The Handbook of Environmental Chemistry 45

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Advanced Treatment Technologies for Urban Wastewater Reuse

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Advanced Treatment Technologies for Urban Wastewater Reuse

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Aims and Scope

Since 1980, *The Handbook of Environmental Chemistry* has provided sound and solid knowledge about environmental topics from a chemical perspective. Presenting a wide spectrum of viewpoints and approaches, the series now covers topics such as local and global changes of natural environment and climate; anthropogenic impact on the environment; water, air and soil pollution; remediation and waste characterization; environmental contaminants; biogeochemistry; geoecology; chemical reactions and processes; chemical and biological transformations as well as physical transport of chemicals in the environment; or environmental modeling. A particular focus of the series lies on methodological advances in environmental analytical chemistry.

Series Preface

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

While a considerable amount of knowledge has been accumulated over the last three decades, as reflected in the more than 70 volumes of *The Handbook of Environmental Chemistry,* there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

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

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

The Handbook of Environmental Chemistry is available both in print and online via www.springerlink.com/content/110354/. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of *The Handbook of Environmental Chemistry* by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló
Andrey G. Kostianoy
Editors-in-Chief

Volume Preface

The ever-increasing shortage of water and the increasing needs for food security of the expanding world population and for irrigation water both in respect to good quality and quantity render the reuse a necessary condition. Currently, sustainable and safe urban water cycles have a high priority on the policy agenda of many countries around the world. Although reuse is accompanied by a number of benefits, several open questions still exist. For example, the applied treatments fail to completely remove biological and chemical microcontaminants, antibiotic-resistant bacteria, and resistance genes. The remaining organic matter in the wastewater after conventional treatment consists of a number of recalcitrant organic compounds including potential endocrine-disrupting compounds; many types of pharmaceutical compounds including antibiotics, disinfection by-products, personal care products, metabolites, and transformation products; and others. This leads to their subsequent release in the terrestrial and aquatic environment through disposal, storage, and reuse applications, which is of major environmental and health concern. Therefore, the identification of technologies that are able to remove such contaminants from wastewater, and the identification of means and solutions to overcome these problems and promote safe reuse practices, is of outmost importance.

Within the last decade much research has been performed in order to eliminate such contaminants present in low concentration (so-called micropollutants) from wastewater by appropriate treatment technologies. The newer ones are applied in addition to conventional treatment technologies. They are most often called "advanced treatment technologies". These mainly include a chemical step such as ozonation, hydrogen peroxide and light-driven technologies, and/or application of adsorption materials as well as filtration processes or combinations of these, in order to remove contaminants from the water. Within the last years there has also been intense research investigating the applicability of such advanced treatment technologies not just for the removal of organic microcontaminants but also for the removal of microorganisms, including bacteria, antibiotic-resistant bacteria, protozoa, and viruses.

Much published material is currently available. However, it is often scattered in different journals and books and is available only among various scientific communities. Therefore, it is timely to bring together this knowledge. In this book the potential and the limitations as well as the pitfalls and the knowledge gaps of the different advanced treatment technologies are presented. This volume offers a detailed overview on the capacity of currently applied and tested treatment technologies and on the integration of advanced processes to remove trace organic contaminants and microorganisms. This book is expected to draw the attention of experts; scientists; practitioners, from various fields of research, including analytical and environmental chemistry, toxicology, and environmental and sanitary engineering; and also treatment plant operators and policy makers.

The editors would like to acknowledge all the scientists involved in the development of the book and for creating the opportunity for fruitful discussions and exchange of ideas and knowledge and their patience with the editors. They would also like to thank warmly their co-workers of their research groups for their support in the daily working routine for giving them time to edit a book in such a vital field for the sustainable development of the urban environments and societies. Special thanks go to Dr. Lida Ioannou and Mr. Toumazis Toumazi (Nireas-International Water Research Center, University of Cyprus), Dr. Oliver Olsson (Institute of Sustainable and Environmental Chemistry, Leuphana University Lüneburg), and Ms. Xiaodi Duan (University of Cincinnati) for their significant contribution and administrative work and support during the development of the book.

The editors would like to express their gratitude to Dr. Andrea Schlitzberger and their team at Springer Publisher who supported in such a wonderful and constructive way the idea to realize this book.

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Contents

Scope of the Book *Advanced Treatment Technologies for Urban Wastewater Reuse*

Klaus Kümmerer, Dionysios D. Dionysiou, and Despo Fatta-Kassinos

Abstract This volume offers a comprehensive overview on the potential challenges and limitations of currently applied and tested treatment technologies, to remove trace organic contaminants.

Keywords Advanced treatment technologies, Antibiotic resistance, Biological and chemical treatment technologies, Contaminants of emerging concern, Wastewater treatment technologies

Urban wastewater treatment plants are regarded as the main sources for the spread of contaminants of emerging concern into the environment. The term refers to a diverse and expanding number of anthropogenic and natural compounds including

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industrial chemicals, compounds present in personal care products, pharmaceuticals, their metabolites, and transformation products formed during wastewater treatment. It is widely accepted that conventional activated sludge systems are inefficient in eliminating such contaminants, resulting thus in their dissemination into the environment. Advanced effluent treatment has also severe limitations depending on the type of treatment and compound to be removed. All of them can only remove certain compounds completely. Some compounds are removed only partially and others are not removed at all. In some cases, such as treatment with ozone or other oxidizing chemicals as well as effluent treatment and drinking water treatment with UV radiation, mostly unknown transformation products are formed which have been shown to be sometimes even more toxic than the parent compounds. The introduction of such compounds into the environment can potentially be even more pronounced when wastewater reuse schemes are implemented in water-scarce regions especially for agricultural and landscape irrigation. Furthermore, all advanced treatment comes along with elevated energy demand.

As a contribution to the knowledge in this field, this book focuses on the application of various technologies for the removal of contaminants of emerging concern, including not only organic chemicals but also antibiotic-resistant bacteria and other mobile resistance elements.

The second chapter presents four well-known and widely used technologies for the elimination of microcontaminants. Membranes, activated carbon, ozonation, and advanced oxidation processes are reviewed with regard to their efficiency in eliminating such contaminants from wastewater effluents. The analysis leads to the conclusion that the presented technologies can be useful for microcontaminant mitigation although none of them seems to be a universal barrier for them when used separately. Depending on the final use of the reclaimed water, the treatment may require the combination of several technologies that could lead to a substantial increase of the cost.

Activated sludge-based processes are environmentally friendly approaches to wastewater treatment. However, as mentioned already, conventional biological treatment alone may not be effective for all microcontaminants present in wastewater. The low removal efficiency of biologically persistent compounds and the presence of hydrophilic ones necessitate the integration of biological treatment with other membrane-based and physicochemical processes to ensure adequate removal at least of some of them. The third chapter provides a brief overview on the integration of advanced treatment processes including activated carbon adsorption, advanced oxidation processes, and high retention membranes with membrane bioreactors for the removal of microcontaminants.

Enhanced performance of biological processes for microcontaminant removal in wastewater treatment plants can be also achieved by adopting various general strategies based on different principles of operation including the increase of the biomass concentration, dynamic operating conditions able to modify the biocenosis composition and to induce alternative metabolic pathways required by xenobiotic biodegradation, and others. The fourth chapter tackles these issues and discusses technologies that involve the addition of adsorption or absorption media, advanced oxidation processes like UV and UV/H_2O_2, and bioreactors operated with attached and granular biomass.

The detection of resistant microorganisms in the effluents of urban wastewater treatment plants disposed into surface water or reused for crop irrigation shows that conventional treatments and disinfection processes do not effectively control the spread of pathogens into the environment. There is a need for new and more effective disinfection processes and technologies. The aim of the fifth chapter is to briefly describe some of the emerging and antimicrobial-resistant microorganisms detected in wastewater, as well as the conventional and advanced available technologies for wastewater disinfection, and to evaluate and discuss their effect on these microorganisms. Moreover, regulations and policies on wastewater reuse are also discussed and compared.

The sixth chapter investigates the potential of different tertiary wastewater treatment technologies to minimize antibiotic-resistant bacteria and resistance genes in wastewater effluents, while the seventh chapter provides an overview on the microcontaminant behavior throughout conventional and advanced chemical and biological systems.

A very popular technology for the abatement of such contaminants, mainly on research level, is heterogeneous photocatalysis, which is often proposed to destroy micropollutants recalcitrant to biological treatment. However, the use of suspension of TiO_2 particles at an industrial scale is not easy. The eighth chapter reports on the evaluation of the efficiency of two photocatalysts immobilized on glass plates and cellulose fibers for the degradation of antibiotic compounds.

The development of integrated systems for wastewater treatment has been investigated in recent years not only for the improvement of control parameters but also to allow the routine reuse of wastewater to be effectively implemented. Chapter nine covers the evolution of the combined use of upflow anaerobic sludge blanket systems and constructed wetlands and also the integration of these technologies with advanced chemical processes.

The tenth chapter tackles the technological developments in treating wastewater by membrane bioreactors. In this chapter, various water reuse issues and standards applied in the USA are reviewed, and the challenges of membrane bioreactor systems and their status of applications are presented.

Reverse osmosis is considered today as a reliable and essential water reclamation technology for producing high-quality water for reuse. The concentrate, which is a waste stream produced from the process, is volumetrically substantial and contains environmentally harmful compounds and therefore can cause severe environmental impacts if disposed of into the environment. The eleventh chapter presents an overview of the concentrate quality and various technologies for treating it. The technologies discussed include mineral recovery, electrochemical desalting, and treatment through adsorption, coagulation, and oxidative degradation. Other alternative strategies including emerging technologies for increasing water recovery rate from water reclamation plant are also discussed.

Potable water reuse through the use of treated wastewater effluents has been practiced for more than 50 years. The majority of projects worldwide are characterized as indirect potable water reuse, where an environmental buffer like groundwater aquifer or a surface water reservoir provides retention, additional attenuation, and blending prior to use as drinking water. Due to the recognition of contaminants of emerging concern occurring in reclaimed water that might exhibit adverse health effects, additional advanced treatment processes have been implemented. With increasing reliability of advanced water treatment processes and operational experience over several decades, the role of the environmental buffer to provide treatment and retention time has been revisited in projects that came online during the last 10 years. Recent trends in direct potable water reuse are presented and discussed in the penultimate chapter.

The book closes with an outlook that provides the reader with information on the potential strategies that could be applied in order to tackle the problems related with the presence of contaminants of emerging concern and wastewater.

Treatment Technologies for Wastewater Reuse: Fate of Contaminants of Emerging Concern

O. González, B. Bayarri, J. Aceña, S. Pérez, and D. Barceló

Abstract The presence of thousands of microcontaminants in wastewaters and their potential risks has drawn a large attention of the scientific community during the last years. The presence of these contaminants is especially controversial when wastewater is considered for reuse because a large number of microcontaminants are frequently not totally removed by conventional wastewater treatment processes. As a contribution to the knowledge in this field, this chapter focuses on the application of four well-known and widely used technologies to the elimination of microcontaminants. Membranes, activated carbon, ozonation, and advanced oxidation processes (AOPs) are deeply reviewed to assess their efficiency and safety in the elimination of these contaminants from wastewater effluents. A brief description of each technology is presented together with a review of their real application, mostly in wastewater treatment plants (WWTPs). A deep analysis of the found data allows to conclude that the four presented alternatives can be useful for microcontaminant mitigation although none of them seem to be a universal barrier for microcontaminants when used separately. In addition, each technology presents drawbacks which demand further research to be overcome. Depending on the final use of reclaimed water, the treatment may require the combination of

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several of the studied technologies although that results in an economic impact which cannot be neglected.

Keywords Activated carbon, AOP, Membranes, Micropollutant, Ozone

Contents

Abbreviations

AOPs	Advanced oxidation processes
BAC	Biological activated carbon
BDPEs	Bromodiphenyl ethers
CAS	Conventional activated sludge
DEHP	Bis-(2-ethylhexyl)phthalate
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EDCs	Endocrine-disrupting chemicals
EEQ	E2 equivalence factor
GAC	Granulated activated carbon
HRTs	Hydraulic retention times
HS	Compound–humic substance
K_{OW}	Octanol–water partition coefficient
MBR	Membrane bioreactor
MF	Microfiltration
NDMA	*N*-Nitrosodimethylamine
NF	Nanofiltration
NOM	Natural organic matter
PAC	Powdered activated carbon
PhACs	Pharmaceutically active compounds
PPCPs	Pharmaceuticals and personal care products
RO	Reverse osmosis

SAT	Soil aquifer treatment
SRTs	Sludge retention times
TDS	Total dissolved solid
UF	Ultrafiltration
WWTPs	Wastewater treatment plants

1 Introduction

The lack of surface water for drinking water production is of growing concern and attracts worldwide attention. In response to the water scarcity, treated wastewater is considered a viable alternative water resource. This book chapter focuses on urban wastewater reuses following passage through wastewater treatment plants (WWTPs). The main applications of urban water reuse are direct or indirect potable reuse and direct or indirect non-potable reuse.

As regards potable water reuse, to our knowledge, direct reuse has been implemented only in Africa [1]. In contrast, indirect potable reuses have been widely accepted by introducing reclaimed water into surface or groundwater bodies. Artificial groundwater recharge is the most widespread practice due to the additional treatment provided by underground transformations and because reclaimed water loses its identity as sewage water. Soil aquifer treatment (SAT) is one of the most regarded practices for indirect potable reuse [2]. To improve wastewater quality, SAT can be combined with preceding advanced treatments. Undoubtedly, the quality of water extracted from a recharged aquifer depends on the introduced water.

Non-potable water reuse includes all water reuse practices other than potable water reuse. Reclaimed water is mainly used for agricultural and landscape irrigation or groundwater recharge. In addition, several cities use reclaimed water for different urban applications such as toilet flushing [3, 4], fire protection, or washing purposes (Fig. 1).

Possible human exposure to reclaimed water puts higher demands on the wastewater treatment in order for the wastewater to be safe for direct or indirect applications. Advanced treatment technologies have been evaluated for improving the quality of reclaimed water in order to prevent potential effects of recalcitrant compounds.

Due to the concern related to the presence of microcontaminants in water sources, several studies on their removal at WWTPs have been carried out at full scale. Nowadays, conventional WWTPs produce water in compliance with major relevant regulations. However, municipal wastewater is considered the primary source of microcontaminants [6] in waterways. A variety of organic microcontaminants, including pesticides, pharmaceutically active compounds (PhACs), personal care products, and estrogens as well as their human metabolites, are not completely removed in WWTPs with conventional treatments, and therefore they are detected in wastewater effluents [7–10]. The presence of microcontaminants is

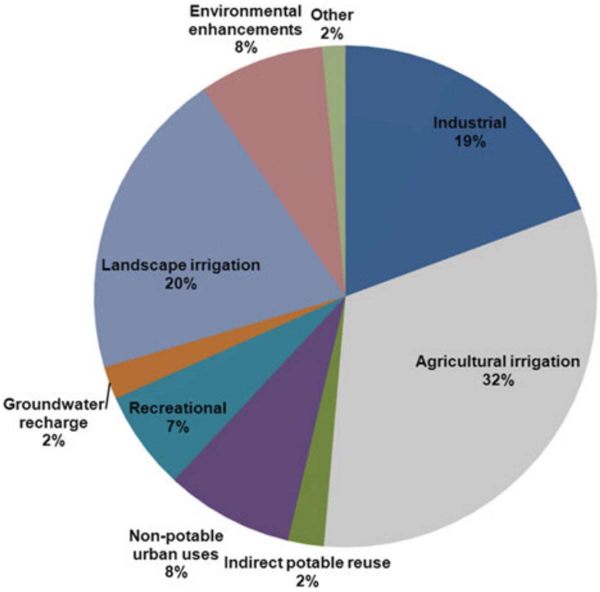

Fig. 1 Global water reuse (Figure adapted from "Municipal Water Reuse Markets 2010" [5])

especially concerning if treated wastewater is being considered for reuse. It has been seen that traditional biological treatment via activated sludge is not very effective for the removal of several of such contaminants. Thus, studies analyzing the efficiency of conventional WWTPs without advanced treatments are presented herein.

Although the non-potable direct reuse of treated effluents may have beneficial effects (e.g., addition of nutrients to the soil), irrigation with reclaimed water, for example, may cause sorption of microcontaminants and metals in agricultural crops and the contamination of groundwater sources [11–14]. Moreover, several studies reported the presence of microcontaminants in agricultural irrigation networks [11, 12].

2 Existing Technologies for Water Reuse

In the last decade, some researchers investigated the efficiency of different advanced water treatment processes for contaminants of emerging concern (CEC) removal to reduce the impact of discharges of reclaimed water into different water bodies [15]. In this work, we review various available technologies for the removal of microcontaminants showing their advantages and disadvantages. The selected technologies presented in this chapter (membranes, ozone, adsorption, and advanced oxidation processes (AOPs)) are those considered more mature and ready to be applied at WWTPs [16, 17]. In fact, most of them are currently being used successfully in WWTPs for different purposes. The elimination rate reported proves that these technologies can eliminate a high fraction of the micro-contaminants present in water. However, the necessity or not of this step must be carefully studied, since all of them are economically and energetically demanding. Thus, their application can be only considered if water conditions and requirements justify it.

Membrane technologies provide an important solution in reuse and recovery of water. Membrane filtration involves the passage of wastewater, usually from biological treatment, through a thin membrane for the purpose of removing particulate material, pathogens, organic matter, nutrients, and dissolved substances not removed by previous treatment processes. Generally, membrane processes are considered the most powerful technologies for removing microcontaminants, and microfiltration (MF) coupled with reverse osmosis (RO) (MF–RO) has become the most widely used technology together with SAT [18].

Ozone is an unstable gas generally produced by electric discharge in a gas phase. Its stability in water is on the order of minutes, requiring on-site generation. Ozone has been used in drinking water and WWTPs since several decades. Thus, ozonation is a mature and quite reliable technology. Currently, ozone is mainly used for disinfection purposes in the production of drinking water. However, since the concern for the presence of several microcontaminants in wastewater is growing up, ozone is being considered a good alternative to control this problem due to its high oxidizing capacity and the ability of generating hydroxyl radicals.

Adsorption is the process of accumulating substances that are in solution on a suitable interface. During adsorption, molecules of a substance (adsorbate) collect on the surface of another substance (adsorbent). Thus, adsorption is considered to be a mass transfer operation, usually from a fluid phase to solid phase. Adsorption process involves the transfer of the adsorbate molecule from the bulk solution to the adsorption site in the adsorbent. Adsorption treatment of reclaimed water is usually thought of as a polishing process for water that has already received normal biological treatment.

AOPs are generally based on an initial generation of hydroxyl radicals (HO·), which then become the system's main oxidizing agent, able to remove a large number of contaminants. In general, contaminants which exhibit the highest levels of oxidation are characterized by high HO· rate constants associated with their electron-rich moieties (e.g., phenols, anilines, olefins, and activated aromatic).

2.1 Membrane Filtration

2.1.1 Membrane Technologies

MF and ultrafiltration (UF) membranes are commonly used for the filtration of municipal secondary effluent. The resultant water from these membrane processes may be used for diverse reuse applications after disinfection. The membrane driving force in MF and UF is the hydrostatic pressure difference or vacuum in open vessels. On the other hand, sieve is the typical separation mechanism. The combination of a biological treatment with MF or UF membranes is called membrane bioreactor (MBR) and is widely used in water reuse systems. MBR is an alternative to the conventional secondary treatment with activated sludge that provides enhanced organic compounds and suspended solid removal. MBRs possess the following advantages over conventional wastewater treatment: high effluent quality, excellent microbial separation ability, absolute control of sludge retention times (SRTs) and hydraulic retention times (HRTs), high biomass content and less sludge bulking problem, low-rate sludge production, small footprint and limited space requirement, and possibilities for a flexible and phased extension of existing WWTPs [19]. The presence of membranes improves the removal of microcontaminants in MBR because of both the intrinsic effect of the membrane and also the increase of SRT. Higher SRTs lead to the diversification of microorganisms, including some slow-growing bacteria such as nitrifying bacteria, which improves the removal of microcontaminants. Sorption to biomass and enmeshment in the membrane biofilm are also important mechanisms of elimination.

MBR technology has demonstrated to meet unrestricted irrigation World Health Organization (WHO) standards by means of a supplemental disinfection [20]. Regarding microcontaminants present in municipal wastewater, MBR technology does not efficiently remove them (see the section on “Microfiltration, Ultrafiltration and Membrane Biological Reactor”). Other applications such as aquifer recharge, surface water augmentation, dual water systems in households, and industrial process water require advanced levels of purification nonaffordable with the technologies above mentioned.

MF and UF membranes are also widely used as a pretreatment step to help prevent fouling of the less permeable nanofiltration (NF) and RO membranes. In contrast to MF and UF, solution/diffusion and exclusion separation mechanisms govern the NF and RO separation. In addition, the hydrostatic pressure difference is the only driving force in NF and RO. In terms of water reuse, NF membranes are commonly used to reduce total dissolved solid (TDS) concentration for specific applications. To this end, NF is also used in conjunction with RO. Both NF and RO are also used to treat pre-filtered effluent (typically with MF or UF) for surface water augmentation or indirect potable reuse applications such as groundwater injection. Also, the two-stage scheme MBR–RO/NF is nowadays increasingly accepted for water reuse. Terms “loose” (low rejection) and “tight” (high rejection) are commonly used to define the overall rejection efficiency of NF and RO membranes. Even though most inorganic and organic constituents and microorganisms are removed, disinfection is required to ensure system reliability in the event of a leak or defect in the membrane and to control the growth of microorganisms in the pipelines.

Figure 2 outlines the effectiveness of each membrane technology in removing the different constituents of wastewater as a function of their size.

