenol	Nano-graphite oxide	421.7	298 K, pH 7.0, 100 mg/L conc., 4 g/L adsorbent dose at 30 min	268.5	98.9%	Zhang et al. (2015)
9	Ni^{2+}	Oxidized CNTs	–	–	49.3	–	Kandah and Meunier (2007)

19.2.2.1 Bioenergy and Environmental Biotechnology

Bioenergy is most commonly the biogas, biofuels, biomass, and biohydrogen energies produced from the use of environmental microbes in the domestic (Xin et al. 2016; Novoveská et al. 2016), industrial (Nakashimada et al. 2002; Wen et al. 2010; Jayashree et al. 2016; Darpito et al. 2015) and other sectors (Wang et al. 2015). Several studies have revealed that the household waste has demonstrated larger bioenergy potential than other types of wastes originating from agricultural and industrial sources (Nakashimada et al. 2002; Wen et al. 2010; Sarris et al. 2014; Darpito et al. 2015; Wang et al. 2015; Jayashree et al. 2016; Xin et al. 2016; Gomes et al. 2016; Novoveská et al. 2016; Estevam et al. 2018; Ferreira et al. 2018; Pachiega et al. 2018). Table 19.3 shows the microorganisms applied to produce different forms of energy from various sources of wastewater.

The production of bioenergy through the retrieval of organic wastes characterizes a substantial waste management alternative as well as a significant environmental pollution abatement strategy.

Table 19.3 Selected microorganisms for the production of energy from wastewater

Types of wastewater	Type of microorganism	Type of energy produced	References
Domestic wastewater	Algae	Biofuel production	Xin et al. (2016)
Municipal wastewater	Microalgae	Biofuel production	Novoveská et al. (2016)
Cassava flour wastewater	Lactic acid bacteria	Biohydrogen production	Gomes et al. (2016)
Olive mill wastewater	*Saccharomyces cerevisiae* MAK-1	Bioethanol production	Sarris et al. (2014)
Food processing wastewater	*Stenotrophomonas* bacterial strains	Electricity generation	Jayashree et al. (2016)
Synthetic wastewater	UMN266 microalgal strain	Bioethanol production	Wang et al. (2015)
Brewery wastewater	Microbial fuel cells	Electricity generation	Wen et al. (2010)
Brewery wastewater	*Chlorella protothecoides*	Biodiesel production	Darpito et al. (2015)
Brewery wastewater	*E. aerogenes* HU-101	Biohydrogen production	Nakashimada et al. (2002)
Poultry, swine, cattle, brewery, dairy, and urban wastewater	*Scenedesmus obliquus*	Biohydrogen	Ferreira et al. (2018)
Brewery wastewater	*Klebsiella pneumoniae*	Biohydrogen	Estevam et al. (2018)
Brewery wastewater	*Anaerobic bacteria consortium*	Biohydrogen	Pachiega et al. (2018)

19.2.2.2 Bioremediation Techniques

The term bioremediation has been used to describe the process of using biological agents such as fungi, bacteria, and algae to remove and detoxify the environmental contaminants, while the microbes are capable of using the chemical contaminants as a source of energy during their metabolic processes (El-Sheekh et al. 2015; El-Sheekh et al. 2016). The efficiency of microbial degradation is restricted by any one of the environmental factors such as moisture content, temperature, nutrient availability, activity of the microorganism, characteristics, and composition of the contaminant(s) and its biodegradability (Chakraborty et al. 2012a, b). This process is also considered as a cleaner, cost-effective, and environment-friendly technology for the removal of pollutants from wastewater (Salgot and Folch 2018).

The principal components of the bioremediation process are the food, nutrients, and microorganisms, which are known as bioremediation triangle (El-Sheekh et al. 2015). The lack of food and nutrients can be a limiting factor to achieve a successful bioremediation process when the microorganisms are found almost ubiquitously. In essence, microorganisms find their food in the water and wastewater where they live. However, water pollutants become a source of additional food for microbial growth. In this aspect, the main goal of any bioremediation technique is to stimulate the microbes with nutrients and chemicals that allow them to destroy the pollutants. Besides, the water pollutants serve two important implications (Fufa et al. 2017): (i) the pollutants provide the required carbon source for microbial growth, and (ii) the microbes acquire energy through the oxidation and reduction reactions by breaking the chemical bonds and transferring the electrons from the pollutants.

Biotechnology has a big role in the bioremediation processes, in terms of utilizing the application of genetic engineering to enhance the cost and efficiency as a key factor to reduce the future burden of toxicants/pollutants in the environment. In this aspect, the biological agents have higher potential for bioremediation; however, for continuous and large-scale water and wastewater treatment, it requires the application of genetic tools for improved efficiency. Genetically modified microbes have proven to be effective for the bioremediation of highly polluted environment (e.g., petroleum spills). *Bacillus thuringiensis* and *Deinococcus radiodurans* have been used for the removal of oil spills and ionic mercury from highly radioactive waste, respectively (Fufa et al. 2017). Bioremediation technologies have been tested for the removal of contaminants from water and wastewater. These include different bioreactor configurations, phytoremediation, bioleaching, bio-stimulation, and composting. There are also "active members of the microbial consortiums" that play a major role in carrying out biodegradation in many polluted environments such as *Nitrosomonas*, *Pseudomonas*, *Penicillium*, *Bacillus*, *Xanthobacter*, *Flavobacterium*, and *Mycobacterium* (El-Sheekh et al. 2015). The aerobic and anaerobic groups of microbes are being used in the bioremediation techniques. In the aerobic microbes, the *Rhodococcus*, *Mycobacterium*, *Pseudomonas,* and *Sphingomonas* are recognized for their degradative capacities of pesticides and hydrocarbon compounds. Recently, there is an increasing attention of bioremediation application such as the dichlorination of the chloroform and trichloroethylene and the removal of polychlorinated biphenyls in the river sediments. In the bioremediation process, microbes could be isolated from all natural conditions prevailing in the environment in order to have an extensive range of adaptability (Salgot and Folch 2018) because: (i) they can survive harsh environmental conditions, and (ii) they can easily survive in the presence of hazardous compounds and in the absence and/or presence of oxygen in wastewater streams. As a classical example, for the bioremediation of heavy metals, the most common class of bacteria belongs to the genera of *Bacillus*, *P. aeruginosa*, *Streptomyces,* and *Pseudomonas*. However, due to the presence of high percentage of cell wall material that exhibits good metal binding potential, many fungal biomasses are more effective for the bioremediation of heavy metals when compared with other class of microorganisms. These include genera of *Rhizopus*, *Saccharomyces,* and *Streptoverticullum* (Salgot and Folch 2018). In a recent study, Werkneh et al. (2018a) investigated the simultaneous bioremediation of selenite and phenol containing oil refinery wastewater using *P. chrysosporium* and one of the end product of this bioremediation process was the formation of biogenic elemental selenium. Depending on the type of wastewater treatment required, there are basically two types of bioremediation: (i) in situ bioremediation–this depends on the principle that the microbes are already present in the polluted site and thereafter the microbes are adapted to the organic pollutants present at the site. The process of biodegradation occurs until all the electron acceptors (in most case oxygen) or nutrients (phosphate and nitrate) attain a limiting (low) concentration. However, it is possible to increase the biodegradation efficiency through the stimulation of natural biotransformation by the addition of nutrients (P and N) to the environment and this process is called enhanced in situ bioremediation; (ii) ex situ bioremediation—is usually an aerobic system and it involves treatment of the contaminated environment (water or sediment) by using a slurry phase system. This type of bioremediation technique can be applied to medium that is readily accessible above the ground surface. There are several important environmental factors that affect the in situ bioremediation process: (i) pH-at the laboratory scale, bioremediation is often studied under neutral pH conditions to which the majority of the bacteria show optimal growth. However, the adjustments of pH enhance the biodegradation rate. The other factors include temperature, water content, nutrient availability, external electron donor availability, the bioavailability of organic pollutants, and the presence of growth and metabolic factors (Kumar et al. 2015).

19.2.2.3 Biotransformation Techniques

Biotransformation is the process of transforming toxic water pollutants into compounds with less toxicity and persistence, which are aided by microorganisms such as fungi, bacteria, and their enzymes (Alvarino et al. 2018). It is well known that the natural transformation process is nonspecific and slow, while the microbe-mediated technologies are gaining importance and widely utilized to generate metabolites with more specificity. Besides, environmental biotransformation is an environmentally induced or natural process used to restore water to its original state by using the indigenous microbes to break down and eliminate the contaminant(s) present in the water body (Alvarino et al. 2018). Biotransformation is a crucial process in the natural attenuation (disposal or reduction) of chemical compounds at the waste site. To make effective use of the environmental biotransformation process, the microorganisms should convert the water pollutants to harmless products/forms, while the environmental conditions allow and facilitate microbial growth

Table 19.4 Comparisons of biological wastewater treatment techniques

Approaches	Benefits	Drawbacks
Anaerobic digestion	– Releases little or no greenhouse emissions and able to produce bioenergy – It can be stored with minimal energy loss	– It is more expensive when compared with energy sources to fossil fuels, since it requires more fuels to generate the same amount of energy – It also expensive concerning the cost of handling the biomass, transporting, extracting, and harvesting
Bioremediation	– It is cost-effective, because it is a natural process – The toxic chemicals are removed/destroyed and they are not merely separated from the environment – Requires low capital expenditure, but requires less energy when compared to other technologies	– The process is slow and requires a longer time; it is not effective to remove heavy metals – The soil for in situ bioremediation requires high permeability – There exists a substantial gap in the understanding of physiology and genetic expression, microbial ecology, site engineering, and site expression, and requires a scientific background in designing the process to be successful
Biotransformation	– Its application contains equipment that is easy to install and commonly available – There exists a minimal disturbance to ongoing site activities. It is less costly than other remediation techniques – To enhance site bioremediation, it should be integrated with other technologies such as soil venting, bioventing, etc. – In many cases, this method does not produce waste products that might require further disposal and treatment	– High concentrations (>50,000 ppm) of less water soluble (hydrophobic) compounds are not readily bioavailable – It is challenging to implement this technology in low permeable aquifers – It requires continuous maintenance and monitoring – The remediation occurs only in channels within the aquifer or in more permeable layers

and activity. Its application should include the manipulation of environmental parameters to achieve high microbial growth rate and a faster specific substrate degradation rate. However, environmental biotransformation techniques also have their drawbacks (Table 19.4) (Speight and El-Gendy 2017).

19.2.3 Bioreactor Configurations in Water and Wastewater Treatment

The packed bed bioreactor (Fig. 19.1a) consists of a fixed bed that is used as a supporting medium for the attachment of microorganisms. This biofilm-based bioreactor technology has widespread applications in the field of wastewater treatment. Contaminant removal is achieved as the wastewater flows through the bed; the pollutants are biodegraded by the attached biofilm (Kureel et al. 2018). In this reactor configuration, it is possible to use the nanomaterials as a filter medium and integrate the advantages of nanobiotechnology processes to reduce the installation and operational costs. A fluidized bed reactor (FBR) (Fig. 19.1b) consists of an upwardly flowing liquid phase and a solid phase that is in a state of fluidization due to the liquid flow. The solid phase here refers to an inert material and the biomass that is attached onto its external/internal surface. This reactor configuration offers high surface area for microbial growth and the microbes get easy access to the substrate, i.e., the pollutants present in the liquid phase. In practice, there are challenges associated with FBR operation: (i) limited biomass growth on the particles, (ii) wash out of biomass leading to variations in solid retention time, (iii) unexpected alteration of flow rate, and (iv) the formation of inactive or dead zones within the reactor. Another reactor type that is extensively used in environmental engineering for the treatment of high strength wastewater is the upflow anaerobic sludge blanket reactor (UASB) (Fig. 19.1c). As the name implies, this reactor configuration is similar to an anaerobic digester and the microorganisms are grown in the form of a blanket of granular sludge at the bottom of the reactor. The wastewater is passed to the vertically designed bioreactor in an upflow mode during which the microbes present in the granular sludge come into contact with the substrate. The granular sludge is spherical in shape and has a size of 1–4 mm, with good settling characteristics. Figure 19.1d shows the schematic of a sequencing batch reactor (SBR). This system is a batch process operated in four consecutive cyclic steps: feed–react–settle and decant. During the settling step of the SBR operation, the wastewater treatment requires more time and reactor volume depending on the type of biofilm growth and its settleability. Otherwise, the operational mode can be programmed to achieve anaerobic, aerobic or anoxic treatment depending on the characteristics of the wastewater and the degree of treatment required. High-rate anaerobic reactors are widely applied for the treatment of industrial wastewaters with organic loading rates as high as 10–15 kg m^{-3} d^{-1}. In some situations, in order to enhance the performance of the UASB reactor, a hybrid system comprising mainly the UASB reactor and an internally packed bed bioreactor (Fig. 19.1e) can also be used.

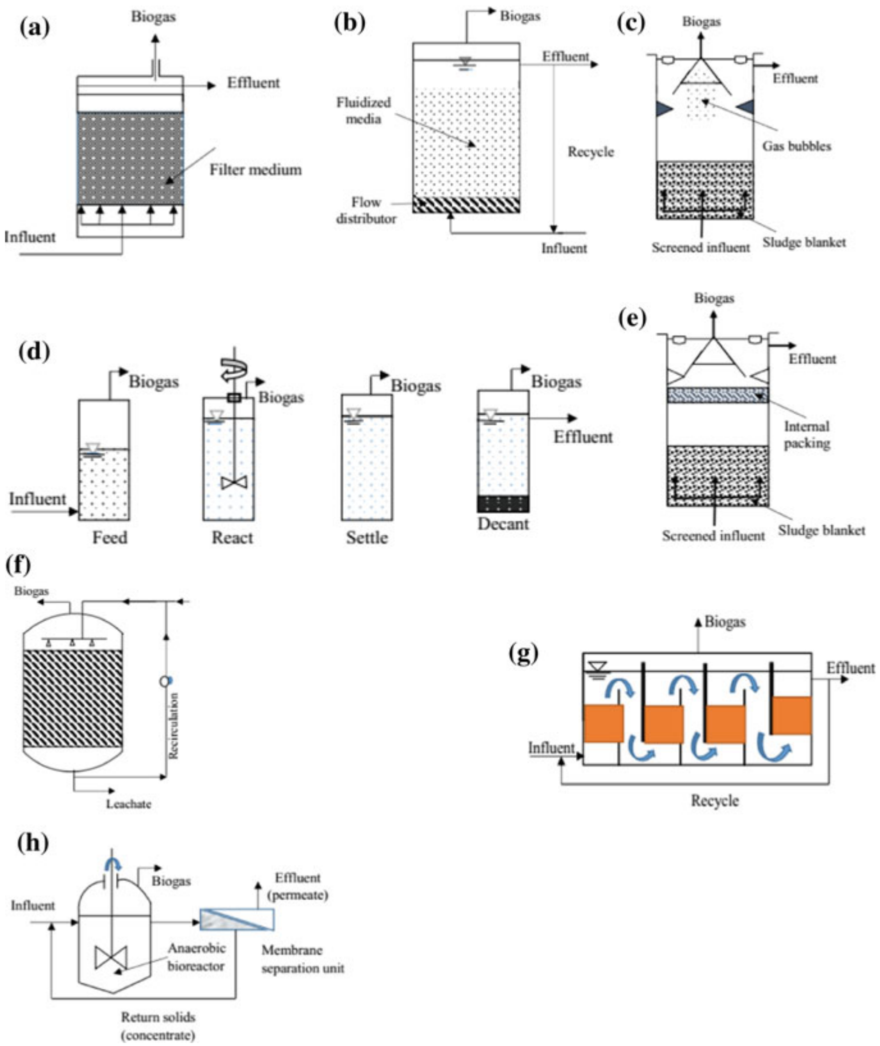

Fig. 19.1 Different bioreactor configurations used for wastewater treatment: **a** packed bed bioreactors (PBB), **b** fluidized bed bioreactor (FBR), **c** upflow anaerobic sludge blanket (UASB), **d** anaerobic sequencing batch reactor (ASBR), **e** hybrid (UASB + packed bed) reactor, **f** leach bed reactor, **g** anaerobic baffled reactor, and **h** anaerobic membrane bioreactor (AMB)

Anaerobic baffled reactor (Fig. 19.1f) can be envisioned as a number of UASB reactors coupled in series. The advantages of this reactor configuration over a single UASB reactor are: to decrease the problems associated with biomass washout and consequently retain higher content of biomass inside the reactor. Besides, this reactor configuration does not require an auxiliary gas–sludge separator. This system is specifically designed to handle low to high strength municipal wastewater in high-temperature areas. A leach bed reactor (Fig. 19.1g) is also used for simultaneous wastewater treatment and biogas production in order to achieve resource recovery. Figure 19.1h shows the schematic of an anaerobic membrane bioreactor (AMB), which has proven to be highly efficient for water and wastewater treatment. AMB offers the following advantages: (i) rapid start-up, (ii) good removal of suspended solids, (iii) low footprint, and (iv) high COD removal efficiency (Guglielmi et al. 2009). As demonstrated in several research works, these reactor configurations can be applied in the field of nanotechnology for water and wastewater treatment.

19.3 Case Study in Water and Wastewater Treatment

There are several case studies where the concept of nanotechnology has been implemented and commercialized at industrial wastewater treatment systems, i.e., in full-scale systems. Wei et al. (2011) studied a full-scale wastewater treatment plant handling wastewater from a food processing factory (Lee Kum Kee Condiment Corporation, Guangdong, China). The reactor configuration used was a jet biogas internal loop anaerobic fluidized bed reactor (JBILAFBR) (Fig. 19.2). This technology requires low energy input, offers good mixing characteristics, and enhances the mass transfer. This reactor required a start-up time of 55 days and the pre-treatment step comprised of settling, coagulation, and air floating. The full-scale reactor had a working volume of 800 m^3, and it was able to handle a maximum COD loading rate of 5.6 kg COD m^{-3} day^{-1} at a hydraulic retention time (HRT) of 24 h. According to the authors, the COD removal efficiency and the biogas production rate were found to be 80% and 350 m^3 day^{-1}, respectively.

As seen from this figure, the raw wastewater is fed into a separating tank wherein oil and other solids present in the wastewater are removed. After that, the effluent is

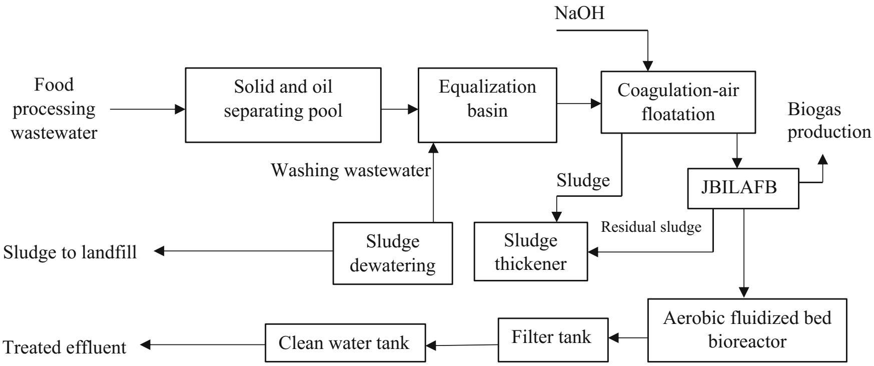

Fig. 19.2 Schematic of the full-scale jet biogas internal loop anaerobic fluidized bed reactor (JBILAFBR) for the treatment of food processing wastewater

transferred to a flow equalization basin in order to ensure continuous flow and stable concentration of the influent. The effluent from the equalization basin then passes to the coagulation-air floating tank (CAFT) for the complete removal of suspended solids and color, and the adjustment of pH. After this step, the wastewater enters the JBILAFBR unit wherein biodegradation occurs and the organic load is reduced to levels that can be easily handled in the anaerobic fluidized bed bioreactor. This process generates biogas which can be recovered and also sludge that can be landfilled or further processed to be used as a fertilizer.

19.4 Toxicological Perspectives of Nano/Biotechnology

Natural and anthropogenic nanoparticles when released or formed naturally in the environment could be transformed, distributed, and transported in water, soil, sediment, and air environments. Such means of transport can have higher impacts on the fate, bioavailability, and toxicity of NPs in the aquatic environment. The widespread application of nanotechnology has also caused a toxicological scare among the end users and the environmentalists. This is due to the poor knowledge about the behavior and fate of nanoparticles in the environment and human health (Fu et al. 2014). The toxicology of nanomaterials depends on their structural properties and chemistry. The mechanisms of toxicity or antimicrobial action on the living organisms are as follows:

(i) Disruption and membrane integrity by the strong electrostatic interaction between the bacteria and the nanoparticles or by rupture of the cell membrane and bacterial agglomeration.
(ii) The reactive oxygen species (ROS) can interact with organelles and indirectly induce the DNA damage as well as protein inactivation leading to cell death and apoptosis in eukaryotes.

The carbon nanotubes and metal oxides that include superoxide anions, hydroxyl radicals, and the leached ions and heavy metal forms an ROS, which usually shows high chemical reactivity (Sayes and Warheit 2009). The ROS generation and the succeeding formation of the oxidative stress acts as the foremost mechanism causing various nanotoxicity problems. The toxicity concern is not on the nanomaterial itself but on its potential reaction within the surrounding environmental conditions. This causes inflammation and oxidative stress, resulting in damaging of membranes, proteins and DNA, unregulated cell signaling, cytotoxicity, changes in cell mortality, cancer initiation and promotion, and apoptosis (Nel et al. 2006; Xia et al. 2008; Zhu et al. 2013). Many authors reported that the production of ROS caused phototoxicity and cytotoxicity by various nanoparticles such as nano-TiO_2 and nano-ZnO, nano-Co, nano-Ag, and nano-Cu (Gurr et al. 2005; Wang et al. 2007; Kang et al. 2008; Hsin et al. 2008; Applerot et al. 2009; Shukla et al. 2011a;

b; Chiang et al. 2012; Yin et al. 2012, 2013; Mei et al. 2012; Girgis et al. 2012; Wang et al. 2013; Fu et al. 2014).

The toxicity of nanoparticles to the microbial community depends on two major factors (Laux et al. 2018): (i) the nature of the nanoparticle such as morphology, size, and chemical nature; (ii) the nanoparticles have the tendency to conjugate with biological molecules in the natural environment that may have various adverse effects on bacteria and other aquatic organism. The interaction of nanoparticles with the microorganism forms ROS that can cause oxidative stress, cell wall damage, membrane disorganization, generation of organic radicals in the absence of light and DNA damage. For example, silver nanoparticles ($\sim$ 1–10 nm) interact with the cell membrane of *Pseudomonas aeruginosa*, phosphorus, and sulfur-containing compounds to cause DNA and cell membrane damage at a concentration of 25–100 mg/L (Morones et al. 2005).

Thus, there is a need to understand the health, environmental, and safety concerns of nanomaterials through a scientific evidence-based approach. Besides, at the country level, the managerial aspects of implementing new policies, legal standards of testing the nanomaterials toxicity on human health, and other life forms and risk assessment should be given high priority. In this respect, China was the first to establish a “national standards effort in nanotechnology with the united working group for nanomaterials standardization” in the year 2003 (Laux et al. 2018). The Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA) recommended different benchmark limit exposure values to monitor the effectiveness of different protective measures being implemented in an 8-h workplace (Locascio et al. 2011; Katsumiti et al. 2015). These include the following:

(a) Metals, metal oxides, and other bio-persistent granular nanomaterials (a density of >6000 kg m^{-3}): A particle number concentration of 20,000 particles per cm^3 in the range of measurement between 1 and 100 nm should not be exceeded.
(b) Bio persistent granular nanomaterials (a density <6000 kg m^{-3}): A particle number concentration of 40,000 particles per cm^3 in the range of measurement between 1 and 100 nm should not be exceeded.
(c) Carbon nanotubes: A provisional fiber concentration of 0.01 fibers per cm^3 should not be exceeded. This is based on the exposure risk ratio for asbestos.
(d) Nanoscale liquid particles (hydrocarbons, fats, and siloxanes): The maximum workplace limit values should be employed owing to the absence of effects associated with the solid particles.

Microbial toxins are also produced by the microorganisms including fungi and bacteria. *Botulinum neurotoxins* (BoNTs) are a well-known potent natural toxin. The family of BoNTs is produced by several toxigenic strains of spore-forming anaerobic *Clostridium botulinum* (Agrawal and Gopal 2013). Bacterial toxins are either endotoxins or exotoxins, where endotoxins are part of the bacteria itself on the outer membrane or it is not released until the bacteria is killed by the immune system, while exotoxins are generated by bacteria and are actively secreted

(Agrawal and Gopal 2013). The other bacterial toxins are tetanus toxin (Agrawal and Gopal 2013), anthrax toxin (Maldonado-Arocho 2009), *Pasteurella multocida* toxin (Orth 2009), subtilase cytotoxin (Paton and Paton 2009), vibrio RTX toxins (Satchell and Geissler 2009), *Helicobacter pylori* toxin (Cover and Atherton 2009), Staphylococcal toxins (Langley et al. 2009), Cyanobacteria toxins (Herrero and Flores 2008), and mycotoxins (Machida and Gomi 2010). The Cyanobacteria, i.e., the blue-green algae, produces another type of toxins in the drinking water system. The effects of these toxins (e.g., anatoxin-a(s), anatoxin-a, saxitoxins, microcystins, cylindrospermopsin, and nodularins) range from liver cancer to neurotoxicity (Rapala et al. 2002). The health effects of cyanobacterial toxins depend on the type of water-related exposure (skin, drinking, and contact) and the chemical structure and physicochemical characteristics of the toxin itself. The prevalence of cyanobacteria and its toxins in water bodies are a major challenge for the treatment of drinking water. Fungal ribotoxins are common toxins of fungal extracellular ribonucleases family, which tend to inactivate ribosomes by the cleavage of a single phosphodiester bond (located on the rRNA) (Agrawal and Gopal 2013). It is evident that further research is needed from a systems perspective on the integration of nanotechnology and environmental biotechnology (nanobiotechnology) in treating water and wastewater. Nanobiotechnology refers to the capability to manipulate and integrate different biological and chemical materials, as well as (bio)processes for applications pertaining to the remediation of contaminated environments.