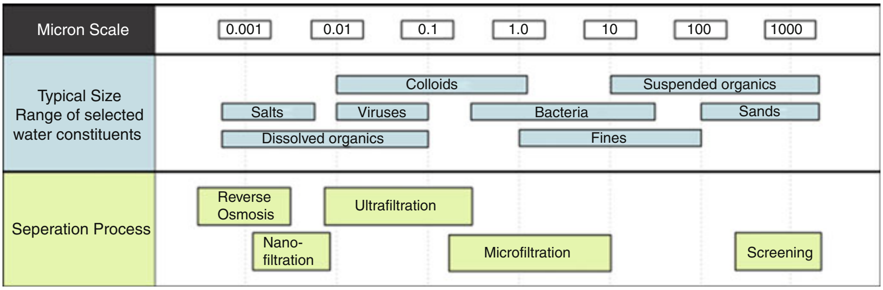

Fig. 2 Size range of constituents in wastewater and operation range of membrane processes

2.1.2 Membrane Separation Mechanisms

Generally, up to four basic mechanisms may be involved in the rejection of solute by membrane processes: sieve, size exclusion (steric effect), adsorption onto membrane, and charge repulsion. To illustrate that, the example of low rejection rate of caffeine by RO membranes due to its physicochemical properties can be used. As a representative of hydrophilic and nonionic compounds, the rejection driven by charge exclusion and adsorption is negligible, and steric exclusion is solely responsible for the retention of caffeine. In addition, the lower molecular weight of caffeine in comparison with other target compounds might result in the decreased removal efficiency during the RO membrane filtration process [21].

These mechanisms are largely dependent on a number of factors, i.e., membrane process type, operating conditions, specific microcontaminant characteristics, membrane fouling, matrix composition, and membrane characteristics. The last factor seems to be more relevant in the case of NF and RO membranes. Although to a lesser extent compared to NF, the retention in RO systems is also membrane type dependent [22].

Recently, major efforts have focused on assessing how matrix characteristics affect the microcontaminant rejection by membranes. According to Nghiem and Coleman [23] and Comerton et al. [24], membrane fouling is likely to contribute to higher rejections of PhACs by NF/RO, especially for some hydrophobic ionogenic compounds. However, other studies reported that organic fouling can both improve and lessen the retention of microcontaminants because membrane fouling has been observed to both increase compound adsorption and decrease mass transport causing higher diffusion of solutes across the membrane [25–27]. The main mechanisms by which fouling seems to influence membrane rejection are the modification of the membrane surface charge, pore restriction, and cake-enhanced concentration polarization.

Regarding the natural organic matter (NOM) present in the matrix, most authors agree with a positive effect over the rejection of microcontaminants. Plakas et al. [28] clarified that an increase in compound rejection may result from the binding of microcontaminants to NOM due to hydrogen bonding, forming NOM–compound complexes that are larger, have an increased negative charge, and/or have a higher affinity for adsorption to the membrane when compared to the compound alone. Sadmani et al. [29] further analyzed the interactions of major organic matter fractions of NOM with the different microcontaminants as a function of their characteristics. They determined that dissolved organic matter (DOM) fractions interact preferentially with neutral microcontaminants, resulting in increased rejection, presumably due to enhanced size exclusion of compound–humic substance (HS) pseudo-complexes arising from dipole–dipole interactions. The increase in rejection can be also attributed to an increase in the negative surface charge of the membranes due to the presence of NOM (electrostatic repulsion) [30]. According to Sahar et al. [31], NOM interactions could be the explanation for the lower removals observed for the microcontaminants present in lower concentrations in the raw sewage since the matrix effect which influences the removal mechanisms would decrease.

The speciation of microcontaminants may result in a significant change in rejection as a function of pH, with much greater retention occurring for ionized, negatively charged compounds. For uncharged microcontaminants, intrinsic physicochemical properties of the molecules play a role in their retention. UF and NF exhibited much higher removals for less polar microcontaminants [32]. The presence of divalent cations, calcium in particular, can also influence the membrane charge and the interaction of compounds and humic acids with each other and the membrane surface. They can have a positive effect on microcontaminant retention but can also interfere with the microcontaminant–NOM complex reducing its formation and thus retention [24, 28, 33]. According to Sadmani et al. [29], an increase in cation concentration leads to a decrease in removal of neutral compounds probably by decreasing the availability of HS interaction sites.

2.1.3 General Disadvantages of Membrane Technologies

Although membrane processes are effective treatments for removing a wide range of microcontaminants, one of their drawbacks is the generation of huge volumes of concentrates that are commonly discharged to water bodies. Although the discharge of membrane retentates is currently not regulated, safe environmental practices would suggest that such a concentrated waste stream should be treated before its release and dilution into the environment. Treating these concentrates would minimize the environmental impacts associated with their discharge or management [21, 34]. Backwash streams need also to be considered especially if chemicals are used in pretreatment or for membrane cleaning. On the other hand, another important drawback of these filtration systems is the high energy consumption associated to the high operation pressures. These reasons, together with the costs associated to fouling problems and replacement of membranes, prevent these technologies to be truly sustainable.

2.1.4 Full-Scale Application Assessment

MF, UF, NF, and RO have been applied during the treatment of municipal effluents in WWTP for water reuse [30, 35–37].

Microfiltration, Ultrafiltration, and Membrane Biological Reactor

MF and UF are widely used processes to efficiently eliminate turbidity. Regarding the rejection of microcontaminants, adsorption onto membrane polymers, as well as interaction with NOM in wastewater, can improve their removal by MF or UF membranes. An advanced water recycling demonstration plant was studied by Khan et al. [22] in order to investigate the effectiveness of MF in the removal of some commonly prescribed PhACs, as well as natural and synthetic hormones found in sewage. They observed partial reduction in concentration for all target compounds that could be attributable to adsorption on the membrane rather than removal by size exclusion. However, they warned that the adsorption capacity of the membrane for a particular compound can reach saturation, and therefore they would desorbed from the membrane when its concentration in the influent becomes lower. Sahar et al. [31] reported that the incorporation of UF after a conventional activated sludge (CAS) system increased the removal of antibiotics (including sulfamethoxazole) by up to 30%, probably due to the activity of the biofilm formed on the membrane surface that incidentally makes the "biomembrane" a tighter physical (enmeshment) and chemical (sorption) barrier. Despite all that, microcontaminants are generally poorly removed during MF and UF because the membrane pore sizes are much larger than the molecular sizes of microcontaminants. Al-Rifai et al. [35] confirmed that MF did not significantly decrease the concentration of 11 PhACs and two nonsteroidal estrogenic compounds. Snyder et al. [36] confirmed that MF and UF membranes have little value for the removal of the vast majority of organic contaminants after studying the removal of a large number of endocrine-disrupting chemicals (EDCs), PhACs, and personal care products. They highlighted the good removal of steroids possibly due to their relatively lower water solubility. However, other compounds did not follow this pattern. The study was evaluated in different pilot- and full-scale plants using secondary non-disinfected effluents and tertiary treated wastewaters.

As commented in Sect. 2.1.1, MBR systems seem to enhance the removal of microcontaminants compared to CAS. Trinh et al. [38] observed good eliminations (>90%) for most of the studied compounds. However, others were incompletely removed (24–68%), including amitriptyline, carbamazepine, diazepam, diclofenac, fluoxetine, gemfibrozil, omeprazole, sulfamethoxazole, and trimethoprim. Similar limited target compound removal was observed in two pilot-scale MBRs using different types of membranes in a WWTP in South Korea. MBR systems were found to be efficient for hormones (e.g., estriol, testosterone, androstenedione) and certain PhACs (e.g., acetaminophen, ibuprofen, and caffeine) with approximately

99% removal. However, the results showed that MBR treatments did not decrease the concentration of the flame retardant TCEP and the PhACs erythromycin, trimethoprim, naproxen, diclofenac, and carbamazepine [39]. Kovalova et al. [40] examined the fate of PhACs and metabolites in a pilot-scale MBR that treated a hospital effluent and reported high removal (>90%) except for the persistent iodinated contrast media. Sahar et al. [31] presented significant but variable eliminations of different microcontaminants in a MBR pilot plant scale operated in a WWTP. Snyder et al. [36] reported that, while the MBRs are effective for reducing the concentration of many EDCs and PhACs from WWTP primary effluents, several compounds remain unaffected, and very few compounds are reduced to below the method reporting limit. They concluded that the removal is likely related to biodegradability of the individual compound.

In summary, MBRs show greater and steadier elimination of microcontaminants compared to CAS systems because of the reasons outlined in Sect. 2.1.1. This improvement is especially evident for hydrophobic compounds. According to Alturki et al. [41], the high removal efficiency for these hydrophobic compounds could be attributed to enhanced residence time in the biological reactor due to ready adsorption to the mixed liquor suspended solids.

From the presented data, it can be concluded that the use of MF or UF membranes alone is not sufficient for microcontaminant removal. Hence, the combination of MF or UF with other processes (e.g., NF or RO) is essential for enhanced elimination of microcontaminants.

Nanofiltration and Reverse Osmosis

Khan et al. [22] compared the effectiveness of NF and RO in the removal of some PhACs and hormones. Retention for individual compounds in NF varies strongly with the membrane type. Comerton et al. [24] studied the rejection of 22 EDCs and PhACs in a MBR effluent. Rejection of EDCs and PhACs by a “loose” NF membrane was poor and variable, which shows that the membrane pore size is large relatively to the compound size. However, the use of a “tight” NF membrane improved the rejection. This was variable and appeared to be influenced by specific compound properties. Rejection was most strongly correlated with compound hydrophobicity, with the more hydrophobic compounds showing higher rejection. Analogue variability was observed for antibiotics by Kosutic et al. [42] for “tight” membranes, with removals higher than 90% and poor removal (<40%) when the rejection of small antibiotic compounds (<200 Da) was assessed. For its part, Yangali-Quintanilla et al. [30] ensured that “tight” NF can be equal to or “better” than RO. The elimination efficiency of NF membranes for different emerging contaminants was very close to that achieved by RO membranes. The average retention efficiency by tight NF was 82% for neutral organic contaminants and 97% for ionic contaminants, while RO was able to achieve 85% removal of neutral contaminants and 99% removal of ionic contaminants. Sang et al. [39] also defended the excellent performance of NF in comparison with RO. RO and NF showed similar excellent removal (>95%) for all the PhACs and flame retardants studied, being the flame retardant TCEP which presented the lowest rejection.

As commented above, the results undertaken by Khan et al. [22] indicated that the RO process was the most effective in the removal of all tested compounds. Only in one case, one of the PhACs (salicylic acid) was identified in the RO permeate. However, hormones appeared to be more difficult to remove, and traces of those compounds were found in the RO permeates. A polyamide RO membrane provided excellent rejection (>90%) of all EDCs and PhACs investigated in a MBR effluent by Comerton et al. [24]. The authors suggested RO as the final step in a water reuse application, where removal of microcontaminants is of particular concern. Garcia et al. [43] studied the efficiency in the removal of 22 "priority" microcontaminants in a municipal WWTP for water reuse using MF and RO. Although MF was able to remove some compounds by more than 50%, the incorporation of RO significantly enhanced the removal efficiency, ranging from 65% to 90% for most microcontaminants other than naphthalene and ibuprofen. All organics other than EDTA, bis-(2-ethylhexyl)phthalate (DEHP), and bromodiphenyl ethers (BDPEs) were effectively removed by RO to concentrations below 50 ng/L in the permeate. The authors compared their full-scale results for naphthalene and ibuprofen with the ones obtained in pilot plant experiments (>99%) and attributed the differences to the lower feed concentrations at full scale combined with more aged membranes. Sui et al. [44] studied the occurrence and removal of 15 PhACs and consumer products in four WWTPs of Beijing, China. Whereas the eliminations achieved by UF did not exceed 50%, all the target compounds except caffeine were not detected in the effluent of the WWTP equipped with RO. Again, Drewes et al. [21] found that in two full-scale RO facilities, target EDCs and pharmaceuticals and personal care products (PPCPs) were efficiently rejected to below detection limit except for caffeine, still detected in the permeates. The study performed by Al-Rifai et al. [35] in one Australian wastewater recycling scheme proved the ability of RO to remove trace organic contaminants including 11 PhACs from various therapeutic categories and nonylphenol and bisphenol A, two nonsteroidal estrogenic compounds. Al-Rifai et al. [45] monitored the removal of these same microcontaminants in a full-scale water recycling plant in Queensland, Australia. The RO membrane process contributed efficiently to the removal of all the microcontaminants except bisphenol A. In contrast to the last two cited studies, nonylphenol presented the worst removal (83%) within different EDCs studied during a pilot-scale sewage treatment equipped with RO [46]. A study analyzing the removal of different PhACs, hormones, and industrial products in a WWTP in Tel Aviv (Israel) revealed that high total removal rates (>93%) were achieved by the both configurations assessed at pilot plant scale (MBR/RO and CAS–UF/RO) [31]. Snyder et al. [36] studied several pilot- and full-scale RO systems monitoring the removals of a large amount of EDCs and PPCPs. RO systems removed nearly all target analytes to below or very near the method reported limit. However, trace levels of some contaminants were still detectable in RO permeates (i.e., the PhACs meprobamate, gemfibrozil, naproxen, sulfamethoxazole, loperamide, and the personal care products TCEP, DEET, and galaxolide). They also observed that the second pass in a double-pass RO was able to remove compounds that were not entirely removed during the first pass.

2.2 Ozonation

2.2.1 Main Concepts and Bases of Ozonation

Ozonation is a mature technology, and the reactions involved in the process are well known. There are two main reaction pathways for microcontaminant elimination by ozone. Ozone can react directly with organic contaminants through an ozone molecular reaction. This reaction is slow and selective. On the other hand, in alkaline waters, ozone can also react with water or other substances, forming the highly oxidant hydroxyl radicals HO·.

Due to its instability and quick reactivity, ozone must be generated on-site using air or high-purity oxygen. Normally, the gas generated contains between 1% and 3% of ozone by weight if initial gas is air and between 8% and 12% if pure oxygen was fed. Ozonation units in WWTPs for secondary effluent disinfection are injecting doses in the range of 3–30 mg ozone L^{-1}.

After the generation, since the concentration of ozone is very low, it is important to ensure a good contact between the gas and the water to ensure a good distribution of ozone and avoid over-concentrations of ozone which can lead to the formation of hazardous by-products.

Furthermore, ozonation presents a reasonable cost of 0.16 € m^{-3} [47] compared to other tertiary treatments.

2.2.2 Full-Scale Application

Due to the several ozonation units already operating in different WWTPs, there are already some studies about the effectiveness of ozonation to eliminate microcontaminants at full scale. Also several studies can be found at pilot plant level. As an example of the use of ozonation at full scale, Table 1 summarizes some details of some works cited in this chapter. In the listed references, ozonation units usually are placed after the secondary treatment, and they come before some sand or carbon filter.

Microcontaminant Removal

The effects of ozonation after biological treatment for microcontaminant removal have been widely studied. Similar results are found if microcontaminants are gathered according to their affinity to react with ozone. There is a first group of compounds which are easily removed below detection limits with an average dose

Table 1 Works at full scale/pilot plant scale about the microcontaminant removal listed for ozonation technology

Authors	WWTP location	Flow rate (m^3 day^{-1})	Equivalent population	Advanced treatment	Microcontaminant: monitored/before adv. treatment/after adv. treatment	O_3 dose	Residence time (min)
Hollander (2009)	Regensdorf (Switzerland)	5,550	25,000	Ozonation + sand filter	220/55/11	0.4–1.2 g O_3: g DOC	4–10
Margot (2013)	Lausanne (Switzerland)	95,000	220,000[a]	Ozonation + sand filter	120/70	2–13 mg O_3 L^{-1}	20–60
Rosal (2007)	Alcalá de Henares (Spain)		3,000	Ozonation (lab plant)	72/54/12	2.4–16 mg O_3 L^{-1}	
Nakada (2007)	Tokiyo	170,000	460,000	Sand filter + ozonation	29/24/19	3 mg O_3 L^{-1}	27
Reungoat (2010)	South Caboolture (Australia)	8,000	40,000	Ozonation + BAC	85/54/4	0.5 mg O_3: mgDOC	15 (O_3)
							18 (BAC)
Reungoat (2011)	Three plants at Australia:			Ozonation + BAC	41/21/11	0.2–0.8 mg O_3: mgDOC	BAC: 9–45
	Caboolture	8,000/	40,000				
	Landsborough	2,000/	10,000				
	Gerringong	900	11,000				

[a] Ozonation studied a pilot plant to treat a maximum flow rate of 100 L s^{-1} (13,000 PE)

of ozone (0.8 g O_3 g^{-1}DOC). Normally, those compounds present second-order rate constants $>10^4$ $M^{-1}s^{-1}$ (regarding to the direct reaction with O_3) such as compounds with aromatic rings, double bonds, or amine moieties, with a high affinity for direct reaction with ozone [6]. There is a second group of compounds with low affinity for O_3 (second-order rate constants $<10^4$ $M^{-1}s^{-1}$) but with high affinity for the strong and unselective hydroxyl radical. An average removal around 60% was achieved for these substances. HO· radical exposure to microcontaminants varies with the EfOM composition (it is sensitive to the addition of coagulants), presence of HO· scavengers (such as carbonate), and pH. Finally, there is a third group which includes those microcontaminants with low affinity to O_3 direct reaction and also to HO·. They formed the group of recalcitrant compounds with low removal (below 40%): atrazine, iothalamic acids, atenolol, diatrizoate, iopromide, mecoprop, benzotriazole, 5-methylbenzotriazole, sucralose, DEET, diazinon, galaxolidone, benzothiazole, microcontaminants with amide groups in general, etc [47, 48].

Regarding to specific removal data, Hollender et al. [6] found that, of the 55 microcontaminants identified after the secondary clarifier, only 11 were detected after the ozonation, using a moderate dose of 0.62 g O_3 g^{-1} DOC. Margot et al. [47] found that the number of microcontaminants with a concentration above 100 ng L^{-1} was reduced from 52 compounds in the effluent of the biologically treated wastewater to 30 compounds after the ozonation with an average ozone dose. Thirteen (13) substances were removed over 90%. Nakada et al. [49] monitored 24 pharmaceutically active compounds. The combination of ozonation and sand filtration with activated sludge treatment led to an efficient removal (>80%) of most of the target compounds, mainly due to the ozonation step. Rosal et al. [50] found that 31 of the 54 microcontaminants detected at influent of the ozonation were below the detection limit using a moderate dose of 6.2 mg O_3 L^{-1}. Reungoat et al. [51] studied the removal of microcontaminants in a reclamation plant. After the main ozonation (0.5 mg O_3 mg DOC^{-1}), 26 of the 54 microcontaminants initially detected were below the detection limits. Among the others, 9 showed a reduction higher than 90%, 13 higher than 70%, and only iopromide and gabapentin were reduced by 55%. Later, the study was extended, and Reungoat et al. [52] investigated the fate of 41 microcontaminants in three full-scale WWTPs using ozonation followed by biological activated carbon (BAC) as advanced tertiary treatment. Twenty-one (21) compounds were found at the influent of the ozonation. Half of them presented a removal higher than 80% after the ozonation. The percentage of removal of the microcontaminants at the different WWTPs was very similar.

The persistent compounds required extended exposure to HO· to achieve significant concentration reductions. Thus, in some of the studies, more extreme conditions were tested, and ozone dose was increased to high values. At the highest ozone dose tested by Hollender et al. [6], 1.4 g O_3 g^{-1} DOC, only two X-ray contrast media still detected the originally 11 recalcitrant compounds. At even stronger O_3 dose conditions (17.6 mg O_3 L^{-1}, equivalent to 2.6 g O_3 g^{-1} DOC), Margot et al. [47] found that even the most resistant microcontaminants were highly removed, with an average elimination of 80%. However, at these O_3 concentrations, cost is much higher, and the generation of bromate is more feasible and so usually is discarded.

Generation of By-Products

One of the main problems faced by ozonation is the generation of some unintended, toxic by-products. For example, when bromide-containing wastewater is ozonized, bromate, a genotoxic carcinogen [53], can be generated. Thus, bromate was recently included in stringent drinking water standards. Both the European Union and the United States Environmental Protection Agency (EPA) established a maximum contaminant level of 10 μg L^{-1}. Normally, bromide concentrations in wastewater are low enough to be below that threshold, but further research about how to minimize their presence is required. More recently, the observation that ozonation results in direct nitrosamine formation [6] indicates a new focus of attention which must be investigated. Nitrosamines are highly toxic, especially to the liver, and are suspected human carcinogens [54]. Recent investigations point to specific precursors of nitrosamines as degradation products of fungicides and even bromide catalysis [55].

Hollender et al. [6] studied the generation of both undesired by-products, and for the highest dose of ozone tested, 1.4 g O_3 g^{-1} DOC, the bromate concentration was never found to exceed 7.5 μg L^{-1}, lower than the 10 μg L^{-1} threshold fixed by EPA or European regulations. The authors also monitored eight nitrosamines, being *N*-Nitrosodimethylamine (NDMA) the most predominant, with concentration up to 21 ng L^{-1}. They found that the amount of NDMA generated during ozonation was only a function of the composition of the influent coming from the clarifier. Only 25% of NDMA was removed with the highest ozone dose. Margot et al. [47] also studied the formation of bromate. Before ozonation, bromate concentration was below the detection limit. After ozonation (0.8 g O_3 g^{-1} DOC), the concentration grew up to 3.7 μg L^{-1}, again below the drinking water standard of 10 μg L^{-1}. The authors found that the formation of bromate was dependent on the ozone dose applied, exceeding the drinking water standard for an ozone dose above 1.4 mg O_3 mg^{-1} DOC. As it can be seen, for the same dose of ozone, different amounts of bromate were measured. This proves the importance of a continuous monitoring of the bromate concentration to be sure that water standards are not overcome since it is affected by the characteristics of the influent.

Due to the process-related formation of reactive transformation products, it is recommended to install a stage with biological activity (e.g., sand filter) after ozonation of the wastewater so that these products can fully biodegrade. For example, sand filter can retain 50% of NDMA generated during ozonation. Biological sand filtration proves as an economic, useful complement to ozonation for elimination of by-products biologically degradable and removal of suspended solids and phosphate [6, 47, 50]. Unfortunately, bromate concentration is not reduced during the sand filtration, and therefore a high ozone dose should be avoided to ensure low bromate concentrations in the effluent [47].

Ecotoxicity of Ozonation Processes

Since the harmful by-products generated by ozone are a concern for the use of this technology, the use of a battery of bioassays as complementary tools to chemical analysis can provide valuable additional information on the water quality and the process efficiency. Furthermore, the bioassays allow taking into account the presence of non-identified compounds, formed transformation products, and/or mixture effects. Generally, bioassays carried out in different studies show that ozonation decreases the toxicity of waters. At average ozone doses, it can be concluded that the mixture of degradation products formed has an overall less harmful potential than the mixture of parent compounds [47, 51, 52].