19.5 Conclusion and Future Perspectives

Nanotechnology and biotechnology are two promising technologies of the twenty-first century, specifically in the field of water and wastewater treatment. Nanotechnologies have demonstrated higher removal efficiency of the pollutants from water and wastewater, but their toxicity is still questionable. Due to their nanoscale size, the assessment and management of the associated risk are often challenging and limited. In natural environments, eukaryotic (microalgae) and prokaryotic (bacteria) microorganisms produce different types of very potent toxins, among which many of these toxins have complex structures and their biological actions are yet to be elucidated. Further research is required: (i) to study the potential hazards of these materials during water and wastewater treatment, (ii) to ascertain the long-term performance of biological techniques in full-scale systems, and (iii) to integrate innovative nanotechnology and environmental biotechnology (nanobiotechnology) for sustainable water and wastewater treatment. The application of chemical agents (nanomaterials) and biocatalysts in an integrated approach should be tested further by considering life cycle analysis (LCA) of the nanomaterial and the potential toxicological risks to human health and the environment.

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Chapter 20
Nanofibers for Water and Wastewater Treatment: Recent Advances and Developments

Leonard D. Tijing, Minwei Yao, Jiawei Ren, Chan-Hee Park, Cheol Sang Kim and Ho Kyong Shon

Abstract Materials of nanofibrous morphology and structure are attractive for solving environmental problems including water-related issues. In recent years, increasing interest is geared on the use of specially designed electrospun nanofibers for water/wastewater treatment applications. The nanofibers can be used in the form of nonwoven structures, as stand-alone membranes, as support layer or as a surface modification layer that enables added functionality to a composite material. Continuous research has been carried out in optimizing the nanofiber membrane design and structure by manipulating material, process and surrounding parameters in the electrospinning process. This chapter highlights the recent advances and developments on the potential and application of electrospun nanofibers for water/wastewater treatment. Comprehensive discussion is presented here on various designs and structures of nanofibers and their applications to water-related treatment and the future prospects of such materials.

Keywords Nanofiber · Membrane · Electrospinning · Desalination
Water/wastewater treatment

20.1 Introduction

Electrospun nanofibers have gained wide interest and attention in recent years (Chronakis 2005; Jiang et al. 2018; Xue et al. 2017). The nanofibers boast attractive properties such as very high surface area, controllable pore sizes, high porosity,

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interconnected pore structure, and adequate mechanical strength that are desirable for many different applications (e.g., biomedical, energy harvesting, clothing, smart materials, sensors, water and wastewater treatment, etc.) (Tijing et al. 2017). The ease of fabrication and functionalization makes it more promising. The nanofibers have also attracted many research activities on their preparation, modification, and treatment capabilities for water and wastewater treatment processes. This is primarily attributed to the filter-like characteristics of nanofiber mats, which are similar to the filters used in the water/wastewater treatment field. Nanofibers as membranes take a center role in this review as most nanofibers reported in literature are prepared in this structure/form. However, nanofibers have also been used as electrodes or adsorbent materials for other processes.

Membrane technology plays a significant role in ensuring water security around the world (Shannon et al. 2008). This is because of its high efficiency, cost-effectiveness, and high performance in treating different types of water sources towards the desired water quality. Among the most common membrane separation processes include reverse osmosis, microfiltration, ultrafiltration, and nanofiltration. Polymeric membranes are the most widely available in the market but still face a number of challenges in terms of fouling, degradation, and their overall stability (Le and Nunes 2016). Hence, there is a surge of research done on improving the polymeric membrane performance by manipulating their design, structure, and physiochemical properties. Most commonly, these membranes are in the form of flat sheet and hollow fiber structures. In recent years, the use of nanotechnology and nanomaterials has considerably improved the development of membranes and especially on the use of electrospun nanofibers (Goh et al. 2016).

In the past two decades, research on nanofibers as materials for water and wastewater treatment (membranes, electrodes, adsorbents, etc.) has surged dramatically with many works done on the nanofiber synthesis, surface modification, nanomaterial incorporation, mechanical and thermal stability improvement, etc. This chapter reviews the recent advances on the developments of nanofibers and their application to water and wastewater treatment.

20.2 Electrospun Nanofibers: Fabrication, Design, and Properties

20.2.1 Introduction to Electrospinning and Nanofibers

Nanofibers loosely refer to fibers having diameters less than 1 μm, and have been gaining wide interests in many applications due to their exciting properties and functionalities (Bhardwaj and Kundu 2010). There are a number of ways to fabricate nanofibers such as template synthesis, melt blowing, self-assembly, nanolithography, and electrospinning. For membrane fabrication especially, electrospinning is the most facile and effective way of producing nanofiber membranes especially with the use of polymeric solutions (Huang et al. 2003; Ahmed et al. 2015). The recent advances on upscaling and mass production capability of electrospinning have greatly increased its potential use and promise for future development of functional materials and membranes (Luana et al. 2013).

Simply, electrospinning uses a high-voltage electric field to force a polymer solution to jet out from a small nozzle opening and elongate while whipping instantaneously towards a grounded collector where it is collected and form a nonwoven flat sheet membrane structure. Figure 20.1 shows a schematic of the electrospinning system. The process itself is simple, yet the optimization of the different parameters such as the material, process, and posttreatment parameters can be challenging, when designing a specific structure and property of the nanofiber membrane. The most common material used for electrospinning is polymer-based materials, with more than 200 of such polymers have been made into different nanofiber structures. Several papers have summarized the various strategies in nanofiber membrane fabrication and modification in recent years including the effect of process/operating parameters, material selection and preparation, and posttreatment conditions (Ahmed et al. 2015; Teo and Ramakrishna 2006; Tijing et al. 2014a). Nanofiber membranes can be divided into three main designs: (1) neat nanofiber membranes, (2) composite nanofiber membranes, and (3) surface-modified/functionalized nanofiber membranes.

The use of nanofiber membranes for water and wastewater treatment applications has attracted wide interest in the last 20 years. This is primarily because of the versatility of the nanofiber formation, where the porosity, pore size, structure, surface properties, and mechanical and thermal stability can be controlled

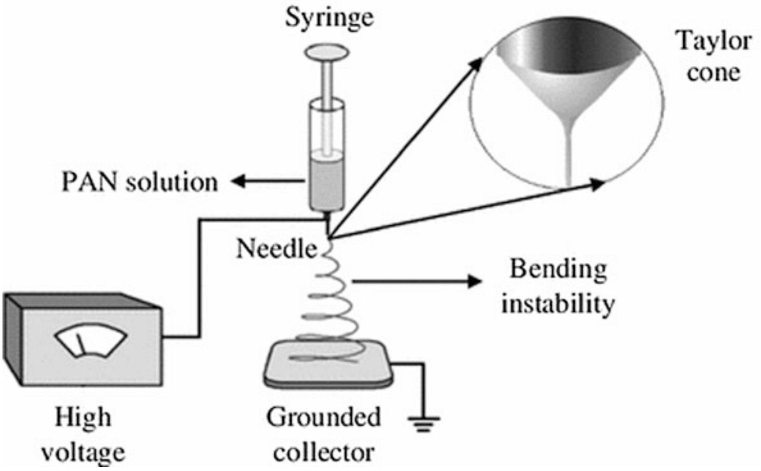


Fig. 20.1 Schematic of electrospinning system showing the three main components: high voltage power supply, syringe containing polymer solution, and grounded collector. The enlarged inset figure also shows the Taylor cone formation when jet overcomes the surface tension of solution to emit fibers. Adapted from Zhang et al. (2014)

(Tijing et al. 2016). Depending on the desired properties, nanofiber membranes can be made into hydrophilic, hydrophobic, omniphobic, highly porous, as support material, as self-standing membrane, as antibacterial or antifoulling membrane, as self-heating membrane, as adsorbent, and many other properties. This chapter reveals the attractive properties and applications of such nanofiber membranes mainly for water and wastewater treatment processes.

20.2.2 Electrospinning Parameters

Electrospinning is a facile technique in producing nonwoven nanofibers mats or membranes. Though the concept and method are quite simple, producing nanofibers with the desired properties and design could be tricky (Tijing et al. 2014a). The material selection and preparation are essential parameters for the resulting nanofibers. The polymer concentration of the solution has a strong effect on the fiber size, the presence of beads, and the electrospinnability of the solution. Conflicting studies have been reported in the literature about the effect of polymer concentration on fiber size, but majority of the reports indicated that high polymer concentration results in bigger fibers, while low polymer concentration produces smaller fibers (Ki et al. 2005). In addition, below a certain threshold polymer concentration (which varies depending on the type of polymer used), there will be higher tendency for sputtering which results in the production of beads-on-string fiber formation. Beads on nanofibers are usually regarded as defects as they can serve as stress points for any external load towards the nanofiber, which consequently affects its overall mechanical properties. However, in some studies, the beads could be a desired design, which adds more roughness and increases surface hydrophobicity (Tijing et al. 2016). The polymer concentration is closely related to the solution viscosity. At higher polymer concentration, solution viscosity in most cases also increases. Thus, it was observed that higher concentration (therefore more viscous) has more chances of clogging in the electrospinning nozzle and eventually block it. Thus, fiber formation is inhibited. Nevertheless, the less viscous solution is also not desired because it could lead to sputtering effect. So that a certain viscosity for a specific polymer solution is required for smooth fiber formation. Another solution parameter that is very much related with concentration and viscosity is the polymer molecular weight. Generally, there is a minimum molecular weight for a specific polymer for it to have good electrospinnability (Tao and Shivkumar 2007; Haghi and Akbari 2007). Hence, the importance of optimizing the solution parameters is essential to fabricate smooth, cylindrical, and uniform nanofiber mat.

For jet formation to proceed, the solution must be conductive enough to improve its charge carrying capability so that the applied electric field can promote the repulsion of charges in the jet that stretches and elongates the polymer until it is collected (Talwar et al. 2010). Polymers innately have charges themselves, thus nanofiber formation is possible. However, the kind of solvent and additives used greatly enhances the conductivity of the solution which also helps in the electrospinnablity of the solution (Kim et al. 2005). Studies have shown that adding salts in the polymer solution increases conductivity thereby increasing the chances of further elongation resulting in thinner fibers. The presence of additives also promotes the formation of nanonets due to charge attraction from neighboring particles (Barakat et al. 2009).

In as much as the material selection and preparation are important factors, the process conditions also dictate much of the resulting nanofiber design and properties. The applied electric field is a requirement for nanofiber formation. This is basically dictated by the applied voltage (Sill and von Recum 2008) and the nozzle tip-to-collector distance (TCD). At high applied voltage, the driving force that helps overcome the surface tension of the solution to emit thin fibers is much greater, hence expecting more charge repulsion resulting in thinner nanofiber formation. However, one must be careful not to increase too much of the voltage as this could also lead to sputtering as the driving force is too high that there is sudden breakage of polymer entanglement at the nozzle tip leading to sputtering. Depending on the polymer used, the applied voltage is usually in the range of 5–40 kV. There is always a threshold voltage for specific kind of material and its solution properties.

As mentioned above, the tip-to-collector distance is also important. At a longer TCD, once the polymer solution is emitted from the nozzle, the longer flight time towards the collector gives higher chance for the solvent to evaporate, thus leading to thinner nanofiber formation (Matabola and Moutloali 2013). On the other hand, too short of TCD would likely result in film formation instead of fibers, as the short flight time is not enough for the solvent to evaporate in air. For most electrospinning setup, optimizing the TCD together with other parameters is essential. Usually, a TCD between 15 and 25 cm is used in many studies. As nanofibers are emitted from the nozzle via applied electric field as driving force, the amount of solution that actually is exposed to the nozzle tip is controlled by the solution feed rate. In most cases, a syringe pump is used to push the solution, and the feed rate is usually 1 ml/h or lower. This is to ensure that there is sufficient amount of solution going to the nozzle, ideally in the same rate of the fiber emission from the nozzle (Matabola and Moutloali 2013). If the solution feed rate is too slow, this usually leads to uneven and nonuniform fiber formation as not enough solution is being emitted. On the other hand, too fast feed rate also leads to beaded fibers as the supply of solution at the nozzle tip is over accumulated. This produces beaded structures, garland, or even ribbon-like fiber formation, as observed by other studies. Hence, it is necessary that a suitable feed rate is used for electrospinning.

Other factors to consider for electrospinning of nanofibers are its ambient condition—especially temperature and relative humidity, and the way it is processed post-fabrication. The surrounding humidity during electrospinning is found to have an important effect on the nanofiber morphology and structure (De Vrieze et al. 2008). At low humidity, i.e., less moisture in air, there is bigger tendency for rapid evaporation of solvents to the air as the air has higher capacity to hold moisture. This usually results in thinner nanofiber formation. On the other hand, high humidity can produce pores on the nanofiber as the moisture in the air can condense on the formed nanofiber. However, if the polymer used is water soluble, high

Table 20.1 Effect of electrospinning parameters on the nanofiber structure and morphology

Electrospinning parameter	Effect
Applied voltage	High voltage generally leads to thinner fibers
Feed flow rate	Most flow rates are limited to 1 ml/h or lower to enable good fiber formation
Tip-to-collector distance (TCD)	Longer TCD results to thinner fibers Very near TCD may produce thin film structure instead of nanofibers
Solution concentration	High concentration may clog the nozzle Low concentration may lead to sputtering
Solution conductivity	High conductivity leads to thinner fibers
Ambient humidity and temperature	Higher humidity leads to pore formation on nanofibers unless if the polymer is water soluble, which leads to thinner nanofiber
Hot-press posttreatment	Increases the mechanical strength of nanofibers mat Reduces pore sizes if there is fusion of fiber nodes

humidity could potentially produce thinner fibers as the moisture in the air helps in further dis solution of the fiber while it is on flight to the collector. The temperature of the environment also has similar effect. Higher temperature (which also could mean drier surrounding) could lead to less viscous solution hence promoting thinner fibers. The post-fabrication treatment methods help in improving the overall mechanical, and morphological properties of the nanofiber membranes. Hot-press treatment in particular, which presses the nanofiber between two hot plates or just exposed to high temperature in an oven, promotes controlled melting of some nanofiber nodes that leads to node fusion thereby increasing the overall mechanical properties. However, this method also reduces the overall pore size and porosity due to the fusion occurrence (De Vrieze et al. 2008). Table 20.1 summarizes the effect of various electrospinning parameters on the nanofiber formation, structure, and morphology.

As a guide, smooth nanofiber formation with uniform fiber sizes is always the ideal structure desired for nanofibers. This can be controlled by manipulating various parameters before, during, and after electrospinning process. The proper optimization of these many parameters for any specific polymer used is necessary to achieve the desired nanofiber morphology and properties.

20.2.3 Electrospun Nanofiber Design and Properties

The versatility of electrospinning to produce nanofibers is one of its most attractive features for many applications. Nanofibers can be designed and prepared in many configurations, structures, and functionalities in a more facile way compared to other material preparation processes. In its basic form, nanofibers are in nonwoven form that resembles a flat sheet mat or membrane. The pore size and porosity are in the range of 0.5–10 μm, and >70%, respectively. The pore size distribution is usually a little wide unless posttreatment processes are done to the nanofiber mat. The nanofibers are formed in an overlapping manner, hence the overall structure is full of voids and less torturous. There is an interconnection of the pores from the surface down to the bottom of the mat. Thus, this kind of structure found its application in water treatment application as filtration membrane. As nanofibers are overlapping, they form surface nano-micro roughness that affects the wettability of the material. If a hydrophobic polymer is used for electrospinning, the resulting nanofiber mat has more pronounced hydrophobicity due to the added roughness. In a similar way, when hydrophilic polymer is used, it becomes more hydrophilic. For most cases, neat or as-spun nanofibers lack some of the desired surface properties for specific applications. Hence, many works have been done on fabricating nanocomposite mats or membranes (Huang et al. 2003; Tijing et al. 2012a, 2014a). Figure 20.2 shows various nanofiber structures and designs that can be fabricated by electrospinning.

Nanocomposite mats or membranes based on nanofibers can be manufactured via direct blending of component materials (usually nanoparticles or nanofillers mixed with polymer solution), by in situ growth of nanoparticles, or by the post-treatment decoration of nanomaterials. The direct blending method can change the morphology of the nanofibers as the filler element changes the rheological properties of the solution, and at the same time adds new functionalities to the resulting

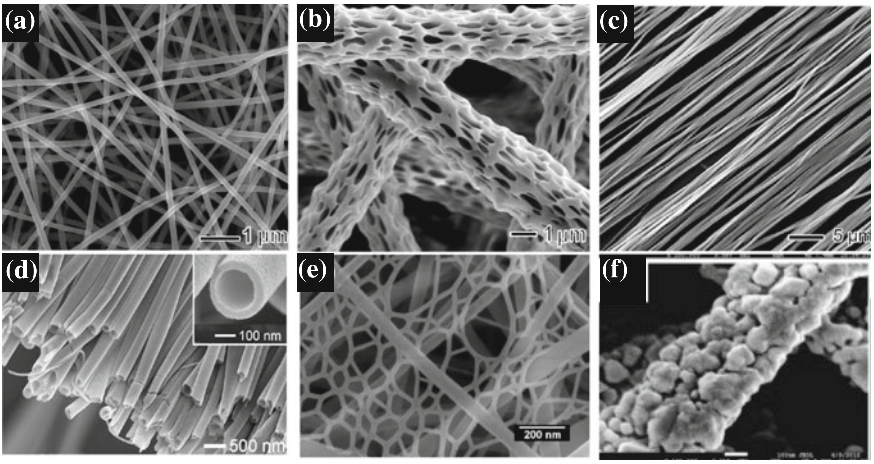


Fig. 20.2 Different nanofiber structures and morphologies that can be fabricated using electrospinning by manipulating electrospinning parameters, nozzle design and collector configuration: **a** conventional randomly oriented nanofibers (reprinted with permission from Xue et al. 2017), **b** internally porous nanofibers (Jingwei et al. 2008), **c** aligned nanofibers (reprinted with permission from Li et al. 2003), **d** hollow nanofibers (reprinted with permission from Li and Xia 2004), **e** nanonet formation within spaces between nanofibers (Wang et al. 2011), **f** Ag nanoparticle with hydrophobic coating, surface-modified nanofiber (Liao et al. 2013)

nanocomposite. This strategy has been investigated in many research studies with inorganic nanoparticles as nanofillers such as TiO_2, SiO_2, carbon nanotubes, graphene, Ag, Au, etc. The inherent properties of these nanofillers provide new functionalities to the nanofibers especially when located on the nanofiber surface. The main challenge for this method is the proper dispersion of these nanoparticles in the polymer solution. To address this dispersion challenge, other researchers impart functionality to the nanofibers by in situ growth of nanoparticles in/on the nanofibers. For example, $AgNO_3$ as a precursor to Ag nanoparticles has been blended in the polymer solution in liquid form, and then after electrospinning, the mat is exposed to UV light to promote the growth of Ag nanoparticles (Tijing et al. 2012b). This gives Ag more bonding with the polymer matrix thereby lowering the chances of release. However, both of the mentioned approaches (blending or in situ decoration) can oftentimes lead to nanoparticles being embedded inside the polymer matrix, which may enhance the overall mechanical properties, but the added functionality of the nanoparticles may not be as effective as they are not directly exposed on the surface. With this in mind, several groups attempted to functionalize nanofibers by surface modification techniques. This involves adding some functional groups on the nanofiber surface via dipping, spraying, layer-by-layer deposition, and other methods as anchors for the succeeding immobilization of nanoparticles (Liao et al. 2013; Formo et al. 2008). This method ensures that nanoparticles are located on the surface of the nanofibers, rather than inside the polymer matrix. Many of the results showed interesting properties such as added omniphobicity, hydrophibicity, hydrophilicity, antibacterial, self-heating, and other desirable functional qualities. The main drawback of this technique though is the need for really strong bonding of the nanoparticle on the surface, otherwise, they will be easily released and can act as secondary pollutant.

Another way of ensuring that nanoparticles are attached on the surface is via the use of coaxial electrospinning technique (Ma et al. 2012). Here, instead of using only a single nozzle, two concentric nozzles are used wherein the inner nozzle (core) is used as the main polymer carrier or host, while the outer nozzle (shell) is provided with functional materials designed to be attached on the surface of the nanofibers. By simultaneously electrospinning these two solutions, one-step nanoparticle-decorated nano-micro fibers can be made. Though this is very promising, there is difficulty in ensuring proper encapsulation of the core nanofibers with shell nanofibers as the two solutions may differ in properties which behave differently at specified applied voltage. Not only is this technique used for nanoparticle decoration, it can also be utilized to make core–shell structure of two different polymers if the design of such is necessary.

In nanofiber electrospinning, the fiber size is in the range of 100–1000 nm, thus the fibers are not really in the true nano range. A new design in the electrospinning research is towards the formation of true nanofibers or commonly called as nanonets, with a fiber diameter range of 50–80 nm. The nanonets are also known as spider web or spider net form. These nanonets are formed via phase separation splitting due to exposure to high electric field (Lian et al. 2013). Nevertheless, this design can be controlled in its formation, providing much higher surface-area-to-volume ratio if all of the nanofiber mat is covered. However, there is difficulty in the full coverage of nanonets of the macrosize of the nanofiber mat. This is an area of great interest for future nanofiber-related work. If one is able to fully capitalize on the nanonet formation, this could provide more reactive sites, and increased porosity overall that might be interesting for filtration applications.

Nanofibers are formed normally in 2D structure, wherein the thickness is very thin while width or length is quite large. However, making a 3D nanofiber structure is very possible and is potentially useful as sorbent materials (Kim and Kim 2007; Wu et al. 2014). One approach to do doing this is through long-time electrospinning at the same area. As electrospinning progresses, the thickness of the nanofibers increases towards 3D structure. Another way is to electrospin several layers of nanofibers, and just stacking them together to make the 3D structure. The main drawback of this is the robustness of such 3D mats as the individual stacked layer may not adhere well with each other. However, recent studies carried a more interesting approaching, by exposing the 2D nanofiber to chemical gas foaming (Jiang et al. 2015), which expands the nanofiber matrix and produce low-density sponge-like material.

New advances in nanofiber design are geared on producing intraporous structure, i.e., having internal pores within each nanofiber. This can be prepared by selectively removing a component from the formed fiber or by inducing polymer-solvent phase separation. The provision of internal porous drastically increases the overall surface area of the nanofibers. Other new works are also on the fabrication of aligned nanofibers (Wu and Qin 2013), instead of nonwoven form. These aligned nanofibers can be used as electrode or for tissue engineering application. Alignment of nanofibers is done by using a rotating drum at high speed, or by manipulating the collector design (Kim and Kim 2018; Kim et al. 2016). Another interesting structure is the hollow nanofiber design, wherein the core part of the fiber is hollow (Li et al. 2005). This type of design is best achieved using a coaxial or triaxial nozzle, whereby the core layer is selectively dissolved by heat treatment or by some other methods.

Overall, nanofibers present very promising potential for a variety of applications especially in water and wastewater treatment. Membranes are now widely used in many of these water/wastewater treatment applications, and the overall characteristics and properties (high specific surface area, high porosity, controllable pore sizes, interpenetrated pore structure, adequate mechanical strength, easily functionalized or surface-modified, etc.) of nanofiber-based membranes are highly desirable for filtration applications. Depending on the process application, the nanofibers can be made into hydrophilic or hydrophobic structure, and can be utilized as a stand-alone membrane, as a support layer, or a host polymer/carrier. The nanofiber structure can also be interesting as an electrode material or as sorbent material. The versatility of electrospun nanofibers makes them one of the most researched materials in the last two decades. Still, more research is needed to fully utilize these nanofibers towards commercial use in water/wastewater treatment.

20.3 Application of Nanofibers in Desalination, Water and Wastewater Treatment

20.3.1 Nanofibers for Desalination and Water Treatment

Nanofibers as Membranes for Membrane Distillation (MD). MD is a hybrid thermal/membrane separation process that works via phase change, and thus a temperature difference is needed between the feed and cold sides (Tijing et al. 2014b). It is one of the emerging technologies that can utilize low-grade heat as an energy source. In usual cases, the feed side is at higher temperature normally around 40–80 °C and the cold side is maintained around room temperature (∼20 °C) (Tijing et al. 2015). With the use of a hydrophobic membrane, the partial vapor pressure difference between the two fluids enables evaporation of the feed side, only allowing water vapor to pass through the membrane and condensed to water in the cold side. Membranes for MD require hydrophobic surface, high porosity, adequate pore sizes with uniform pore size distribution, high liquid entry pressure, and adequate mechanical strength (Yao et al. 2017). All of these properties can be designed via nanofiber membrane structure using the electrospinning technique. Hence, in the last 10 years, studies using nanofiber membranes for MD have seen exponential surge due to their interesting and desirable properties. The membrane properties and structure play a very important role in the process. Studies using nanofiber membrane exhibited high water flux while maintaining high salt rejection. In comparison, the usual membrane used for MD tests is commercial PVDF or PTFE flat sheet membranes, which perform at relatively lower flux and have wetting issues. Our previous review article on the use of nanofibers for MD presents the promising potentialities of nanofiber membranes (Tijing et al. 2014a). Recent studies have focused on membrane development and modification especially on the design of nanofiber membranes with added omniphobic properties, i.e., able to reject almost all kinds of fluid, including low surface tension liquids (see Fig. 20.3). Nanofiber membranes are attractive in this design as the nanofibers themselves provide already rough surfaces, and can be further improved towards reentrant surfaces or to have much lower surface energies to provide omniphobic surfaces (Woo et al. 2017a; Lee et al. 2016; Deng et al. 2018).

Various research groups aimed at making dual-layer membranes, superhydrophobic membranes, and Janus-type membranes for MD. Dual-layer bicomponent composite nanofiber membrane utilizing two wettability properties of both sides of the membrane was prepared and tested for direct MD and obtained high flux of 30 L/m^{2}h (LMH) (Tijing et al. 2014b). Additional investigation using different dual-layered nanofiber membrane designs were done and tested using air gap MD and compared with commercial membranes, and still obtained very high fluxes and high salt rejection using 3.5 wt% NaCl solution as feed (Park et al. 2015). Another study made a different approach, wherein they electrospun polyvinyl alcohol nanofibers incorporated with Triton-X directly on polypropylene (PP) mat. The PP mat, in this case, serves as the hydrophobic layer facing the feed, and the

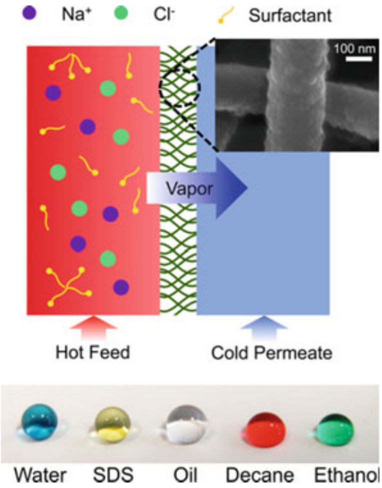


Fig. 20.3 (Top) Schematic of the membrane distillation system showing modified nanofiber membrane (SEM image inset) that has omniphobic properties; (bottom) photographic images of liquid droplets on modified nanofiber membrane providing resistance to wicking from liquids with different surface tensions. Adapted from Lee et al. (2016)

electrospun PVA/Triton-X nanofiber serves as the hydrophilic support layer facing the permeate (Ray et al. 2017). They found 1.5–2 times higher flux of this dual-layer membrane compared with PP mat alone. However, the process mechanism is not clearly elucidated. Nanoparticles are also quite commonly used as nanofillers to improve the nanofiber properties. The incorporation of carbon nanotubes (Tijing et al. 2016), graphene (Woo et al. 2016), TiO_2-FTCS (Ren et al. 2017a) into and on nanofibers has added functionality and improved wettability (superhydrophobicity) on the nanofiber membranes that result in improved flux and salt rejection performance even for high salinity brines. Posttreatment of nanofiber membranes has also been found to improve the overall properties of the membrane by increasing its mechanical strength, and enabling smaller and more uniform pore sizes (Yao et al. 2017).