Reungoat et al. [52] found that more than 87% reduction of estrogenicity was observed in the ozonation stage of all the three reclamation plants studied. Even at the lowest dose of 0.2–0.3 mg O_3 mg^{-1} DOC, high removal of estrogenicity was achieved. Nonspecific toxicity, measured with Microtox test, was reduced around 30–40% showing that new by-products generated during ozonation were less toxic to Microtox test than the former ones. In another study [51], authors carried out more specific measurements after a treatment train composed by ozonation + BAC. Authors carried out different bioassays to measure specific toxic actions: Ah receptor response (removal of 62% of dioxin and dioxin-like activity), genotoxicity effects (removal of >93%), neurotoxicity effects (removal of >90%), and phytotoxicity effects (removal of 75%). If only ozonation step is considered, the specific toxicity values of the listed bioassays notably decreased. For example, estrogenicity effects present 90% of removal after the main ozonation. Margot et al. [47] did a similar study but with different bioassays, arriving to similar conclusions. They monitored the photosynthesis inhibition (removal of 82%), the algae growth inhibition (75%), and estrogenic activity (89%). Finally, they also found that ozonation clearly reduced the fish early-life stage toxicity of the effluent.

In spite of the good perspectives for ozonation presented in most of the literature, there are also some works which warn about the necessity of further research to consider ozonation a totally safe technology. Actually, some studies show an increase of toxicity of wastewater effluent due to the formation of toxic by-products during the ozonation stage [56–58]. Petala et al. [56] found that ozonation of secondary effluents with high doses of ozone may increase the toxic potential (Microtox test) or mutagenic activity (Ames test) of the stream. Mutagenic activity was usually reduced when ozone dose and contact time were increased. Magdeburg et al. [57] monitored the toxicity of a secondary effluent with in vivo test battery before and after ozonation and sand filtration. Authors used one aquatic plant and five invertebrate species. They found that ozonation induced an increase of toxicity for three of the tested systems, assuming the generation of adverse by-products. After sand filtration, toxicity levels were reduced up to the levels at the outlet of the secondary effluent or even lower. A similar study was carried out by Stalter et al. [58]. They evaluated the variation of toxicity after a conventional secondary treatment followed by an ozonation + sand filter unit, by means of the fish early-life stage toxicity test. They found that ozonation decreases the estrogenic activity. However, authors also showed that ozonation produced a development retardation in fishes, probably due to the generation of toxic by-products. That negative effect disappeared after sand filtration, proving that the by-products are easily degradable or adsorbable.

According to the overall results, it may be assumed that usually the outlet flow presented a lower toxicity than the inlet. However, since there are also some studies which warn about the generation of toxic by-products, further research is required to know the operation parameters that make ozonation a safe technology. The controversy that use of ozone presents is clear. The necessity of a proper design of the ozone reactor and a careful study of the operation parameters as contact time seem obvious [47].

Disinfection and Other Contaminants Removal by Ozonation

With regard to other parameters, ozonation proves to be an excellent tool for disinfection purposes. Ozonation is able to disinfect the effluent greatly, with removal of coliphage virus below the detection limit (5 UFP ml^{-1}) (>95% removal) and a reduction over 97% in the concentration of fecal bacteria; this level is below the European standard for good bathing water quality [47].

If other contaminants (DOC, phosphorous, NO_3^-) are monitored, ozonation is not very effective against them. For example, DOC removal is normally very small in an ozonation unit, proving that it is difficult for ozonation to achieve the complete mineralization of microcontaminants. Ratios of 10% of DOC removal can be found in literature [51, 52]. Thus, if required, it is convenient adding a complementary step after ozonation to decrease those parameters.

2.3 Adsorption

2.3.1 Main Concepts and Basis of Adsorption with Activated Carbon

Adsorption is a technology widely used in wastewater treatment, and several types of materials have been tested as absorbents. However, although there are a large variety of adsorbents in the market, most of the adsorption units in WWTPs use activated carbon due to economic reasons. Activated carbon is generated by a pyrolysis process at 700°C. After the pyrolysis process, the obtained chair is "activated" being exposed to oxidizing gases as steam or CO_2 at high temperatures (800–900°C). There are different types of activated carbon according to the pore sizes and the particle size, with a different adsorption capacity. The two types of activated carbon more frequently used are powdered and granulated activated carbon.

Powdered activated carbon (*PAC*): It refers to particles with a diameter less than 0.074 mm and an apparent density between 300 and 700 g L^{-1}. PAC presents a large surface to volume ratio with a small diffusion distance. PAC is usually fed directly to other process units in the treatment process. Since both DOM and microcontaminants adsorb onto the activated carbon, the PAC stage is best located after extensive biological treatment in order to minimize competition and the PAC consumption. PAC also offers the advantage of being used seasonally when risk of microcontaminants may be greater (e.g., low-flow events) [36].

When loaded with microcontaminants, PACs should be disposed, but recirculation of the spent PAC to the biological treatment before its elimination can additionally improve the global microcontaminant removal efficiency without impacting the quality of the biological treatment [47]. This configuration enhances microcontaminant removal by 10–50% comparison with the application without recycling [59].

Granulated activated carbon (*GAC*): It has a diameter greater than 0.1 mm and an apparent density between 400 and 500 g L^{-1}. The higher diameter and lower head loss allow it to be used in dedicated vessels. As with PAC, residence time is the major factor that affects the yield of the process. GAC usually is loaded in the contactor (frequently a fixed bed reactor), and the wastewater passes through it. Adsorption capacity is reduced with operation time, so it is very important to plan periodically regenerations, especially to avoid desorption and releasing of hazardous components to the effluent [17].

There is also a variation of GAC called *biological activated carbon* (*BAC*). BAC is a type of GAC with a biofilm in the surface which adds biological activity to the GAC properties. The major advantage of the BAC system is that the recalcitrant organic matter removed from water is firstly adsorbed into the macropores, where it is detained long enough to promote its slow biodegradation by attached bacteria, also leading usually to continuous bioregeneration of the GAC [60].

2.3.2 Full-Scale Application of Adsorption Process for Wastewater Treatment

Adsorption is considered as a good option for the removal of microcontaminants due to the wide amount of compounds that can be retained. The rate of adsorption of the microcontaminants to the activated carbon and the contact time will be key parameters for the final contaminant removal achieved. The first one is the function of the properties of both adsorbate (K_{OW}, pKa, molecular size, aromaticity versus aliphaticity, and presence of specific functional groups) and adsorbent (surface area, pore size and texture, surface chemistry, and mineral matter content) [40]. The contact time is fixed with the design of the unit. In PAC systems, 1–3 h contact time is normally provided compared to contact times of typically less than 30 min in GAC where the effluent is passed through a packed bed. The presence of competing solutes for the adsorption sites, as dissolved organic carbon (DOC), is also important when microcontaminant removal is pursued [47, 59].

Activated carbon has been widely used in WWTP as PAC, GAC, or BAC form. Therefore, there are a number of studies which have applied these technologies to

Table 2 Works at full scale/pilot plant scale about the microcontaminant removal listed for adsorption technologies

Authors	WWTP location	Flow rate (m^3 day^{-1})	Equivalent population	Advanced treatment	Microcontaminants: monitored/detected before adv treatment/detected after adv. treatment	PAC/GAC concentration	Residence time (min)
Boehler (2012)	Kloten/ Opfikon (Switzerland)	–	60,000	PAC	38/37/26	10–20 g PAC m^3	
Snyder (2007)	Facility 1	–		PAC	–/14/1	–	–
	Facility 2	–			–/21/18		
Grover (2010)	Swindon (UK)	–	155,000	GAC	14/8/4	–	–
Sang (2007)	Seven plants at South Korea	–	–	GAC	26/14/0	–	–
Margot (2013)	Lausanne (Switzerland)	95,000	220,000[a]	GAC + sand filter/GAC + UF	120/70	3–5 GAC g L^{-1}	40–170 water/ 2–17 days GAC
Reungoat (2010)	South Caboolture (Australia)	8,000	40,000	Ozonation +BAC	85/54/4	0.5 mg O_3: mgDOC	15 min (O_3)
							18 min (BAC)
Reungoat (2011)	Three plants at Australia:			Ozonation + BAC	41/21/11	0.2–0.8 mg O_3: mgDOC,	BAC: 9–45 min
	Caboolture	8,000/	40,000				
	Landsborough	2,000/	10,000				
	Gerringong	900	11,000				

[a] GAC studied at a pilot plant at a maximum flow of 10–15 L s^{-1} (ca. 1,700 PE)

microcontaminant removal at real WWTPs. Table 2 shows the characteristic of the WWTPs of some of the most complete works listed in this chapter focusing on the use of adsorption as microcontaminant removal technology.

Microcontaminant Removal

As it is expected, better removal of microcontaminants is achieved for higher doses of activated carbon and longer retention time. Also, electrostatic and hydrophobic interactions seem to play an important role in the adsorption process. Positively charged substances usually present a very high removal, independently of their hydrophobicity. PAC usually is charged negatively due to the layer formed by EfOM over the surface of the carbon particle, mainly attracting positively charged compounds. With regard to hydrophobic interactions, Rogers et al. [61] provided a general rule of thumb for applying octanol–water partition coefficient (K_{OW}) to the estimation of adsorption: log $K_{\mathrm{OW}}<2.5$ indicates low sorption potential, $2.5<\log K_{\mathrm{OW}}<4$ indicates medium sorption potential, and log $K_{\mathrm{OW}}>4$ indicates high sorption potential. Thus, the most hydrophilic compounds are eliminated to a lesser extent [47].

Margot et al. [47] carried out an extensive study and monitored 70 compounds present at the inlet of the PAC slurry reactor with a moderate concentration (10–20 mg PAC L^{-1}). Authors found that 32% of microcontaminants presented a very good affinity for PAC and more than 90% was removed. Almost all were either positively charged (five substances) or neutral (seven substances) at the pH of the wastewater, covering a broad range of hydrophobicity (log D_{ow}[1] from −1.3 to 3.7). Around 38% of analyzed microcontaminants presented a medium affinity for PAC and had, on average, between 70% and 90% removal, including six neutral and six negatively charged compounds. Thirty percent of monitored microcontaminants composed of neutral or negatively charged compounds (including all the hydrophilic contrast media) showed poor or very variable affinity for PAC with an average removal between 11% and 66%. A higher PAC dose of 60 mg L^{-1} was tested during one campaign, leading to more than 90% removal for those substances with a low PAC affinity.

Better results were reported by Boehler et al. [59]. They monitored 19 microcontaminants before and after adding PAC in a WWTP, and at least 80% of each microcontaminant was removed by the PAC with a dose of 15 g PAC m^{-3}. Also DOC was greatly reduced, with an elimination of around 45%. It was also proved that the performance of PAC in eliminating microcontaminants depends upon PAC dose and contact time, the molecular structure and behavior of the targeted compound, as well as the water/wastewater composition. Grover et al. [62] studied the effect of installing a GAC unit at the effluent of an urban WWTP at Swindon (UK).

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[1] Log D_{OW} is a corrected form of the octanol–water partition coefficient (log K_{ow}) determined for nonionic substances, to account for the molecule dissociation or protonation at pH 7.

Authors monitored three representative EDCs and five detected PhACs. Two EDCs were below detection limit after the GAC unit, and 64% of the third one was removed. With regard to the PhACs, concentrations were substantially reduced in post-GAC effluents. On average, the additional removal of PhACs by GAC was between 17% for propranolol and >98% for indomethacin. Also estrogenic potency of the effluent was estimated by means of E2 equivalence factor (EEQ). It was found that EEQ was reduced from 2.2 to 14.6 ng L^{-1} before GAC to <0.5 ng L^{-1} after GAC, proving that the final effect of the water had notably decreased. In South Korea, Sang et al. [39] studied the elimination of different chemicals during drinking water and wastewater treatment processes at full- and pilot-scale by GAC technology in seven WWTPs and drinking water plants. Sang et al. [39] monitored 26 microcontaminants (PhACs, hormones, antibiotics, personal care products, flame retardant). The authors found that the conventional water treatment processes (e.g., coagulation and sand filtration) tested were inefficient. However, the monitored microcontaminants were removed below detection limits, thanks to the GAC step.

Another important factor when using activated carbon refers to the remaining adsorption capacity at a given moment. If adsorption capacity is exhausted, the activated carbon can only perform a biological degradation, but for those microcontaminants which have escaped from traditional biological reactor, removal may be very poor. Thus, exhausted activated carbon reactors (several BACs perform on this way) can be useful to remove biodegradable by-products generated by prior advanced treatments but not to eliminate microcontaminants. For example, Snyder et al. [36] studied the performance of two full-scale GAC installations installed in water plants for removing 29 microcontaminants including PhACs, personal care products, pesticides, steroids, fragrances, and antimicrobials. The first installation uses on-site GAC regeneration to ensure the activated carbon was capable of adsorbing organic compounds. Authors found that all the microcontaminants monitored were below detection limit except atrazine, but with a removal higher than 90%. On the other hand, the second installation does not replace regularly the GAC, and it was exhausted. On this case, the GAC column shows a very poor removal of the organic microcontaminants monitored. However, Reungoat et al. [52] studied the effect of three BAC units installed in WWTP after ozonation units with different results. They monitored 21 microcontaminants before and after the BAC unit. Authors found that BAC units could further remove all the remaining microcontaminants. Fifteen microcontaminants presented removals higher than 80%.

It is also interesting to underline that human PhAC metabolites usually are much less removed by activated carbon than the original compound. Indeed, the liver or kidney transforms the pharmaceutical drugs to more polar and hydrophilic compounds, so they can be easily eliminated through the urine or bile, but then there is a weaker tendency to be absorbed by activated carbon [63].

Ecotoxicity of Activated Carbon Processes

Since no by-products are generated by adsorption process, an improvement in the indicators of the bioassays is expected after the activated carbon treatment, as it is proved experimentally. Margot et al. [47] carried out an ecotoxicological evaluation of PAC use. Around 85% of toxicity was removed by PAC reactor. Photosynthesis inhibition was strongly reduced (87%) as well as algae growth inhibition (84% of removal) and estrogenic activity (88% of removal). Furthermore, PAC significantly decreased the toxicity of the WWTP effluent on the development of rainbow trout embryos for all end points measured: the overall survival of the fish, the hatching success, the swim up, the individual development (weight and size), and the induction of estrogenic effects. In the same line of results, Reungoat et al. [52] carried out a nonspecific toxicity test (bioluminescence inhibition test with *V. fischeri*) before and after different BAC units in three different WWTPs. Authors measured a removal between 13% and 54% of nonspecific toxicity. The units were installed after an ozonation unit which achieve a removal of 30–40% of toxicity. Overall, the combination of ozonation and BAC filtration could achieve removals of 50% for DOC and more than 90% for a wide range of microcontaminants as well as a reduction of 70% of nonspecific toxicity and more than 95% of estrogenicity. Thus, BAC process proved to be an excellent complement to ozonation step.

Microcontaminant Removal by Adsorption

Regarding DOC elimination, activated carbon can show a good performance. For BAC reactor, DOC removals up to 48% have been reported [52]. Similar values of DOC removal were found in PAC+UF units. PAC shows a good performance for phosphorus, NH_4, and BOD_5 removal and a complete removal of TSS, intestinal bacteria, and coliphages [47].

Finally, activated carbon proved to be technically feasible at large scale in municipal WWTP. For example, PAC presents a reasonable cost of 0.18 € m^{-3} [47], very similar to ozonation.

2.4 *Advanced Oxidation Processes (AOPs)*

The AOPs covered in this section are UV/H_2O_2, photo-Fenton, heterogeneous photocatalysis, and O_3/H_2O_2.

2.4.1 General Disadvantages of AOPs

The main disadvantages of AOPs are their high chemical requirement and/or the energy consumption, which are reflected in high operating costs. Regarding the use of H_2O_2, there are significant limitations associated with its use. For example, the additional costs and complexities associated with chemical storage, handling, and injection may limit its attractiveness, and the residual H_2O_2 must also be quenched in some applications prior to environmental discharge.

Similarly to the use of ozone, AOPs (except in cases under very drastic oxidation conditions) do not commonly result in complete mineralization of microcontaminants. Therefore, the major concern is the formation of oxidation by-products (or transformation products) from microcontaminants. To further reduce parent compounds and oxidation by-products, biological post-filtration (sand filtration or activated carbon filtration) can be considered.

2.4.2 Water Reclamation: Full- and Pilot-Scale Application

The UV/H_2O_2 full-scale process installed after a RO membrane in a water reuse facility studied by Snyder et al. [36] showed significant degradation of the four target microcontaminants still present in the permeate of the RO. De la Cruz et al. [64] reported very high removals for 22 selected microcontaminants (15 PhACs, 2 X-ray contrast media, 1 corrosion inhibitor, and 4 biocides/pesticides) in an effluent from a municipal WWTP using a UV/H_2O_2 pilot-scale process (cylindrical reactor chamber of 37 L equipped with five lamps of 150W each emitting at 254 nm). They carried out experiments at different flow rates and H_2O_2 concentrations and concluded that a concentration of 50 mg H_2O_2/L and a residence time of 10s provided the most economical setting and the best microcontaminant elimination (global degradation >88%). However, they reported a global degradation of only 26% working at much lower flow rate with UV alone. Only two (diclofenac and ketoprofen) microcontaminants reached more than 80% degradation. Sang et al. [39] determined that a UV pilot-scale treatment applied after RO and NF processes did not contribute significantly to microcontaminant removal. Another bench-scale UV/H_2O_2 process study performed by Kim et al. [65] showed that 90% removal efficiency was reached in 39 of the 42 PhACs found in a WWTP secondary effluent. The UV dose (254 nm) was 923 mJ/cm^2, and the contact time and H_2O_2 concentration were 5 min and 7.8 mg/L, respectively. They found that only few PhACs (especially ketoprofen, diclofenac, and antipyrine) were significantly removed by UV radiation alone. The removal efficiencies of macrolide antibiotics such as clarithromycin, erythromycin, and azithromycin resulted very low even by the introduction of UV doses 20 times higher than common disinfection doses and contact times of 15 min. Good removal of microcontaminants cannot be expected by the UV processes alone and let alone at the radiation doses applied for disinfection of treated water in WWTPs (40–140 mJ/cm^2). The addition of H_2O_2

to the UV processes reduces drastically the UV energy required for the effective PhAC removal.

Snyder et al. [66] studied the degradation of steroids, PhACs, pesticides, and industrial chemicals by ozonation at pilot scale. TCEP, musk ketone, and meprobamate were not well removed. They concluded that the addition of H_2O_2 caused little benefit and even in some cases decreased the efficiency of O_3. Ozone with addition of H_2O_2 was assayed in at pilot scale in a water reclamation plant for removing several steroid hormones and PPCPs. Results showed considerable removal efficiency (N90%) for almost all of the target contaminants, except TCEP (13%), TCPP (26%), atrazine (69%), meprobamate (80%), and ibuprofen (83%) [67, 68].

Chi et al. [69] assessed the performance of a heterogeneous Fenton's pilot-scale process to remove different EDCs and PPCPs from three different municipal WWTP secondary effluents. The system incorporated a modified polyacrylonitrile catalyst which allowed to decompose >90% of the EDCs and >40% of PPCPs using 200 mg/L of H_2O_2 in 3 h residence time working at natural pH. According to them, the system showed great potential in the removal of low levels of PPCPs and EDCs when compared to homogeneous Fenton's, photo-Fenton's, electro-Fenton's, and photocatalysis on TiO_2. Solar photo-Fenton and solar TiO_2 photocatalysis were studied at pilot scale as tertiary treatments for the remediation of 66 microcontaminants present in municipal WWTP effluents by Prieto-Rodríguez et al. [70]. Photo-Fenton (pH 2.8) achieved 90% of microcontaminant elimination in short reaction times using 5 mg Fe^{2+}/L and 60 mg H_2O_2/L. It also proved to substantially eliminate the degradation products. However, solar photocatalysis with TiO_2 resulted very inefficient in terms of treatment time and accumulative energy compared to solar photo-Fenton. They highlighted the potential of solar photo-Fenton as tertiary treatment in municipal WWTPs, with estimated treatment costs in the range of <0.4 €/m^3, which is very competitive compared with more mature processes.

2.4.3 Treatment of Retentates

Because there is an urgent need for environmentally friendly management options for RO brines, diverse technologies for the treatment of RO brines have been investigated. Although more conventional treatments have been studied for this purpose (coagulation/flocculation, activated carbon adsorption, ozonation, electrochemical oxidation, river bank filtration among others), AOPs appear to be appropriate for the treatment of these waste streams that are highly concentrated in recalcitrant microcontaminants [34]. Authors evaluated the efficiency of UV/H_2O_2 for mitigation of 11 PhACs present in RO brines of a wastewater reclamation facility. Although high oxidant doses were necessary to ensure the complete removal of all the monitored microcontaminants, authors conclude that UV/H_2O_2 process appeared to be a promising and efficient tool for treating these concentrates. There is still a lack of studies and information about the efficiency of

AOPs in removing microcontaminants from these complex matrices and improving the quality of the effluents.

2.5 Overall Comparison

In Table 3, a comprehensive comparison among the different technologies is presented. Although each individual microcontaminant can behave differently with each technology, if an overall comparison is made, it is found that the highest rejection of microcontaminant is presented by RO or NF, although they also present some drawback as the generation of a waste stream. Activated carbon presents an efficacy for microcontaminant removal very similar to ozonation. AOPs show a good potential for microcontaminant removal but the technology is less tested at full-scale level.

3 Overall Conclusions

In this chapter, four technologies for eliminating the microcontaminants present in the effluents of WWTPs have been reviewed: adsorption, membranes, AOPs, and ozonation. The choice has been done since they are well known, already used in existing WWTP. Therefore, its specific utilization for the removal of microcontaminants may be done easily. All treatments prove to be feasible at large scale and for long-term operation in real WWTP conditions. However, given the wide range of properties exhibited by microcontaminants, there is no single treatment process that provides an absolute barrier to all chemicals. To minimize their presence in treated water, a sequence of diverse treatment processes seems suitable. However, other considerations must be taken into account to ensure the viability of the solution since the most restrictive technologies are economically expensive and energetically demanding. Therefore, it is necessary to carry out more research to improve and make them more efficient.

Finally, the main conclusions for each technology are listed below.

3.1 Membrane Filtration

The use of MF or UF membranes alone is not sufficient for microcontaminant removal. Therefore, the combination with other membrane processes (i.e., NF or RO) is essential for enhanced elimination of microcontaminants. All analyzed data indicate that NF and RO could be considered as a powerful tool to mitigate the presence of most of microcontaminants present in municipal wastewaters.

Table 3 Comparison of different technologies focused on microcontaminant removals

Technology	Pros	Cons	Compounds easily removed	Compounds hardly removed
Ozonation	Does not generate a waste stream	Potential generation of hazardous by-products	Microcontaminants with electron-rich moieties: aromatic rings, double bonds, or amine moieties	Microcontaminants with low affinity to O_3 direct reaction and also to HO: atrazine, iothalamic acids, carbamazepine, diatrizoate, iopromide, mecoprop, benzotriazole, 5-methylbenzotriazole, sucralose, DEET, diazinon, galaxolidone, benzothiazole, amide functional groups
	Excellent disinfectant	Ozone is toxic and explosive. Safety measures required	Microcontaminants with second-order rate constants $>10^4\ M^{-1}s^{-1}$ (direct reaction with O_3)	
	Oxidate microcontaminants; no further treatments needed	Installation requires qualified personnel	Hydrophobic or positively charged microcontaminants	
	Good performance in bioassay test	Poor removal of DOC		
	High removal of some specific compounds	Efficiency affected negatively by the presence of EfOM: prior removal required		
Adsorption (activated carbon)	Adsorbs a wide variety of contaminants	AC does not destroy contaminants	Hydrophilic ($k_{OW} > 4$) or negatively charged microcontaminants	Hydrophobic ($kOW < 2.5$) or positively charged microcontaminants
	Easy operation	Microcontaminants can be released to effluent if AC is not regenerated		Gabapentin, diatrizoate, iothalamic acid, Irgarol, propranolol, DEET
	Good performance in bioassay test	Efficiency affected negatively by the presence of EfOM: prior removal required		High molecular or colloidal compounds
	BAC offers adsorption and biodegradation	Periodic regeneration required		
	PAC can be used seasonally, when required			
	Good removal of DOC			

Membranes (RO/NF)	Reduced labor requirements, can be automated easily	RO and NF do not destroy contaminant	Hydrophobic, ionic compounds	Hydrophilic, nonionic, and low molecular weight compounds
	Most inorganic and organic constituents and microorganisms are removed (especially with RO)	Disposal of concentrate		Variable and poor rejection with "loose" NF for several compounds
		Desorption of sorbed chemicals from membrane		Worse rejection in RO studies: hormones, salicylic acid, naphthalene, ibuprofen, DEHP, BDPEs, caffeine, bisphenol A, nonylphenol, meprobamate, gemfibrozil, naproxen, sulfamethoxazole, iopromide, TCEP, DEET, galaxolide
		High investment required		
		High energy consumption		
		Membrane fouling		
		Periodic membrane replacement required		
		Performance declines over time		
AOP	Does not generate a waste stream	Potential generation of hazardous by-products	Most of target compounds due to the non-selectivity of HO·	
	Non-selectivity of HO	Chemical and/or energy consumption		
	Rapid reaction rates	Installation requires qualified personnel		
	Easily automated and controlled	Subsequent quenching required if a strong oxidant is used		
		Complex chemistry must be tailored to specific application		

There is some controversy about how membrane selectivity affects the efficiency of membranes in microcontaminant removal. In general, it seems that there is a tendency for an expected decrease in microcontaminant rejection with decreasing membrane selectivity. However, some authors consider that conductivity rejection does not appear to be a reliable indicator to assess the removal efficiency of microcontaminants by NF/RO membranes.

In general, microcontaminant removal efficiency would follow the next order: RO > "tight" NF > "loose" NF. However, different comparative works [22, 39, 43, 71] concluded that, although the retention of microcontaminants by NF is lower than that obtained by RO, the latter has demonstrated only marginally increased rejection in comparison with NF.

There are different points of view about the appropriateness of NF or RO to mitigate the microcontaminant problem. According to some studies, it would be questionable, unless desalination is a requirement, that the use of RO is preferable than the use of NF. Its higher operational costs incurred from higher pressure operation would not justify the additional purification achieved in comparison with NF. Other studies remark that not even the RO can serve as an absolute barrier to microcontaminants. Therefore, additional treatment processes should be considered to be incorporated aside the RO to ensure complete removal of such substances. In addition, an important point to be taken into account is that NF and RO require significant amounts of energy, which may lead indirectly to greater environmental risks than the presence of minute concentrations of organic contaminants. Thus, careful consideration must be given to the actual costs and benefits of these processes simply for the removal of microcontaminants [36].

It is also important to consider brine disposal associated with RO and NF membranes. The rejected compounds are merely concentrated in brine streams which must be disposed of properly since brine would be expected to have much greater toxicity than the influent water.

3.2 Adsorption

Adsorption with activated carbon has proved to be an efficient tool for removal of microcontaminants. Since it adsorbs a wide variety of compounds, EfOM competes strongly for the active site, decreasing the adsorption rate of microcontaminants. Thus, it is convenient to install the activated carbon unit as a tertiary treatment after an operation which reduces organic matter. Activated carbon adsorbs easily hydrophobic and positively charged compounds although other interactions as hydrogen bond formation and pi–pi interaction between microcontaminants and the activated carbon surface seem to be important. Since there is no transformation of the compounds, no hazardous by-products are expected. Thus, bioassays reviewed show a less toxic effluent after the adsorption treatment. Finally, use of PAC as tertiary treatment and the reuse of it in the biological reactor (a kind of countercurrent system) show efficiencies 10–50% higher. PAC can also be added seasonally to face peaks of contamination. GAC is not so flexible but requires a smaller residence time.

3.3 Ozonation

Ozone is a useful technology for microcontaminant removal. In most of the studies reviewed, it achieves great results with removal over 80% for several of compounds analyzed. However, the rate of removal proves to be very dependent on the type of contaminant. Ozone is efficient in the oxidation of compounds with electron-rich moieties, which react directly with ozone. A second group of compounds less efficiently removed includes those compounds which react with radical HO·. Finally, there is a group of recalcitrant compounds which present a low reactivity with molecular ozone or hydroxyl radical.

The main concern when using ozone for wastewater treatment is the generation of hazardous by-products as bromate, nitrosamines, or other unknown species which can increase toxicity of the effluent. At normal operation conditions, those compounds seem to be generated in very small amounts, below the recommended thresholds proposed by recognized official organisms. To minimize this risk, it is very important to assure a good contact between gas and liquid. It is also advisable to install a barrier unit after the ozonation process. For example, a sand filter has proved to be very effective on those scenarios where ozonation produced an increase on toxicity or to eliminate nitrosamines.

3.4 Advanced Oxidation Processes

The efficiency of AOPs for organic contaminant removal has been well proven at laboratory scale. The non-selectivity of these AOPs is a great advantage and guaranty. Nobody doubts about the potential of AOPs to degrade microcontaminants. However, more studies at pilot and full scale are needed in order to determine the optimal operational conditions and elaborate consistent and reliable cost evaluations.

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Trace Organic Contaminants Removal by Combined Processes for Wastewater Reuse

Faisal I. Hai, Luong N. Nguyen, Long D. Nghiem, Bao-Qiang Liao, Ismail Koyuncu, and William E. Price

Abstract The term trace organic contaminant (TrOC) refers to a diverse and expanding array of natural as well as anthropogenic substances including industrial chemicals, chemicals used in households, compounds and their metabolites excreted by people and by-products formed during wastewater and drinking-water treatment processes. Activated sludge-based processes (e.g. membrane bioreactor) are environmentally friendly approaches to wastewater treatment. However, conventional biological treatment alone may not be effective for all TrOCs that are known to occur in municipal and industrial wastewater. The low removal efficiency of biologically persistent and hydrophilic TrOCs necessitates the integration of MBR with other membrane-based and physicochemical processes to ensure adequate removal of TrOCs. Because MBRs can produce effluent with low turbidity and bulk organic content, significant synergy can be realised when it is integrated with other advanced treatment processes. In addition, given the small physical footprint of the MBR process, it is possible to deploy these integrated systems for decentralised water recycling applications. This chapter provides a brief overview of the integration of advanced treatment processes including activated carbon adsorption, advanced oxidation processes and high retention membranes (e.g. nanofiltration and reverse osmosis) with MBR for TrOC removal.

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Keywords Adsorption, Advanced oxidation processes, Bioaugmentation, Membrane bioreactor, Wastewater reuse, Trace organic contaminant

Contents

Abbreviations

AC	Activated carbon
AOP	Advanced oxidation processes
BAC	Biologically activated carbon
CAS	Conventional activated sludge
COD	Chemical oxygen demand
DO	Dissolved oxygen
EDG	Electron donating group
EWG	Electron withdrawing group
FO	Forward osmosis
GAC	Granular activated carbon
GEM	Genetically engineered microorganisms
HRT	Hydraulic retention time
MBR	Membrane bioreactor
MD	Membrane distillation
MDBR	Membrane distillation bioreactor
NF	Nanofiltration
OMBR	Osmotic membrane bioreactor
PAC	Powdered activated carbon
PACT	Powdered activated carbon treatment
RO	Reverse osmosis
SRT	Sludge retention time
TN	Total nitrogen
TOC	Total organic carbon
TrOCs	Trace organic contaminants

1 Introduction

One of the most pervasive problems affecting people throughout the world is inadequate access to clean water and sanitation. Such issues are expected to grow worse in the coming decades, with water scarcity occurring globally. Water reuse and recycling is a pragmatic approach to reduce the pressure on our water resources and the environment. However, the occurrence of trace organic contaminants (TrOC) in secondary treated effluent and sewage-impacted water bodies in the range from a few nanogram per litre (ng/L) to several microgram per litre (μg/L) is a major obstacle for the implementation of water reuse [1, 2]. TrOCs are a diverse group of chemicals including pesticides, pharmaceuticals and personal care products, industrial chemicals, steroid hormones, phytoestrogens and UV filters [3–5]. TrOCs are biologically active and can, therefore, impose acute and chronic toxicity on aquatic organisms, accumulate in the ecosystem and cause loss of biodiversity as well as a range of possible adverse effects on human health. Given the potential adverse impact of TrOCs on human health and the environment as well as their ubiquitous occurrence in municipal sewage, their removal during wastewater treatment has become a vital issue in recent years. Intensive treatment is required to eliminate the risks to human health and aquatic ecological wellbeing when secondary treated effluent is used as water source in water reclamation. Table 1 summarises the advantages and disadvantages of the available techniques for TrOC removal from water/wastewater. All methods listed here have some inherent advantages and drawbacks, and a universal standalone process applicable for majority of the TrOCs is yet to be developed [3–5]. In general, the advanced processes are more energy intensive and complex in operation than conventional ones. Biological processes are considered environmentally friendly, so it is logical to investigate ways to improve their performance for TrOC removal. The membrane bioreactor (MBR) process consists of a biological reactor integrated with membranes that combine clarification and filtration of an activated sludge process into a simplified, single-step process [26]. Over the past decade, submerged MBR processes have experienced unprecedented growth in domestic and municipal wastewater treatment/reuse. Application of MBR technology for industrial wastewater treatment has also gained attention because of the robustness of the process [27]. In this chapter, advanced technologies for the removal of emerging TrOCs from wastewater for reuse purposes are systematically reviewed and discussed. In particular, MBR-based hybrid processes for TrOC removal are delineated.

2 Wastewater Reuse and MBR

Water scarcity is a major global challenge and is being further exacerbated due to continuing population growth, industrialisation, contamination of available freshwater sources and increasingly irregular weather patterns. In the Earth's hydrologic

Table 1 Available technologies for trace organics removal from water and wastewater (adapted from [3])

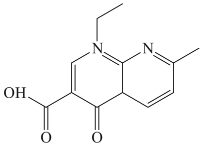
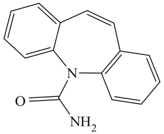
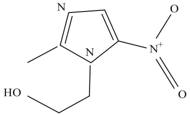
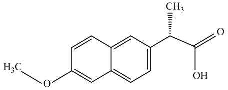
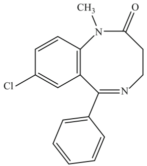
Process	Advantages	Disadvantages	Reference
Chemical coagulation	An economical conventional treatment process widely used for turbidity and colour removal	Produces large quantity of sludge; the available coagulants were not developed aiming at trace organics removal, therefore, removes only selected groups of trace organics	[6–11]
Electrocoagulation	Potential of achieving both adsorption and degradation and removal of both soluble and insoluble organics	Inherent limitations are secondary pollution (from chlorinated organics, heavy metals) and high cost (electricity); compound-specific removal has been reported by the few available references regarding trace organics removal	[12, 13]
Activated carbon adsorption	Well-established tertiary treatment option; removal of wide variety of trace organics	Competitive adsorption leads to early breakthrough of several groups of compounds; difficult regeneration and costly disposal of potentially hazardous spent adsorbent	[14–16]
Nanofiltration/ reverse osmosis	Good removal of a large range of trace organics via size exclusion and electrostatic repulsion	A considerable degree of complexity associated with the separation process; production of concentrated sludge; adsorption to membrane surface and subsequent diffusion of the hydrophobic organics through the membrane	[17–19]
Advanced oxidation processes	Degradation of various trace organics by generation of a large number of highly reactive free radicals, surpassing the conventional oxidants by far in efficiency	Pretreatment almost always necessary to remove suspended solids, radical scavengers and competing ions; formation of toxic by-products; expensive and very few full-scale plants	[20–22]
Membrane bioreactor (MBR)	Excellent removal of significantly hydrophobic trace organics in a single-step compact biological process	Inefficient removal of hydrophilic and persistent trace organics requiring a polishing step	[23–25]

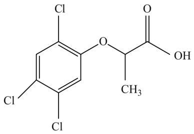
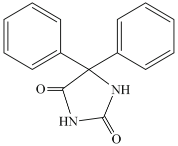
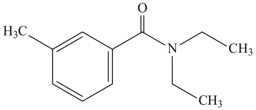
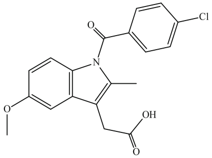
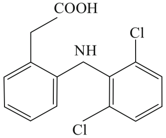
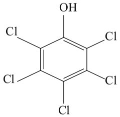
cycle, freshwater supplies are fixed and constant [28–30]. Furthermore, due to environmental pollution, the quality of the planet's water gradually deteriorates, presenting challenges for the major users. Increasing demand for water and drought and water scarcity are now critical issues faced by many urban and rural communities worldwide. There is a growing interest in using nontraditional water resources such as wastewater by means of water reclamation and water recycling for long-term sustainability. In comparison to the conventional activated sludge (CAS) process, MBRs have several major advantages including a smaller footprint, more flexibility for future expansion, scaleup and better effluent quality in terms of removal of pathogens and suspended solids and nutrients [31]. In addition, sludge separation is not dependent on the influent characteristics or the flocculation state of the biological suspension as the floc size is much larger than the membrane pores [28]. The biomass concentration can also be (up to 10 times) higher than in CAS, resulting in a much more intensive treatment process in comparison to CAS [28]. Thus, MBRs have appeared as a significant advancement over the CAS processes for wastewater reuse [32]. In addition to the conventional chemical contaminants and pathogens, the presence of TrOCs in treated sewage is an emerging concern associated with water reclamation. MBRs can potentially achieve better removal of TrOCs than conventional CAS processes due to their ability to operate under longer solid retention times (SRT), higher biomass concentrations and complete retention of suspended solids. Compared to CAS processes, MBRs may provide additional removal mechanisms for TrOCs: (1) the membrane serves as an effective barrier to solids, onto which many TrOCs can be adsorbed and this cake layer on the membrane can potentially prevent the escape of some extracellular enzymes and soluble oxidants creating a more active biological mixture capable of degrading a wider range of carbon sources, and (2) the longer SRT in MBR may facilitate additional biological transformation of TrOCs [4].

3 TrOC Removal by MBR

Considerable research efforts have been devoted to the assessment of TrOC removal by MBR treatment. The reported data ranges from near-complete removal for some compounds to almost no removal for several others. For example, Reif et al. [33] observed a significant removal of ibuprofen (98%), naproxen (84%) and erythromycin (91%) by a pilot-scale MBR. The author also reported a moderate removal (>50%) of sulfamethoxazole and musk fragrances (i.e. galaxolide, tonalide and celestolide). On the other hand, carbamazepine, diazepam, diclofenac and trimethoprim were poorly removed (<10%). Nghiem et al. [34] also confirmed the possibility of achieving good treatment of bisphenol A (90%) due to both biodegradation and adsorption. By contrast, sulfamethoxazole removal was solely attributed to biodegradation, and its lower removal (50%) is due to this compound having low biosorption because of its low hydrophobicity as manifested by a low $\log D_{[\mathrm{pH}=7]}$ of -0.22 ($\log D$ is the logarithm of distribution coefficient, which is the ratio of the sum of concentrations of the solute's various forms in octanol to the sum of the concentrations of its forms in water at a given pH) [34]. Table 2 presents examples of variations in the reported removal of different TrOCs and the same TrOC in different studies.

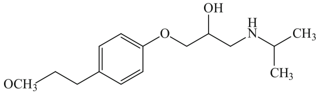
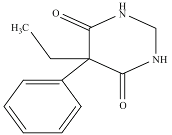
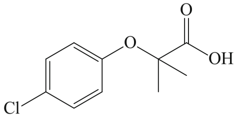
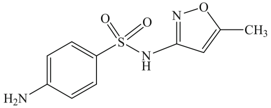
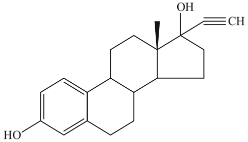
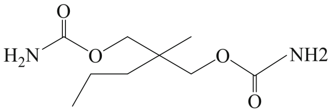
Table 2 Examples of variations in the reported removal of different TrOCs and the same TrOC in different MBR studies

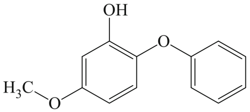
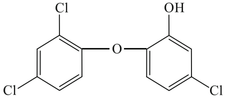
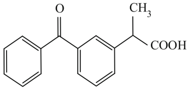
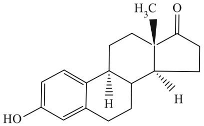
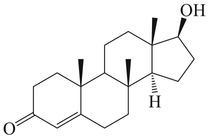
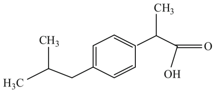
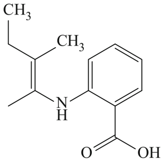
Compounds (molecular formula) (CAS)	Chemical structure	Reported removal (%)	References
Nalidixic acid ($C_{12}H_{12}N_2O_3$) (389-08-2)		0–5	[35]
Carbamazepine ($C_{15}H_{12}N_2O$) (298-46-4)		2–32	[36–39]
Metronidazole ($C_6H_9N_3O_3$) (443-48-1)		0–40	[37, 40]
Naproxen ($C_{14}H_{14}O_3$) (22204-53-1)		0–50	[40–42]
Diazepam ($C_{16}H_{13}ClN_2O$) (439-14-5)		25–27	[33, 42]

Fenoprop ($C_9H_7Cl_3O_3$) (93-72-1)		0–60	[37, 43]
Dilantin ($C_{15}H_{12}N_2O_2$) (57-41-0)		13–50	[41, 44]
DEET ($C_{12}H_{17}NO$) (134-62-3)		6–94	[2, 41]
Indomethacin ($C_{19}H_{16}ClNO_4$) (53-86-1)		39–47	[45]
Diclofenac ($C_{14}H_{11}Cl_2NO_2$) (15307-86-5)		0, 27.6, 32.1, 50.6, 80, 81.5	[15, 37, 46]
Pentachlorophenol (C_6HCl_5O) (87-86-5)		0–95	[25, 40, 46]

(continued)

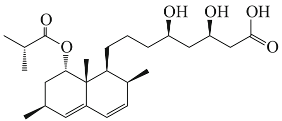
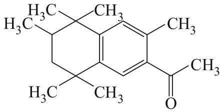
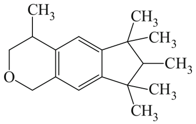
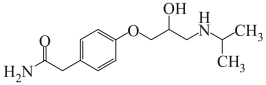
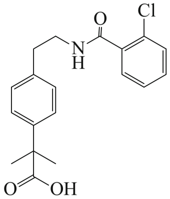
Table 2 (continued)

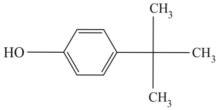
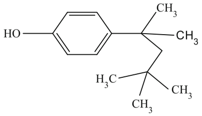
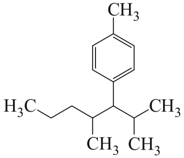
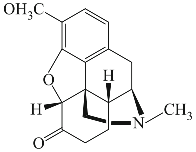
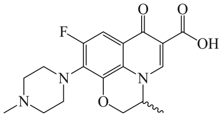
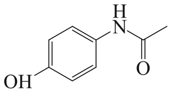
Compounds (molecular formula) (CAS)	Chemical structure	Reported removal (%)	References
Metoprolol ($C_{15}H_{25}NO_3$) (51384-51-1)		50	[47]
Primidone ($C_{12}H_{14}N_2O_2$) (125-33-7)		12–90	[17, 40]
Clofibric acid ($C_{10}H_{11}ClO_3$) (882-09-7)		32.5–82.5	[17, 48]
Sulfamethoxazole ($C_{10}H_{11}N_3O_3S$) (723-46-6)		12–80.5	[24, 42]
17-α ethinyl estradiol ($C_{20}H_{24}O_2$) (57-63-6)		33.3–94	[37, 43]
Meprobamate ($C_9H_{18}N_2O_4$) (57-53-4)		54.6–86.5	[2]

Oxybenzone ($C_{14}H_{12}O_3$) (131-57-7)		42–99.6	[48]
Triclosan ($C_{12}H_7Cl_3O_2$) (3380-34-5)		60–91	[15, 37]
Ketoprofen ($C_{16}H_{14}O_3$) (22071-15-4)		61.7–97.8	[37, 42, 46]
Estrone ($C_{18}H_{22}O_2$) (53-16-7)		92–100	[15, 37]
Testosterone ($C_{19}H_{28}O_2$) (58-22-0)		83.3	[40]
Ibuprofen ($C_{13}H_{18}O_2$) (5687-27-1)		70–99	[43, 44, 48]
Mefenamic acid ($C_{15}H_{15}NO_2$) (61-68-7)		76.9–93.2	[42]