A recent study used nanofibers as a coating material to a hollow fiber membrane via continuous electrospinning for use in MD (Su et al. 2017). The hollow fiber membrane served as the collector and the nanofibers were directly collected on the surface of the hollow fiber membranes (see Fig. 20.4). MD performance results of these nanofiber-hollow fiber membranes indicated a good flux of 17 LMH at feed and permeate side temperatures of 60 and 20 °C, respectively. Superhydrophobic titania nanofibers modified with fluorination was recently prepared and tested for its DCMD performance (Fan et al. 2017). The titania nanofibers showed higher flux (12 LMH) and maintained excellent rejection (99.92%) compared with corresponding ceramic membranes.

Nanofiber membranes for MD pose promising results so far and have been competitive in overall performance compared with existing microfiltration membranes. Still lacking though is the long-term performance tests of most reported nanofiber membranes for MD, and also dealing with scaling and fouling problems when exposed with challenging waters. However, the potential of nanofiber membranes for MD is looking positive, though the issues of energy source and

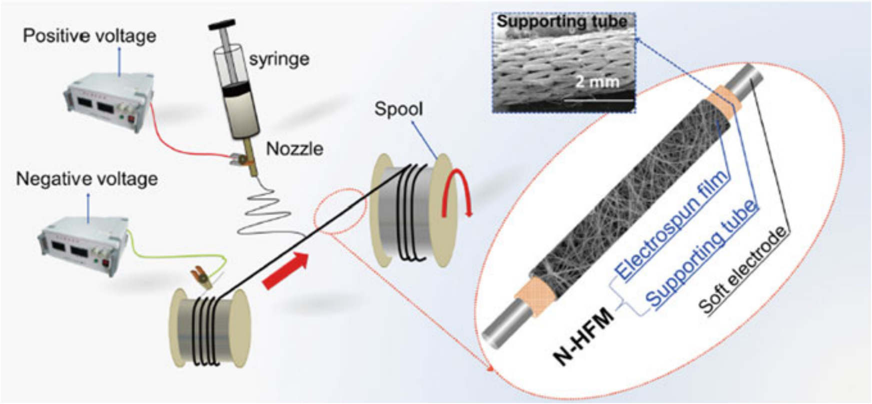


Fig. 20.4 Schematic of the fabrication strategy of directly coating nanofiber onto hollow fiber support Su et al. (2017)

niche application are still some of the challenges to delve more into the MD research space before commercialization will be realized.

Nanofibers as Membrane Support Layer for Forward Osmosis (FO). FO uses a semipermeable membrane between two fluids with different osmotic pressures. This osmotic pressure difference drives the water from the feed solution to pass through the membrane and dilute the draw solution (Phuntsho et al. 2011). Thus, the FO membrane is very essential to the process (Xu et al. 2017). A selective membrane with low internal concentration polarization (ICP) is desirable. There have been promising developments in FO membranes and processes in the last decade. FO membranes are usually made of three parts: very thin selective layer, a middle layer, and a backing/support layer for mechanical stability. In recent years, nanofiber layers utilized as middle or backing layer have been investigated to reduce the ICP effects in FO.

Tian et al. (2017) investigated the effect of silica nanoparticle incorporation on a polyetherimide (PEI) nanofiber support layer of FO membrane subjected to heat-pressing on their FO performance via reduction of ICP effects. The silica/PEI-supported thin film composite membrane showed higher porosity and pore sizes and exhibited higher osmotic water flux. Their result showed an optimum content of 1.6 wt% of silica to produce 83% porosity and the smallest structural parameter of 174 μm. When deionized water as feed and 1.0 M NaCl solution as draw solution were used, 42 and 72 LMH were obtained when the active layer is facing the feed, and when the active layer is facing the draw solution, respectively. Park et al. (2018) designed a PVDF nanofiber support layer coated with cross-linked PVA to improve the hydrophilicity of the membrane and overall reduce the ICP effects. Interfacial polymerization was used to make the polyamide selective layer. Using 1 M NaCl and deionized water as draw and feed solution, respectively, high water flux of 34.2 LMH was achieved using their PVA-coated PVDF nanofiber-supported membrane with structural parameter as low as 154 µm.

In most laboratory experiments using nanofibers, the nanofibers are designed and produced in the laboratory. However, commercial nanofibers are now available for various applications (e.g., air filtration) and are mostly supported with backing layers. Chowdhury et al. (2017) decided to investigate the use of commercial unsupported nanofiber membrane (from DuPont) to apply interfacial polymerization and tested for FO performance. Interestingly, this nanofiber membrane with selective polyamide layer produced twice the water flux and one-tenth of the reverse solute flux compared with corresponding commercial TFC FO membrane. The mechanical integrity of this nanofiber membrane was also high enough and is even better than typical electrospun materials found in the laboratory.

A promising upscaling strategy for the use of continuous fabrication of nanofiber-supported FO membrane with interfacial polymerization has been reported (Son et al. 2018). In this study, nanofibers were directly electrospun onto a heated (150 °C) collector that sandwiches the nanofiber layer, and then thereafter, interfacial polymerization is applied (see Fig. 20.5). The researchers tested the fabricated thin film nanocomposite membrane in engineered osmosis and obtained high permeability of 30 LMH with excellent selectivity (17 g/m^{2}h and 0.57 g/L).

Nanofiber membranes in FO show promising results achieving high fluxes and reduced ICP influence, however, as the FO membrane needs a thin selective layer, the synthesis of the dense polyamide top layer remains a challenge. This is because the structure of the nanofiber layer is not smooth, there is a high tendency for the top selective layer to be delaminated as not all of the surface are adhered well on the crevices or valleys of the overlapping nanofibers. Besides, during the polyamide interfacial polymerization, there is a high tendency for the PA layer to penetrate the pores of the nanofiber membranes which are generally bigger in size. In addition, the mechanical integrity of unsupported nanofiber membrane is also put into

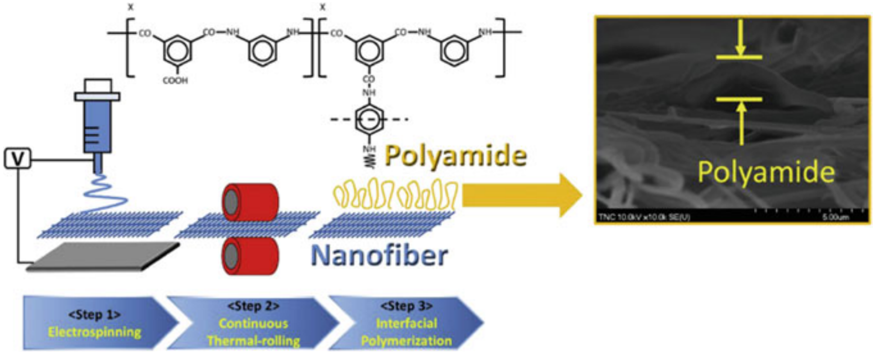


Fig. 20.5 Schematic of the three steps to fabricate thin film nanofiber composite membrane via electrospinning, thermal rolling, and interfacial polymerization. The inset shows the cross section of the fabricated nanofiber support with polyamide layer. Adapted from Son et al. (2018)

question, thus there is still lots of room for improvement in the use of such nanofibers for FO.

Nanofibers as Electrodes for Capacitive Deionization (CDI). Capacitive deionization is based in electrosorption technique wherein cations and anions from a saline solution are adsorbed on the electrodes via the application of electric potential usually less than 2 V on two oppositely charged electrodes. The electrosorption behavior is primarily dependent on the electrode material (Porada et al. 2012). The material needs the following properties for it to be ideal for CDI: a) large surface area, large capacitance, high conductivity, high electrochemical stability, and easy to manufacture (Oren 2008). With these electrode criteria in mind, electrospun nanofibers that are carbonized and boasting of high specific surface area are highly potential materials as electrodes. In addition, the ease in adding functionalities to electrospun nanofibers makes them more attractive as electrode materials. Hence, a number of recent research have been conducted on designing nanofiber as electrode materials for CDI.

Among the materials, electrospun porous carbon nanofibers have gained quite an attention for CDI electrode. However, the microporosity of such carbon nanofibers is less desirable as an electrode as it offers resistance to ion transport in inner pores and could act as deep trap sites. Thus, to address this challenge, Wang et al. (2016) developed hierarchical porous carbon electrode with tailored structures for CDI. The structure is a combination of micropore, mesopores, and macropores, which they claim to promote mass transport. Their fabrication strategy was to combine electrospinning with poly(vinylpyrrolidone) template method (Fig. 20.6). The resulting hierarchical porous carbon nanofiber electrode obtained an adsorption capacity of 7.61 mg/g and the charge efficiency was 23.7%. The adsorption capacity and the charge efficiency were better by 1.87 and 1.51 times, respectively, compared with those of the traditional parallel flow by CDI structure. Another group (Zhang et al. 2018) also synthesized hierarchical porous carbon nanotubes/graphene/carbon nanofibers obtaining very high salt capacity of 36 mg/g and large retention absorbing capability of 96.9%. However, the cost of this electrode may be a challenge due to the materials used.

Liu et al. (2016a) investigated the CDI application performance of carbon nanofibers-reinforced 3D porous carbon polyhedral network. The carbon nanofibers were prepared by electrospinning of polyacrylonitrile (PAN) nanofibers as precursor followed by carbonization. This new design of electrode showed an electrosorption capacity of 16.98 mg/g at 1.2 V using 500 mg/L NaCl solution, which was better compared to baseline electrospun carbon nanofibers. Some metal oxides such as ZrO_2 (Yasin et al. 2017), TiO_2 (Yasin et al. 2018), and MnO_x (Zhao et al. 2017a) are also available materials for CDI electrodes as they possess properties that are desirable for CDI such as high durability in the aqueous solution, and good hydrophilicity to improve electrode wettability.

Nanomaterials including nanofibers could be promising materials for use as CDI electrodes due to their many interesting properties and functionalities that can lead to improved desalination performance (Gaikwad and Balomajumder 2016).

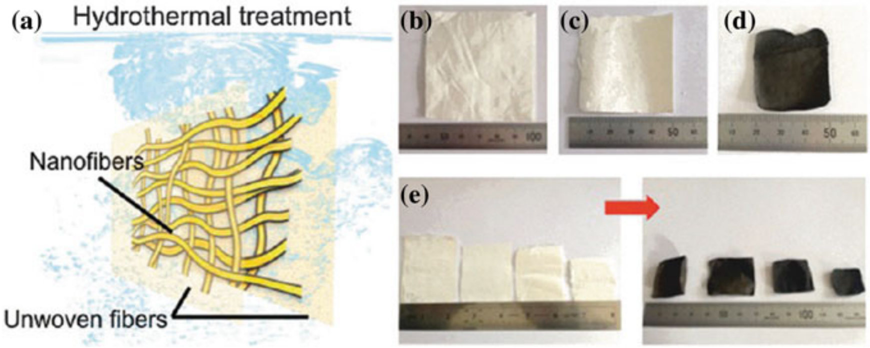


Fig. 20.6 **a** Schematic of the modified PVP-template method to prepare monolithic porous carbon nanofibers, **b–e** photographic images of PVP nanofibers, PVP-removed porous nanofibers, carbon nanofibers, and porous carbon nanofibers, respectively. Adapted from Wang et al. (2016)

However, many of the studies reported lack economic analysis of the use of such materials, which may increase their cost. Also, the stability of such nanofiber/nanomaterials needs to be further investigated.

Nanofibers as Barrier/Mid-layer for Reverse Osmosis (RO). RO is considered as the state of the art in desalination and continues to be used for new desalination plants around the world. It has high desalination efficiency yet it still is a very energy-intensive process (Shenvi et al. 2015). The membrane is the heart of the RO process providing the barrier needed for selective permeation. But aside from being highly selective, the good membrane should minimize fouling formation and should have the high mechanical stability to withstand the high pressure applied to the membrane. Thin film composite membranes, which contain a dense thin selective layer and a porous polymeric support layer, are the most commonly used type of membranes in RO (Xu et al. 2013). Several researches have been done to improve the performance of the RO membrane and one of the recent ones involved the use of nanofibers as an additional layer material of the RO membrane. However, nanofibers are usually not prepared for RO test due to exposure to very high pressure that nanofiber membrane may not be able to withstand.

A recent interesting RO membrane design by Wang et al. (2017a) incorporated ultrafine cellulose nanofibers as the barrier layer, electrospun PAN nanofibers as the mid-layer, and poly(ethylene terephthalate) nonwoven mat as the mechanical support. This makes up as an ultrafiltration membrane, and the addition of the interfacially polymerized polyamide top selective layer makes it a thin composite membrane that can be used for RO application. In addition, the spray coating technique was also utilized to control the thickness of the selective layer during polymerization. This new membrane design with nanofiber incorporation has achieved 96.5% rejection using 500 ppm NaCl as feed and a flux of 28.6 LMH under 0.7 MPa pressure, which was comparable with high flux commercial RO membrane. A previous study (Yoon et al. 2009) of the same group also utilized

PAN nanofibers as middle layer having micropores, and interfacial polymerization was directly done on the surface for use in nanofiltration membranes. This also showed high permeability and comparable selectivity with those of thin composite membranes available in the market.

Nanofibers as Porous Floating Membrane for Solar Steam Generation. Desalination, in general, is still an energy-intensive process, thus as a way to reduce energy cost while maintaining good process efficiency, solar desalination comes into the picture. Solar desalination, in this case, refers to the use of solar energy as a heat source to separate water molecules from the salts and impurities via evaporation–condensation process. Solar distillation process has been used for a long time by just simply exposing a wide area of seawater to the sun, and letting the evaporation to occur, and capturing the vapors via a cooling plate to condense back to pure water (Kabeel and El-Agouz 2011). However, this process takes a long time to occur as the mechanism is based on bulk heating rather than just surface heating of the surface water. Recently, a few studies were carried out designing floating materials on the saline water, wherein the floated porous materials have the ability to absorb solar heat and heat itself up thereby providing localized heating of the interface between the material and surface water, enabling more rapid evaporation (Wang 2018). The water then passes through the porous structure of the material and proceed with the condensation (Chen et al. 2018a; Zhou et al. 2016a). Nanofiber membranes with or without photonic or light-absorbing particles have been tested for such application.

Chen et al. (2018a) investigated the efficacy of a nanofiber-based composite film loaded with plasmonic gold nanoparticle on its solar steam generation. Figure 20.7 shows the schematic of the solar generation process and the new nanofiber-based membrane for solar steam generation. With the very good mechanical stability of the nanofiber film, the evaporation rate was found to be 1.424 kg/m^{2}h with a solar vapor efficiency of 83% when exposed to one sun exposure. They also claimed that

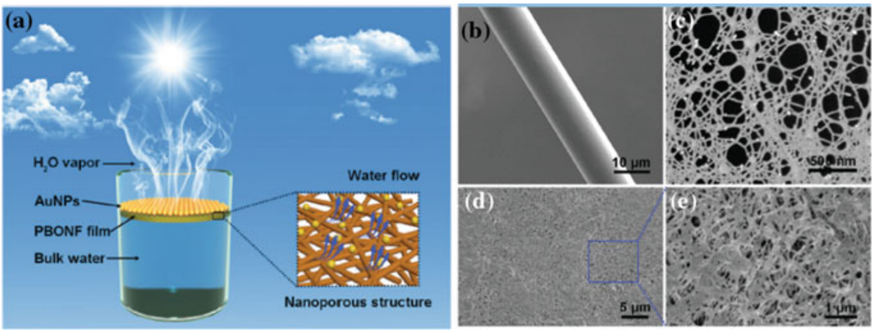


Fig. 20.7 **a** Schematic of the solar-driven steam generation using nanoporous AuNP/poly(*p*-phenylene benzobisoxazole) (PBO) nanofiber composite films. SEM images of **b** PBO microfiber, **c** PBO nanofibers and its **d** top and **e** surface views. Adapted from Chen et al. (2018a)

the material can be readily reused, hence indicating its promising potential for clean water production, even to the point of suggesting that it can be used in space environments.

Nanofibers as Adsorbent or Filters for Contaminant Removal from Water. With exploding population and rapid development in agriculture, manufacturing, and mining, the availability and use of more products like pesticides, fertilizers, chemicals, and heavy metals have led to increased leakage/discharge their constituents into groundwater. Such contaminants, which are very complex and difficult to eradicate, can seriously influence the ecosystem in groundwater, aquifers, and soil. Therefore, developing groundwater remediation strategies is of high necessity to address the challenges in the increasingly serious groundwater pollution.

Groundwater remediation technologies are basically classified into two ways: pump and treat technology (P&T) and in situ remediation technology. For P&T (Truex et al. 2017), contaminated groundwater is pumped out from the aquifer and then treated externally in a treatment building. Thus, all the surface water treatments such as adsorption, filtration, and advanced oxidation processes (AOPs) can be utilized for groundwater remediation. This also opens up for the possibility of using nanofibers as main or substrate material for the mentioned treatment processes that can be utilized for P&T groundwater remediation.

For in situ groundwater remediation, methods are very limited due to the complex geological conditions, difficulties in construction, and the instability of sampling and detection. Classical treatments include permeable reactive barrier (PRB) technology and direct injection of adsorbents, oxidizers, or reducing agents. As nanofibers can be made into membranes, they can also be potentially utilized as materials for PRB that can be placed into the aquifer to block the plume and treat groundwater.

Nanofiber for groundwater remediation can be used in two forms based on the dominant role in the treatment process. One is to utilize nanofiber itself to remove contaminants in the groundwater. The other is to employ the nanofiber as a carrier or substrate to facilitate immobilization of the existing materials/technologies used for groundwater remediation. For example, nanofibers have been used in adsorption and filtration due to their high specific surface area and easy surface functionalization. (Haider et al. 2015). Heavy metals (like chromium, copper, cadmium, lead, arsenic, and mercury) and organic pollutants (chloride organics, dyes and etc.) are the main contaminants in groundwater generally remediated by adsorption process (Aliabadi et al. 2013). Adsorption works mainly via affinities (like physical affinity, electrostatic interaction, chemical chelation, and complexation) between contaminants and functional groups on adsorbents (Huang et al. 2014). Studies have shown that polymers containing different functional groups such as amino, carboxyl, phosphoric, etc., have good complexation affinities toward metals ions and were commonly selected to fabricate nanofibers for heavy metal adsorption (Haider et al. 2015). Polyacrylic acid (PAA) with a large number of –COOH group is widely used as a complexing agent. Many researchers introduced PAA into nanofiber and use it for heavy metal adsorption. Chitpong and Husson (2017) grafted PAA polymer onto poly(glycidyl methacrylate) (PGMA) nanofiber and the fabricated PAA-PGMA membrane obtained good removal of cadmium with maximum capacities that exceeded 160 mg/g. Xiao et al. employed electrospun PAA/PVA nanofibers for the removal of metal ions from aqueous solution. The nanofiber membrane showed the exceptional removal of copper ions (91% removal within 3 h) and it also showed superb selectivity in the presence of calcium ions (Xiao et al. 2010).

Nanofiber can also be fabricated as membranes used into filtration process for groundwater remediation. Permeability, rejection capability, and service life are the three most important factors for the selection of membrane in filtration process. Permeability and rejection capacity are mainly determined by pore size, porosity, surface charges, and hydrophilicity. Pore size and porosity can basically be controlled by changing the fiber size of nanofiber membrane. Electrospun nanofiber can easily be manipulated to control fiber size from nanoscale to microscale by changing polymer concentration, introducing additives or adjusting electrospinning parameters. Therefore, some studies have reported using electrospun nanofiber membranes into microfiltration (MF) and ultrafiltration (UF) processes. Bae et al. (2016) fabricated a polyethersulfone (PES) electrospun nanofiber membrane and employ the membrane into MF for the removal of bovine serum albumin (BSA). Wang et al. (2017b) prepared regenerated cellulose nanofiber membranes surface-grafted with water-insoluble poly(HEMA) or water-soluble poly(AAS) chains via the ATRP method for ultrafiltration of water. The surface hydrophilicity of the nanofibers can be modified by introducing materials with hydrophilic functional groups such as –COOH and –OH. Jang et al. (2015) introduced graphene oxide (GO, with –COOH and –OH) into electrospun polyvinylidene fluoride (PVDF) nanofiber for MF process and the PVDF-GO achieved three times improvement in permeation flux. For the removal of charged contaminants, surface charges on the nanofiber can be modified by introducing charged polymer. Interestingly, for the adsorption process, nanofibers should be introduced with opposing electrical charge to contaminants for a better attraction and immobilization of contaminants. However, on the contrary, for the membrane filtration process, nanofibers are expected to have same electrical charge with contaminants to increase the rejection of contaminants and alleviate membrane fouling from the affinity of foulants by electrostatic repulsion effect. Han et al. prepared a surface-charged PVDF nanofiber MF membrane through a direct sulfonation reaction, which both increased the rejection of contaminants and reduced the fouling by improving electrostatic repulsion between membrane surfaces and charged polystyrene (PS) latex suspensions as feed solution (Han et al. 2011).

However, individual nanofibers have some restrictions and are not adequate to cope in treatment with all the contaminants in groundwater. Incorporating with other materials/technologies in the existing groundwater remediation can both improve the performance of nanofiber and existing remediation technology. For instance, nanoscale zero-valent iron particles (nZVI), with its the high reactivity towards a broad range of contaminants, have been a commonly used material/

technology for in situ groundwater remediation (Tosco et al. 2014). However, nZVI particles themselves are prone to agglomeration and sedimentation (Xue et al. 2018; Liu et al. 2014a). Traditional methods to combat agglomeration are to add surfactants (Tian et al. 2018), and stabilizers (Schiwy et al. 2016) to maintain the uniformity and activity of nZVI particles. Nevertheless, those auxiliary additives and contaminants adsorbed on nZVI may be released and can be a source of secondary pollution if not properly retrieved (Lefevre et al. 2016). Electrospun nanofiber membrane with its high specific surface area, recyclable and easily functionalized properties is an ideal material for nZVI immobilization to avoid agglomeration and sedimentation. With nanofibers as carrier, it provides an opportunity for regeneration of the membrane, thus avoiding the release of nZVIs and potential secondary pollution. (Yang et al. 2014). A study by Liu et al. (2014b) immobilized nZVI onto polyacrylonitrile (PAN)-based oxidized mat to reduce water contaminants (including methylene blue and trichloroethylene), and their results showed excellent performance on the removal of the target contaminants. Another study reported on the use of chitosan fiber-supported nZVI particles, which showed excellent sorption performance for inorganic arsenic uptake at concentration ranging from 0.01 to 5.00 mg/L (Horzum et al. 2013). Ren et al. (2017b) successfully immobilized 48.8 wt% nZVI onto a high ratio of PAA/PVA nanofiber mat and the nZVI–PAA–PVA had high removals to both methylene blue and copper ions.

Nanofiber can also be a support layer for other filtration processes or active layer based on other materials. Bahmani et al. (2017) employed electrospun polyethylene terephthalate (PET) nanofiber scaffold as a support layer to increase mechanical strength and fabricated PAN nanofiber as an active layer onto the PET scaffold. The thin film composite (TFC) membrane showed 172–520% higher flux and improved rejection of arsenate ions when compared with the UF membrane.

For the risk control of potential pollution from nanofiber, researchers also developed biodegradable and recyclable nanofiber to avoid secondary pollution. Varanasi et al. (2015) developed a biodegradable and recyclable cellulose nanofibre composite, which showed a decent water flux of 80 LMH and MWCO of 200 kDa in UF process.

The interesting and desirable properties of nanofibers such as large specific surface area, controllable fiber sizes, ease of fabrication, high flexibility to surface modification, and strong compatibility with other technologies make them highly potential for use in water treatment and groundwater remediation. However, still there are a number of challenges that need to be addressed on the use and design of nanofibers, for example, generally weaker mechanical properties, the less tested long-term performance and stability, mass production issues, among others, thus continuous and more rigorous research are still needed to fulfill its promising potential.

20.3.2 *Nanofibers for Wastewater Treatment*

Nanofibers as Membrane for Membrane Bioreactor (MBR). The feasibility of using nanofiber membranes for MBR application has recently been investigated by several groups. Nanofiber membranes share similar pore sizes with MF membranes in the range of 0.1–10 μm, making them applicable for MBR process which uses MF membranes. Bjorge et al. were the first group to investigate the performance of nanofibrous membranes in MBR application (Bjorge et al. 2009, 2010). They utilized polyamide (PA) nanofibers for their MBR process. Based on their results, they found that nanofibers suffered rapid decay of flux because of the irreversible fouling formed on the electrospun membrane. The PA nanofibers were also found to have low removal efficiency for pathogen removal, even though the integration of Ag nanoparticles promoted the removal of Gram-negative bacteria. Their report did not provide much positive result on the use of nanofiber membranes but gave a glimpse of potential opportunities for improving the nanofiber design and properties. Later, Bilad et al. improved the nanofibrous PA membrane performance in MBR by heat-treating the membranes (Bilad et al. 2011). Rapid flux decay was prevented, as the heat treatment greatly improved the integrity and mechanical strength of the nanofiber membranes; hence, the heat-treated electrospun membranes showed comparable flux performance to the commercial membranes (Fig. 20.8). Also, their use of more hydrophilic PA6 improved the permeation flux in MBR. However, the authors suggested further studies on the electrospun membrane improvement as the heat-treated nanofibrous membranes still suffered the intrusion of sludge in long-term operation, which led to the gradual increase in the fouling formation.