(continued)

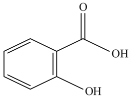
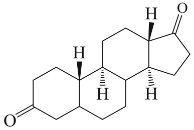
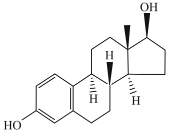
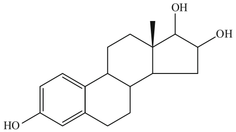
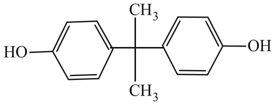
Table 2 (continued)

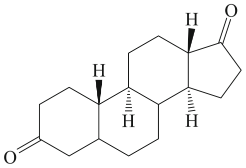
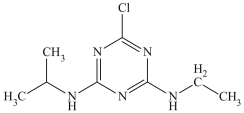
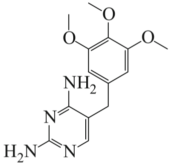
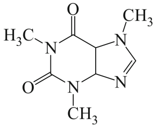
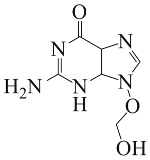
Compounds (molecular formula) (CAS)	Chemical structure	Reported removal (%)	References
Pravastatin ($C_{23}H_{36}O_7$) (81093-37-0)		83–90	[45]
Tonalide ($C_{18}H_{26}O$) (21145-77-7)		87.2	[44, 47]
Galazolide ($C_{18}H_{26}O$) (1222-05-5)		87.5	[36]
Atenolol ($C_{14}H_{22}N_2O_3$) C29122-68-7)		87.5	[44, 47]
Bezafibrate ($C_{19}H_{20}ClNO_4$) (41859-67-0)		76–97	[36, 44]

4-*tert*-butylphenol ($C_{10}H_{14}O$) (98-54-4)		80–99	[15, 37, 42]
4-*tert*-octylphenol ($C_{14}H_{22}O$) (140-66-9)		76–99	[15, 37, 42]
4-*n*-nonylphenol ($C_{15}H_{24}O$) (25154-52-3)		85–99	[15, 37, 42]
Hydrocodone ($C_{18}H_{21}NO_3$) (125-29-1)		92	[2]
Ofloxacin ($C_{18}H_{20}N_3O_4$) (82419-36-1)		92–94	[36]
Paracetamol ($C_8H_9NO_2$) (103-90-2)		90–99	[17, 36]

(continued)

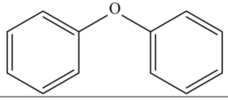
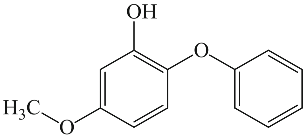
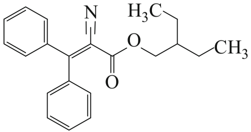
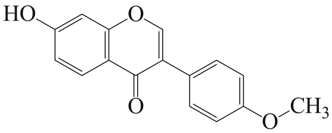
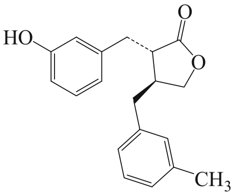
Table 2 (continued)

Compounds (molecular formula) (CAS)	Chemical structure	Reported removal (%)	References
Salicylic acid ($C_7H_6O_3$) (69-72-7)		85–96	[15, 25, 37]
Androstenedione ($C_{19}H_{26}O_2$) (63-05-8)		93–100	[2]
17-β-estradiol ($C_{18}H_{24}O_2$) (50-28-2)		95–100	[15, 25, 37]
Estriol (E3) ($C_{18}H_{24}O_3$) (50-27-1)		90–100	[15, 25, 37]
Bisphenol A ($C_{15}H_{16}O_2$) (80-05-7)		92–100	[15, 37, 39]

Acetaminophen ($C_8H_9NO_2$) (103-90-2)		52–96	[2, 42, 44]
Atrazine ($C_8H_{14}ClN_5$) (1912-24-9)		5–30	[48, 49]
Trimethoprim ($C_{14}H_{18}N_4O_3$) (738-70-5)		97–100	[40]
Caffeine ($C_8H_{10}N_4O_2$) (58-08-2)		98–100	[17]
Acyclovir ($C_8H_{11}N_5O_3$) (59277-89-3)		100	[50]

(continued)

Table 2 (continued)

Compounds (molecular formula) (CAS)	Chemical structure	Reported removal (%)	References
Benzophenone $(C_{13}H_{10}O)$ (119-61-9)		100	[48]
Oxybenzone $(C_{14}H_{12}O_3)$ (131-57-7)		100	[48]
Octocrylene $(C_{24}H_{27}NO_2)$ (6197-30-4)		85	[48]
Formononetin $(C_{16}H_{12}O_4)$ (485-72-3)		90–95	[48]
Enterolactone $(C_{18}H_{18}O_4)$ (78473-71-9)		90–95	[48]

MBRs have been widely reported to achieve superior performance over that of CAS in terms of basic water quality parameters. However, there have been several conflicting reports on whether MBRs can offer enhanced removal of TrOC compared to that achieved by CAS treatment. Cirja et al. [23] noted that the removal rates differed from one compound to another; however, no discernible difference between CAS and MBR could be detected. Oppenheimer et al. [51] reported no significant difference in removal efficiencies of ibuprofen, triclosan and caffeine by both CAS and MBR process. Bernhard et al. [52] reported that treatment by MBR resulted in significantly better removals compared to CAS for poorly biodegradable compounds such as diclofenac, mecoprop and sulfophenyl carboxylates which were attributed to the long SRT in MBR. Radjenovic et al. [45] reported that the removal of pharmaceuticals in MBRs was better for several compounds (e.g. naproxen and ketoprofen) and at least similar for others (e.g. carbamazepine and diazepam). Kimura et al. [53] found that compounds with a complex chemical structure, for example, ketoprofen and naproxen, were not eliminated at all in CAS treatment, but could be removed partially by MBRs. While MBRs may not necessarily always yield higher removal efficiencies, they are nevertheless advantageous because they exhibit a more consistent performance and shorter lag times, indicating a superior response to fluctuating influent concentrations [4]. Additionally, MBRs offer the advantages of increased plant flexibility through more compact installation and allow modification of design to fine-tune biological performance.

4 Factors Affecting TrOC Removal by MBR

TrOC removal efficiency by MBR may depend on the physicochemical properties of the compounds and the operational parameters of the wastewater treatment plant. Physicochemical properties of trace organics have been reported to significantly govern their removal efficiency by MBR treatment. Adsorption of TrOCs on sludge particles, driven primarily by hydrophobic interaction, appears to be one of the key mechanisms controlling removal efficiency during MBR treatment. Hydrophobic compounds ($\log D > 3.2$) adsorbed on sludge can be retained by membrane, and further biodegradation by biomass in the reactor can occur. For instance, the removal efficiency of the significantly hydrophobic compound steroid hormones and alkyl phenolic compounds has been consistently reported to be 95–99% [17]. Tadkaew et al. [25] investigated the removal of 40 trace organics with molecular weight ranging from 151 to 455 g/mol by MBR treatment. Their results showed that compounds with molecular weight of more than 300 g/mol were relatively well removed, while the removal of those below 300 g/mol varied greatly from almost no removal to more than 95% removal. However, it was noted that the compounds with molecular weight above 300 g/mol also possessed higher hydrophobicity.

For hydrophilic compounds ($\log D < 3.2$), sorption is no longer a dominating removal mechanism, and the removal of these compounds is much more strongly influenced by their intrinsic biodegradability [25]. In this context, the presence of specific functional groups in TrOC structures has been reported to influence the removal efficiency of MBR treatment [25, 40, 54]. Tadkaew et al. [25] systematically demonstrated that compounds with strong electron withdrawing group (EWG) (e.g. halogen, amide and carboxyl) are more resistant to MBR treatment, while the removal of compounds possessing both electron donating group (EDG) (e.g. hydroxyl, amine and methyl) and EWG can substantially vary depending on the number and type of the functional groups. Cirja et al. [23] also reported that the removal rates of xenobiotics by MBR are related to the physicochemical characteristics of the compounds. Kimura et al. [40] reported that removal efficiencies of the pharmaceutically active compounds studied (clofibric acid, diclofenac, ibuprofen, mefenamic acid and naproxen) were dependent on their molecular structure such as number of aromatic rings or inclusion of chlorine: chlorinated compounds (e.g. clofibric acid and diclofenac) were not effectively removed by MBR. The functional group and hydrophobicity of compounds may also have a combined effect on their removal efficiency. For example, Hai et al. [49] demonstrated that there was a combined effect of halogen content (weight ratio) and hydrophobicity on the removal of halogenated trace organic compounds in MBR. Compounds with high halogen content (>0.3) were well removed (>85%) when they possessed high hydrophobicity ($\log D > 3.2$), while those with lower $\log D$ values were also well removed if they had low halogen content (<0.1). Figure 1 presents a semi-quantitative framework of the impact of the physicochemical properties ($\log D$ and functional groups) on the removal (biodegradation and biosorption) of TrOCs.

In addition to the physicochemical properties of trace organics, their removal also depends on operating conditions such as temperature [37, 55, 56], hydraulic retention time (HRT) [57], SRT [52, 58, 59], mixed liquor pH [60] and dissolved oxygen (DO) concentration [61, 62]. Hai et al. [37] studied the removal of trace organics by MBR as a function of temperature and reported that while the removal of hydrophobic compounds was stable at a temperature between 10 and 35°C, the removal of hydrophilic compounds was lower at 10°C than that at 20°C. However, at 45°C, it was found that the removal efficiency for most trace organics deteriorated. Thus, it was concluded that the optimum temperature for all tested TrOCs ranged between 20 and 35°C. Increased SRT values have been shown to improve removal for most TrOCs studied by Clara et al. [58], although beyond 25–30 days, this parameter appeared not to be significant. Tadkaew et al. [60] investigated the removal of ionisable and non-ionisable trace organics by MBR treatment using different mixed liquor pH ranging from 5 to 9. High removal efficiency of the ionisable compounds was observed at a pH of 5, while removal efficiency of two non-ionisable (bisphenol A and carbamazepine) compounds was independent of the mixed liquor pH. Similarly, Urase et al. [63] found that higher removal rate of some acidic pharmaceuticals such as ketoprofen, ibuprofen, clofibric acid, gemfibrozil, fenoprofen, ketoprofen, naproxen, diclofenac and indomethacin by MBR treatment was observed at lower pH (pH = 4.3–5). On the other hand, the removal of neutral

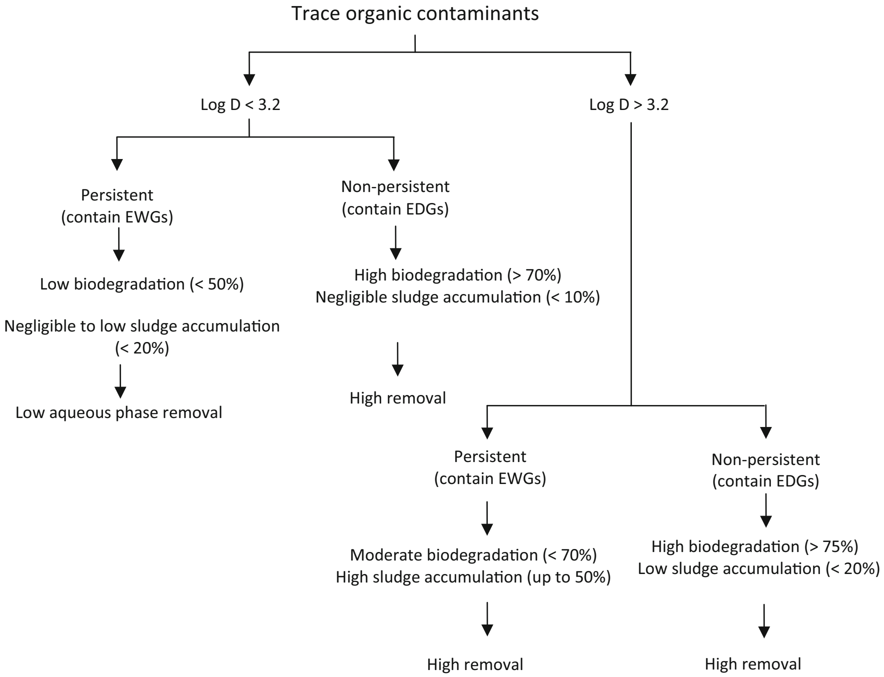


Fig. 1 A semi-quantitative framework of the impact of the physicochemical properties (log*D* and functional groups) on the removal (biodegradation and biosorption) of TrOCs (adapted from Wijekoon et al. [48])

compounds 17α-ethinylestradiol, carbamazepine, propyphenazone and benzophenone was not significantly affected by bioreactor pH.

Only a few studies have specifically investigated the effect of different redox conditions or DO concentration in the bioreactor on the removal of trace organics. The reported results revealed mostly insignificant difference between aerobic and anoxic MBRs in terms of TrOC removal. For example, Clara et al. [36] and Abegglen et al. [64] reported negligible level of removal of carbamazepine using different configurations of MBR (sequential anoxic–aerobic MBR and aerobic MBR). However, there are some studies which have reported better removal under anoxic environment, either in MBR or in batch tests. For example, Hai et al. [61] reported carbamazepine (a persistent trace organic) to be degraded only under anoxic environment in their batch tests. In MBR treatment, the removal of carbamazepine was found to be 68% and less than 20% under anoxic and aerobic conditions, respectively [61]. Joss et al. [62], on the other hand, reported that the degradation of estrone takes place under both anoxic and aerobic conditions but achieves higher degradation rate in aerobic conditions (DO = 2–3 mg/L). Stasinakis et al. [65] reported better removal of diuron during batch tests under anoxic environment (>95%) in comparison to that in aerobic condition (60%). Zwiener and Frimmel [66] also showed that diclofenac was not degraded in short-term biodegradation tests under aerobic conditions, whereas it was degraded under anoxic conditions.

5 MBR-Based Hybrid Processes for TrOC Removal

The tightening of water quality regulations and the inefficiency of conventional treatment processes have been strong drivers behind the emergence of alternative treatment technologies for efficient elimination of TrOCs. When deployed on an individual basis, advanced treatment processes exhibit some inherent drawbacks and do not offer a complete barrier to a broad range of TrOCs that may occur in municipal wastewater. To overcome this, the concept of combined processes such as coupling of MBR with nanofiltration (NF) or reverse osmosis (RO), activated carbon adsorption, advanced oxidation processes (AOP) such as ozonation and UV irradiation has been tested. Furthermore, innovative configurations such as osmotic membrane bioreactor (OMBR) and membrane distillation bioreactor (MDBR) have also been explored. This section provides a review of recent literature on the combination of MBR with different physicochemical treatment processes.

5.1 Combination of MBR with High Retention Membranes

5.1.1 MBR and Nanofiltration and Reverse Osmosis

NF and RO membrane filtration processes to date have been used to produce high-quality water from surface water or nontraditional sources such as brackish, seawater or secondary treated wastewater. Recent studies have demonstrated the excellent capacity of NF and RO membranes to remove a large range of TrOCs in pilot and full-scale applications [67]. Physicochemical parameters such as molecular size, hydrophobicity and polarity as well as feed solution composition are considered important factors which govern NF and RO efficiency [18]. According to Nghiem et al. [68], the removal of some hydrophobic compounds can be lower than that predicted based solely on a size exclusion mechanism. This is because hydrophobic compounds can also adsorb to NF and RO membranes and then diffuse through the dense polymeric matrix, resulting in considerable transport of these compounds across the ultra-thin active skin layer. Another potential drawback of the NF and RO processes is membrane fouling which can be caused by the deposition of bulk organic or colloidal matter on the membrane surface if the feed solution is not adequately pretreated. Therefore, there is a scope to combine MBR with NF or RO filtration to achieve an overall high TrOC removal.

The complementarity between MBR and NF or RO filtration has been recently demonstrated [17, 43]. Nguyen et al. [43] used NF and RO filtration to treat effluent from a lab-scale MBR, which was used to treat 22 diverse TrOCs from a synthetic wastewater. The authors reported greater than 90% removal of compounds, which were negligibly removed by MBR alone, by the combined process. Consequently, the combination of MBR with NF or RO filtration resulted in an overall removal of 90% to complete (or removal to below the analytical detection limit) of all 22 TrOCs. Alturki et al. [17] reported effective removal of hydrophobic and biodegradable TrOCs by an MBR. The hydrophilic TrOCs, which passed through the MBR, were effectively removed by the following NF or RO membranes. In these short-term studies, membrane fouling was negligible when the NF and RO membranes were fed with MBR permeate. The application of MBR-NF or RO system has been also tested in pilot scale [69–71]. Dolar et al. [70] used a pilot-scale MBR-RO unit to treat 20 TrOCs from a real municipal wastewater. A significant variation in the removal (negligible—95%) was achieved by the MBR system, while the authors obtained an excellent overall removal of the target TrOCs with removal efficiencies of about 99% by the combined MBR-RO system. This observation clearly demonstrates the complementarity between MBR treatment and RO filtration. Similarly, Sahar et al. [71] obtained above 99% removal of 11 TrOCs from municipal wastewater by a MBR-RO system. Cartagena et al. [69] examined the possibility of producing better water quality from municipal wastewater using an MBR-NF/RO pilot plant. The results showed that the high quality of water produced was suitable for reuse. In addition to achievement of high (>95%) removal of salinity, total organic carbon (TOC) and total phosphorous, the set-up achieved over 95% removal of the ten selected TrOCs. Apart from the posttreatment of MBR effluent, recent developments integrating NF membrane with bioreactors (NF-MBR) are also interesting [72]. Zaviska et al. [72] employed a ceramic nanofiltration membrane with a bioreactor to investigate the removal of two pharmaceutical compounds. The results showed that the TrOCs were poorly degraded by activated sludge but were retained by the membrane. Such configurations form a new system which has been termed as high retention membrane bioreactor (HR-MBR) in the recent literature [73]. The high retention membrane separation process can effectively retain TrOCs, thus prolonging their retention time in the bioreactor and potentially enhancing their biodegradation [73]. HR-MBR has a great potential for efficient TrOC removal, but there are certain technological challenges (e.g. low permeate flux and membrane fouling) that must be addressed before it can be implemented in full scale.

5.1.2 Osmotic Membrane Bioreactor

In the forward osmosis (FO) process, a “draw” solution of high concentration (relative to that of the feed solution) is used to induce a net flow of water through a semipermeable membrane into the draw solution, thus effectively separating the feed water from its solutes. In other words, FO utilises an osmotic pressure

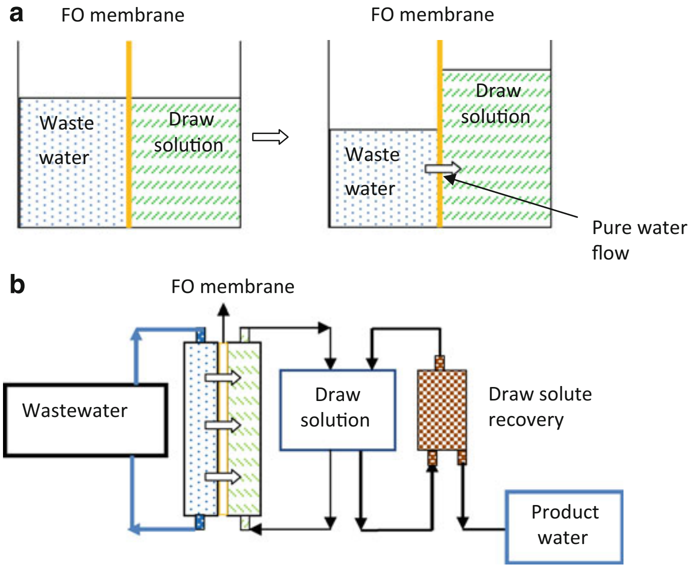


Fig. 2 Schematic diagram of (**a**) the concept of forward osmosis (*FO*) and (**b**) FO set-up for water/wastewater treatment

differential to drive the permeation of clean water across the membrane into the draw solution (Fig. 2) [74]. Water movement due to osmotic pressure differences does not require any input of external energy and offers an alternative manner through which water can be extracted from wastewater with much lower energy requirement [75]. FO process is an emerging water treatment technology, which has low fouling propensity [76], simple configuration and low energy consumption [77].

The removal of TrOC by the FO process has been reported in some recent studies. Cartinella et al. [78] demonstrated that FO can completely remove steroid hormones (e.g. estrone and estradiol). Cath et al. [79] reported a high removal of some TrOC such as diclofenac (99%), gemfibrozil (80%), naproxen (90%) and salicylic acid (72%). Alturki et al. [80] studied the rejection of 40 selected TrOCs by FO system using HTI membrane and sodium chloride as a draw solution. The rejection efficiency varied from 10% to 100%, depending on the hydrophobicity and volatility of the compounds. The variation in the rejection of TrOCs was also reported by Hancock et al. [81].

A concept to combine the FO process with MBR forms an innovative OMBR (Fig. 3). The OMBR inherits advantages of both MBR and FO processes. Permeate production in the OMBR is driven by differences in osmotic pressure instead of hydraulic pressure, resulting in lower fouling propensities [83]. The FO membrane can retain small and persistent TrOCs in the biological reactor, thus significantly increasing their retention time in the reactor and subsequently facilitating their biodegradation. To prove this hypothesis, Alturki et al. [82] investigated the

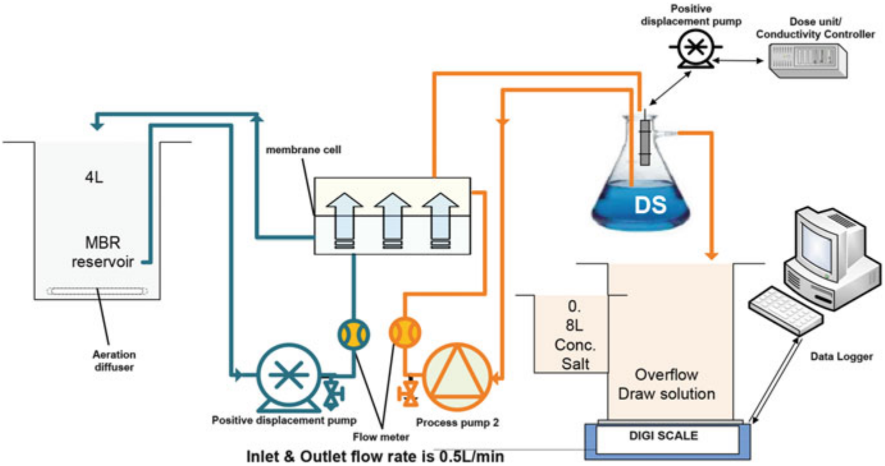


Fig. 3 Schematic diagram of OMBR system for TrOC removal (adapted from Alturki et al. [82])

performance of an OMBR on the removal of a range of 50 TrOCs. The OMBR system achieved up to 80% removal of 25 out of 27 TrOCs with molecular weight higher than 266 g/mol. However, the removal of the remaining 23 compounds was very scattered. The authors also observed deterioration of biological activity of the OMBR system over time, possibly due to the build-up of salinity in the reactor. In another study, Lay et al. [84] investigated the removal of four pharmaceuticals in an OMBR over an experimental duration of 73 days. The authors reported that the OMBR was generally able to achieve excellent product water quality. The pharmaceuticals were completely rejected by the FO membrane. The high rejection of the pharmaceuticals by the FO membrane allowed these compounds to be concentrated in the bioreactor, which could enhance their rate of biodegradation. While the complementarity between the MBR and FO processes is evident, the OMBR process is still in its infancy and challenges such as requirement of water recovery from the draw solution, low water fluxes and reverse solute leakage need to be overcome.