Moradi et al. developed electrospun membrane using PAN, a polymer with high mechanical and thermal stability. Moreover, PAN is also one of the easiest

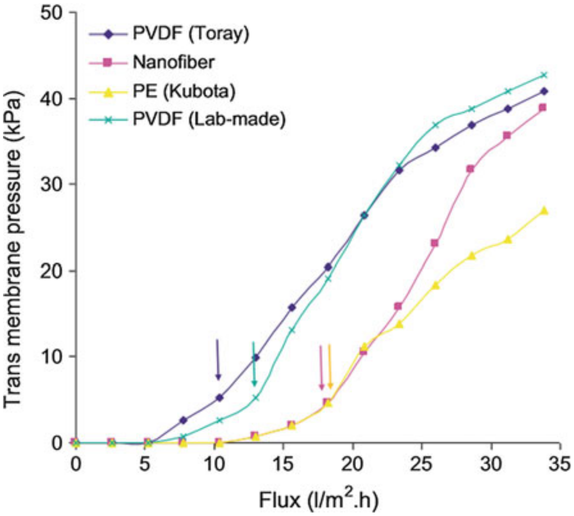


Fig. 20.8 The flux stepping profiles of electrospun and commercial membranes (Bilad et al. 2011)

polymers to electrospin to fabricate nanofiber membranes (Moradi et al. 2018). The authors also considered high fouling resistance of PAN to be an interesting property that is attractive for MBR application. The antifouling resistance of PAN membranes was further improved with the aid of fumarate alumoxane nanoparticles, integrated into the membrane matrix. The nanoparticles, at optimal concentrations, greatly improved the fouling resistance by increasing the hydrophilicity of the membranes, owing to the rich hydroxyl and carboxylate groups on the nanoparticle surfaces. However, too high concentration of the fumarate alumoxane nanoparticles also led to aggregation, blocking nanofibrous membrane pores, and hence reduced permeation flux in MBR (Moradi et al. 2018). Overall, the PAN nanofibrous membranes loaded with nanoparticles showed promising performance with greatly reduced irreversible fouling in MBR.

Nanofibers as Membrane or Adsorbent for Oil–Water Separation. Owing to frequent oil spill accidents in recent years, there is an increasing need for novel and efficient technologies for oil/water separation. Gravity-driven membrane separation, an energy-efficient versatile technology, is generally considered one of the most promising technologies (Arslan et al. 2016). For proper separation of oil and water emulsion using gravity-driven method, one important factor needed for the separation materials is the engineered surface wetting properties, either to be superhydrophobic and superoleophilic, or superhydrophilic and underwater-superoleophobic. Electrospinning is a desirable technique to produce membranes with pore size, and pore size distribution suitable for gravity-driven applications, which also boast of ease in surface modification and functionalization. The relatively easier approach to fabricate membranes for oil/water separation was to directly electrospin low surface tension polymer membranes; polystyrene, polyvinylidene fluoride, or polytetrafluoroethylene membranes had been fabricated in one-step electrospinning (Kim et al. 2013; Zhou and Wu 2015; Qing et al. 2017). Although without modification, these membranes showed superhydrophobic and superoleophilic properties, thus performing efficiently in oil/water separation process. Some other researchers developed approaches to impart superhydrophobicity and superoleophilicity to the hydrophilic membranes by surface modifications. Li et al. coated the silver nanocluster on the nanofibrous PAN membranes, followed by superhydrophobization; thus, a high contact angle and low sliding angle of water were realized, and the membranes could treat the oily wastewater for 30 cycles with good stability (Li et al. 2014). Arslan et al. developed perfluoro-modified electrospun cellulose acetate membranes through sol-gel methods; the modified membranes had a high water contact angle but low oil contact angle, which worked well in oil/water separation for 5 cycles (Arslan et al. 2016). Chen et al. chose the elastic polyurethane and chromatic polydiacetylenes for electrospinning because of their high mechanical stability and chemical resistance; after UV treatment, and later on heat treatment, the membranes became superhydrophobic with water contact angle higher than 155°, which could remain stable even after 1000 stretching cycles. The elastic nanofibrous membranes maintained high removal efficiency for 12 cycles (Chen et al. 2018b) (Fig. 20.9). Liu et al. improved the hydrophobicity of PVDF nanofiber membrane through incorporating ZnO nanoparticles and fluorination posttreatment. These modification processes made the nanofiber membranes superhydrophibic (water contact angle of 171°) while maintaining the oil contact angle of 0° (Liu et al. 2016b). The modified PVDF membrane showed much improved antifouling resistance and oil/water separation efficiency for dozens of cycles. One research group investigated electrospun membrane formed from carbonaceous materials, as they argued that the polymer membranes were prone degradation from chemical cleaning, which is necessary in oil/water separation (Tai et al. 2014). SiO_2-Carbon membranes were fabricated using electrospinning, and after being coated with silicone, the inorganic membrane became superhydrophobic and superoleophilic, while maintaining its high chemical and thermal stability. The other benefit of such membrane was that, unlike polymer membranes, its wettability was not affected by pH of the wastewater.

The other approach of gravity-driven membrane separation for oil/water separation was using superhydrophilic and underwater-superoleophobic membrane. To achieve such membrane surface property, surface modification was necessary.

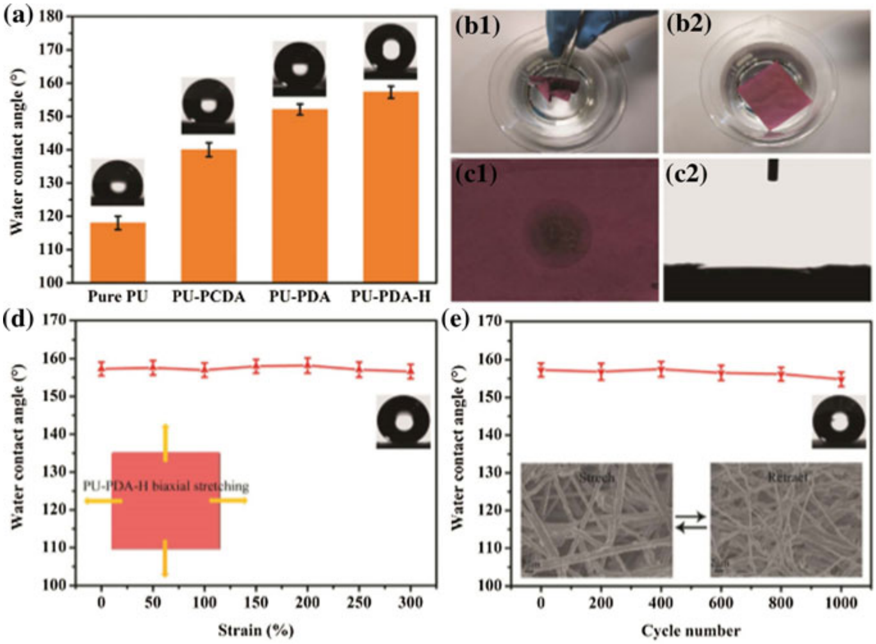


Fig. 20.9 **a** Water contact angle of different PU membranes; **b** immediate rising of PDA-modified PU membranes, which is immersed in water by an external force; **c** photograph of an oil droplet on PDA-modified PU membrane with oil contact angle of 0°; **d** water angle of PDA-modified PU membranes under various strains, and the inset shows the schematic of membranes under biaxial stretching; **e** water contact angle of PDA-modified PU membranes after 1000 stretching cycles, and the inset shows the SEM images of stretched and retracted membranes after 1000 stretching cycles (Chen et al. 2018b)

Ahmed et al. directed coated cellulose–ionic liquid solution on electrospun PVDF membrane to modify its surface properties. This led to superhydophilic property (water contact angle of 0°) and superoleophobic underwater (dichloromethane contact angle of 169° underwater) (Ejaz Ahmed et al. 2014). The membranes showed high separation efficiency for most types of oil. Obaid et al. modified the polysulfone electrospun membranes surface by generating one thin layer of polyamide on top, and its contact angle of water dropped from 130° to 13° (Obaid et al. 2015). The membrane maintained three consecutive cycles of high water flux in oil/water separation. Hydrophilic inorganic additives, SiO_2, and graphene oxide had also been individually incorporated into the electrospun nanofibrous membranes, and hence greatly decreased the contact angle of water (to around 20°). These membranes had improved oil/water separation efficiency and durability (Zhang et al. 2017; Islam et al. 2017). Membrane surface with hierarchical structure was achieved on the cross-linked polyacrylonitrile/hyperbranched polyethyleneimine electrospun membranes; thus, it had a water contact angle of 0° and underwater oil contact angle of 163°. The composite membranes achieved strong antifouling property, so it maintained high flux and rejection in 10 cycles (Wang et al. 2018).

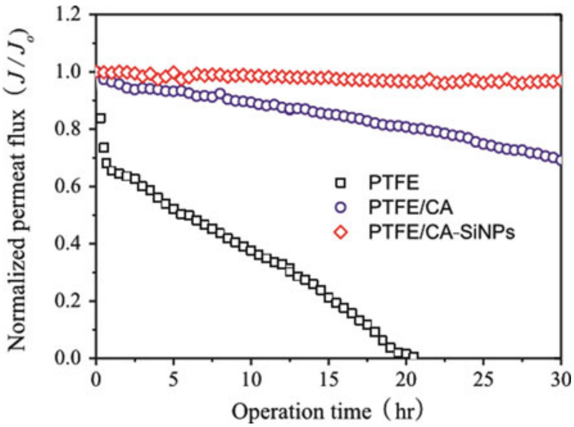
For the sake of improved versatility with a controllable surface wettability, smart materials were introduced in the electrospun nanofibrous for gravity-driven oil/water separation membranes. Responsive to the pH of the wastewater, these membranes could switch between superhydrophobic/superoleophilic and superhydrophilic/underwater-superoleophobic (Li et al. 2015; Cheng et al. 2017). In addition, incorporated with decanoic acid, the modified electrospun polyimide membrane could become superhydrophilic from superhydrophobic, if exposed to ammonia vapor (Mino et al. 2017).

Nanofibers as Omniphobic Membrane for Produced Water Treatment. Produced water, mainly from oil field or gas field, is becoming a major challenge for wastewater treatment under current tightening environmental regulation, as its high total dissolved solids make reverse osmosis, the currently most efficient water separation technology, impractical (Woo et al. 2017b). Therefore, membrane distillation, one of few technologies able to treat highly saline wastewater, was being developed as a solution. However, low surface tension compounds and oil emulsion, commonly found in the produced water, made the hydrophobic membrane susceptible to membrane wetting, which could greatly affect the permeation performance and even halt the operation (Yao et al. 2018). Due to its controllable pore size range and ease of modification, electrospun nanofiber membranes were developed into barriers with anti-surfactant and anti-low-surface-tension-compound properties. Till now, two major approaches were established: (1) Omniphobic membrane surface; (2) Janus membrane (superhydrophilic and underwater oleophobic surface layer with superhydrophobic or omniphobic bottom layer). Through CF_4 plasma treatment, Woo et al. modified the electrospun PVDF membrane to obtain omniphobicity on its surface (Woo et al. 2017b). The omniphobic membrane had high contact angle of both water and low surface tension liquids (mineral oil and methanol), as well as a greatly decreased water sliding angle to 50° if the membranes had been plasma-treated for more than 15 min. When treating real produced water containing high concentrations of surfactant in the configuration of DCMD, while the commercial membrane suffered rapid wetting, the modified electrospun membranes had no wetting issues and maintained stable flux and 99.99% salt rejection. Alternately, coating 1H,1H,2H,2H-perfluorodecyltriethoxysilane followed by heat treatment could impart omniphobicity to PVDF-HFP nanofiber membranes (An et al. 2018). The modified membrane had high contact angle for both water and oil, and the property of omniphobicity was robust even under harsh circumstances. Without an expense to performance, the omniphobic membrane successfully treated the produced water containing surfactant of sodium dodecyl sulfate for more than 2 h. Electrospun inorganic membranes could be modified to acquire omniphobicity as well. Huang developed omniphobic silica-based membranes with high surfactant resistance (Huang et al. 2017a). The omniphobicity of membrane was contributed by two factors: reentrant structures induced by coaxial technique (sheath solution for second scale nanostructure), and low surface tension after being dip-coated in 1H,1H,2H,2H-perfluorodecyltriethoxysilane. The omniphobic electrospun silica membrane had very high contact angle and stable MD performance against wetting when treating produced water containing surfactants.

To further improve the wetting resistance, Huang et al. developed a Janus membrane containing an omniphobic substrate (Huang et al. 2017b). PVDF-HFP membrane substrates containing cetyltrimethylammonium bromide were fabricated using electrospinning, and coated with fluorinated silica nanoparticles thus the substrate became omniphobic. Then, a layer of silica nanoparticles, chitosan, and perfluorooctanoate was spray-coated on the omniphobic substrate, forming a Janus membrane. The Janus membranes, showing greatly improved wetting and fouling resistance against troublesome compounds (oil emulsion and surfactant) in the produced water, had no degradation of flux and rejection performance for 10 h MD operation. An alternate approach to form a hydrophilic layer in a Janus membrane was electrospinning. A nanofibrous network comprising both cellulose acetate and silica nanoparticles could be simultaneously coated on a hydrophobic PTFE substrate in one-step electrospinning; a low water contact angle of 40° and high underwater oil contact angle of 154° were achieved (Hou et al. 2018) (Fig. 20.10). For 30 h, the electrospun-modified Janus membrane had stable performance treating saline water which contained oil-in-water emulsion.

Nanofibers as Membrane or Adsorbent for Dye Wastewater Treatment. Organic dye contaminants, greatly found in textile wastewater, posed great risks to both ecological system and human health. As these contaminants had high resistance against heat, and oxidizing light, treatment before their discharge was the best approach to minimize their impacts. Various physiochemical treatment processes, including adsorption, filtration, coagulation–flocculation, biological treatment, chlorination, electrochemical, and photocatalytic degradation, had been developed (Chen et al. 2018c). Membrane electrospinning has simple manufacturing processes and could conveniently acquire various functions with controllable pore sizes; thus,

Fig. 20.10 Normalized permeate flux for the commercial PTFE membrane and the fabricated composite membranes in the DCMD experiments. The saline oil-in-water emulsion with 600 mM NaCl and 1000 mg/L crude oil was used as the feed. The flow rate at feed and permeate side were 70 L/H (Hou et al. 2018)



a great number of dye treatment technology had been developed based on electrospun nanofiber membranes.

Direct filtration had been developed to separate the dye compounds from the water. Zhao fabricated β-cyclodextrin-based electrospun membranes which had a high flow rate of 150 ml/min for five cycles when separating cationic dye methylene blue from anionic dye methyl, owing to the strong electrostatic repulsion between the carboxyl groups on the membrane and the negative electricity of anionic dyes (Zhao et al. 2015a). Incorporating graphene oxide in the PVDF spinning solution, Ghaffar et al. developed a membrane having 99% selectivity towards cationic dyes with a flux of 439 LMH (Ghaffar et al. 2018). On the other side, electrospun membranes had been specifically designed to reject the anionic dyes by incorporating nanomaterials in the hydrophilic membranes. With the addition of 0.5 wt% SiO_2 in the spinning solution, the PVA nanofiber membrane was able to remove 98% of Direct Red 23 with a high flux of 1711 LMH (Hosseini et al. 2018). Coated with graphene oxide with the aid of polydopamine, the electrospun PEN membrane was able to remove 92.6% Direct Blue 14 with a flux of 141.5 LMH (Zhan et al. 2018). Electrospun membranes capable of removing both cationic and anionic dyes were also developed. Shi and coworkers fabricated branch-like carboxylated MWCNTS/Chitosan nanofiber membranes; they had high rejection of both methylene blue (86%) and methyl orange (83%) while maintaining high flux higher than 3500 LMH (Shi et al. 2016). Multilayer electrospun nylon-6 membranes were the alternate approach to achieve such rejection. With greatly decreased pore size owing to multilayer and increased thickness, the nanofiber membranes achieved high removal rejection with relatively low flux of 16 LMH (Yu et al. 2018). Incorporated with graphene oxide, the multilayer nylon nanofiber membranes had improved rejection of both methylene blue (99%) and methyl orange (95%) without sacrificing the flux performance (Chen et al. 2018c). Treating dye wastewater via MD with electrospun membrane was also explored. PDMS/PVDF nanofiber membrane showed high flux and rejection rate and greatly reduced irreversible fouling when treating anionic crystal violet (Vaselbehagh et al. 2017).

Electrospun membranes could be used as adsorbents, another approach treating dye in the wastewater. Some researchers used the nanofibers as carriers of adsorbents, and poly (vinyl alcohol) (PVA) was the most common one. Various adsorbents, including poly (acrylic acid), graphene oxide, polyethyleneimine, and chitosan, had been coated on the PVA membranes; these adsorbent membranes had high adsorption capacity in multiple consecutive cycles (Yan et al. 2015; Xing et al. 2017; Zhu et al. 2017; Habiba et al. 2017a). To improve durability, Gopakumar et al. developed adsorbent membrane based on PVDF membranes (Gopakumar et al. 2017). Cellulose acetate nanofiber was incorporated into PVDF membranes and modified by Meldrum's Acid; thus, the membrane obtained a high adsorption capacity of crystal violet of 3985 mg/g. After modification, the nanofiber membranes alone could work as adsorbent. Amine-modified electrospun polymer membranes could adsorb methyl orange at a capacity of 312.5 mg/g (Satilmis and Uyar 2018). Although having lower adsorption capacity of methylene blue than the electrospun polymer adsorbent membranes, inorganic electrospun membranes made of zeolites were successfully fabricated; they were easier and faster for separation and reuse than the raw form of the minerals (Saepurahman and Hashaikeh 2015).

Similar to the adsorbent membrane, the electrospun nanofiber membranes could work as carriers of the nanoparticles that photo-degrade the dyes. Li et al. incorporated TiO_2 nanoparticle, a photocatalyst, on electrospun poly (methylmethacrylate) membranes, which degraded Methylene Blue stably in 5 consecutive cycles (Li et al. 2017a) (Fig. 20.11). Others coated Ag@AgCl or $H_4SiW_{12}O_{40}$ on electrospun cellulose acetate membranes, and the membranes degraded methyl orange efficiently in three successive cycles (Zhou et al. 2016b; Li et al. 2017b). Electrospun membranes made of inorganic photocatalyst materials was a more direct approach to remove the dyes in wastewater. PVP (or PVA) is generally used as a temporary carrier in the electrospinning process and is burned off after the membranes are formed. Various materials, such as MoS_2, TiO_2, and SiO_2, can be made into inorganic nanofiber membranes (Ren et al. 2018; Singh et al. 2017; Yang et al. 2017; Wang et al. 2017c). To improve the degradation efficiency, additional particles ($CoFe_2O_4$, Pt, and MnO_2) were incorporated to impart hierarchical structure to the membrane surface. The inorganic membranes were able to degrade the dyes in multiple cycles. Also, activated carbon nanofiber membranes can degrade dyes. Electrospun membranes made of PAN, a precursor of activated carbon, had porous hierarchical structure (Zhu et al. 2018; Lin et al. 2017) after exposing to high thermal treatment. Also, the oxidation power of the carbon materials could be enhanced by the incorporation of cobalt into the spinning solution (Lin et al. 2017). After carbonization, the nanofibrous membranes could degrade the dye efficiently in five consecutive cycles.

Nanofibers as Adsorbent for Removal of Heavy Metal Ions from Water/Wastewater. Heavy metal pollutants in the wastewater pose serious challenges to human health because they are highly carcinogenic and hard to be decomposed or biodegraded. Adsorbents had been developed to deal with the threat; however, regeneration of the conventional adsorbents has serious difficulties. Due to their

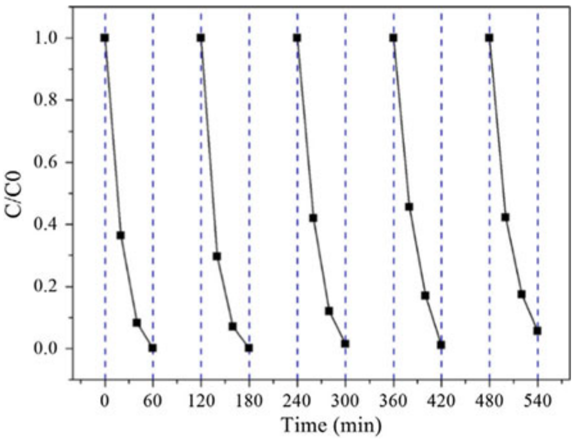


Fig. 20.11 Photodegradation of methyl orange by TiO_2@PMMA during in five consecutive cycles (dye concentration at 10 mg/L) (Li et al. 2017a)

tunable pore size, high surface to volume ratio, and integrity, electrospun membranes were considered suitable as adsorbent of heavy metal ions from wastewater (Li et al. 2018).

Chitosan, capable of binding heavy metal ions, had been selected to fabricate electrospun membranes. To increase the adsorption capacity, PVA or poly (ethylene oxide) (PEO) was mixed with chitosan in the spinning solution; hence, the electrospun nanofiber membranes had increased pore size owing to decreased crystallinity (Li et al. 2018; Habiba et al. 2017b; Shariful et al. 2017). To further enhance the adsorption capacity of chitosan membranes, various additives, including zeolite, halloysite nanotubes, and graphene oxide, had been used (Hadi Najafabadi et al. 2015). The chitosan-based electrospun membranes achieved a high removal efficiency of Cr(VI), Cu(II), Pb(II), Zn(II), and Fe(III) in multiple cycles. Also, chitosan, cross-linked with rectorite, could be loaded onto electrospun nanofiber substrate by electrospinning simultaneously. Huang et al. developed chitosan-rectorite nanospheres embedded in aminated PAN nanofiber membranes to efficiently treat Pb(II) (Huang et al. 2018); Tu and coworkers also fabricated chitosan-rectorite nanospheres embedded polystyrene (PS) membranes to adsorb Ca(II) (Tu et al. 2017). Even without additives, PS membranes alone exhibited impressive adsorbent properties.

Alcaraz-Espinoza et al. developed hierarchical composite membranes by applying polymerization of polyaniline on the PS nanofiber membranes; the membranes could remediate Hg(II), Cd(II), Pb(II), Cr(VI), and Cu(II) ions efficiently (Alcaraz-Espinoza et al. 2015). Due to their high mechanical strength, PAN nanofiber membranes had been greatly used as the base/substrate of the membrane adsorbent. Zhao and colleagues developed an amino-rich hydrothermal carbon-coated electrospun PAN membranes which could absorb both cationic and anionic pollutants. The membranes had high removal efficiency in five successive cycles (Zhao et al. 2017b). Kim specifically developed Prussian blue embedded PAN membranes to remove radioactive Cs from the wastewater (Kim et al. 2018).

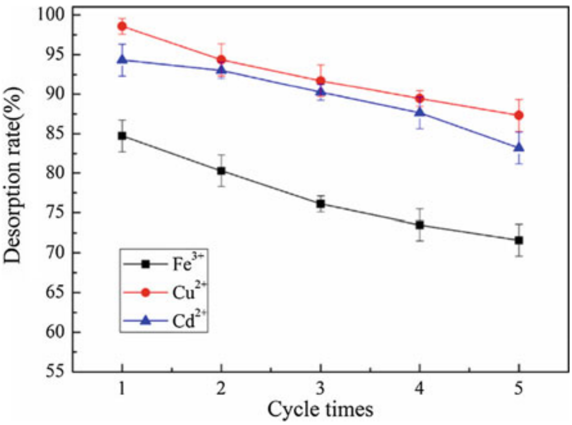


Fig. 20.12 Desorption percentages of Fe(III), Cu(II), and Cd(II) ions upon regeneration of electrospun AOPAN/RC blend nanofiber membranes for 1–5 cycles (Feng et al. 2018)

Alternately, a grafted phosphorylated PAN nanofiber membrane gained high adsorption performance towards Pb(II), Cu(II), Ag(I), and Cd(II); the removal efficiency remained high in four cycles (Zhao et al. 2015b).

Chen et al. synthesized adsorbents by intercalating ethylenediaminetetraacetic acid into layered double hydroxides; then they were embedded into the PAN spinning solution, and were encapsulated in the polymer matrix during electrospinning (Chen et al. 2018d). The composite membranes showed strong Cu(II) removal (Feng et al. 2018) (Fig. 20.12). Amidoxime groups could be imparted to PAN and blended with regenerated cellulose; the electrospun PAN membranes showed strong adsorption of Fe(III), Cu(II), and Cd(II). In five consecutive tests using the membranes, the adsorption and desorption rate of the heavy metal ions remained high. Cheaper polymers such as cellulose, PVA, or PVC were also used as base polymer for electrospun membranes, which were modified to acquire heavy metal adsorption ability (Wu et al. 2015; Islam et al. 2015; Cai et al. 2017). On the other hand, inorganic electrospun membranes, made of silica nanotubes or Hematite, were developed (Nalbandian et al. 2016; Wang et al. 2015). No requirement of modification, both natural membrane absorbents had strong adsorption capacity of heavy metals, and higher mechanical strength and chemical resistance than their polymer counterparts.

20.4 Summary and Future Prospects

The use of nanofibers for water and wastewater treatment is gaining fast ground for promising future use. This is primarily due to the many interesting and controllable properties and functionalities that can be designed for nanofiber membranes. The surge in nanofiber-related research for desalination, water, and wastewater treatment in the last decade provides evidence of its wide interest in various fields, may it be academe or industry. However, there are still a number of challenges that needed to be overcome before full commercialization can be realized especially for emerging applications. One of the biggest challenges that many are always curious about is the upscaling potential of the nanofiber fabrication. Though many new equipment have sprung providing glimpse of mass production potential, still if further modifications are needed after electrospinning, this could pose additional challenge. However, the future of electrospun membranes seems to be bright as advances in nanotechnologies in terms of precision and efficiency are making the electrospinning technique more viable with ease of operation. Also, newer nanomaterials and innovative surface modification methods are being realized, hence making it more attractive to apply to nanofibers with high surface area and porous structure that are essential for efficient membrane filtration process.