5.1.3 Membrane Distillation Bioreactor

Membrane distillation (MD) involves a combination of water evaporation and vapour condensation within an integrated process encompassing water vapour transportation through the pores of a hydrophobic membrane via a transmembrane temperature gradient [75]. Permeate production starts from water evaporation and transportation through the membrane pores, finally condensing on the permeate side of the membrane. The rejection of TrOC by MD process has been recently demonstrated by Wijekoon et al. [85]. A complete rejection was observed for almost all of 29 selected TrOCs (except 4-*tert*-octylphenol (54%) and oxybenzone (81%)) in this study. However, it is important to note that during MD operation, TrOCs continuously accumulate in the feed reservoir, necessitating further treatment of the concentrate. Phattaranawik et al. [86] studied a novel MDBR, which integrates a bioreactor (e.g. activated sludge) with MD unit. Biodegradation in the bioreactor and membrane rejection are the two mechanisms that account for the overall pollutant removal in such an MDBR. Goh et al. [87] observed that the high organic and nutrient in wastewater can aggravate membrane wetting in the MD process. This problem can be mitigated by using MDBR wherein the bioreactor removes organic matters (e.g. carbohydrates and proteins) [87]. Permeate production within such system are driven by the vapour pressure difference across an unwetted membrane pore [75]. Moreover, the usual MD operation temperature is in the range from 30 to 80°C. Therefore, in the MDBR process, the biological reactor can be operated at thermophilic conditions and the bioreactor often requires the implementation of a thermophilic microflora. The use of thermophilic bioreactor may also result in an enhanced biodegradation of organics and low sludge yield [88].

In an MDBR, the MD unit can be submerged within the bioreactor with the membrane unit in direct contact with the mixed liquor or side stream to the bioreactor (Fig. 4). Posttreatment of MBR effluent by MD [85] and treatment by an integrated sidestream MDBR [89] have been recently explored for TrOC removal. Wijekoon et al. [85] demonstrated that MD complemented well with MBR to allow complete or near-complete (>95%) removal efficiency of all 29 TrOCs tested. The results from this study also shed light on the prospect of integrating MD with bioreactor for TrOC removal. Wijekoon et al. [89] subsequently studied the removal performances of 25 TrOCs, which occur ubiquitously in municipal wastewater, by a novel MDBR using a thermophilic bioreactor. Although salinity build-up occurred gradually, which affected the bioreactor performance in terms of total nitrogen and TrOC removal, the MDBR process achieved a high overall removal (>95%) of all TrOCs.

5.2 *Combination of MBR with Adsorption*

The idea of application of activated carbon adsorption in conjunction with an MBR has given rise to two modes of application: (1) posttreatment of MBR permeate by passing it through a granular activated carbon (GAC) column and (2) direct addition of activated carbon (mainly powdered activated carbon—PAC) into MBR.

5.2.1 Granular Activated Carbon and MBR Systems

While PAC is added directly into MBR, GAC is used in a packed bed reactor. In comparison to investigations involving drinking-water treatment, only a handful of studies have investigated GAC adsorption as an option for tertiary treatment of

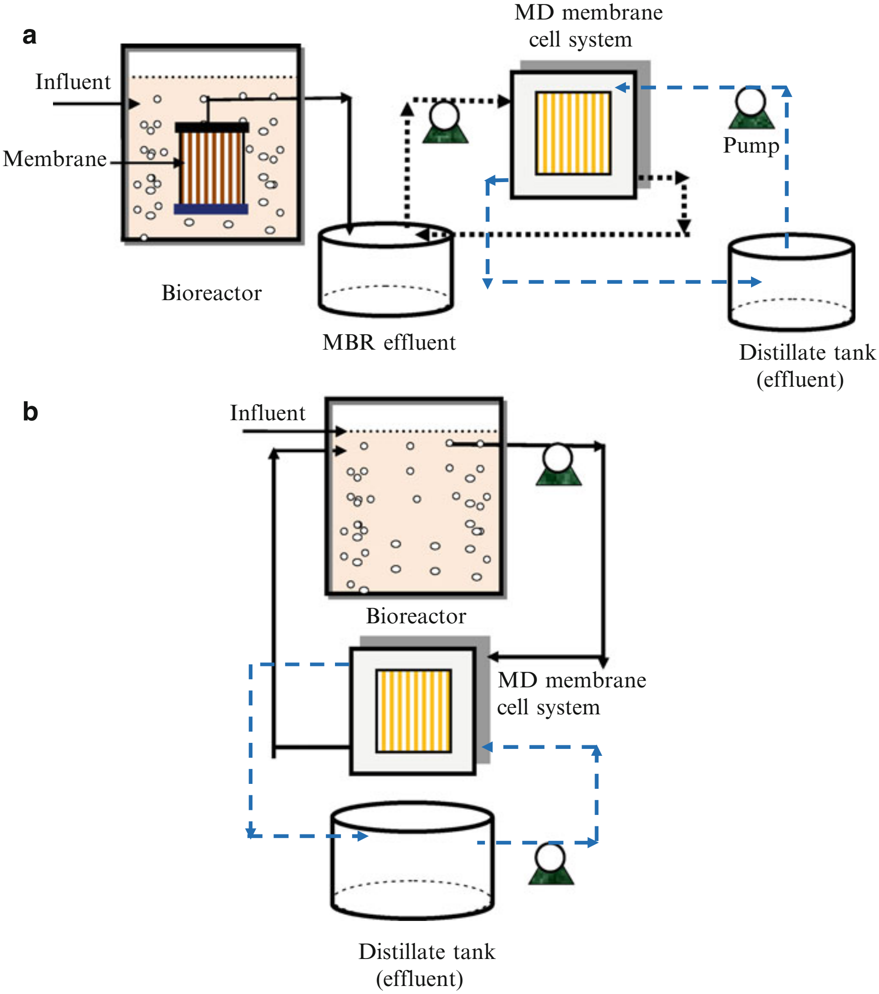


Fig. 4 Schematic diagram of combination of MD with MBR system: (**a**) Posttreatment of MBR effluent with MD and (**b**) integrated MDBR

conventional biologically treated wastewater [14, 90, 91]. It has been noted in these studies that the adsorption of TrOC on activated carbon decreases due to competition with bulk organic matter for adsorptive sites. In fact, competition with bulk organic matter for adsorptive sites has important implications for the lifetime and serviceability of GAC columns. For efficient adsorption of TrOC, it is recommended that the feed to GAC column has a low bulk organic content. Because MBR can produce suspended solids-free permeate with low TOC content, adsorption on GAC may be a suitable posttreatment option for MBR permeate. In such a system, GAC can specifically target the residual trace organics in MBR permeate without any significant interference from the bulk organics. Nguyen et al. [15] demonstrated that GAC could complement MBR treatment very well as a posttreatment process. The MBR-GAC system showed high removal of all selected TrOCs including those that are hydrophilic and persistent to biological degradation. However, under a prolonged operation time, the TrOCs start penetrating (breakthrough) the GAC column [15, 46]. Therefore, regeneration or replenishment of GAC is required.

Although GAC is predominantly used in packed bed columns, direct addition of GAC to the bioreactor can also be done if settling of GAC can be prevented by applying adequate mixing/aeration. Thuy et al. [92] investigated the treatability of phenolic compounds by direct dosing of GAC to MBR. Relatively low values of phenol adsorption on GAC and biomass, and high maximum substrate removal rates obtained from a biokinetic experiment, proved that the removals were mainly due to biodegradation.

5.2.2 Powdered Activated Carbon and MBR Systems

PAC is generally added directly into other process units [93]. The first application of PAC into biological treatment systems was called powdered activated carbon treatment (PACT) process [94]. The PACT process is based on the concept of simultaneous adsorption and biodegradation. This has been reported to be effective for treating toxic organic pollutants such as dyes [95]. Orshasky et al. [96] compared three processes for the removal of phenol and aniline: biological treatment, adsorption on PAC and simultaneous adsorption and biodegradation within the PACT process, among which the PACT process achieved the highest removal. Dosoretz and Böddeker [97] reported an enhanced removal of organics and colour by CAS reactor to which PAC had been added. However, due to short sludge retention time in CAS, a portion of carbon is wasted frequently along with the withdrawn sludge. As compared to that in CAS, the use of PAC in MBR may be more effective.

A PAC-added MBR combines three individual processes, namely, physical adsorption on PAC, biological degradation and membrane filtration, in a single unit where all of these processes can occur simultaneously. In the PAC-MBR, membranes provide a physical barrier preventing the passage of PAC, thus ensuring retention of the organic compounds adsorbed on the PAC that otherwise would not be rejected by the membrane alone. High biological activity may also be achieved when PAC is added into MBR because PAC helps microbial growth on surface [98]. The use of PAC for organics adsorption and subsequent biodegradation also has the advantage that the effects of shock loads or toxic concentrations of pollutants can be buffered as a result of their adsorption onto and diffusion into the PAC particles. This results in physical separation of the toxic materials from the biological catalyst and ensures that the microbes are able to continue their metabolic activities [99]. Addition of PAC to MBR can thus improve effluent quality and provide stability against shock loading [98, 100] (Fig. 5).

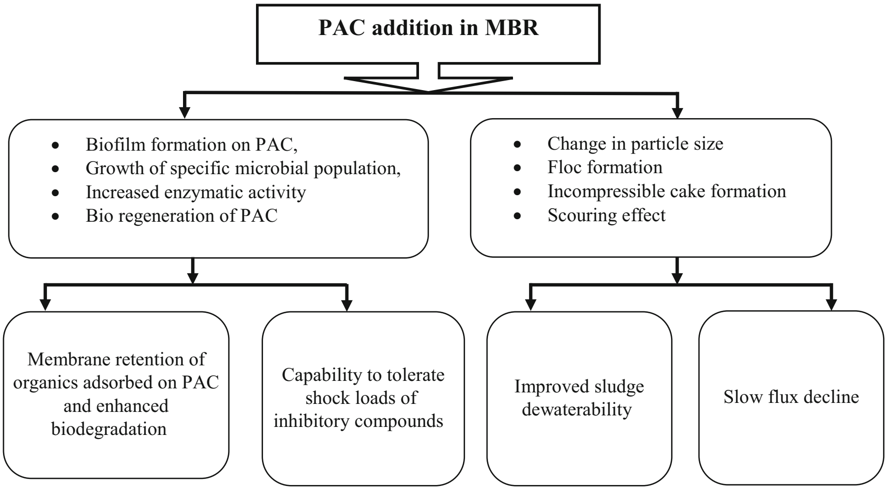


Fig. 5 Potential advantages of addition of PAC to MBR

PAC-MBR equipped with either microfiltration (MF) or ultrafiltration (UF) modules has been reported for the treatment of landfill leachate and refinery wastewater as well as for the removal of refractory organic matter from secondary sewage effluent [101]. Hai et al. [102] reported excellent stable decolouration of a wastewater containing two dyes (Poly S 119 and Orange II) by a PAC-MBR. Improved decolourisation due to adsorption and close contact of dye as well as dye-degrading enzyme on PAC, which was added into the MBR, was observed in this study. Simultaneous PAC adsorption within fungi MBR thus resulted in multiple advantages including adsorption of dye and prevention of enzyme wash-out, eventually leading to enhanced dye degradation. Munz et al. [103] reported the synergistic effect of PAC addition to an MBR treating tannery wastewater. In their study, PAC was shown to reduce the negative effects of natural and synthetic tannins that are toxic. A PAC dosage of 10 g/L improved significantly the leachate treatment by a PAC-MBR hybrid system [104].

In recent years, a few studies on the performance of TrOC removal by MBR coupled with PAC have been published [24, 38, 39]. Available studies show positive effects of PAC addition on MBR performance for the removal of TrOC. For example, Li et al. [24] demonstrated an improved removal of two different pharmaceuticals (sulfamethoxazole and carbamazepine) by a PAC-MBR system. Serrano et al. [39] investigated the removal of several recalcitrant pharmaceuticals, namely, carbamazepine, diazepam, diclofenac and trimethoprim by adding PAC into the aeration tank of a CAS reactor. The results demonstrated that this approach is a successful tool to improve the removal of the more recalcitrant compounds (carbamazepine, diazepam, diclofenac and trimethoprim) which were removed by up to 85%. In another study on biodegradation of trace compounds in an aerobic MBR, it was found that PAC dosage of 500 mg/L reduced trihalomethane precursor by over 98% [105]. Nguyen et al. [38] evaluated the performance of PAC addition

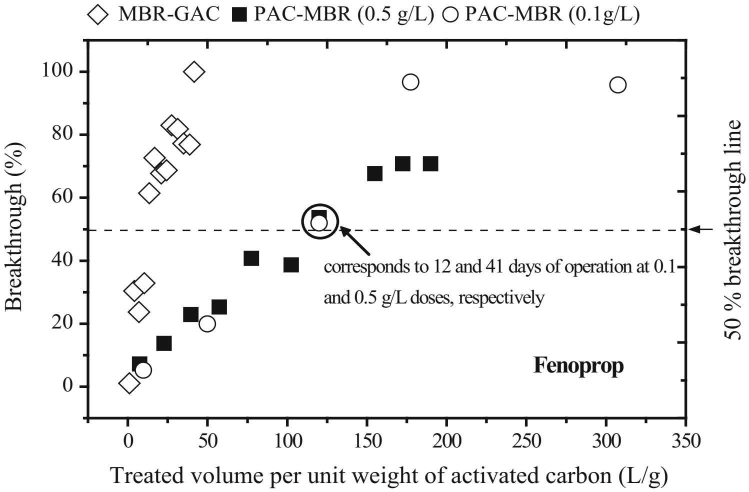


Fig. 6 Comparison of breakthrough profiles of fenoprop as a marker compound in different systems, namely, GAC posttreatment (MBR-GAC) and PAC addition to MBR (PAC-MBR) taking into consideration activated carbon usage rate (adapted from Nguyen et al. [106])

on the removal of 22 widespread TrOC in an MBR. The results showed that in addition to a high removal of readily biodegradable and hydrophobic compounds, the addition of PAC resulted in an immediate improvement in the removal of all biologically persistent and hydrophilic compounds. However, under a prolonged operation time, a gradual drop in the removal of seven biologically resistant and hydrophilic compounds was inevitable. Charged compounds, particularly fenoprop and diclofenac, demonstrated the fastest breakthrough. Thus, the authors suggested that frequent but smaller-dose addition of PAC is required for stable removal and efficient PAC use. Results from this study suggested that "biologically activated carbon" wherein adsorption, biodegradation and PAC regeneration may occur simultaneously was not fully established. This may be attributed to two likely reasons: (1) under competition with other organic compounds in the synthetic wastewater, only a small fraction of the PAC added to the MBR can be effectively utilised for adsorption of TrOC, and (2) pore blockage by bulk organic matter including products of microbial degradation and dead microbial cells reduces the adsorption capacity of target compounds on PAC. Based on a simple comparison from the long-term performance stability and activated carbon usage points of view, PAC-MBR (PAC dosing into MBR) appeared to be a better option than MBR-GAC (GAC posttreatment) treatment [106] (Fig. 6). The better performance of PAC-MBR over MBR-GAC can be attributed to the higher surface area per unit weight of PAC. In addition, due to the larger particle size as well as the characteristic arrangement of GAC in a packed column, mass transfer hindrance may be more severe in the posttreatment GAC column.

5.3 Coagulation and MBR Systems

The application of chemical coagulation/flocculation using coagulants such as alum, ferric chloride and polyaluminium chloride as pretreatment before MBR has been used for treatment of industrial wastewater such as dairy [107] or piggery effluents [108]. Similar to PAC, coagulants, when directly added to MBR, have been found to reduce membrane fouling, possibly due to modification of the particle-size distribution of the mixed liquor suspended solids. Zou et al. [109] added $Fe(OH)_3$ to an MBR to enhance the treatment of dye wastewater and to mitigate membrane fouling. Even at a 25% higher volumetric loading rate, the coagulant-amended MBR achieved about 10% higher dye removal than a conventional MBR.

Coagulation treatment is mostly ineffective in terms of TrOC removal [6–11]. However, certain musk fragrances and pharmaceuticals such as diclofenac can be effectively removed using coagulation [3]. Electrocoagulation shows the potential of achieving both adsorption and degradation and removal of both soluble and insoluble organics. However, to date, only compound-specific removal by electrocoagulation has been reported [12, 13]. Interestingly, diclofenac has been reported to be poorly removed by MBR. It is also noted that some of the hydrophobic compounds, such as hormones, which are reported to be significantly removed by MBR treatment, were poorly removed by coagulation treatment. Given the complementary nature of these processes, it is likely that simultaneous addition of coagulant into MBR may enhance the removal of TrOC. However, this aspect has not been explored in the literature.

5.4 Combination of MBR and Advanced Oxidation Processes

The low background organic matter content and the absence of suspended solids in MBR effluent are of particular benefit for the combination of the MBR technology with the AOP [20–22]. In addition to enhanced TrOC degradation, combination of MBR and AOP can minimise some of the inherent limitations of AOP. For example, the presence of suspended solids in the influent can absorb and scatter UV radiation, thus reducing the overall process efficiency. This section presents available literature on the combination of MBR and AOP such as MBR-UV oxidation, MBR-ozonation and photo-Fenton-MBR system.

5.4.1 MBR and UV Oxidation

UV oxidation is an advanced treatment process that can be very effective for the removal of TrOC. However, influent with a high bulk organic content and/or high turbidity would require a very high UV dosage, rendering the process economically unattractive [1, 110]. Thus, this process is mostly used as a polishing step. Previous studies have shown that UV oxidation is capable of oxidising taste and odour-causing pollutants such as geosmin and methyl *tert*-butyl ether [111] and pesticides such as atrazine [112]. Topical antimycotic drugs naftifine, sulbentine, cloxiquin, tolnaftate and chlorphenesin have been shown to be light sensitive [113]. Packer et al. [114] reported that diclofenac is subject to rapid photodegradation, while ketoprofen and naproxen are mildly photodegraded. Nguyen et al. [43] demonstrated that UV oxidation can be effective for many but not all TrOCs. For example, the removal efficiencies of TrOCs by UV oxidation varied significantly from as low as 30% (e.g. carbamazepine) to almost 100% (e.g. pentachlorophenol and triclosan) [43]. As noted above, the effectiveness of UV oxidation may be reduced by the presence of bulk organic matter in wastewater [115]. Chong et al. [115] noted that to ensure rapid photocatalytic reaction rate, the turbidity of the target wastewater should be kept below 5 NTU for optimal UV light utilisation and photocatalytic reaction. MBR technology is nowadays recognised for its many demonstrated benefits and reliability for producing high-quality effluent. Due to the biological degradation and membrane filtration, MBR provides effluent with low organic content and turbidity (<0.2 NTU) [116].

Because MBR treatment and UV oxidation are capable of removing TrOC by different degradation mechanisms, a hybrid system involving both technologies can take advantage of their complementary nature. For example, chlorinated TrOCs (e.g. diclofenac, triclosan, fenoprop and pentachlorophenol), which were resistant to MBR treatment, were well removed by UV oxidation [43, 117]. In this connection, Nguyen et al. [43] observed a significant removal of 22 TrOC by MBR-UV system. The compounds, which were poorly removed by either MBR or UV, were very effectively removed by combined MBR-UV. For example, the removal efficiency of an anticonvulsant drug carbamazepine by MBR and UV separately was $32 \pm 17\%$ and $30 \pm 7\%$, respectively. By contrast, posttreatment of the MBR effluent by the UV system at a contact time of 7.5 min achieved exceptionally high removal efficiency and resulted in an overall removal of carbamazepine of 96%, which is significantly higher than that achieved by either treatment separately (Fig. 7). Laera et al. [118] reported that the integration of MBR with UV/TiO_2 photocatalysis in a system with a recycling ratio of 4:1 resulted in 95% removal of carbamazepine.