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Chapter 21
Current Trends of Electrospun Nanofibers in Water and Wastewater Treatment

Aiswarya Devi Sekar and Matheswaran Manickam

Abstract The increased disposal of highly hazardous organic pollutants without sufficient treatment into the natural water bodies has become an immediate threat to the living organisms. Pesticides, surfactants, halogens, polycyclic aromatic hydrocarbons, microorganisms, dyes, and other contaminants need to be removed completely by facile and eco-friendly technology. Among various advanced materials, nanofibers symbolize a next generation of nanocatalyst that offers unique properties to overcome water pollution crisis as compared to conventional catalyst. Electrospinning is a most proficient method for the fabrication of nanofibers. Metal oxide nanofibers such as zinc oxide, titanium dioxide, zirconium dioxide, etc. are attractive material for wastewater treatment due to their capability of total mineralization of organic contaminants under atmospheric conditions with greater removal efficiency. These composite nanofibers, due to their synergetic effect promotes the production of hydroxyl radicals by enhancing their light absorption and better photon harvest property, thereby reduce the recombination of semiconductor surfaces and complete removal contaminant occurs. Thus, this review highlights the recent trends of nanofibers as adsorbent, photocatalyst, filter media, and sensor in water and wastewater treatment.

Keywords Nanofiber · Electrospinning · Nanocatalyst · Wastewater treatment

21.1 Introduction

According to the recent study, the human population will be nearly 9 billion in the earth by 2050 and supply of fresh water to this huge population will become one of the critical problems to be addressed (Ray et al. 2016; Sahay et al. 2012). Hence, there is a need for innovative and novel technologies to facilitate the desalination,

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water reclamation, and water/wastewater treatments (Peng et al. 2016; Thenmozhi et al. 2017). Nanofibers are one of the most intensively studied and versatile class of one-dimensional nanomaterials, with diameter less than 100 nm (Lim 2017; Xue et al. 2017). Owing to their unique properties such as small diameters with excellent pore interconnectivity, high porosity, and surface-to-volume ratio, nanoparticles are made to attain much interest and consideration in the wide range of research and in applications such as healthcare, energy, filtration, catalysis, electronics, protective clothing, bioengineering, and environmental (Balamurugan et al. 2011; Lim 2017, Zhu et al. 2017; Song et al. 2017). Also, in recent years, the nanofibers have acquired much attention to develop pioneering materials with suitable properties to meet the challenges in water and wastewater treatment (Mokhena et al. 2015).

Numerous strategies have been used to produce nanofibers such as drawing, templates synthesis, phase separation, self-assembly, electrospinning, etc. Whereas electrospinning is a top-down method for nanofabrication, which has been recognized as an efficient technique for the production of uniform nanofibers with controlled dimension and morphology; The low cost, simplicity, proficiency, and versatility nature made electrospinning to be adopted for scale-up of nanofibers at an industrial scale (Mokhena et al. 2015; Peng et al. 2016). The electrospun nanofibers possess high surface area, chemical reactivity, low density, as well as enhanced charge separation with improved light absorption and dye adsorption in photocatalysis (Kumar et al. 2014). Few applications of nanofibers are highlighted as follows; nanofibers (i) as photocatalysts (Mohamed et al. 2016b) can chemically break down the organic contaminants and self-regenerate, (ii) as nanoabsorbents (Li et al. 2015) for the removal of heavy metals electrospun into mats for filters (Zander et al. 2016). Moreover, these nanofibers offer high porosity, a large number of active sites for metal binding, small sizes, regeneration, and faster removal of contaminants (Peng et al. 2016). Recently, Anjum et al. have stated that nanofibers are playing a proficient role in the elimination of organic dyes, heavy metals, and microorganisms from wastewater (Anjum et al. 2016). In recent times, the metal oxides or nanoparticles can be incorporated in the nanofibers to enhance the performance (Ray et al. 2016). The facile electrospinning process is used to fabricate a variety of materials into nanofibrous structures with metal oxides/ceramics such as CuO, Fe_2O_3, TiO_2, and NiO; mixed metal oxides such as $NiFe_2O_4$; $TiNb_2O_7$, and $LiMn_2O_4$; composites such as PVA/TiO2, carbon/SnO2, graphene/TiO2, Nylon-6/gelatin, and collagen/hydroxyapatite (Kumar et al. 2014).

In addition, Ray et al. have reported that the uniform pore size of electrospun nanofibers was a significant feature for membranes, which made them be utilized in water purification applications (Ray et al. 2016). Also Balamurugan et al., have affirmed the potential of nanofibers in water filtration by cheaper and portable units consuming less energy (Balamurugan et al. 2011). With this perception, this chapter presents the recent development of nanofibers and its application in water and wastewater treatment.

21.2 Outline of Nanofiber Fabrication

Since 1902, the E-spinning is the most effective method that has known to produce uninterrupted fibers with diameters down to a few nanometers, which shares the characteristics of both electrospraying and conventional solution dry spinning (Ramakrishna et al. 2010). The basic principle of electrospinning was demonstrated in our previous review chapter (Devi et al. 2018). In addition, to enhance the quality of conventional electrospinning technique, several variations were adopted in this method such as multineedle, needleless, and co-electrospinning or coaxial electrospinning and the current scenario was given in Fig. 21.1a (Lim 2017; Valle et al. 2016). Even though electrospinning was a versatile technique to fabricate fiber, it has certain drawbacks such as the requirement of specialized equipment, high electrical potential, and electrically conductive targets.

To overcome these drawbacks, recently several novel strategies have emerged for fabrication of nanofiber at a larger scale and higher throughput manner such as CO_2 laser supersonic drawing, solution blow spinning, plasma-induced synthesis, centrifugal jet spinning, and electro hydrodynamic direct writing methods (Lim 2017). However, electrospinning is an existing versatile technique to produce nanofibers for various applications, including filtration, desalination, and wastewater treatment (Ray et al. 2016; Xue et al. 2017). The various types of nanofibrous materials are discussed in the following section.

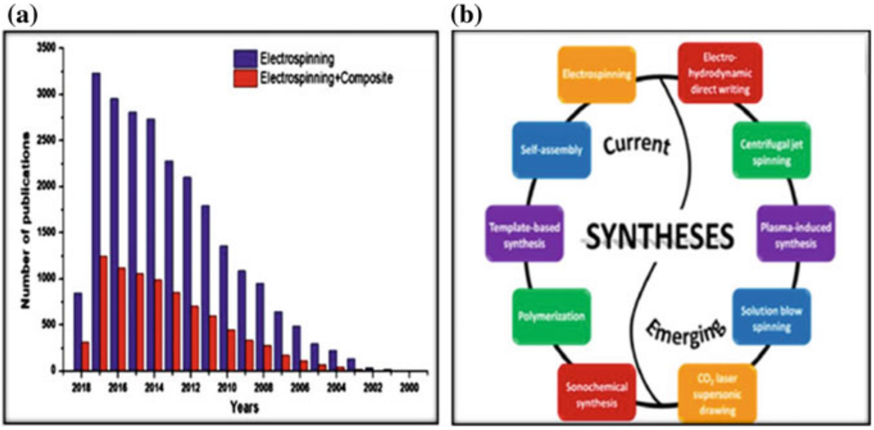

Fig. 21.1 **a** The annual number of publications with topics of "electrospinning" and electrospinning + composite", provided by the search engine of Web of Science before March 30th, 2018. Reproduced from (Jiang et al. 2018) with permission from the Royal Society of Chemistry, **b** Different strategies nanofibers of synthesis, ranging from current methods (e.g., electrospinning, self-assembly, and polymerization and template-based synthesis) to emerging strategies (e.g., solution blow spinning, centrifugal jet spinning, and electrohydrodynamic writing). Reprinted from (Lim et al. 2017) with permission from Copyright © 2017 Elsevier

21.3 Nanofibers for Water and Wastewater Treatment

In the recent era, the electrospinning technique has become one of the crucial processes that influenced the research and development on water treatment applications (Ray et al. 2016). Besides the remarkable properties mentioned, nanofibers may be further functionalized to enhance their potential. Based on the application, different types of nanofibers can be fabricated, such as polymeric (Synthetic and natural), carbon, ceramic, or composite nanofibers in different shapes such as porous, core–shell/hollow fiber with random or aligned assemblies through electrospinning process (Malwal and Gopinath 2013).

21.3.1 Natural and Synthetic Polymer Nanofibers

Any polymers with adequately high molecular weight can be electrospun into nanofibers. More than 100 synthetic and natural polymers have been productively fabricated into nanofibers through electrospinning (Feng et al. 2013). Natural polymers are with unique properties such as biocompatibility, biodegradability, and non-toxicity. Natural polymers such as cellulose, chitosan, collagen, gelatin, silk, DNA, fibrinogen, hyaluronic, and alginate were efficaciously fabricated into nanofibers for a wide range of application. Furthermost, they possess unique functional groups to adsorb various heavy metals through different mechanisms such as ion exchange, chelation, and electrostatic attraction in wastewater treatment. But the drawback of few natural polymer is their solubility and biodegradation in an aqueous medium. This made them restricted to be the most applied in water treatment (Mokhena et al. 2015). Hence, this paved the way for utilization of synthetic polymers in water treatment. Synthetic polymers such as polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), PVA, PAA, polyacrylamide (PAM), and polyethyleneimine (PEI) are water soluble and can directly be electrospun into nanofiber using water as solvent and devoid of toxic organic solvent. However, their nature of swelling or collapsing upon moisture made them restrained in water treatment application. Resolution to this problem is using water-insoluble synthetic polymers such as polybutylene terephthalate (PBT), polyvinylidene fluoride (PVDF), PCL, polylacticco-glycolic acid (PLLA), polyethylene terephthalate (PET), polystyrene PS, polysulfone (PSF), PAN, PU, polybutylene succinate-co-butylene terephthalate (PBST), polyhydroxyalkanoates (PHA), polybutylene succinate (PBS), polyimide (PI), polymethyl methacrylate (PMMA), PVC, polytrimethylene terephthalate (PTT), polycarbonate (PC), polybenzimidazole (PBI), polymer vinyl acetate (PVAc), polyvinyl butyral (PVB), and polyethylene-co-vinyl acetate (PEV). These above said polymers were electrospun into nanofibers and are used for water treatment applications (Si et al. 2014; Feng et al. 2013).

21.3.2 *Unaligned and Aligned Nanofibers*

The alignment/orientation of the fibers primarily depends on the type of collector used such as pin, plate, cross bar, rotating rods or wheels, drum, liquid bath, disk, etc. The choice of a suitable collector depends mainly on the nature of application associated with the fabricated nanofibers. Static collectors result in the production of unaligned, randomly oriented nanofiber (Mondal and Sharma 2016). Figure 21.2a represents the FE-SEM image of the PAN nanofibrous membranes which indicates randomly oriented three-dimensional (3D) nonwoven membranes with a uniform diameter of 200–300 nm (Si et al. 2014). Rotating collectors are used to produce partially/ well-aligned nanofiber (Mondal and Sharma 2016). The strong elongation of the roller makes the fiber to be aligned. Figure 21.2b shows the highly aligned PMIA nanofibers (Si et al. 2014).

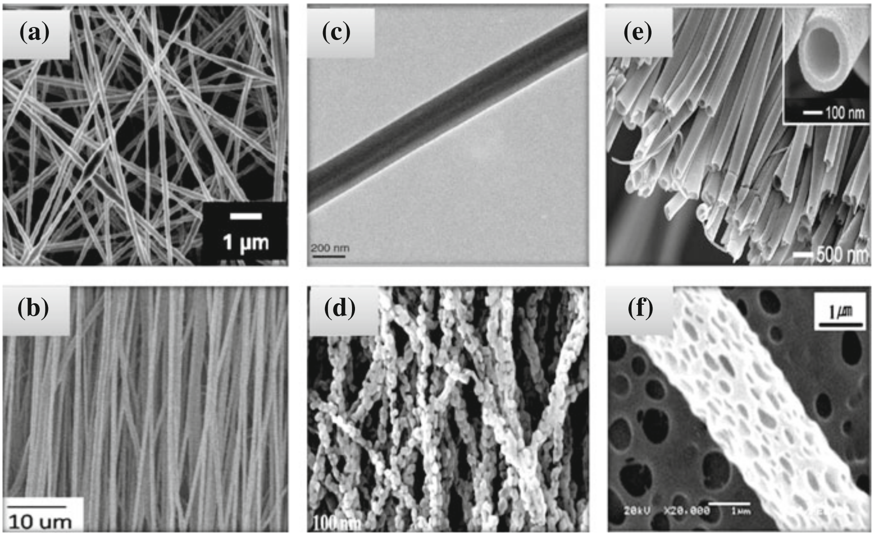

Fig. 21.2 Various structures of electrospun nanofiber. **a** PAN nonwoven nanofibers (random orientation), Reproduced from (Si et al. 2014) with permission from Copyright © 2014 Springer. **b** Radially aligned fiber orientation, Reproduced from (Ramakrishna et al. 2010) with permission from Copyright © 2010 Springer nature, **c** TEM image of C/SnO_2 core–shell nanofibers, Reproduced from (Wei 2012) permission from Copyright © 2012, Elsevier. **d** FEEM micrographs of ZnO metal oxide nanofibers fabricated by calcining at 650 °C temperature, Reproduced from (Mondal and Sharma 2016) permission from Inventions, MDPI. **e** SEM image of TiO_2 hollow nanofibers, Reproduced from (Xue et al. 2017) permission from Inventions Copyright © 2017, American Chemical Society. **f** SEM images of porous PLLA fibers at room temperature (21 °C), Reproduced from (Thenmozhi et al. 2017) with permission from Copyright © 2017, Elsevier

21.3.3 Composites, Ceramics, and Carbon Nanofibers

Recently, a large number of research works have been fascinated to fabricate incorporated composite nanofibers/functional nanofibers due to its compositions, structures, and functionalities. The composite nanofibers can be easily fabricated by incorporating a variety of materials (polymer and polymer, polymer and nanoparticle) into nanofibers and optimizing the nanofibrous architectures, either during one-step electrospinning or two/multichannel spinnerets (two or more than two solutions)/nozzles or through post-modifications with nanoparticles or a secondary polymer (Liao et al. 2017; Jiang et al. 2018 review). In another study, Thenmozhi et al. have reported that research publications after 2010 dealt mainly on the applications of E-spun fibers in many fields using functionalized polymers, nanoparticle incorporated fibers, and metal oxide composite nanofibers (Thenmozhi et al. 2017). When compared to pure material, these composite nanofibers can provide high porosity, better mechanical and structural properties such as high modulus and strength to weight ratios, provide electrospun polymer nanofibers applications in the filtration and water treatment application (Zhang et al. 2012; Jiang et al. 2018).

Equally the impact of electrospun ceramic nanofibers has been well recognized and applied in water remediation processes. Ceramics include metal oxides, non-oxides (such as carbides, nitrides, silicides, or borides), and their composites. Ceramic nanofiber can be fabricated by a typical process that involves three major steps: (i) preparation of a stable colloidal suspension (the sol) from a sol–gel precursor, a polymer, and a solvent; (ii) fabrication of composite nanofibers by electrospinning; and (iii) generation of ceramic nanofibers through selective removal of the organic component by calcination or solvent extraction (Mondal and Sharma 2016; Xue et al. 2017). Moreover, Malwal and Gopinath have stated that membranes with ceramic nanofibers show advantages over polymeric membranes with higher porosity, greater chemical, and physical stability in extreme conditions and capable to withstand the harsh chemical treatment. All these properties make them economically suitable to be used in water and wastewater treatment (Malwal and Gopinath 2013).

The intrinsic brittleness of the free-standing ceramic nanofibrous mats is still a technological challenge. To overcome this, large area CNF sheets with high mechanical strength can be easily fabricated. In addition, compared to polymeric filters their higher chemical resistance makes them suitable for filtration (Faccini et al. 2015). Al-Anzi BS and Siang have stated that the use of electrospun carbon fibrous membrane for oil–water separation has more advantages when compared to the conventional pressure-driven filtration membranes, because of its high energy efficiency (separation by gravity), significantly high permeate fluxes, and separation performance (Al-Anzi and Siang 2017). Generally, the CNFs from PAN precursor by electrospinning was the most reported method and PAN is a well-known precursor for the traditional microsized carbon fibers. Other precursors, such as cellulose, PVDF, PVA, PAA, PI, PBI, and polybenzoxazine (PBZ), have also been reported (Si et al. 2014).

21.3.4 Porous, Core–Shell, and Hollow Nanofibers

Recent advances in electrospinning technique have allowed fabricating porous, core–sheath, and hollow nanofibers of composites (McCann et al. 2005; Jiang et al. 2018). Amid various classifications of electrospinning, coaxial has got much consideration due to the fabrication of improved nanofibers such as, hollow, core–shell, and uni-axially aligned nanofibers (Thenmozhi et al. 2017). Nanofibers with hollow, core–shell, or porous structures have many potential applications. Based on the basic electrospinning setup, two syringes feed inter-separated and coaxial "'Inner fluid"' and "Outer fluid" to spinneret and Fig. 21.2c presented the core–shell fiber. The core solution is fed into the inner spinneret (mineral oil) while the shell solution (polymeric solution that may include a polymer, a catalyst, a solvent, and a sol–gel precursor) is transported into the outer one. Coaxial fibers are collected on the metal substrate under high-voltage conditions. These coaxial nanofibers are either core–shell/hollow nanofibers with walls made of inorganic/polymer composites or ceramics, whereas selective removal of the cores results in hollow nanofiber (Feng et al. 2013). The porous nanofibers can be created with a unique topology by choosing precise environment was shown in Fig. 21.2e. Two approaches have been explored for producing porous nanofibers: (i) selectively eliminating one of the components from the fibers and (ii) inducing polymer–solvent phase separation by rapid cooling of fibers prior to complete solidification (Xue et al. 2017). Mondal and his coworker have reported that due to their high surface area, the applicability of porous nanofibers is more ample and broad in contrast with core–shell and hollow nanofibers in the field of filtration and catalysis (Mondal and Sharma 2016). However, the composite core–sheath or hollow nanofibers were prepared most for catalysis, sensors, and electronic devices, and the porous membranes exhibit prominent potential to be applied in water treatment (Liao et al. 2017).

21.4 Applications of Nanofibers in Water and Wastewater Treatment

21.4.1 Adsorption

Adsorption is simple, inexpensive, and effective strategy for treating the polluted water, when compared to the other existing treatment methods and it was depicted in Fig. 21.3a–d (Peng et al. 2016). At this juncture, highly porous nanofibers with large surface area, tailored pore structure, flexibility of surface functionalization, and self-standing properties made them recognized as adsorbents for removal of pollutants from drinking water and wastewater (Terra et al. 2017; Ray et al. 2016). Also, nanofibers facilitate the more availability of functional groups disclosed to the target contaminants for their removal (Peng et al. 2016). In the following part, removal of the major class of pollutants like heavy metal ions and organic contaminants are dealt.

Take a lead with heavy metals. The polystyrene nanofibers functionalized with dithizone (DZ) as the absorbent were reported to absorb lead (II) at pH 8.5 and desorb it by three times under acidic conditions, recording a breakthrough capacity of 16 μg mg^{-1} (Deng et al. 2011). Following that, the removal of persistent organic pollutants such as antibiotics, hormones, pesticides, and dyes from water and wastewater should be equally concerned. The adsorption of ciprofloxacin (CIP), bisphenol (BPA), and 2-chlorophenol (2-CP) the three organic chemicals on electrospun polyacrylonitrile (PAN) CNFs was investigated by Li et al. using carbon nanofibers (CNFs). The adsorption capacities of three pollutants CIP, BPA, and 2-CP on CNFs were of 2-CP (6.18 mmol/g) >BPA (4.82 mmol/g) >CIP (0.68 mmol/g) (Li et al. 2015). Madhumita Bhaumik et al. have synthesized polypyrrole–polyaniline nanofibres (PPy–PANI NFs), with interconnected structures for the removal of Congo red (CR) from aqueous solutions. This study revealed adsorption capacity of 99.5% color removal with 0.1 g of PPy–PANI NFs (Bhaumik et al. 2013). Thus, the polymeric nanofibers membrane acts as an attractive adsorbent of toxic heavy metal ions and organic pollutants by adsorption/chemisorption and electrostatic attraction mechanisms (Ray et al. 2016; Terra et al. 2017).

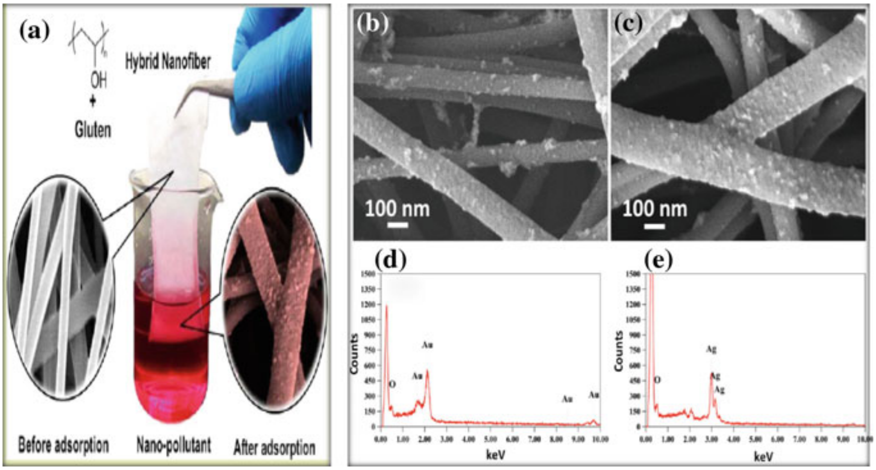

Fig. 21.3 **a** Adsorption of nanopollutant by hybrid nanofiber, **b** SEM image of PVA/gluten (5 wt%) after the extraction of Au NPs and **c** SEM image of PVA/gluten (5 wt%) after the extraction of Ag NPs on the surface of the nanofiber, **d** EDS spectra of the Au and (B) EDS spectra of the Ag on the fiber surface, Reproduced from (Dhandayuthapani et al. 2014) permission from Inventions Copyright © 2014, American Chemical Society

21.4.2 Photocatalysis

In wastewater treatment, photocatalysis is one of the most widely utilized inexpensive and sustainable methods for treating heavy metals, toxic organic pollutants, and microorganisms (Peng et al. 2016). Photocatalysis is a process of initiating photoreactions (oxidation/reduction) with aid of a solid catalyst (semiconductor) got irradiated by UV or visible light and it was presented in Fig. 21.4a–c

After absorption of photons with energy (hν) larger than the bandgap energy (Eg) of the photocatalyst, electrons from the valence band (VB) are excited to the conduction band (CB), making electron–hole pairs. These electron–hole pairs either recombine or act as powerful oxidizing/reducing agents to produce reactive species during (·OH, O_2^{-}, and H_2O_2) photocatalytic reactions (Kumar and Gopinath 2016; Terra et al. 2017).

Thus, the oxidation of organic pollutants and reduction of heavy metal ions will occur (Wu et al. 2015). Even though semiconducting metal oxide nanoparticles appear as promising photocatalyst, their strong affinity to agglomerate and hard to separate from the wastewater have confines their usage in photocatalytic activity (Kumar et al. 2014). With this regard, incorporation of semiconductor metal oxide nanoparticles in polymer nanofibers was introduced to overcome the limitations of powder nanoparticles (Peng et al. 2016). In photocatalysis generally, TiO_2, ZnO,

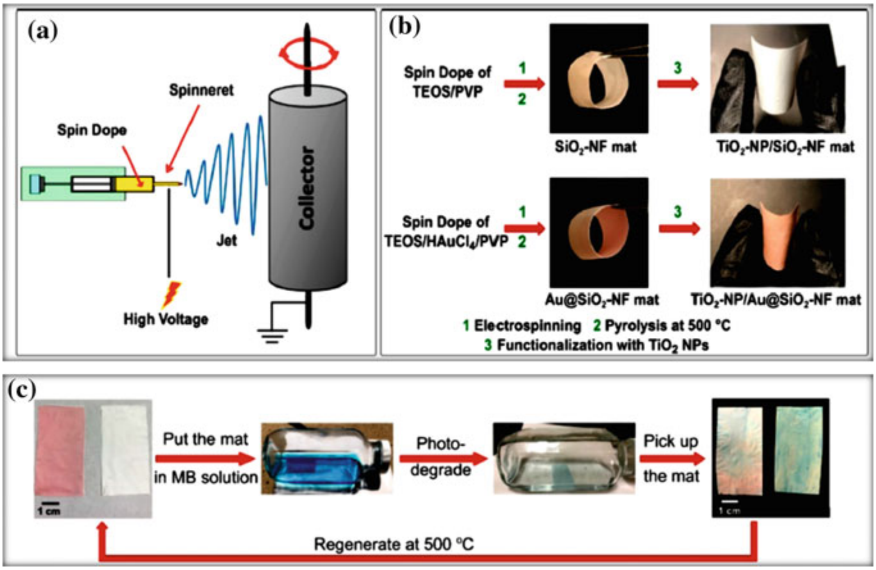

Fig. 21.4 **a** Schematic of electrospinning setup. **b** Schematic illustrating the formation process of the TiO_2–NP/SiO_2–NF and TiO_2–NP/Au@SiO_2–NF nanofibrous composite mats. **c** Flowchart showing the setup of dye degradation experiment and recycling of the TiO_2–NP/SiO_2–NF and TiO_2–NP/Au@SiO_2–NF composite mats. Reproduced from (Zheng and Zhu 2018) permission from Inventions Copyright © 2017, American Chemical Society

Fe_2O_3, CeO_2, and WO_3 semiconducting metal oxide NFs have been used as catalysts to degrade the toxic heavy metals and hazardous organic compounds (Kumar et al. 2014). Thus, the recent studies on the photocatalytic degradation of heavy metals, organic pollutants, and microorganisms are discussed here subsequently. Composite PA_6@FexOy and core–sheath CNF@SnS_2 nanofibers also have reported to exhibit prominent photocatalytic performance for the degradation of Cr (VI) from aqueous solution (Li et al. 2013; Zhong et al. 2016]. PAN–CNT/TiO_2–NH_2 composite nanofiber was tested for the degradation of organic dyes such as methylene blue (MB) and indigo carmine (IC). PAN–CNT/TiO_2–NH_2 composite nanofiber has delivered complete removal of both dyes in the acidic pH (Mohamed et al. 2016a). Lei Liu and his coworkers have demonstrated about a novel multifunctional TiO_2 nanofibrous functionalized with Ag nanoparticles. This multifunctional nanofibrous mat exhibited the excellent photocatalytic activity of methylene blue degradation by 80.0 and 99.9% bacteria inactivation under solar irradiation within 30 min (Liu et al. 2012).

In another study, the as-synthesized composite nanofiber showed a distinctive performance in adsorption, the photocatalytic activity of methylene blue, and antibacterial activity against *E. coli* (Saud et al. 2015). Thus, the synergistic effect of metal oxide nanoparticle and functionalized components played a vital role in water purification. Also, these studies have provided a new intuition to prepare advanced and scalable photocatalytic composite membrane materials for water and wastewater treatment.