5.4.2 MBR and Ozonation

Ozone (O_3) has been shown to degrade TrOC during wastewater treatment and water reuse applications [119]. Ozone reacts with TrOC through either direct reactions or through the formation of free radicals, including the hydroxyl radical ($HO^\bullet$) [120]. The efficiency of a combined MBR and ozonation process for TrOC removal has been assessed in different operational modes. Figure 8 presents three different configurations of MBR-ozonation systems. Pollice et al. [35] compared the performance of integrated MBR-ozonation and MBR-post ozonation for the

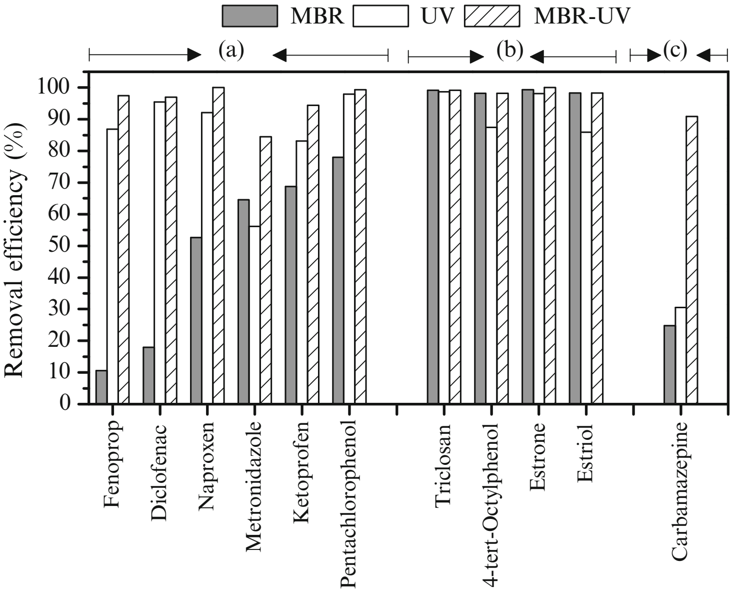


Fig. 7 TrOC removal efficiency by MBR, UV and combined MBR-UV systems. (**a**) Low and moderate removal by MBR and high removal by UV (overall high removal), (**b**) high removal by either MBR or UV (overall high removal) and (**c**) low removal by both MBR and UV but significant removal by combined MBR-UV (data sources: [43, 117])

removal of an antibacterial product nalidixic acid. The results showed that the integrated process was more efficient than the MBR-post ozonation by virtue of higher removal of ozonation by-products and lower ozone dose requirement. A similar observation was reported by Laera et al. [121]. The abundance of ozonation by-product in the final effluent of the integrated process was 20-fold lower than that of MBR-post-ozonation process [121]. Mascolo et al. [50] achieved a similar removal of an antiviral drug (acyclovir) by both the configurations; however, the integrated process again was more beneficial in terms of removal of specific ozonation by-products.

5.4.3 MBR and Fenton Oxidation

The Fenton oxidation process is based on the generation of highly reactive hydroxyl radicals from H_2O_2 using an iron catalyst [75]. Pretreatment by Fenton oxidation may completely degrade the target pollutants or enhance their biodegradability, producing a biocompatible effluent which can then be completely mineralised by biological processes [122]. For example, Feng et al. [123] observed that Fenton process was effective to enhance the biodegradability of dye wastewater for enhanced removal in a subsequent MBR. The overall process produced a final effluent which met the criteria of urban recycling water. A real wastewater

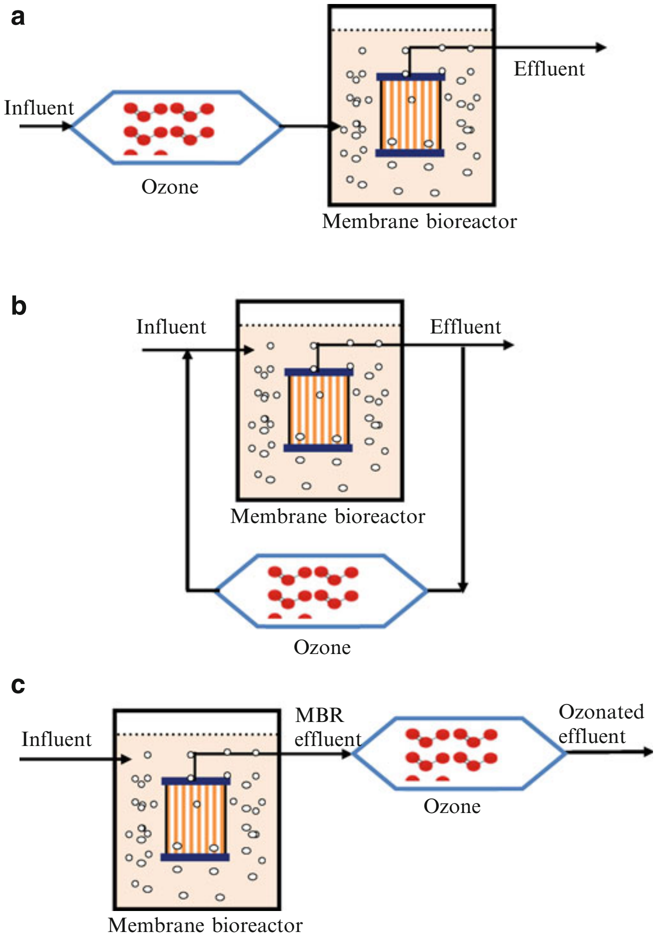


Fig. 8 Schematic diagram of (**a**) pre-ozonation-MBR, (**b**) integrated MBR-ozonation and (**c**) MBR-post ozonation systems

containing a non-biodegradable antibiotic nalidixic acid (45 mg/L) was pretreated by Fenton oxidation [124]. The authors reported that nalidixic acid completely disappeared after 190 min of solar photo-Fenton treatment. The overall TOC degradation efficiency of the combined system was over 95%, of which 33% corresponded to the photo-Fenton process. Biodegradability and toxicity bioassays as well as economic analysis showed that in order to remove the recalcitrant compound, while avoiding excessive cost of advanced oxidation, photo-Fenton degradation should be continued until the total degradation of nalidixic acid before switching to a biological treatment. On the other hand, Sánchez Peréz et al. [125] examined posttreatment of MBR effluent by Fenton oxidation for the removal of fungicide thiabendazole. They observed a complete removal of thiabendazole by the combined process, even though the MBR accomplished a negligible removal of the compound. The authors noted that a complete removal of suspended solids and a significant removal of bulk organic matter by the MBR may enhance the degradation of thiabendazole by Fenton oxidation.

5.5 Bioaugmented MBR for TrOC Removal

Bioaugmentation is the term used to describe the addition of cultured microorganisms, which are capable of biodegrading or transforming specific contaminants, to the indigenous microbial community in a bioreactor. The application of bioaugmentation technique to conventional biological treatment processes is challenging due to the possibility of washout of the added culture. MBRs use MF or UF membranes for solid–liquid separation and, therefore, are suitable for applying bioaugmentation. Recent studies have explored the use of specific bacterial strains and fungi (e.g. white-rot fungi) for removal of different categories of resistant compounds. Genetically engineered microorganisms (GEM) are also being utilised. For example, Qu et al. [126] studied the removal of bromoamine acid (1-amino-4-bromoanthraquinone-2-sulfonic acid), widely used in synthesis of anthraquinone dyes, and also the microbial population changes in a laboratory-scale MBR augmented with *Sphingomonas xenophaga* QYY. The augmented MBR demonstrated relatively stable treatment performance, and the introduced strain coexisted well with the indigenous microbial community.

The bacterial strain *Paracoccus denitrificans* W12, which could utilise pyridine as its sole source of carbon and nitrogen, was added into an MBR to enhance the treatment of a pharmaceutical wastewater. The performance of bioaugmented and conventional MBR was compared in terms of chemical oxygen demand (COD), total nitrogen and phosphorus removal and pyridine removal. The results showed a similar removal of COD, total nitrogen and total phosphorus between the bioaugmented and non-bioaugmented MBRs. However, significant removal of pyridine was achieved by the bioaugmented MBR [127]. Cirja et al. [128] also reported an enhanced removal of nonylphenol by an MBR bioaugmented with *Sphingomonas* sp. strain TTNP3. Ghyoot et al. [129] examined the behaviour of a 3-chlorobenzoate degrading *Pseudomonas putida* BN210 in a CAS system and an MBR. Although molecular techniques indicated that the strain BN210 disappeared or survived only in low cell numbers in both the reactors, the MBR showed higher resistance towards shock loading of 3-chlorobenzoate in terms of improved COD removal. Molecular characterisation of the isolates strongly suggested that in the MBR, the element containing the gene for 3-chlorobenzoate metabolism had been in situ disseminated from the initial inoculum to contaminant bacteria, which had invaded the reactor and which finally became the dominant strains to continue degradation.

Bioaugmentation using GEM is also a promising way to remove recalcitrant TrOC from wastewater. For example, Liu et al. [130] incorporated an atrazine chlorohydrolase gene of *Pseudomonas* sp. into an *Escherichia coli* strain and inoculated to an MBR. The authors achieved efficient (above 90%) and stable removal of atrazine, which is reported to be persistent to conventional biological treatment process [130].

Recently, white-rot fungi, which are able to degrade lignin, a highly resistant compound in woody plants, have been evaluated for the degradation of TrOC [131]. Significant removal of various resistant compounds by white-rot fungi makes them a potential candidate for bioaugmentation. In fact, bioaugmentation of white-rot fungus *Coriolus versiscolor* into an MBR has been reported to enhance the removal of dyes from a textile effluent [132, 133]. Yang et al. [134] tested an MBR containing a mixed microbial community including the white-rot fungus *Trametes versicolor* for the treatment of a synthetic wastewater containing two TrOCs, namely, bisphenol A and diclofenac. The authors reported that at TrOC loading rates below 500 μg/L · d, diclofenac and bisphenol A removal was 55% and 80–90%, respectively. In a more comprehensive study, Nguyen et al. [135] investigated the performance of a *T. versicolor*-augmented MBR on the removal of 30 selected TrOCs. Results in that study highlight that a mixed culture of bacteria and a white-rot fungus in a fungus-augmented MBR can achieve better TrOC removal than a system containing fungus or bacteria alone. The results showed that bacteria complemented well the degradation of TrOC by fungal MBR.

6 Summary and Future Outlook

The combination of MBR treatment with various physicochemical processes has been comprehensively reviewed in this chapter. The MBR technology produces high-quality effluent in terms of turbidity and bulk organic removal. However, the removal efficiency of TrOCs by MBR is variable. Particularly, biologically persistent and hydrophilic TrOCs are inefficiently removed by MBR treatment, necessitating posttreatment of the MBR permeate. This chapter has shown that the MBR technology can be combined with various treatment processes to achieve significant removal of varieties of TrOCs from wastewater. Overall, the combined processes inherit the advantages of each process and give an enhanced overall performance. High retention membranes such as NF and RO membranes can achieve efficient retention of many TrOCs. However, severe membrane fouling restricts application of high retention membranes in direct filtration of wastewater. A number of studies have shown significant removal of TrOCs by other advanced processes such as activated carbon adsorption and AOP. However, at the present stage of development, TrOC removal efficiency by these techniques depends on the dosage and applied contact time as well as the wastewater matrix. This chapter also highlights some novel MBR configurations, namely, osmotic MBR and MDBR. The potential benefits of combined systems having MBR at the core to treat the wide varieties of TrOCs from wastewater have also been highlighted. However, in practice, there are many factors affecting TrOC removal by these techniques. These include both structural and physicochemical characteristics of the TrOC as well as operating parameters of the processes, which require fine-tuning. It is also noteworthy that most of the data available to date are from laboratory-scale studies. Further research is still needed for full-scale validation, scaling up and system optimisation and to improve our overall understanding of the complementarities between MBR and other physicochemical processes.

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Enhanced Biological Wastewater Treatment to Produce Effluents Suitable for Reuse

M. Concetta Tomei, Guido Del Moro, Claudio Di Iaconi, and Giuseppe Mascolo

Abstract Enhanced performance of biological processes for xenobiotic removal in municipal and industrial wastewater treatment plants can be achieved by adopting the following general strategies based on different principles of operation: increase of the biomass concentration (i.e., using biofilm, immobilized cell, and granular sludge reactors); dynamic operating conditions able to modify the biocenosis composition and to induce alternative metabolic pathways required by xenobiotic biodegradation; two-phase systems, which optimize the substrate delivery to the microorganisms on the basis of their metabolic demand; and combined treatment processes utilizing synergistic physical/chemical methods.

In this chapter, the three following strategies for enhancing the biological process are presented and discussed:

- Addition of adsorption or absorption media
- Advanced oxidation processes: UV and UV/H_2O_2
- Bioreactors operated with attached and granular biomass

The proposed alternatives have been chosen as representative examples of promising technological solutions still under investigation. For each alternative a short presentation including the principle of operation, the realized applications and potentialities, as well as a case study is reported.

Keywords Advanced oxidation processes, Attached biomass, Combined treatment, Enhanced biological treatment, Granular biomass, Sorption, Wastewater reuse

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Contents

Abbreviations

4 t-OP	4-tert-Octylphenol
AC	Activated carbon
AOPs	Advanced oxidation processes
BPA	Bisphenol A
C	Concentration
C_0	Initial concentration
COD	Chemical oxygen demand
DCP	2,4-Dichlorophenol
DOM	Dissolved organic matter
E1	Estrone
E2	17β-Estradiol
EC_{50}	Effective concentration that gives the half-maximal response
EDs	Endocrine disruptors
EE2	17α-Ethynylestradiol
GAC	Granular activated carbon
GSBR	Granular sequencing batch reactor
HPLC/MS	High-performance liquid chromatography-mass spectrometry
MMTD	5-Methyl-1,3,4-thiadiazole-2-thiol
MW	Molecular weight
OLR	Organic loading rate
PE	Population equivalent
PCB	Polychlorinated biphenyl
PLC	Programmable logic controller

PVC	Polyvinyl chloride
SBBGR	Sequencing batch biofilter granular reactor
SBR	Sequencing batch reactor
SIM	Selected ion monitoring
TOC	Total organic carbon
TPPB	Two-phase partitioning bioreactor
TSS	Total suspended solids
UV	Ultraviolet
Vis	Visible
VSS	Volatile suspended solids
WWTP	Wastewater treatment plant

1 Introduction

Water reuse, regardless of whether the intent is to augment water supplies or manage nutrients in treated effluent or save energy and money in an industrial production, has positive benefits that are also the key motivators for implementing innovative technologies at wastewater treatment plants (WWTPs). These benefits for municipal wastewater include improved agricultural production; reduced energy consumption associated with production, treatment, and distribution of water; and significant environmental benefits, such as reduced nutrient and pollutant loads to receiving waters due to reuse of the treated wastewater. Even more evident are the motivations of water reuse in industry: in the last century, the rapid development has improved the standard of living and quality of life for millions of peoples causing a 50-fold increase in industrial production. Therefore, the industrial water demand and pollution dramatically increased and in developed countries, industrial water demand accounts for 50–80% of the total demand. It is also worth noting that, in the last decades, in many countries the high rates of consumption have exceeded capacity to compensate the depletion of water sources causing a driving up the cost of raw water for industrial applications. Besides the cost, there are more important environmental safety motivations: the industrial effluent discharge may exceed the natural self-purification capacity of the receiving water body and depleting the dissolved oxygen below levels, which can support aquatic life. Moreover, the intensive and prolonged groundwater use in the industry caused severe damage to aquifers and their recharge capacity resulting in a progressive and serious decrease of groundwater levels. In this context, recycling and reusing industrial wastewater is an attractive alternative for environmental protection and cost-effective if compared to the use of raw water [1].

Required quality characteristics of municipal and industrial effluents suitable for reuse, in addition to efficient COD and nutrient removal accomplished in conventional WWTPs, are mainly related to the presence of xenobiotic compounds (i.e., poorly biodegradable chemicals) and pathogens (the latter only for municipal and mixed wastewater) [2].

Wastewater treatment technologies are available for mitigating chemical and microbial contaminants, including both engineered and natural treatment systems. The required degree of treatment varies according to the specific input, the reuse application, and the related water quality requirements. The technological solution can be adapted to meet the effluent quality criteria. Conventional treatments involve solid/liquid separation (primary and secondary settling), biological treatment, and disinfection. More efficient treatment systems are based on the combination of physical, chemical, and biological processes employing multistage treatment approaches to enhance biological treatment such as adsorption, air stripping, ion exchange, filtration, chemical coagulation, and precipitation.

In this chapter, the three following alternatives to be combined with the conventional biological treatment for performance enhancement are considered:

- Addition of adsorption or absorption media
- Advanced oxidation processes (AOPs): UV and UV/H_2O_2
- Bioreactors operated with attached and granular biomass

For each alternative a short presentation including the principle of operation, the realized applications and potentialities, as well as a case study is reported. The focus is on xenobiotics and the proposed technologies can be in principle applied to both municipal and industrial wastewater for the removal of different groups of xenobiotics. Operating conditions have to be optimized depending on the characteristics of the contaminants and it has to be taken into account the different type of xenobiotics and their different order of magnitude of concentration in municipal and industrial wastewater, which can significantly affect the removal efficiency.

2 Technological Alternatives to Enhance Biological Processes for Xenobiotic Removal: An Overview

Enhanced performance of biological processes for xenobiotic removal in municipal and industrial WWTPs can be improved by adopting several strategies, which can be realized in practice through different technological solutions [3]. A general, simplified classification of the available strategies is reported below:

- Increase of the biomass concentration (by, e.g., using biofilm, immobilized cell, and granular sludge reactors) with the concomitant beneficial effect of increasing the process kinetics and reducing the substrate/biomass ratio.
- Dynamic operating conditions: in this case, the variability of the reaction environment promotes the development of microorganisms more resistant to substrate toxicity and able to degrade “bioresistant” compounds. Typical example is the sequencing batch reactor (SBR).
- Two-phase systems, which deal directly with substrate inhibition by reducing aqueous phase concentrations via sequestration into a second, immiscible phase,

Table 1 Overview of the technological solutions for enhancing biological process performance in xenobiotic removal (modified from [3])

Principle of operation	Technologies
Increase of biomass concentration	Attached biomass
	Fixed bed
	Expanded bed
	Fluidized bed
	Pulsed bed
	Adsorptive support media
	Immobilized biomass
	Fixed bed
	Membrane
	Fluidized bed
	Adsorptive immobilizing agent (added of granular activated carbon (GAC), GAC)
	Granular biomass
	Continuous reactor (for anaerobic processes)
	Granular sequencing batch reactor (GSBR)
	Sequencing batch biofilter granular reactor (SBBGR)
Dynamic operating conditions	Sequencing batch reactors (SBRs)
	Suspended biomass
	Biofilm on inert or adsorptive support media
	Granular biomass
Two-phase systems	Two-phase partitioning bioreactors (TPPBs)
	Liquid-liquid – organic solvents as partitioning phase
	Encapsulated – organic solvents in polymer matrices
	Solid/liquid – polymers as partitioning phase
Integrated treatment: biological plus	Different reactor configurations depending on the process sequence
Absorption/adsorption	Adsorptive support (GAC)
	Absorptive polymers (commercial and/or waste polymers)
Oxidation	Ozone
	Advanced oxidation processes (AOPs)
Photochemical	UV radiation
	Photocatalysis

and re-release of the substrate driven by metabolic substrate demand and maintenance of thermodynamic equilibrium.

- Combined treatment processes utilizing synergistic physical/chemical methods. Physical methods are based on the use of sorption media added to the biological tank or employed as tertiary treatment. Chemical methods can be used to initially modify (detoxify) the substrates, before the biological treatment, in case of low or non-biodegradability of the xenobiotic compounds (e.g., landfill leachates, pharmaceutical effluents) or as post-treatment (tertiary treatment) as a polishing step in order to remove the residual organic compounds. They include oxidation with ozone or AOPs including photochemical treatment such as UV/H_2O_2 and photocatalysis.

Table 1 shows an overview of the available technologies applied in bioreactors and their principle of operation.

Biofilm, SBRs, and membrane bioreactors were extensively investigated and are largely applied in full-scale plants, while research activities are still in progress on aerobic granular reactors and on some immobilized cell systems mainly related to their transfer on practical applications. Given the wide spectrum of possible derived technological solutions, further investigations are still required on two-phase systems and on combined physical/chemical and biological processes. The alternatives proposed in this chapter have been chosen as representative examples of promising technological solutions (still under investigation) of the various possible strategies to increase the performance of biological processes in the removal of xenobiotics both in municipal and industrial wastewater treatment plants.

3 Adsorption/Absorption Processes

3.1 Activated Carbon and Precursors: Potentialities and Realized Applications

Activated carbon (AC) is the classical adsorbent generally utilized in WWTPs to improve their performance in the removal of xenobiotic compounds. It has been extensively investigated and applied in full-scale plants from decades, and its main peculiarity is to be aspecific so suitable for adsorption of a wide spectrum of molecules characterized by different functional groups. Additional AC advantages are the very high specific surface (up to 2,000 m^2/g) and the possibility of using the AC in different technological solutions as powdered activated carbon (PAC) or in granular form (GAC). The possible alternatives of AC application on WWTPs range from the simple addition into the bioreactors (operated in conventional mode or with membranes) [4] to the employment as tertiary treatment in biofilters. GAC also offers a reactive support for the biomass growth so adding a chemical-physical reaction step to the biological one. Detected removal efficiencies are generally very high ($\geq 90\%$) for some compounds within classes of compounds found in urban wastewater such as pharmaceuticals, pesticides, endocrine disrupting compounds, personal and house care compounds, and other compounds (e.g., phenols, chlorinated compounds, hydrocarbons, dyes, etc.) present in industrial wastewater [4].

Certainly, AC is characterized by really high demonstrated potentialities in xenobiotic removal and remains one of the preferred solutions in dealing with slow/not biodegradable compounds. Nevertheless, AC application, especially in tertiary treatment, is hindered by its high price and by the environmental cost of the production/regeneration step. It is also worth noting that in adsorption processes the contaminant removal consists in a mass transfer between phases: there is not a degradation of the compounds whose amount remains unchanged in the environment being just removed from the aqueous phase and concentrated in the sorbent medium. So two more steps are required in this case: to regenerate the adsorbent for reuse and to ultimately degrade, or dispose, the contaminants if there are no alternatives for their reuse.

Overcoming these drawbacks led to research aiming at identifying adsorbent materials less expensive, easier to regenerate, and more contaminant specific. These last two features are of relevance especially for industrial wastewater, not only for the expected increased removal efficiency but also for the possibility of selectively recovering and reusing the compound in the production cycle.

In order to reduce the cost of the AC production and to increase the environmental sustainability of its utilization, different raw materials have been investigated as possible precursors: some of these materials include woody residuals of plants, shells and stones of fruits, asphalt, metal carbides, carbon blacks, and polymer scraps. Moreover, different types of coal, which already exist in a carbonaceous form, have been modified to produce activated carbon. Although activated carbon can be produced from almost any raw material, it is most cost-effective and environmentally sustainable to use as precursor waste materials, which have been demonstrated effective in producing a good-quality adsorbent medium. For example, activated carbons produced from coconut shells are characterized by high micropore volume, making them the most commonly used raw material for applications where high adsorption capacity is needed. AC produced from olive, plum, apricot, and peach stones yields highly homogeneous adsorbents with significant hardness, resistance to abrasion, and high micropore volume. An interesting possibility as plastic waste recycling is the activation of PVC scrap after HCl removal, and this results in an activated carbon which is a good adsorbent for methylene blue. Activated carbons have even been produced from tire scrap. The choice of a precursor is determined by the resulting physical properties after activation, i.e., specific surface area of the pores, pore volume and pore volume distribution, composition and size of granules, and chemical structure/character of the carbon surface [5, 6]. Another element to be taken into account is the cost of the plant for both investment and energy demand: in critical situations, like the ones characterizing the developing countries, recovered wastes are a valuable source allowing the low-cost AC production, which is a prerequisite for its application.