21.4.3 Filtration

Filtration is one of the traditional method used for eliminating suspended particulates (particles and microorganism) from water using permeable material by applying pressure as drive force (Ramakrishna et al. 2010). Yet, the filtration system has few disadvantages such as necessity of high pressure, more power consumption, costly and usage of chemicals were restricting the effective utilization of the system. To rectify this scenario and to meet the scarcity of drinking water, a porous membrane material with high efficiency, high stability, low cost, and eco-friendly fabrication process were intended to be used in filtration (Mokhena et al. 2015; Peng et al. 2016). At present, polymeric materials such as poly (acrylonitrile)–poly (vinyl chloride), poly (acrylonitrile), poly (vinylidenefluoride), and polysulfone copolymers are used for manufacturing drinking water membranes (Peng et al. 2016). Though considerable advancements were made in the membrane to improve its efficiency Still fouling, and chemical stability are the most important problems to be solved (Ramakrishna et al. 2010; Mokhena et al. 2015). Thus, it is necessary to modify the properties of membranes to enhance the efficiency of water filtration, since various nanofiber materials have been industrialized (Balamurugan et al. 2011; Mokhena et al. 2015). Based on pore size microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and forward osmosis

(FO) are the classifications of the filtration system. Amid these, nanofibrous membranes were investigated for MF and UF application because of their potential to eliminate suspended solids, microorganism, and other substances, while permitting the water to pass and it was shown in Fig. 21.5a, b (Modesti et al. 2015; Feng et al. 2013). Thereby nanofibers overcome the limitations of the conventional membrane. Also, the low operation pressure, high flux, high retention of multivalent anion salts, relatively low investment and low operation and maintenance costs of nanofibers making them be utilized for the removal of particles and microbes (Ramakrishna et al. 2010; Peter et al. 2018).

The application of nanofiber membranes in particles and microbes' removal from the water was presented in the following sections. The electrospun nanofibers have attracted more researchers due to its prefilter ability to remove the large particles (submicron to micron size) before the raw water is fed into the membrane system (Feng et al. 2013; Balamurugan et al. 2011).

Mirko Faccini et al., have fabricated carboneous nanofibrous membranes using polyacrylonitrile (PAN) as backbone and studied filtration of nanoparticle (Au, Ag,

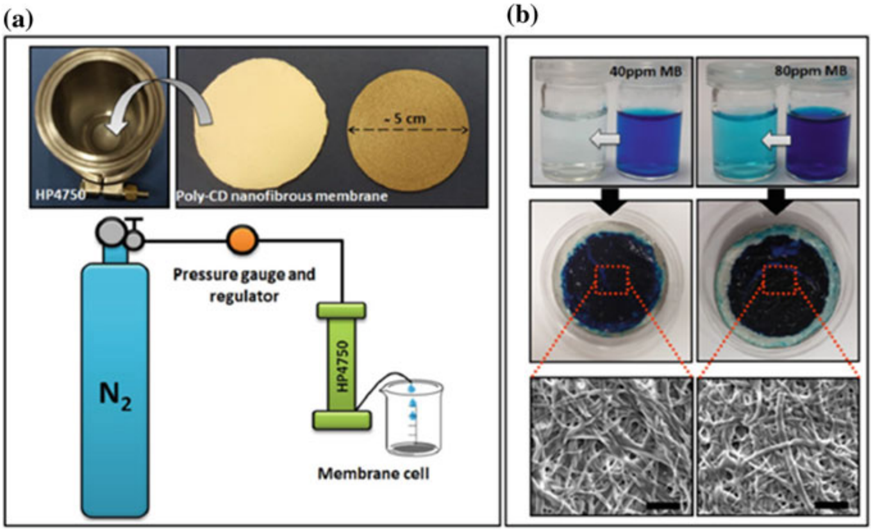

Fig. 21.5 Filtration performance of poly-CD nanofibrous membrane. **a** The photographs of membrane cell part of HP4750 dead-end system and the cropped poly-CD nanofibrous membrane with a definite active filtration area (14.6 cm^2). The schematic view of HP4750 filtration system. For each test, 50 mL solution is passed through the poly-CD nanofibrous membranes with a definite N_2 pressure. Then, the permeated solution is collected in a clear beaker. **b** The visual illustration of the MB solutions prepared at two different MB concentrations (40 and 80 mg/L) before and after filtration test. The photographs and SEM images (scale bar—10 μm) of the poly-CD nanowebs exposed to these two concentrated MB solutions during the experiments. As clearly seen, both the macroscopic visual appearance and the fibrous morphology of poly-CD nanofibers were protected under such applied pressure. Reproduced from (Celebioglu et al. 2017) with permission from Springer Nature

and TiO_2) and size (from 10 to 100 nm in diameter) from aqueous solutions. The results presented the retention percentage of Au NPs as 95% of average diameters 100, 50, and 25 nm; 99% of retention for Ag NPs irrespective of their particle sizes and 94.1% for TiO_2 NPs for average diameter of 10–15 nm (Faccini et al. 2015). A multifunctional electrospun PET nanofiber membranes with fiber diameters as low as ca. 100 nm was fabricated and tested for its filtration efficiency with latex beads with sizes (30–2000 nm). Through gravity filtration, greater than 99% of beads as small as 500 nm were removed. Quaternary ammonium and biguanide biocides functionalization reduced the fouling by delivering 6 log reduction for both gram negative and gram positive bacteria (Zander et al. 2016). Katherine Peter et al. have demonstrated the synergetic effect of SDS (sodium dodecyl sulfate) and iron oxide nanoparticles composite performance for heavy metal sorption. Their results have proposed the treatment of lead at drinking water in a filtration system showed that small amount of material can provide an individual's annual drinking water requirement ($\sim$5 g composite/L/day for tap water containing $\sim$300 μg/L Pb) (Peter et al. 2018). As like the particles the importance of eliminating bacteria and viruses from water is essential. Sato et al. have demonstrated the removal of bacteria and virus using a novel nanofiber. Composite membrane consists of cellulose ultrafine fibers infused into a PAN ENM on nanowoven substrate. Addition of positive-charged cellulose fibers aided in viruses removal by attracting the slightly negatively charged viruses and the E. coli removal was 6-log (99.9999%) (Sato et al. 2011). Recently, Kumar and Gopinath have tested the silver nanoparticles (Ag NPs) incorporated carboxylated multiwalled carbon nanotubes (MWCNTs) grafted aminated polyacrylonitrile (APAN) based nanofibrous membrane for the removal of toxic heavy metals and bacteria present in water. Their results depicted 90% of filtration efficiency for As removal and complete removal of bacteria (Kumar and Gopinath 2016). Thus, the above reports conferred that with the better understanding, efficient nanofilters membranes can be designed and developed both for biological and wastewater treatment applications.

21.4.4 Sensors

Chemical sensors are used for selective diagnosis and recognition of ions and molecules. Currently, numerous research works have involved in enhancing the sensitivity, robustness, and lifetime of chemical sensor materials (Terra et al. 2017). The sensing material incorporated on nanofiber also plays an important role in the sensitivity of detection and chemical contact of pollutant by improving the detection sensitivity and response time, and reduces the concentration detection value [lowest detection value (LOD)]. Also when compared to other nanomaterials, the 1D nanofibers hold ample benefits such as easily tailored structure, large surface area, porosity, contamination free, and easy posttreatment process. The inherent properties of electrospun nanofibers make it highly sensitive for the detection of selected pollutants (Mokhena et al. 2015). Anitha Senthamizhan and her coworkers

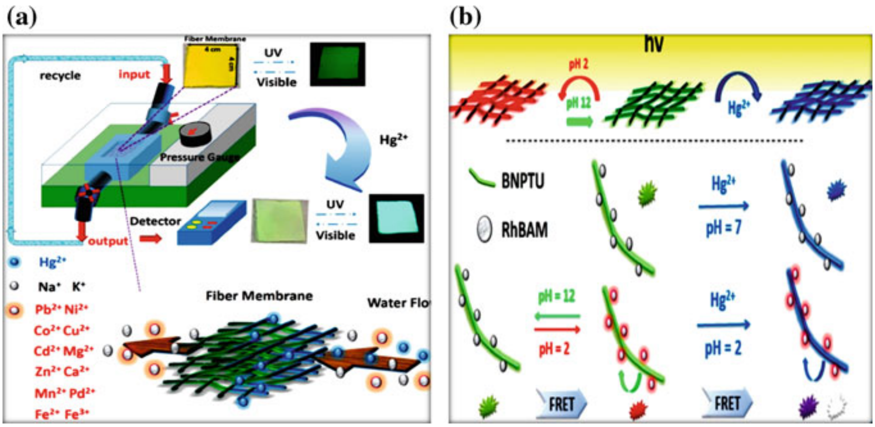

Fig. 21.6 **a** Schematic illustration of a probe filter microfluidics system for real-time metal-ion sensing using an ES nanofiber membrane. **b** Effect of FRET on the fluorescence emission colors of multifunctional environment-sensing ES nanofibers. Reproduced from (Liang et al. 2017) permission from Copyright © 2014, American Chemical Society

constructed an electrospun fluorescent gold nanocluster (AuNC) decorated polycaprolactone (PCL) nanofibers (AuNC*PCL-NF) for real-time visual monitoring of Hg^{2+} at ppt level in water. The prepared AuNC*PCL-NF, delivered to be free of excess ligand, prioritized the selective Hg^{2+} over competent metal ions such as Cu^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} present in the water (Senthamizhan et al. 2015).

Recently, Liang et al. have fabricated Novel red–green–blue (RGB) fluorescence probe with poly(methyl methacrylatete-*co*-1,8-naphthalimide derivatives-*co*-rhodamine derivative electrospun (ES) nanofibers to detect pH and mercury ions (Hg^{2+}) from aqueous solution. Their RGB probe depicted the detection of Hg^{2+} with the change of color from green to blue. Whereas the fluorescence emission probe was selectively for pH detection, it exhibited nonfluorescent for (pH 7) and strong red fluorescence (pH 2) was deliberated in Fig. 21.6a (Liang et al. 2017). Table 21.1 lists few applications of electrospun nanofibers in water and wastewater applications. Thus, the above presented studies with porous nanofibrous membranes have potential application in water purification.

21.5 Conclusion

The fabrication of nanofibrous membranes for water and waste treatment through electrospinning was a facile, environment-friendly, and acceptable strategy. 1D nanostructures including polymers, nonmetals such as carbon fibers, metals, carbides, metal oxides, organic and inorganic composites can be fabricated and utilized

Table 21.1 Various applications of nanofibers in water and waste water treatment

Sl. No	Material	Nature	Applications	References
1	β-cyclodextrin functionalized poly (acrylic acid) (PAA)	Nanofiber	Adsorption of cationic dye **methylene blue** (MB)	Zhu et al. (2017)
2	PAN-CNT/TiO_2-NH_2	Nanofiber	Adsorption of **chromium**	Mohamed et al. (2017)
3	PA6/PPy	Nanofiber	Adsorption of **atrazine**	Yang et al. (2015)
4	PAN-CNT/TiO_2-NH_2	Nanofiber	Photocatalytic reduction of **chromium**	Mohamed et al. (2016a)
5	ZnO/(0.5wt%) CuO	Nanofiber	Photocatalytic **MB dye degradation**	Naseri et al. (2017)
6	$TiO_2 - NP/SiO_2$ and $TiO_2 - NP/Au@\ SiO_2$	Nanofiber	Photocatalytic **MB dye degradation**	Zheng and Zhu (2018)
7	Chitosan/PMMA	Nanofiber membrane	Filtration of chromium	Li et al. (2016)
8	Elctrospun graphene oxide functionalized on polyacrylonitrile (PAN) fibers	Nanofiber	Filtration **(protein rejection)**	Lee et al. (2018)
9	(PVA-co-PE) (NFM) decorated by chitosan (CS) and graphene oxide (GO)	Nanofiber	Disinfection of **microorganism**	Liu et al. (2017)
10	Glutathione-Ag-Cu alloy NPs incorporated in Nylon 6 polymer	Nanofibers	**Sensing Ni^{2+}** in water	Ondigo et al. (2016)
11	Novel red–green–blue (RGB) fluorescence probe with poly(methyl methacrylatete-*co*-1,8-naphthalimide derivatives-*co*-rhodamine	Nanofibers	**Detect** pH and mercury ions (Hg^{2+})	Liang et al. (2017)

based on the desirable application. They hold very high surface-area-to-volume ratio, highly porous, tailored pore structure, the flexibility of surface functionalization, and self-standing properties making them be utilized for various water and wastewater treatments such as adsorption, photocatalysis, filtration, and sensors. In this chapter, the different types of nanofibers and their application in removal of dyes, heavy metals, microorganisms, organic pollutants from the water were discussed elaborately. Also, in recent years, many researchers have paid more attention in the functionalities of electrospun nanofibers to enhance their application at an industrial scale. Even though plenty of literatures are available in electrospun NFs, some challenges remain in real-time application of nanofibers in water treatment process. Though there are several challenges, further research on improving the fabrication process and physicochemical properties of nanofibrous membrane will remove the pollutants at real-time process in the forthcoming years.

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Chapter 22
Nanotechnological Interventions for the Decontamination of Water and Wastewater

Chanchpara Amit, Chandarana Helly, Madhava Anil Kumar and Sunita Varjani

Abstract Nanotechnology has created revolution in all fields of developmental research and technology which includes environmental aspects too. At the present scenario, there is a global demand for potable water and treatability of wastewater and the constraints are mainly due to the climate change associated with global population growth. In order to combat the present haphazard, novel treatability methods that upgrade the existing method of treatment should be adopted. The interventions of notably advanced nanotechnology to upgrade the traditional water treatment and wastewater engineering render new opportunities. The advent of nanotechnology in all aspects of science and technology is because of their distinct special characteristics at the nanoscale level such as greater specificity, larger surface area and high loading capacity for improved catalysis as well as high reactivity. And also to the aforementioned features, the nanomaterials have advantageous mechanical, electrical, optical and magnetic properties which are significantly different from the conventional materials. This chapter envisages the overall use of distinct nanomaterials in all the treatment aspects of water and wastewater.

Keywords Nanomaterials · Nanosorbents · Nanocellulose · Nanomembranes

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22.1 Introduction

Water is the crucial useful resource on the earth for the survival of all life and as a precious substance for human sustenance. The hastily extending human populace is carefully related to the long-term global water demand and global climate alternate. The expected global human populace can be accelerated by 6.3 billion in 2050 (Gehrke et al. 2015). Presently, human society is undergoing the trouble of meeting the demandable quality of potable water for consumption, irrigation and business utilities, which is a sparkling situation at the global level. Growing human population with overexploitation of groundwater and surface water has resulted in water scarcity over the sector for beyond few many years. As a consequence, the call for freshwater is growing dramatically, especially for meal manufacturing, on account that 70% of the sector's freshwater withdrawals are already consumed for agricultural irrigation. According to United Nations Children's Fund (UNICEF) in 2015, 844 million people still lack a basic water service and among them almost 159 million people still collect drinking water directly from rivers, lakes and other surface water sources. The primary position of organic and inorganic pollution plays from the commercial and agricultural activities. The real problem of consuming water and sanitation in growing international locations is that too many people lack get admission to secure and less expensive water components and sanitation. The spread of an extensive range of impurities in floodwater and groundwater has emerged as an essential problem globally, because of population growth, fast development of industrialization and prolonged-term droughts. The presence of contaminants in terms of heavy metals, inorganic compounds as well as biological pathogenic compounds is threat to betterment of human dwelling and proper sanitation facilities along with ecological surrounding. Therefore, constraint to removal of such contaminant/pollutant has become prior focus for researchers.

Wastewater is any water that has been unfavourably contaminated by natural contamination, microorganism, emanating from mechanical operations and disintegrates the initial water quality. It might be sub-isolated into (a) municipal wastewater (fluid waste discharged through home houses and industrial sectors) and (b) industrial wastewater (fluid waste released by methods for mechanical and farming games). For the treatment of wastewater, prior consideration is the components identified with waterborne disease and needs to be verified that the treated water is free from any contaminant that may antagonistically affect the strength of individuals and nature. In conventional treatment methods, the wastewater is treated in stages, i.e. at initial stage course and settleable inorganic solids are removed. In the primary stage, suspended solids by means of physical forces are put off; the secondary stage majorly eliminates the biodegradable compounds and the third stage mainly comprises filtration and disinfection for the removal of biological pathogenic compounds. For developing a cost-effective wastewater treatment technology with small place requirements, nanotechnology offers the competencies as they entail the use of nanoscale materials. Nanomaterials usually have an excessive reactivity and diploma of functionalization, large unique surface place, size-based properties and so forth.

22.2 Magnetic Nanomaterials

Water contamination by means of pollution emanating by the point and non-point sources has become principal environmental concern. Several parameters other than choice of the fine and reliable technique for wastewater remedy are an exceedingly complex mission, such as inclusive of the exceptional models to be met and the performance and additionally the cost are to be kept in mind. For choice of water and wastewater remedy, few elements must be taken into consideration, treatment adaptability and final performance, reprocess of remedy dealers, environmental safety and friendliness. Numerous techniques like adsorption, precipitation, reverse osmosis and filtration are drastically used for water and wastewater remedy. Improvement of cost-effective and contaminant removal green magnetic nanomaterials have attracted pervasive interest. Mainly, the usage of magnetic nanomaterials (NMs) as adsorbents offers convenient elimination of contaminants by means of applying outside magnetic fields.

22.2.1 Advantages of Magnetic NMs and Their Characteristics

Many technologies are practical for the synthesis of magnetic NMs with the combination of superparamagnetic property that is prepared via co-precipitation, thermal decomposition, microemulsion, sonochemical reactions, hydrothermal reactions, hydrolysis and thermolysis of precursors, waft injection syntheses, and electrospray syntheses. The unique characteristic like magnetism offered in the form of small ferromagnetic NMs turns out to be amazing to treat water and wastewater. The major surface area and superparamagnetic property had led them to be attractive and are hugely helpful to fabricate the materials of diverse forms.

Diverse types of magnetic NMs are in life like ferrites, metallic, coated ferrites and steel. Magnetism is developed stopping them to agglomerate at zero magnetic fields; usually, silica-covered magnetite is in utility to enhance the reactivity of magnetic NMs. The benefits of silica-covered magnetic NMs can be summarized as higher colloidal stability when you consider that they do no longer magnetically agglomerate lets in strong covalent bonds with functionalization molecules and keeps first-rate magnetic debris. Naked magnetite NMs are vulnerable to air oxidation and get amassed in watery frameworks. Metal nanoparticles may be useful because of excessive magnetic second belongings. Hence, for the product of these nanoparticles in various capacity handles, the adjustment of the iron oxide particles by surface alteration is satisfactory. The magnetic structure of the surface area layer, that is, generally substantially one of a kind from that within the centre of the nanoparticles, may have an incredible impact at the magnetic residences of nanoparticles.

The blend of magnetite NMs has been seriously grown currently for its fundamental restorative pastime as well as for some innovative bundles, together with attractive reverberation imaging, ferrofluids for sound framework, attractive centred medication transport and attractive chronicle media. Fundamentally, the utilization of magnetite NMs as adsorbents in water cure bears a convenient technique for keeping separated and disposing of the contaminants by method for making utilization of outer attractive fields. As discussed, the types and traits of magnetic NMs and its synthesis manner are of fantastic concern. Synthesizing of magnetic NMs will show the huge utility in the percentage contaminant removal in addition to degradation.

22.2.2 Application of Magnetic NMs in Pollutant/Contaminant Removal

The magnetite-miniaturized-scale NMs are from biomedical to ecological applications. One of the utilizes is in water decontamination: in high inclination attractive division, magnetite NMs brought into defiled water will tie to the suspended particles or overwhelming metals and settle to the base of the liquid, allowing the contaminants to be evacuated and the magnetite trash to be reused.

22.2.2.1 Removal of Heavy Metals

In conjunction with adsorption technique, magnetic NMs are utilized in aggregate with photocatalysis, oxidation manner for the elimination of radioactive and carcinogenic debris as well, making it an important treatment device within the case of heavy metals brought into water structures. Those heavy metals can enter watersheds because of diffusion of business methods that produce and in use.

22.2.2.2 Removal of Pathogenic Bacteria

Elimination of pathogenic bacteria from drinking water by the use of magnetic NMs has been carried out with excessive efficiency and no huge toxicity. Magnetic NMs were introduced with electrostatic interaction and photocatalysis response for the elimination of pathogenic bacteria. Elimination of exceedingly ability contaminants from consuming water is a critical utility, as it significantly reduces the health risks related to consuming infected water. Pathogenic bacteria are fatal to human fitness, requiring cost-effective and safe tactics to avert from the ingesting the contaminated water (Xu et al. 2014).

22.2.3 Recent Advances in Wastewater Treatment by Magnetic NMs

These days, there are various reports of attractive nanoparticles as promising adsorbents for substantial steel disposal because of their remarkable favours, together with large specific surface area, helpful separation from water and smooth functionalization. Current research has shown the development of infiltration techniques, i.e. fabrication of magnetic NMs as a magnetic mesh filter out with upgraded parameters consisting of diameter, distance and the number of layers. In a magnetic mesh filtration method, the magnetic filter out is constructed through which contaminated water is handed and later purified water is acquired. Adsorbed contaminants are evacuated from the clear out by means of regeneration and recovery strategies (Wei et al. 2017). Be that as it may, the recovery of attractive nanoparticles would not be a simple task. In this way, a leap forward could be done by methods for the change of a procedure that licenses green to seize of attractive nanoparticles beneath an incredibly low attractive region and simultaneously has simple recuperation capacity to avoid contamination. A brief comparison of different nanomaterials used for water and wastewater treatment is given in Table 22.1.

Within the current research on wastewater remedy, chitosan has gained much interest as an effective adsorbent to get rid of various forms of dyes as well as heavy metal ions. Chitosan is biodegradable, biocompatible natural cationic polysaccharide. Fe_3O_4–chitosan micro- and nanoparticles are very promising for the removal of dye from wastewater due to their low price of production and high removal efficiencies (Balaji et al. 2016). The extended degrees of natural carbon in sewage wastewater during current years impose an extraordinary task to the present wastewater treatment process. Researches were done to synthesize and functionalize magnetic NMs with surface modifiers for biochemical and environmental applications (Lakshmanan et al. 2014; Seenuvasan et al. 2014; Seenuvasan et al. 2013). The development of customized NMs, with attractive properties and exorbitant adsorption ability for a broad scope of mixes, manages to address these unpredictable rising natural contaminants.

However, the adsorption and attractive detachment process especially sketches or a little degree in a static clump mode. Silver, gold and palladium metallic nanoparticles had been extensively contemplated for the wastewater treatment. Silver NM is an antimicrobial specialist to inactivate the coliform microorganisms in the wastewater, and gold NMs impregnated palladium has been utilized to degrade trichloroethane from groundwater. Metal oxide NMs such as TiO_2, ZnO and CeO_2 have been widely utilized for the degradation of contaminants in the

Table 1 Various nanomaterials for water treatment

No.	Types of NMs	Targeted pollutant	References
1	Zero-valent iron nanoparticles from *Spinacia oleracea*	Reduction of biochemical oxygen demand (BOD) and chemical oxygen demand (COD)	Turakhia et al. (2018)
2	Core–shell iron nanoparticles	Separation of Au, Ag, Ni and Cu	Ling et al. (2018)
3	Gold nanoparticles	Degradation of 4-nitrophenol	Teimouri et al. (2018)
4	Zero-valent iron nanoparticles	Removal of Cd^{2+}	Vidmar et al. (2018)
5	Diatomite decorated with polyethylenimine-functionalized pyroxene nanoparticles	Removal of total organic carbon (TOC)	Hethnawi et al. (2018)
6	Forsterite nanoparticles	Reclamation of cerium ions (Ce^{3+}) from synthetic wastewater	Srivastava et al. (2018)
7	Zinc oxide nanocomposites	Dye removal from textile effluent	Nakkeeran et al. (2018)
8	Zero-valent iron nanoparticles	Removal of TOC, COD and phenols from tannery wastewater	Vilardi et al. (2018a)
9	Iron/copper nanoparticles	Reduction of phosphorus and COD	Amen et al. (2018)
10	TiO_2/silica and ZnO/silica composites	Degradation of Reactive Blue 19	Maučec et al. (2018)
11	Novel sorbent	Removal of Pb(II)	Wang and Wang (2017)
12	TiO_2 nanoparticles using leaf extract of *Jatropha curcas* L.	Photocatalytic degradation of tannery wastewater	Goutam et al. (2017)

wastewater. Because of an exorbitant surface area and higher photolytic properties, metallic oxide NMs are considered as better photocatalysts for water decontamination (Lu et al. 2016). Utilization of nano-TiO_2 and Cu_2O anodes in electrocatalytic oxidation framework demonstrated the effective oxidation of natural contamination and better COD disposal charge end up expressed. In latest years, diverse zero-valent steel nanoparticles, together with Fe, Zn, Al, Ag and Ni in water pollution remedy, have drawn huge interest. The surface area and small in length contribute most of its extremely good overall performance in the removal of contaminants by adsorption. With the powerful elimination of contaminants through adsorption, precipitation and oxidation-discount reactions, nano zero-valent NMs had been implemented for removal of large contaminants consisting of halogenated natural compounds, nitroaromatics, organic dyes, phenols, heavy metals, inorganic anions along with phosphates and nitrates, metalloids and radio factors. Notwithstanding many advantages, there are some hazards, together with aggregation, separation trouble from degraded systems. Thus, remedies to such issues, numerous changes are taking place to beautify the performance of contaminant removal (Lu et al. 2016).

In standard, the attention in this discipline is still no longer sufficient, and further studies must be performed to strengthen know-how inside the location of safety and biocompatibility research. Particularly, for lengthy time period toxicity research, the ability effects on human and environmental fitness should be essentially addressed. In addition, there is a demand for novel water treatments to get rid of micropollutants by adopting water treatment frameworks. Nanoengineered substances, comprising nanoadsorbents, nanometals, nanomembranes and photocatalysts, offer the limit with respect to novel water innovation that can be easily customized to buyer-specific bundles; in the end, there might be a dreadful part ongoing enthusiasm inside the utilization of designed magnetite nanoparticles in wastewater treatment. Be that as it may, vulnerabilities over the wellness impacts and natural predetermination of these nanomaterials need to be tended to sooner than their sizable application. Concentrates on their predetermination and effect inside the earth are required because of the releases as of now happening to the earth. Employment of NMs for wastewater remedy is superior to other technology but have limitations which include separation from very last effluents and adverse eco-toxicological consequences. Those shortcomings are hindering its utility in the wastewater remedy and studies towards the development of noble NMs, consisting of magnetic NMs, which may be without problems recovered from the effluent.

22.3 Nanomembranes

Membrane's innovation is betting an undeniably more significant part as unit tasks for natural quality oversee, aid mending, contamination counteractive action, power creation and ecological checking (Khulbe and Matsuura 2018). In water treatment, layer technology might be utilized for a colossal range of applications beginning from molecule evacuation to normal expulsion and desalination (Yu et al. 2017). Table 22.2 represents the types of nanomembranes for water decontamination.

22.3.1 Zeolite Ceramic Membrane

Recent research says that natural zeolite-based hollow fibre ceramic membrane is used for the removal of chromium from the aqueous streams. Zeolite is a hydrated aluminosilicate mineral normally found in nature, and clinoptilolite is the most plentiful wellspring of characteristic zeolite found over the globe, making it among

Table 2 Different types of nanomembrane available for water treatment

No.	Types of nanomembranes	Targeted pollutant	References
1	TiO_2 thin-film composite membranes	Removal of humic acid	Cheshomi et al. (2018)
2	Hollow fibre ceramic membrane	Removal of chromium	Adam et al. (2018)
3	Electrospun nanomembrane	Water filtration	Lee et al. (2018a)
4	Composite polymeric membranes	Water distillation	Bhran et al. (2018)
5	Dual-layered electrospun nanofibrous membranes	Water desalination	Khayet et al. (2018)
6	Photocatalytic membrane	Water purification	Coto et al. (2018)
7	Pd/GO/BNC membrane	Removal of toxic organic dyes	Xu et al. (2018)
8	Crystalline nanocellulose/poly (vinyl alcohol-co-ethylene nanofibrous membrane)	Adsorption of heavy metal ions	Zhu et al. (2017)

the least-expensive common zeolite sources in the market. This mineral is made out of symmetrically stacked alumina and silica tetrahedron and frames an open and stable three-dimensional (3D) structure with a negative charge, and this charge is responsible for the adsorption of certain charged particles. Along these lines, this element has made the normal zeolite a potential substantial metal cation's adsorbent and expels Cr (VI) from the wastewater (Adam et al. 2018).

22.3.2 *Electrospun Nanofibre Membranes*

A silver nanowire-polyacrylonitrile/thermoplastic polyurethane composite membrane is used for water disinfection as the electrospun nanofibres are known to have high connectivity among pores, ensuring filterability of the membrane as well as mechanical and electrochemical rigidity (Tan et al. 2018). Graphene oxides are blended with the nanoscale polyacrylonitrile (PAN) strands by electrospinning, and these ensuing composite nanofibers are used for the water purification. The blending of graphene oxide with PAN nanofiber films enhances their mechanical strength. The polymeric nanofiber materials with hydrophilic matrices can be more advantageous for water purification (Lee et al. 2018a). The modification in electrospun nanofiber layers to fabricate polymeric nanofibers renders the agglomeration of metals in water, and the modified membrane adsorbs the pollutants and filters the heavy metals in wastewater by the electrostatic forces and also desorbs, thus paving a possibility of recycling (Wei et al. 2018).

22.4 Nanosorbents

Nanometals are usually microspheric which enhances the adsorption of heavy metals, and nanosized metallic oxides such as MgO, CaO and ZnO are best adsorbents as they are environmentally compatible (Vilardi et al. 2018b; Kumar et al. 2018). Zero-valent metals (ZVMs) are widely used to remove contaminants from water with their large surface area and reactivity, and these traits make them to be used in advanced oxidation processes (Nidhesh et al. 2018; Awual et al. 2018). The utilization of iron oxide nanometals in water treatment has gained attention because of their use as nanosorbent as well as immobilization matrix. Zinc oxide has a permeable nanostructure with greater surface area for the adsorption of heavy metals (Kumar et al. 2013). Sorption is a reliable technique for wastewater cleanup and the method involves the initial transport of the pollutant from the water to the sorbent surface, then adsorption on the sorbent surface and finally transport inside the sorbent.

22.4.1 Carbon-Based Nanosorbents

Carbon-based nanomaterials have been significantly used for the adsorption of numerous pollutants from water, and activated carbon is one of its kind as they have adsorptivity. Activated carbon is available at very low cost and has high excellent resistance against attrition losses (Huang et al. 2018; Lee et al. 2018b; Bernstein et al. 2017). Agro-based residues bear good physico- and biochemical properties, which makes them a potential source of activated carbon (Menya et al. 2017; Kumar et al. 2017).

22.4.2 Carbon Nanotubes

Carbon nanotubes (CNTs) are materials of framed networks wrapped into a tube shape either as a solitary layer or as different layers (Trivedi and Alameh 2017). Single-walled CNTs comprise the round and hollow state of a solitary shell, whereas multi-walled CNTs are made out of various layers of sheets, and these CNTs have been extensively used for the water desalination (Das et al. 2018). Polypyrrole-coated oxidized multi-walled CNTs are used to adsorb heavy metals and pesticides from the aqueous solution (Nyairo et al. 2018; Tonski et al. 2018).

Table 3 Nanocellulosic materials in adsorbing pollutants for water and wastewater

No.	Nanocellulose	Targeted pollutant	References
1	Cellulose nanocrystals	Victoria Blue 2B	Voisin et al. (2017)
2	Nanocellulose	Chlorpyrifos	Moradeeya et al. (2017)
3	Carboxy cellulose nanofibers	Lead	Sharma et al. (2018)
4	Crystalline nanocellulose	Heavy metals	Zhu et al. (2017)

22.5 Nanocellulose

Nanocellulose is a substance that has good surface area, compound latency and adaptable surface chemistry science, and nanocellulose-based adsorbents have attracted researchers because of their ability to regenerate after several adsorption–desorption cycle (Moradeeya et al. 2017). Nano cellulose and its modified surfaces are characterized for their adsorptivity and selectivity (Voisin et al. 2017). Table 22.3 shows the efficacy of nanocellulosic materials in water and wastewater treatment.

Hydrophobic nanocellulose is used for the oil separation from water (Rafieian et al. 2018). Nanocellulose also has the ability to work for the coagulation–flocculation treatment of municipal wastewater, wherein the use of nanocellulose substantially reduced the chemical oxygen demand in an extremely settled suspension, with flocculants (Suopajärvi et al. 2013).

22.6 Conclusions

The advent of nanotechnology can greatly impact the wastewater treatment, and the nanomaterials with high surface area, better reactivity and sensitivity with the ability to self-assemble on targeted pollutants make them more reliable for water as well as wastewater treatment. In pursuit, the development of technological solutions in terms of economic factors and eco-friendly considerations should be made.

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Chapter 23
Application of Microbial Fuel Cell in Wastewater Treatment and Simultaneous Bioelectricity Generation

Thanh Ngoc-Dan Cao, Shiao-Shing Chen, Saikat Sinha Ray, Huy Quang Le and Hau-Ming Chang

Abstract The overpopulation in the future will result in burning issues of our environment and the negative effects of global warming, environmental pollution, and habitat loss in the worldwide human community. Moreover, the nonrenewable natural resources such as fossil fuels and clear water are consumed at the speed faster than their rate of regeneration. Worldwide demand has increased year by year, which is required to exceed production from known and anticipated resources. Last but not least, the demands of water used in agriculture, industries, and supporting population growth have increased and become of the most challenges in later centuries. Under those circumstances, there are prerequisites for finding alternative renewable energy resources and cost-effective wastewater treatment technologies with less energy expenditure. Among various technologies that have been well investigated, microbial fuel cell might be the potential candidate to administer with the recent situation of wastewater–energy nexus. In general, the microbial fuel cell is a cross-disciplinary technology so that survey area has extended to energy, material sciences, biology, and environment. In this chapter, we aim to present the possibility of generating electricity in MFC from a wide range of organic waste and hazardous wastes. In addition, the integrations between microbial fuel cells and other technologies are also introduced which have supposedly made great opportunities to concurrently reach sustainable energy production, efficient wastewater treatment, and reuse.

Keywords Microbial fuel cell · Electricity generation · Wastewater treatment

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23.1 Introduction

Although fossil fuels have served mankind for over several years, how far these fossil fuels can be used while the fact that they are going to vanish soon from our lives. Furthermore, the major drawback of utilizing fossil fuels is that conversion of fossil fuels into electricity or fuels is polluting the environment by the emission of carbon dioxide, nitrogen oxides, sulfur dioxide, volatile organic compounds, heavy metals, and fine particles. Global warming, climate changes, and related issues are consequences that humankind has to face if there is no rethinking about switching to green and clean energy as soon as possible. Currently, due to the rapid process of industrialization and urbanization, the amount of wastewater has been increased and required to pass through treatment processes before being discharged into water bodies. Therefore, developments of suitable and reliable technologies for wastewater treatment have been considered as a tremendous need. In conditions of sustainable development, the treatment system should recover energy to offer a self-sufficient energy. Thus, the ideal energy form in this instance should be gained from wastewater sources and directly converted into electricity.

Among reported technologies for harnessing energy, microbial fuel cell (MFC) is considered as a promising candidate, which provides two major benefits including wastewater treatment and simultaneous energy generation. Its recent developments have passed through the historical timeline demonstrated in Fig. 23.1 dating back through the years. In the early stage, Dr. M. C. Potter, a Professor of Botany at the University of Durham, reported that microorganisms disintegrate organic compound contributing to the liberation of electrical energy (Potter 1911). In 1931, Cohen (1931) introduced the early bacterial battery (so-called MFC) producing the high voltage of 0.5–0.9 V when *Proteus vulgaris* was cultured. Although these explorations were very potential, they had not been gained any interests until the 1970s when mediators were found to enhance the power and current density by adding them to the medium of MFC (Allen 1972). Theoretically, several microbes in the anodic chamber do not have the ability to transfer electrons directly to anode since the components of their outer membranes contain non-conductive lipid membrane, and lipopolysaccharides inhibiting electron transfer. Therefore, the addition of mediators could accelerate the transfer of electrons. However, the use of mediators produces some disadvantages limiting MFC application such as high cost, toxicity, and instability of synthetic mediators; hence, their use is removed in most of MFC research resulting in mediator-less MFC (Kim et al. 1999a). In the cathode chamber, the application cathode catalyst is one of the major challenges to improve the performance of MFC which is required to have high redox potential, durability, and availability. Furthermore, biocathode was introduced to replace chemical catalysts which were expected to reduce the cost and toxicity of MFC (He and Angenent 2006). In terms of configuration, dual-chamber MFC has shown its disadvantages in power generation due to high internal resistance, oxygen leakage through the membrane, and extensive cost of aeration. Therefore, in 2004, Liu and Logan (2004) developed a single-chambered

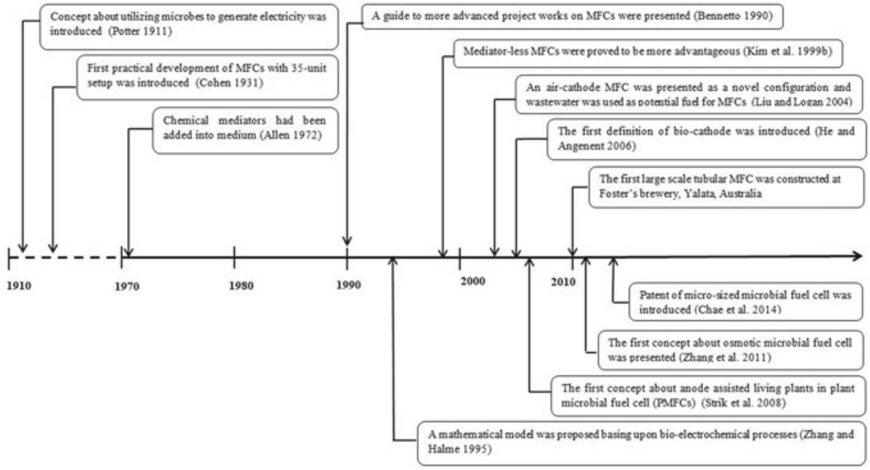

Fig. 23.1 Brief timeline of the development of microbial fuel cell (MFC)

MFC to overcome weaknesses of conventional configuration which achieved the high power density of several thousand mW/m^2. Recently, besides studies conducted about conventional MFC, there are several integrations of MFC and other technologies to produce multi-benefit systems such as living plant-microbial fuel cell (PMFC) (Strik et al. 2008), osmotic microbial fuel cell (OsMFC) for water purification or reducing wastewater effluent (Zhang et al. 2011), or membrane bioreactor coupled with microbial fuel cell (MFC–MBR) for improving wastewater treatment efficiency (Ren et al. 2014). Detailed information about them will be discussed further in this chapter.

The popularity of MFC rose during the last few years with many attempts to make its real application come true. An enormous number of works done in MFC can be referred through several reviews on MFC and latest developments. Different points of reviews have been published such as comprehensive configurations, characterizations, and evaluation of performances (Logan et al. 2006; Du et al. 2007), microbial activities (Rabaey and Verstraete 2005; Logan 2009), relations of conventional anaerobic digestion and MFCs for biogas production (Pham et al. 2006), electrode modifications with catalysts (Nitisoravut et al. 2017; Sonawane et al. 2017), various kinds of electron acceptor (Ucar et al. 2017; He et al. 2015), and feeding substrates (Leong et al. 2013). For membrane modification or alternative materials, there are many works have been done in reviews of ion exchange membrane (Winfield et al. 2016), ceramic membrane (Dhar and Lee 2013; Kokabian and Gude 2015), and recent advances separators and challenges for membranes MFC (Nitisoravut and Regmi 2017). However, due to limit of this chapter, we will just discuss the major benefit of MFC in wastewater treatment. In addition, several developments based on integrations with other technologies were presented such as plant MFC (Zhu et al. 2016), osmotic MFC for desalination and wastewater treatment (Ren et al. 2014), and membrane bioreactor MFC (Nitisoravut and Regmi 2017). However, due to the limit of this chapter, we will just discuss the major benefit of MFC in wastewater treatment. In addition, several developments based on integrations with other technologies were also presented such as plant MFC (Zhu et al. 2016), osmotic MFC for desalination and wastewater treatment (Ren et al. 2014), and membrane bioreactor MFC (Logan 2009).

23.2 Background of Microbial Fuel Cell

23.2.1 Fundamentals of Microbial Fuel Cell

Microbial fuel cell (MFC) is described as a system that uses bacteria as the catalysts to oxidize organic and inorganic matter and generate current. As can be seen from Fig. 23.2a), a basic MFC unit is constructed by three important components such as anode chamber, cathode chamber, and separator as a barrier placed between those two chambers. Bacteria and the organic compound are confined to the anode chamber of an MFC where anaerobic conditions are maintained while electrons and protons are released in this side. The cathode is maintained under aerobic condition by additional air sparging (dual-chamber MFC) or direct air facing (single-chambered MFC or air-cathode MFC as displayed in Fig. 23.2b). The ion-selective membrane placed between both anode and cathode parts of MFC plays major roles in (1) providing the transfer bridge of protons from anode to cathode via ion exchange membrane; (2) constructing a solid barrier to prevent waste in anode chamber from contaminating cathode chamber; and (3) preventing oxygen leakage from cathode to anode breaking the anaerobic environment. During

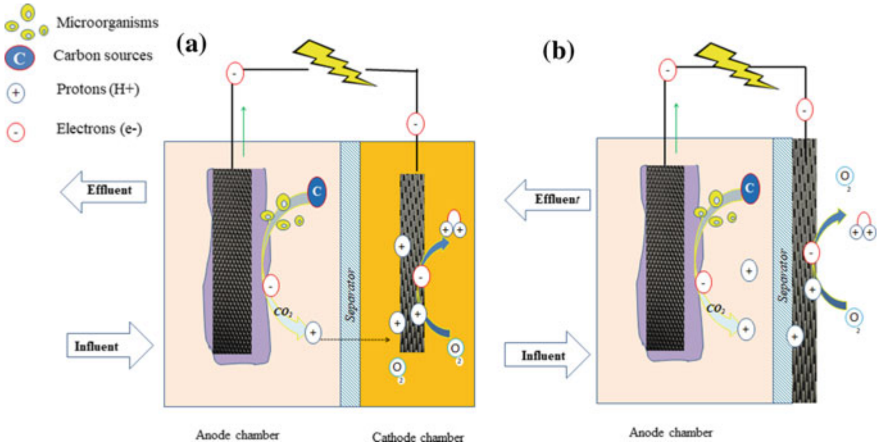

Fig. 23.2 Schematic of **a** a conventional MFC (two-chambered MFC), **b** an air-cathode MFC (single-chambered MFC)

operation when the external circuit is closed, electrons combine with protons and oxygen to produce water. Initially, ferricyanide $K_3[Fe(CN_6)]$ and potassium permanganate have been used as catholyte filled in cathodic chamber in MFC but regular replacement is one of its disadvantages. Besides, oxygen is the most popular electron acceptors since it has high oxidation potential, low cost, and availability. However, low performance is caused by large overpotential due to slow kinetics of oxygen reduction at plain carbon material so that coating catalysts on the cathode are necessary to enhance its performance.

23.2.2 Role of Microorganism in Microbial Fuel Cell

It is worth to say that MFC is unique since it uses microorganisms instead of the metal catalyst as other fuel cells that bacteria oxidize organic matter and transfers electrons to the anode. With the presence of microorganisms in the anode chamber, the oxidation of substrate creates an overall energy loss since microorganisms actually derive energy of oxidation of feeding fuel. Indeed, oxygen is prevented in anode side since any optional bacteria will use oxygen as a terminal electron acceptor instead of anode in the dissimilarity respiratory chain of the microbes in biofilm; hence, an anaerobic environment is compulsory to remain in the anodic chamber. Kim et al. (1999b) revealed the useful insights of exoelectrogenic bacteria and relation to other bacteria affecting power production. Accordingly, there are three ways for the microorganism to use exocellular electron transfer and result in power generation in an MFC including (1) cell respiration, (2) directly transferring to another cell, and (3) cell–cell communication. Recently, it has been proven that ferrous-reducing bacteria such as *Shewanella putrefaciens* and the *Geobacteraceae* strains, such as *Geobacter sulfurrenducens* which are active electrochemically, can directly transmit electrons to the anode electrode by cell respiration. Among them, in 1999, Rabaey et al. (2005) found that *Shewanella putrefaciens* was first shown as direct proof of electrical current generation in an MFC by a dissimilatory metal-reducing bacterium (*Gammaproteobacteria*). To support cell–cell communication, bacterial conducting pili (nanowires) used for electron transfer to the electrode and between bacterial cells was first reported with *Geobacter sulfurreducens* (Gorby et al. 2006) and then in *Shewanella* and other microorganisms (Logan et al. 2006; Leong et al. 2013; Daud et al. 2015). In recent years, the number of reports of microorganism in MFC revealed that few strains individually produce power densities as high as the ones from mixed cultures. However, MFC using mixed cultures (e.g., wastewater) would be able to produce substantially greater power densities than those in pure cultures due to high resistance to significant changes in environment and operational condition.

23.3 Application of Microbial Fuel Cell

23.3.1 Bioelectricity Production and Organic Removal

23.3.1.1 Types of Substrates Used in MFC

Recently, great attention has been paid to the microbial fuel cell (MFC) due to their use of a variety of biodegradable substrates for feeding. A large number of artificial and wastewater as actual substrates have been reviewed (Pant et al. 2010). In order to remain the substrates condition, most of MFC studies have been conducted using pure compounds such as acetate, glucose, sucrose, an amino acid as cysteine, or a protein as bovine serum albumin (Firdous et al. 2018). For instance, Liu et al. (2005) reported about the use of acetate as substrate in MFC generating power density of 506 mW/m^2 at influent COD of 800 mg/l. Similar to acetate, glucose is another popular substrate but it is a fermentable substrate; hence, low Coulombic efficiency is a result of electron loss by competing bacteria and limit electricity production (Chae et al. 2009). On the other hand, the organic high strength wastewater cause serious environmental issues resulting in the ammonium pollution due to nitrogen-rich effluents. Many kinds of wastewater released from industrial sources such as vegetable oil wastewater (Moharir and Tembhurkar 2018), food waste leachates (Shen et al. 2018), dairy manure (Kelly and He 2014), and cheese wastewater (Feng et al. 2008) were investigated in MFC. Among them, brewery wastewater can be effectively treated using MFC, but that achievable power density will depend on wastewater strength, solution conductivity, and buffering capacity (Lu et al. 2009). Moreover, MFC is considered as a promising sustainable approach to reuse starch processing wastewater containing 4852 mg/l of chemical oxygen demand that could be used as substrate to produce electricity of 239.4 mW/m^2 (Chouler et al. 2016; Santoro et al. 2013). Power densities obtained with these substrates vary with MFC configurations but they are generally higher with pure compounds. Another substrate source, human urine, and domestic wastewater have been used in MFC recently since it is huge volumes and produced worldwide (Feng et al. 2008). The summary of efficiency of different substrates used in MFC is demonstrated in Table 23.1. In order to make the comparison within references, power was normalized using per unit volume of the cell (mW/m^3) and per unit area of the anode surface area (mW/m^2).

23.3.1.2 Effects of Organic Loading Rate (OLR)

The rate of fuel feeding to the anode chamber is an important factor that influences MFC function (Mansoorian et al. 2013). The highest current density and power in 48 h operation was achieved since at low OLR, fuel cells need more time to achieve maximum current density and power, but at higher OLR the system quickly approaches to maximum current density and power. Another reason may be the

Table 23.1 Different substrates used in microbial fuel cell (MFC) and maximum power density produced

Type of wastewater	Specific source	Concentration (COD, mg/l)	Configuration	Power densities	COD removal (%) and others	CE (%)	References
Industrial wastewater	Brewery wastewater	2250	Air-cathode MFC	205 mW/m^2 (5.1 W/m^3) at R_{ext} = 1000 Ω	87%	10	Lu et al. (2017)
		3197 ± 979	Air-cathode MFC (tubular configuration)	1.61 mW/m^2 (0.44 W/m^3) at R_{ext} = 10 Ω	94.6 ± 1%	13.9	Dong et al. (2015)
		800–1000	Air-cathode MFC	0.097 kWh/m^3 at R_{ext} = 10 Ω	87.6% 86.3% (suspended solid removal)	8	Mansoorian et al. (2013)
	Food processing wastewater	1900	Two-chambered MFC	230 mW/m^2 at R_{ext} = 20 kΩ	86% 79% (BOD_5)	21	Sangeetha and Muthukumar (2011)
		7760	Two-chambered MFC	123.8 mW/m^2	98.9%	–	Oh and Logan (2005)
		8920 ± 150	Two-chambered MFC	81 ± 7 mW/m^2 at R_{ext} = 117 Ω Hydrogen production 210 ± 56 ml/l	95%	–	Lu et al. (2009)
	Starch processing wastewater	4852	Air-cathode MFC	239.4 mW/m^2 at R_{ext} = 120 Ω	98%	8	Min and Logan (2004)
		686 ± 18	Air-cathode MFC (flat plate MFC)	242 ± 3 mW/m^2 at R_{ext} = 33 Ω	26 ± 2%	21	Huang and Logan (2008)
	Paper recycling wastewater	800	Air-cathode MFC	501 ± 20 mW/m^2	73 ± 1% 85 ± 2% (cellulose)	16 ± 2	Patil et al. (2009)
	Chocolate processing wastewater	1459	Two-chambered MFC	3.02 A/m^2 at R_{ext} = 100 Ω	75%	–	Katuri et al. (2012)

(continued)

Table 23.1 (continued)

Type of wastewater	Specific source	Concentration (COD, mg/l)	Configuration	Power densities	COD removal (%) and others	CE (%)	References
Agricultural wastewater	Slaughter processing wastewater	4850	Two-chambered MFC	578 mW/m^2 (6.4 W/m^3) at R_{ext} = 100 Ω	93 ± 1%	64 ± 2	Kim et al. (2008)
	Swine wastewater	8320 ± 190	Air-cathode MFC	261 mW/m^2 at R_{ext} = 200 Ω	92% 83% ($NH_4{}^+$ –N removal)	26	Min and Logan (2004)
	Casava mill wastewater	16,000 (86 mg/l cyanide)	Two-chambered MFC	1771 mW/m^2 at R_{ext} = 200 Ω	72%	20	Yazdi et al. (2015)
Domestic wastewater	Municipal wastewater	1000	Air-cathode MFC (flat plate MFC)	72 ± 1 mW/m^2	42%	–	Chouler et al. (2016)
	Septic wastewater	600	Air-cathode MFC (designed as MFC-stack)	142 ± 6.71 mW/m^2 at R_{ext} = 100 Ω	95–87.5%	22–8	Greenman et al. (2009)
	Urine	–	Air-cathode MFC	0.58 W/m^3 at R_{ext} = 1 kΩ	–	–	Du et al. (2007)
Landfill leachates		12,900–35,300	Two-chambered MFC	~1000 μW/m^2 at R_{ext} = 500 Ω	34% (BOD removal)	47	Du et al. (2007) and Venkata Mohan et al. (2007)

CE (Coulombic efficiency) is defined as the ratio of actual Coulombs transferred to the anode, to the theoretical Coulombs or maximum Coulombs if all organic matters are completely oxidized in the anode chamber

R_{ext} is applied external resistance adaption intensity of microorganism in wastewater and inoculum (Jadhav and Ghangrekar 2009). This may be due to the fast growth rate of fermenting bacteria in comparison to the bacteria that are electrochemically active. On the other hand, high feeding rate causes incomplete fuel consumption and the substitution of other electron acceptors in competition with the anode and this will lead to low efficiency.

23.3.1.3 Effect of Temperature

Temperature as an important ecological factor affects biofilm development and microbial metabolic activity. A function of temperature was examined altogether with water strength fed with brewery wastewater (Pham et al. 2006). Decreasing the temperature from 30 to 20 °C reduced the maximum power density from 205 mW/m^2 (5.1 W/m^3, 0.76 A/m^2 at 30 °C) to 170 mW/m^2 (20 °C). Other ranges of temperature such as 20–35 °C and 8–22° were investigated (Mei et al. 2017). Operation under a higher temperature range of 20–35 °C favored higher COD removal efficiency of 90% and lower current of 0.7 mA and CE of 1.5%. At low temperature range of 8–22 °C, although the COD removal efficiency of MFC decreased (59%), higher current (1.4 mA) and CE (5%) were produced. However, the unfavorable lower temperature would decrease COD removal efficiency; hence, methanogens growth would be eliminated and caused the loss of charges and increasing the Coulombic efficiency. On the other hand, another study indicated that at a lower operating temperature below 20 °C, the electrochemically active bacteria could remain action (Jadhav and Ghangrekar 2009; Gil et al. 2003; Li et al. 2008a).

23.3.1.4 Effect of pH

According to fundamentals of MFC, proton transferred through a membrane which would cause changes in pH of anode and cathode side influencing on MFC performance. Therefore, pH is considered one of the key parameters concerned to control and evaluates overall MFC performance through proton transfer and internal resistance. If no buffer solution is used as catholyte in MFC, there will be an obvious pH difference between the anodic and cathodic chambers, though theoretically there will be no pH shift when the reaction rate of protons, electrons, and oxygen at the cathode equals the production rate of protons at the anode (Gil et al. 2003; Li et al. 2008a, b). Difference pH increases the driving force of the proton diffusion from the anode to the cathode chamber and forms a dynamic equilibrium. According to references, the maximum efficiency of MFC was achieved at pH 7 of catholyte (Wang et al. 2011). In anode chambers, low pH inactivates microorganism and decreases the function of MFC. To improve the proton availability as a limiting factor in electricity generation, Wu et al. (2017) found that adding acid is similar to supply more protons for cathodic reaction and solve issues related to the slow proton transport rate.

23.3.2 Removal of Hazardous Wastes

23.3.2.1 Heavy Metal Removal

The demand of using metal resources is increasing resulting in the increase in their value. In addition, the requirement of removing heavy metal pollutants from water sources has become a serious issue since they are considered as hazardous wastes causing damage to human body and genetic problems. Therefore, recovery of heavy metals from industrial wastewater, mining wastewater, and leachate is concerned to reduce the environmental problems. In MFC, heavy metals could act as electron acceptors since they have high redox potential and possible to be reduced at cathode. Basically, by reduction reaction that occurs on cathode surface, heavy metal ions are removed as solid form as precipitation on cathode (e.g., Ag^+ is precipitate in Ag) or transformed to nontoxic form (e.g., Cr^{6+} is converted to Cr^{3+}). The present section was proposed to communicate about the effects of specific types of heavy metals on MFC's performance and detailed information of their performances are demonstrated in Table 23.2.

Mercury (Hg^{2+})

Mercury and its compounds are widely used in paint, pulp and papermaking, color-alkali manufacturing industry, oil refinery, battery manufacturing industry, and pharmaceutical processing. However, water-containing mercury contaminates can seriously damage human's health. Unlike other technology used to treat mercury ions which are considered to be high cost and hazardous by-product, MFC used Hg^{2+} as a kind of potential electron acceptor due to its high standard potential. Removal of Hg^{2+} as an electron acceptor of MFC was successful under the condition of lower initial pH of 2 and high Hg^{2+} concentration of 100 mg/L resulted in higher maximum power density of 433.1 mW/m^2 (Li et al. 2008b).

Hexavalent Chromium (Cr^{6+})

The electroplating industry is considered as a factor causing critical pollution problems since it discharges wastewater containing heavy metals such as cadmium, copper, and chromium. Hexavalent chromium usually occurs as highly soluble and highly toxic chromate ions. Additionally, the accumulation of Cr^{6+} in living tissues throughout the food chain causes many serious health problems such as kidney and liver damages. The extensive use of Cr^{6+} in many industries and the disposal of Cr^{6+} containing wastes have resulted in Cr^{6+}-induced environmental contamination (Li et al. 2009). Therefore, it is important to remove Cr^{6+} in wastewater discharged from the electroplating industry. Under the acid condition, Cr^{6+} ion accepts six electrons and thus is reduced to Cr^{3+} ion. As reported by Gupta et al. (2017), under

Table 23.2 A short summary of metal contaminant in wastewater which are able to be removed/recovered by microbial fuel cells

Metal contaminants	Removal efficiency (%) or reduction rate	Power density (mW/m^2)	References
Mercury Hg^{2+} (E^0 = +0.911 V)	93.84% (at pH 2.0)[a]	433.1	Tandukar et al. (2009)
	97.3 ± 2.6	20.98 W/m^2	Li et al. (2008b)
Chromium Cr^{6+} (E^0 = +1.33 V)	0.46 $mgCr^{6+}$/g VSS h	55.5	Wang et al. (2008)
	99.5% (at pH 2.0)	1600	Zhang et al. (2012)
	87.5–100% depending on initial concentration	150	Huang et al. (2011)
	75.4 ± 1.9%	970.2 ± 20.6	Zhang et al. (2012)
	94 ± 8%	6.4 W/m^3	Li et al. (2009)
Vanadium V^{5+} (E^0 = +0.991 V)	67.9 ± 3.1%	970.2 ± 20.6	Xue et al. (2013)
	75.8%	0.6 mA	Li et al. (2016)
Arsenite As^{3+}	40%	477	Heijne et al. (2010)
	100%	752.6 ± 17	Tao et al. (2011)
Copper Cu^{2+} (E^0 = +0.286 V)	84% (anaerobic condition) 43% (aerobic condition)	0.43 W/m^2 (anaerobic condition) 0.8 W/m^2 (aerobic condition)	Choi et al. (2014)
	>96%	339 mW/m^3	Abourached et al. (2014)
Cadmium Cd^{2+} (E^0 = −0.403 V)	90%	Supplied energy by Cr^{6+}-MFC	Choi and Cui (2012)
	90%	3.6 W/m^2	Ho et al. (2017)
Silver Ag^+ E^0 = +0.799 V)	99.91%	4.25 W/m^2	Wen et al. (2011)
	83.73–92.50%	5396–3385 mW/m^3	Wu et al. (2014)

[a] Number was calculated based on achieved results of references
E^0 is electrode potential reduction (V)

the condition of pH 2, 99.5% Cr^{6+} and 66.2% total Cr were removed by MFC and a power density of 1600 mW/m^2 was produced. Similarly, Zhang et al. (2010) reported that Cr^{6+} at 100 mg/l were simultaneously removed during 150 h with initial pH 2 with the power density of 150 mW/m^2 (0.04 mA/cm^2). Another study employed a new material for cathode so-called alumina (AA)/nickel (Ni) nanoparticles (NPs)-dispersed carbon nanofiber (CNF) in MFC for simultaneous electrochemical reduction of Cr^{6+} and generation of bioelectricity (Hao et al. 2016).

Vanadium (V^{5+})

The use of MFC in pollutant removal is vanadium (V) removal which is commonly found in wastewater of vanadium mines and pentoxide processing activities. It can be successfully used in MFC since it has high redox potential in acidic conditions. For instance, about 26.1% V removal was obtained which were accompanied by the maximum power density of about 614.1 mW/m^2 after 72 h of operation (Heijne et al. 2010). In terms of investigating the suitable carbon sources influencing vanadium (V) reduction, acetate generated the highest maximum power density of 589.1 mW/m^2 with V removal of 77.6% (Tao et al. 2011).

Copper (Cu^{2+})

The mining and metallurgical industries are major sources of copper emissions to the environment. High concentration of copper could become toxic for living life forms depending on its concentration. Hence, removing copper from wastewater of those sources is very important. A metallurgical MFC was proposed to combine copper removal and recovery which produced 0.43 W/m^2 under anaerobic condition and 0.8 W/m^2 with oxygen was supplied and Cu^{2+} was removed simultaneously more than 99.88% (Choi et al. 2014). Different concentrations of Cu^{2+} and applied external load were investigated to reveal their influences on the performance of MFC. At initial concentration of 6412.5 ± 26.7 $mgCu^{2+}/L$, it generated power density of 339 mW/m^3 and removal efficiency of >99% (Abourached et al. 2014).

Cadmium (Cd^{2+})

Cadmium is highly toxic to humans and can exist extremely long biological half-life greater than 20 years in environment. It can cause negative impact on human health such as flu-like symptoms (chills, fever, and muscle pain), damage lung, and other kidney, bone, and lung diseases. Hence, removal of cadmium from wastewater is important to protect public health and environment. In fact, Cd^{2+} ions have low reduction potential ($E^0 = -0.403$ V) so that it could not be removed by MFC unless power and voltage generation would be insufficient. Therefore, a dual-chamber MFC containing Cr^{6+} ($E^0 = +1.33$ V) can generate energy as a redox-flow battery containing MFC for complementing Cd^{2+} wastewater and reduced it to metal. In particular, Cr^{6+}-MFC generated power density of 22.5 W/m^2

was higher than the power density of 2 W/m^2 supplied to MFC to reduce 90% Cd^{2+} to metal (Li et al. 2016). In single-chambered MFC, about 90% Cd was removed which might relate to biosorption and precipitation in reactor during operation, and high power generation of 3.6 W/m^2 was produced (Wang et al. 2016).

Arsenic (As^{3+})

Arsenic is one of the most toxic elements commonly existing in groundwater and surface water, and it is a well-known carcinogen and its toxicity depends on its oxidation state. Particularly, two types of predominant forms of arsenic in water are As(III) and As(V), while the former is more toxic than the latter with higher migration. Spontaneous anaerobic oxidation of As(III) to As(V) in MFC was introduced in 7 days with a maximum power density of 752.6 ± 17 mW/m^2 and TOC removal efficiency of 84% (Wu et al. 2017).

23.3.2.2 Antibiotics

Antibiotics, one of the important groups of pharmaceuticals in human and veterinary medicine, are widely used in the prevention and treatment of diseases and have detected in various aquatic environments such as wastewater, surface water, groundwater, and drinking water. As can be seen in Table 23.3, MFC performances on various antibiotic treatments are demonstrated. The question that is still largely unaddressed is the effect of the toxins on the performance of electroactive biofilm-based MFC accomplishing removal of COD in pharmaceutical wastewater treatment. Biodegradation of sulphamethoxazole and its degradation product such as 3-amino-5-methylosoxazole (3A5MI) by MFC were investigated. Approximately, 85% of 20 ppm SMX was degraded within 12 h and 3A5MI can be further mineralized. An antibacterial activity test showed that the biotoxicity of SMX toward *Shewanella oneidensis MR-1* and *Escherichia coli DH5*α was greatly reduced after MFC treatment (Schneider et al. 2015). The bioelectrochemical response of an electroactive mixed-culture biofilm in MFC to different tobramycin concentrations was reported (Miran et al. 2018). Experimental results demonstrate that the electroactive biofilm-based MFC is robust against antibiotics at the level of μg/L but sensitive to changes in antibiotic concentration at the level of g/l. In another study, MFC was developed to be a biosensor for fast determination of the susceptibility of two tested pathogenic bacteria against 10 different beta-lactam antimicrobial agents belonging to different classes and subclasses (Wang et al. 2011). Another study has proved that biodegradation was the main process for sulfamethoxazole removal compared to sorption by sulfamethoxazole acclimatized cultures and that the process results in efficient removal of SMX in MFC mode (Wang et al. 2016).

Table 23.3 A short summary of antibiotics contaminant in wastewater which are able to be removed by microbial fuel cells

Antibiotic species	Classification	Removal efficiency (%) or reduction rate (%)	Power density (W/m^2)	References
Penicillin	β-lactam	98	101.2 W/m^3	Wang et al. (2015)
Sulphamethoxazole	Sulfonamides	85	–	Miran et al. (2018)
		70	–	Song et al. (2013)
		83.3	240	Wang et al. (2017)
Metronidazole	Nitroimidazoles	85.4	141.94	Zhou et al. (2018)
Tetracycline	Tetracycline	79.1	251.14	Strik et al. (2008)
Sulfadimidine	Sulfonamide	99	*Performance was inhibited with additional antibiotics*	Deng et al. (2012)
Aureomycin	Tetracycline	100		
Roxithromycin	Semi-synthetic macrolide	100		
Norfloxacin	Fluoroquinolone	100		

23.4 Integrations of MFC with Other Biotechnologies for Additional Benefits

Although many descendants of an MFC have been introduced, several specific integrations will be mentioned in this section such as plant-microbial fuel cell (PMFC), forward osmosis microbial fuel cell (OsMFC), and microbial fuel cell-membrane bioreactor (MFC–MBR).

23.4.1 Integrating Microbial Fuel Cells with Living Plants (PMFC)

A very first communication about living plant-microbial fuel cell (PMFC) defined as green electricity production with living plants and bacteria in fuel cells was published in 2008 (De Schamphelaire et al. 2008; Kouzuma et al. 2014; Takanezawa et al. 2010). It is a kind of microbial solar cells which deploys living plants and bacteria supporting to convert solar energy into green electricity. In PMFC, the plant's root fuels the electrochemically active bacteria by excreting rhizodeposits or root exudates. Rhizodeposition of plant roots is the loss of organic compounds into the soil, including sugars, organic acids, polymeric carbohydrates, enzymes, and dead-cell material. The integration of the MFC technology with photosynthetic organism makes the PMFC technology renewable and the organic matter that is converted into energy was recently generated by photosynthesis (see Fig. 23.3).

It is necessary to investigate the impact of PMFCs on the rhizospheric environment and plant physiology as well as the microbial community (Timmers et al. 2010). Increased plant diversity by mixing with shade-requiring, hardy, or evergreen plants can improve the resistance of microorganisms community against the fluctuation of light intensity and temperature. PMFC can be used to reduce methane emission in wetland and paddy fields. Living rice plants are potential to apply in PMFC since paddy field farming became the dominant form of growing rice

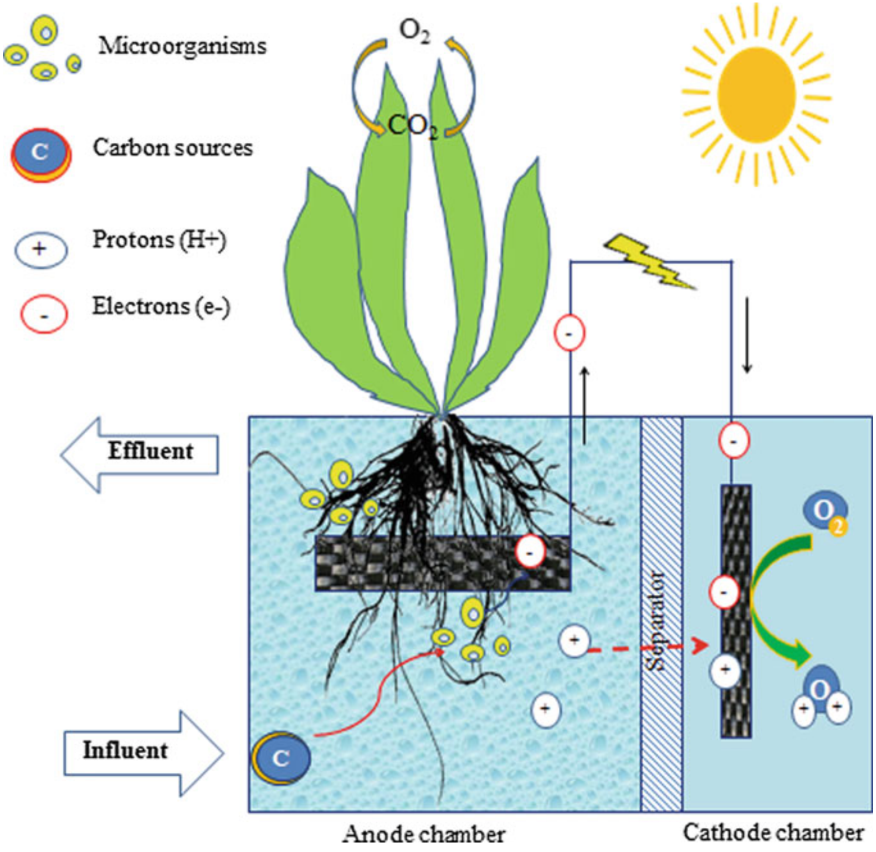

Fig. 23.3 Schematic of a plant-microbial fuel cell (PMFC)

especially, in Asian countries. As a promising approach for harvesting green energy of the natural world, rice plants were examined in PMFC by Moqsud et al. (2017). However, rice plants need special care to grown and lifetime is short. In order to find alternatives to rice plants, many species were tested in PMFC and prove long-term electricity generation in a system such as *Spartina anglica* (Xu et al. 2018) and water plants—*Phragmites australis* (Helder et al. 2012b) and *Juncus effusus*, *Typha orientalis*, and *Scirpus validus* (Helder 2012), since they are widespread in wetland systems. Another design of PMFC with flat plate was expected to increase power output and decrease internal resistance since the distance between anode and cathode was reduced and transport resistance was eliminated (Wetser et al. 2017). To examine influences on PMFC processes, design criteria for PMFC proposed to enhance renewable energy generation were reported for further understanding about this biotechnology and its developments in future (Wetser et al. 2015). A tubular PMFC was successfully designed which can be directly installed in wetlands without the need for active pumping or aeration with an in situ start-up of the bioanode and biocathode (Helder et al. 2012a).

A chemical ferricyanide cathode can be replaced by a biological oxygen-reducing cathode in a PMFC (Moqsud et al. 2015). A nitrate-less, ammonium-rich medium that contains all macro- and micronutrients with a balanced amount of bicarbonate buffer was developed (Habibul et al. 2016). Compost from organic waste mixed with soil to grow rice plant generated voltage and power density at 2 times and 3 times, respectively, higher than only soil used (Xu et al. 2018; Wang et al. 2016). Bioelectrochemical reduction of Cr^{6+} in PMFC through secrete root exudates was evaluated which might provide a new insight for Cr^{6+} removal from wastewater (Zhang et al. 2011). Constructed wetlands have been successfully applied to secondary treatments of domestic sewage, leachate, rainfall runoff, and industrial effluent. In a bigger scale of PMFC, constructed wetlands combined with MFC (aka CW-MFC) could purify the wastewater while the mechanism is similar to PMFC (Ge et al. 2013).

23.4.2 Integrating Microbial Fuel Cells with Forward Osmosis (OsMFC)

In recent years, there are many studies about enhancing MFC performance by utilizing forward osmosis (FO) membrane and simultaneously demonstrated the feasibility of extracting water from wastewater/seawater (see Fig. 23.4).

The development of OsMFC is supposed to gain advantages of both forward osmosis and MFC technology. In addition, a novel OsMFC was introduced using FO membrane as a separator and its performance was evaluated by using artificial seawater as catholyte (draw solution) (Werner et al. 2013). In this study, OsMFC produced more electricity than conventional MFC, likely due to better proton transport with water flux pass through the FO membrane based on osmotic-driven

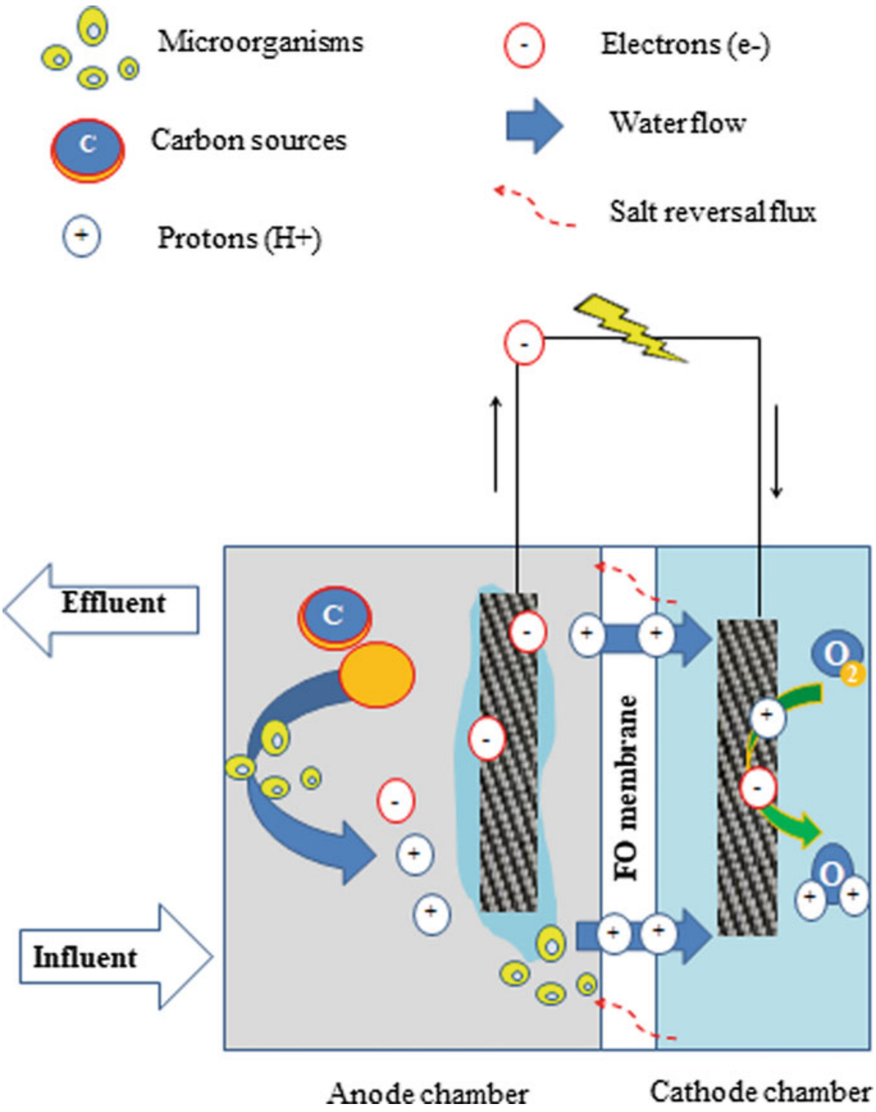

Fig. 23.4 Schematic of osmotic microbial fuel cell (OsMFC)

force. Among those studies adopted, synthetic anode feeding substrate to operate OsMFC, Ge and He (2012) used real domestic wastewater which was more complex substrates to examine OsMFC. About 4.5 W/m^3 of power density was generated along with water flux of 2.15 LMH with the recirculation rate of catholyte from 100 to 3000 mL/min. Previous studies applied aeration for remaining oxygen supply as electron acceptors which are considered to be a limitation of OsMFC development since it is required extensive energy. Due to that reason, air-cathode microbial osmotic fuel cell (MOFC) was operated without relatively energy consumption for aeration (Hou et al. 2016). Maximum power production of 43 W/m^3 and carbon source was removed up to 90%; however, a small amount of acetate crossed the membrane to the catholyte. Only sodium chloride is a suitable candidate as catholyte solutes with good performance in both electricity generation and water flux comparing to calcium chloride, potassium phosphate buffer (PPB), and glucose (Neoh et al. 2016). Additionally, Li et al. (2014) reported different integrations consisting of MFCs and osmotic membrane bioreactors (OMBRs) using new thin-film composite (TFC) membrane which enhanced the power density generated by MFC unit from 3 to 11.5 W/m^3 and removed effectively organic (>95%) and phosphorous (>99%). However, there is still little information about developments of OsMFC until now which might associate to selecting suitable catholyte since a draw solution could perform well in FO process but may not function as good catholyte in MFC. Moreover, scale-up of this system is not as easy as PMFC since PMFC can install in wetland system with all natural environmental provided, while OsMFC requires suitable draw solutes and mitigating salt leakage through membrane which may affect microorganism activity in the anolyte.

23.4.3 Microbial Fuel Cell-Membrane Bioreactor (MFC–MBR)

Meanwhile, developments of membrane bioreactor (MBR) provide a promising approach and become the largest market for other membrane system treating wastewater such as microfiltration, nanofiltration, and ultrafiltration (Wang et al. 2012). In order to improve permeates quality, mitigate membrane fouling, and sustain the performance of reactors, integrating MBR with other technologies is supposedly good options for a multi-advantage approach for wastewater treatment. Among integrations, there is an approach proposed to enhance the overall efficiency of wastewater treatment by integrating MFC and MBR (Wang et al. 2013). Energy consumption has to be evaluated properly since it is a key parameter introducing this integration in wide application. Additionally, biofouling was expected to be controlled by using a shorter hydraulic retention time (HRT) while obtaining high power production. To utilize effectively oxygen supply for aeration tank, biocathode of MFC was applied resulting effective removal efficiency of the system along with stable current generation of 1.9 ± 0.4 mA in 40 days of operation (Tian et al. 2015). A novel electrochemical membrane bioreactor (EMBR) was designed similar to air-cathode MFC so that no aeration was consumed and the use of the non-woven cloth was useful to filtrate wastewater (Ren et al. 2014). This novel configuration offers several advantages relating to fluid leakage through cathode, accumulations of inorganic salts, and decrease of pH gradient adapting for long-time operation. In addition, nitrification and denitrification reactions occurred without oxygen involving. Another integration was developed by combining MFC with hollow fiber membrane bioreactor generating maximum power density of 2.18 W/m^3 ($R_{\text{ext}} = 50\ \Omega$) (Li and He 2015). Li and He (2015) introduced an anaerobic fluidized-bed membrane bioreactor (MFC-AFMBR) to effectively treat domestic primary effluent which was evaluated and electrical energy of 0.0197 kWh/m^3 was produced slightly higher than the required energy for operation (0.0186 kWh/m^3). Controversially, Pandey et al. (2016) conducted a study about bioelectrochemical reactor (MBER)-based anion exchange membrane (AEM) membrane which showed that system produced 0.03 kWh/m^3 less than consumed 0.09 kWh/m^3 (Kaewkannetra et al. 2011). However, advantage of this MBER design is a combination of anaerobic (anode chamber) and aerobic process (cathode chamber), and organic input to aerobic process is supposedly low resulting in less requirement of aeration energy, slow production of sludge, and low membrane fouling while involving electricity generation.

23.5 Challenges and Further Developments

Microbial fuel cell technology has been discussed as a potential alternative sustainable wastewater treatment with energy production for years. Until now, the number of paper published with keyword “microbial fuel cell (MFC)” has reached to over thousand results indicating that MFC still gains a lot of concerns from other scientists all over the world. MFC is a kind of flexible technology since it gives us more rooms to improve its performance by modification of its components, integrating with other technologies, and treating various kinds of substrates which not only reduce pollution but also self-sufficient electricity generation. Specifically, MFC is the only technology that can directly generate electricity out of waste, without the input of external/additional energy. According to information mentioned in this material, the developments of MFC have never stopped until an ideal MFC system is found for practical application in the same situation with membrane technology. Although MFC is a complicated technology, it is a cross-disciplinary collaborator with many fields of study, the continuous research into such technologies that we may find solutions to our global environmental problems. Furthermore, more and more upcoming generations of MFC have been introduced to improve the drawbacks of MFC itself, such as osmotic microbial fuel cells (OsMFC), plant-microbial fuel cell, and integration of MFC with membrane bioreactor (MBR). Optimistically, MFC will be successfully applied in wastewater treatment plant contributing to the developments of environmental engineering and solving recent environmental issues.

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