3.2 Polymers: Principle of Operation in Two-Phase Systems, Potentialities, and Realized Applications

As an alternative to AC for xenobiotic removal, many adsorbents of mineral, organic, or biological origin were investigated: zeolites, clays, silica beads, and low-cost adsorbents, i.e., industrial by-products, agricultural wastes, biomass, and polymeric materials (organic polymeric resins, macroporous hyper-cross-linked polymers, modified polysaccharides) are significant examples [7]. Among them, polymeric materials have been demonstrated to be a valid technological solution given their significant advantages consisting of high selectivity, biocompatibility with the biomass (when directly employed in the bioreactors), easy regeneration and reuse, and low price. In addition, polymer application allows a wide spectrum of technological configurations ranging from the simple addition to the aeration thanks to more complex layouts including separate operation units. In each unit the polymer can be tailored for the specific compound (in terms of functional groups) to be removed (or recovered) and in the most suitable shape for the different bioreactor configurations (packed bed, fluidized bed, etc.).

Moreover, depending on the xenobiotic concentration level, polymers can be employed as classical absorbent or as partitioning phase in two-phase systems, namely, two-phase partitioning bioreactors (TPPBs). The latter option has been extensively investigated in the last years because, differently from the simple adsorption process, it allows the ultimate biodegradation of the contaminant, even if it is potentially inhibitory or toxic for the biomass. The selective partitioning of target molecules is the rationale behind the design and operation of TPPBs, which are characterized by the aqueous phase (containing the biomass) and a partitioning phase (an organic solvent or a polymer) that acts to selectively sequester toxic molecules and to deliver these substrates to the biocatalyst based on the microbial demand. The polymers operate via absorption (not adsorption) similarly to organic solvents [8]. With this configuration, the microorganisms are exposed to reduced toxicity levels being the substrate delivery completely driven by the cellular metabolic processes: in fact, when the biodegradation occurs in the aqueous phase, the xenobiotic compound transfers from the partitioning to the water phase to restore the thermodynamic equilibrium with consequent low/nontoxic substrate concentrations in the liquid phase [9].

This approach has been demonstrated effective to treat a wide variety of toxic organic contaminants present in industrial wastewater including phenol [10], substituted phenols [11], biphenyl [12], indole [13], polyaromatic hydrocarbons [14], and PCBs [15]. The high concentration levels of these contaminants faced by the biomass were successfully reduced and higher removal efficiencies were observed in comparison to single-phase systems. More recent is the TPPB application to municipal wastewater; in this case the reaction environment is quite different: there are low xenobiotic concentrations with a not specialized biomass for their biodegradation, and both factors tend to reduce the biodegradation kinetics. In this case the utilization of absorptive polymers in view of the realization of a TPPB is under investigation and promising results have been reported by Ouellette et al. [16] and Villemur et al. [17]. They observed high absorption capacity of the polymer Hytrel 8206 (DuPont Co., USA) for six endocrine disruptors (EDs) (estrone, 17-β-estradiol, estriol, 17-α-ethynylestradiol, bisphenol A, and 4-n-nonylphenol) commonly found in effluent from WWTPs. In addition, they provided a preliminary validation of a two-phase system operated with Hytrel and enrichment cultures degrading the six EDs.

A new opportunity for TPPBs, attractive in terms of environmental sustainability, is to utilize waste polymeric materials as the partitioning phase. Recent experiments have demonstrated the feasibility of this strategy for the bioremediation of hydrocarbons by employing used automobile tires [18]. It is worth noting that employment of used automobile tires provides an opportunity not only for reducing the initial polymer cost to near zero but also for utilizing a waste material for positive environmental purposes. In the proposed case study, automobile tire pieces have been employed as the partitioning phase in a TPPB to biologically degrade 2,4-dichlorophenol (DCP), a highly toxic compound (effective concentration $EC_{50} = 2.3\text{–}40$ mg/L [19, 20]), found in many industrial effluents of pesticide and herbicide production and, in minor extent, also in municipal wastewater being chlorophenols used as preservatives.

3.3 Case Study: 2,4-Dichlorophenol Removal in Two-Phase Systems Operated with Commercial Polymers and Tires

3.3.1 Experimental

Feasibility of DCP removal in a two-phase system operated with commercial polymers has been demonstrated in a previous study [21], and, more recently, the possibility of realizing the process utilizing tires has been investigated [22, 23]. Obtained results are really encouraging and a short summary is presented in this subparagraph.

DCP biodegradation kinetics was investigated in batch and in a sequencing batch reactor operated in conventional (single phase with suspended biomass) and TPPB mode (with Tone P787 and tire addition) under mixed and aerated condition. Tone P787 (Dow Chemical Canada Inc.) is a poly-caprolactone polyester (density 1.145 g/cm^3 and melting point 60°C) in form of spherical beads of 4 mm diameter. Tires are cut into small pieces of ~ 4 mm, and in the proposed approach, used tires do not require excessive pretreatment: they are utilized after simple cryogenic pretreatment and steel and fiber separation followed by a multistep water washing. DCP biodegradation was performed with a mixed culture previously utilized to degrade phenolic compounds whose development is detailed elsewhere [24]. The culture was acclimatized over a 3-month period to DCP as a sole carbon and energy source. In the acclimatization phase, DCP concentration was gradually increased (from 60 up to 250 mg/L). Representative results of kinetic tests are reported in Figs 1 and 2 for batch tests and SBR tests, respectively.

3.3.2 Results and Discussion

Results confirmed that the biomass in the single-phase batch system was completely inhibited, while significant removal efficiencies of 85% and 68%

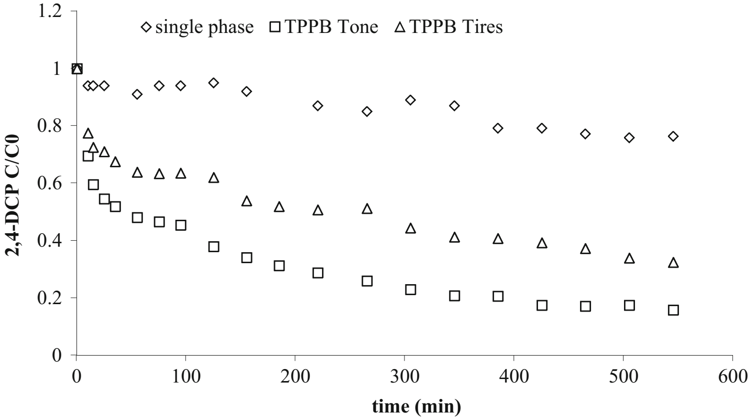

Fig. 1 DCP concentration profiles detected in parallel batch tests performed in single- and two-phase mode. Initial concentration, $C_0 = 134$ mg/L; biomass concentration, X = 1,890 mgVSS/L; tone and tires fraction, 5% v/v

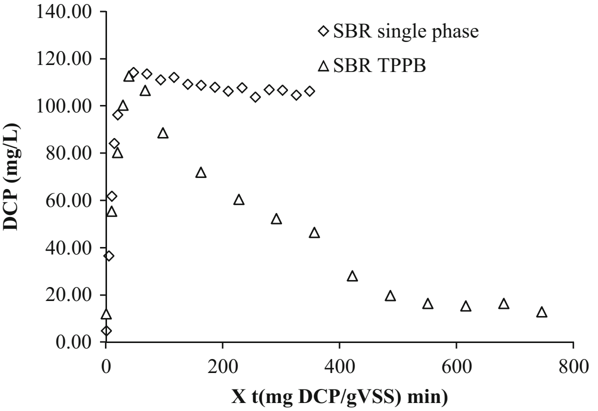

Fig. 2 DCP concentration profiles detected in the SBR reactor operated in single-phase and TPPB mode. Influent concentration, 200 mg/L; biomass concentration, X = 1,200–1,600 mgVSS/L; tire fraction, 5%; exchange ratios (ERs), 0.5 for single-phase SBR and 0.72 for TPPB-SBR

were observed for the two-phase batch bioreactors operated with Tone P787 and tires, respectively. Effectiveness of used automobile tires as the partitioning phase in TPPBs has been demonstrated by their performance comparable to that obtained with commercial polymers for the treatment of DCP. Kinetics tests in the TPPB-SBR highlighted the potentialities of tires which, compared to the conventional systems, where no removal is observed, allowed to achieve a removal efficiency of ~90% at an influent load 30% higher than the one applied to the conventional bioreactor.

4 UV and UV/H_2O_2

4.1 Principle of Operation

A growing interest has been observed in the area of UV-activated processes which is mainly due to (1) the continuous decrease of the cost of UV lamps, (2) the possibility to avoid UV lamp fouling by employing noncontact reactors, and (3) the simultaneous use of UV and chemical oxidants (e.g., ozone or hydrogen peroxide) [25, 26]. UV-based treatments are suitable for degrading organic pollutants from wastewater that contain low amount of suspended solids that would cause light scattering and optical absorption.

When UV light is absorbed directly by H_2O_2, hydroxyl radicals ($HO^{\bullet}$) are generated by photolysis of the –O–O– peroxidic bond ($H_2O_2 + h\nu \rightarrow 2HO^{\bullet}$). Hydrogen peroxide absorbs light (depending on its concentration) in the range of 185–300 nm; the highest hydroxyl radical yields are obtained when short-wave ultraviolet radiations (200–280 nm) are used. Consequently, low-pressure mercury lamps having an emission at 253.7 nm are particularly suited for the photolysis of H_2O_2 and thus very effective for the degradation of recalcitrant organic pollutants in UV/H_2O_2 processes. Hydroxyl radicals mainly oxidize organic compounds, recombine with other hydroxyl species to form hydrogen peroxide, or initiate a radical chain degradation of hydrogen peroxide [27]. Hydroxyl radicals can attack organic molecules by abstracting a hydrogen atom, adding hydroxyl groups, or transferring electrons [28]. Pharmaceuticals are a class of organic pollutants that recently have emerged due to many documented cases of water and wastewater contamination by estrogens, cholesterol-lowering drugs, pain relievers, antibiotics, caffeine, antidepressants, and many others [29–32]. These compounds reach waterways mainly through the discharge of wastewaters both raw and treated. Additional pollution sources are direct emissions from production sites, disposal of surplus drugs in households, excretion after applications for human and animal medical care, or therapeutic treatment of livestock on field. The conventional treatments carried out at WWTPs (i.e., preliminary, primary, and secondary) usually do not effectively remove pharmaceutical derivatives. Therefore, in order to meet the quality's standards required for wastewaters discharge, the effluents contaminated by pharmaceutical derivatives must be pre- or posttreated by appropriate processes such as UV-based treatments [33].

4.2 Potentialities and Realized Applications

Most pharmaceuticals are photoactive, i.e., absorb both UV and visible light. Various studies have demonstrated that many pharmacologically active compounds can be photodegraded, since they generally contain aromatic rings, heteroatoms, and other functional groups that allow absorption of light or produce reactions with photosensitizing species that induce their photodegradation in natural water [34]. Irradiation with UV light is a well-established method for water disinfection and is increasingly used to treat pharmaceutical-contaminated wastewater. Therefore, photolysis and photochemical processes may play important roles in the removal of pharmaceutical compounds from water [35]. It was demonstrated that while the only photolysis generates degradation by-products, the addition of reactive species such as the hydroxyl radical can degrade these by-products, with specific degradation rates between 10^7 and 10^{10} M^{-1} s^{-1}. Consequently, there is considerable interest in processes based on the generation of hydroxyl radicals for pharmaceutical removal from waters [36, 37].

4.3 Case Study: Degradation of Pharmaceutical Intermediates

In the selected study pharmaceutical wastewater containing intermediates derived from antibiotics' production was utilized. These compounds are not completely removed by conventional biological treatments leading, ultimately, to potential groundwater or surface water contamination. The target pharmaceutical intermediate [5-methyl-1,3,4-thiadiazole-2-thiol (MMTD)] is used for the synthesis of cefazolin, a cephalosporin antibiotic [28]. MMTD is potentially harmful because it might play an important role in the pathophysiology of hypoprothrombinemia and hemorrhage [38, 39]. Of course, the case of MMTD is one example among several pharmaceutical compounds that can be found in wastewater. However, the authors are confident that the technique can also be applied to other compounds.

Figure 3 shows a diagram of the treatment plant for processing the pharmaceutical wastewater whose effluent was used in this work. The plant includes storage tanks, an equalization stage, a conventional biological treatment stage, and a clarifier.

As can be observed in Fig. 3, the MMTD concentration is 3–5 g/L in the storage tanks and after the complete biological treatment it is reduced to 0.3–3 mg/L. Therefore, the effluent must be treated by appropriate physical/chemical processes such as UV treatment. In the study, two issues have been specifically tackled: (1) the assessment of the effectiveness of UV and UV/H_2O_2 treatments for removing MMTD and (2) the identification of by-products formed during such treatments.

4.3.1 Experimental

A 0.6 L cylindrical Pyrex glass reactor was used for performing degradation experiments in batch mode. A low-pressure 17 W mercury arc lamp (Helios Italquartz, Italy) emitting at 254 nm was employed as UV radiation source for UV/H_2O_2 experiments. In a typical experimental test, 500 mL of a solution of the

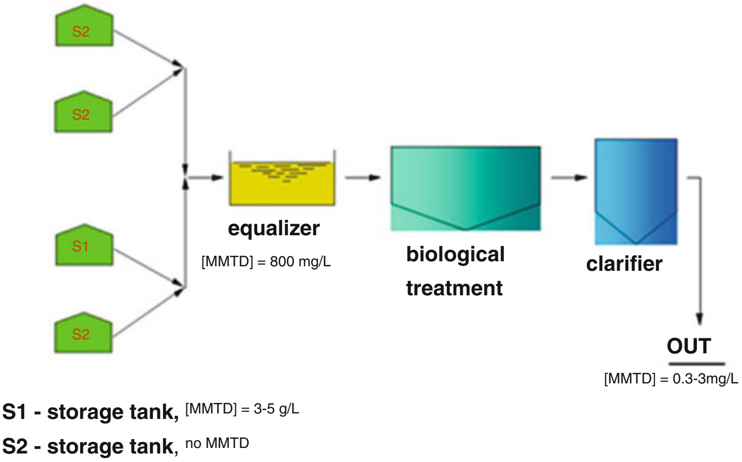

Fig. 3 Schematics of the plant treating the pharmaceutical wastewater whose effluent was used in this study

selected organic pollutant freshly prepared, kept under constant magnetic stirring (about 500 rpm/min), was subjected to irradiation by immerging the lamp (fixed at the central axis) in the reactor. The reactor light path was 1.8 cm. The lamp was previously heated for about 20 min and then placed in the cylindrical quartz tube. The lamp was calibrated by actinometry experiments using potassium peroxodisulfate and uridine following procedures reported elsewhere [40, 41]. From such experiments the average incident photonic flux was 2.8×10^{-6} Einstein/s at 20°C which corresponds to a power output (fluence) of 48 W/m^2 and an effective reactor light path of 1.85 cm. MMTD quantum yield was calculated with a known procedure [42]. In a typical photochemical experiment, 500 mL of MMTD aqueous solution was put in the reactor, and for UV/H_2O_2 experiments, the appropriate amount of H_2O_2 was added in order to have an H_2O_2/MMTD molar ratio of 100/1. Afterwards, the UV lamp was introduced into the reactor, and at each fixed time, a 5 mL sample was taken and immediately analyzed by HPLC.

UV measurements for actinometry measurements were performed with a Cary 1E UV-Vis spectrophotometer (Varian). The residual concentration of MMTD at various reaction times was determined by HPLC/MS-MS analysis by an Acquity chromatographic system, equipped with an autosampler, a photodiode array detector (Waters) interfaced to an API 5000 mass spectrometer (AB Sciex) by means of an electrospray ion source. Five μL samples were injected by a Rheodyne valve equipped with a 10 μL loop and eluted at 0.050 mL/min through a BEH C18 column, 1.0 × 150 mm, 1.7 μm. The detection limit was about 0.005 mg/L and reproducibility was within ± 5%. By-product identification was performed by HPLC/MS. Samples, injected by the autosampler, were analyzed by running a gradient, from 10/10/80 (1% acetic acid in methanol/methanol/water) to 10/70/20 in 10 min, which was maintained for 3 min. The flow from the HPLC-UV, set at 254 nm, was split to allow 200 μL to enter the turboionspray interface. Total organic carbon (TOC) analysis was carried out by a TOC-5050 analyzer (Shimadzu, Tokyo, Japan) equipped with a platinum catalyst on alumina spherical support. The quantitative determination of nitrite, nitrate, and sulfate were carried out by ion chromatography using a Dionex 4000i LC system (Dionex, Sunnyvale, CA, USA) equipped with an ASRS-ULTRA suppressor, operating in recycled mode, and a conductivity detector. Samples, injected via a 50 μL loop, were eluted at a flow rate of 1 mL/min through an analytical column (IonPac AS-14 250 × 4 mm) equipped with a precolumn (IonPac AG-14 50 × 4 mm) by an aqueous buffer solution of sodium hydrogenocarbonate/sodium carbonate 1.0 mM/3.5 mM.

4.3.2 Results and Discussion

Figure 4 shows the comparison between experiments carried out in deionized water and in real matrix for the treatment with UV only (4a) and with UV/H_2O_2 (4b), respectively. For the treatment with UV only (Fig. 4a), it was found that the real wastewater effluent matrix has a strong positive influence on the degradation rate of MMTD. Specifically, after 30 min, all MMTD was eliminated in wastewater effluent, while in deionized water, even after 90 min, a total degradation was not obtained. This trend can be explained by the fact that under UV irradiation, dissolved organic matter (DOM) can be involved in positive mechanisms, which can improve the indirect degradation of the compound. Light absorption can promote photosensitizer molecules present in DOM to their excited state. A variety of pathways may deactivate such state, leading to the formation of singlet molecular oxygen, which can react rapidly often forming peroxidic products [43]. Instead, for the treatment with UV and hydrogen peroxide (Fig. 4b), there was no difference between performing experiments in real or synthetic matrix. In both cases removals are obtained equal to 100% after 10 min of reaction.

In Fig. 5 the MMTD chemical structure and its decays during the investigated treatments (i.e., H_2O_2, UV, and UV/ H_2O_2) are reported. This figure shows that the sole H_2O_2 was not effective in degrading MMTD. Conversely, both UV and UV/H_2O_2 treatments effectively removed MMTD even with different rates. In fact, whereas UV/H_2O_2 treatment completely removed MMTD within about 10 min, the same goal was achieved in more than 1 h when only UV was used. During the experiments carried out using the sole UV, it has been possible to calculate the MMTD quantum yield (12 mmol·Einstein^{-1}) and the extent of MMTD removal (<1%) when a 250 J/m^2 UV dose was applied, i.e., the dose commonly used to disinfect drinking water [44].

The calculated very low value of the MMTD removal extent confirms that UV disinfection and UV organic degradation operate at very different fluence scales. The "speedup" effect observed in the presence of H_2O_2 (see Fig. 5) is due to the photolysis of H_2O_2 ($H_2O_2 + h\nu \rightarrow 2\ HO^{\bullet}$) that gives rise to the formation of hydroxyl radicals. These radicals, which can be generated even by other methods [44], are known to react with organics at high rates and with poor selectivity [45].

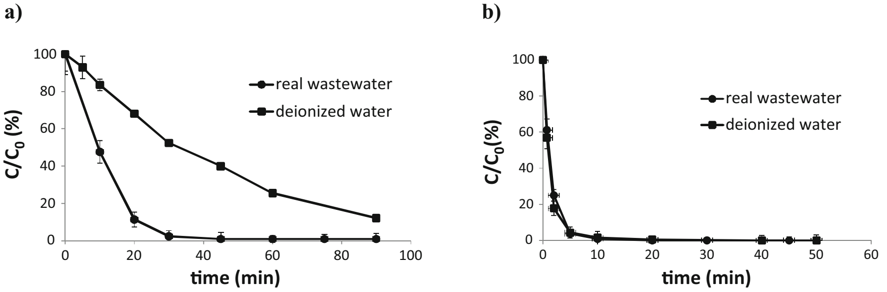

Fig. 4 MMTD treatment in deionized water and real wastewater with UV only (**a**) and with UV/H_2O_2 (**b**)

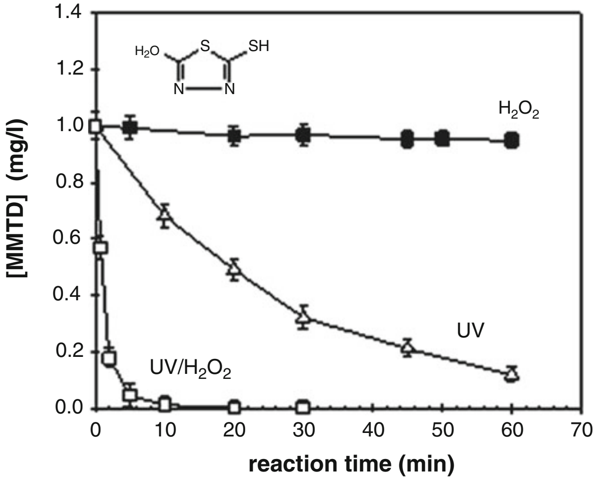

Fig. 5 MMTD structure and decays during H_2O_2, UV, and UV/H_2O_2 treatment. H_2O_2 initial concentration (when used) 26 mg/L

In order to assess whether, as claimed in [46], the degradation by HO$^{\bullet}$ causes a certain grade of MMTD mineralization, chemical parameters (TOC, $SO_4^{=}$, NO_3^{-}) proving such an expectation were monitored during the reaction. The obtained results, depicted in Fig. 6, show that in spite of the fast MMTD disappearance (see Fig. 5), the corresponding mineralization rate results much slower. In particular, after 4 h, an almost stoichiometric formation of $SO_4^{=}$ was recorded, whereas the extents of carbon and nitrogen mineralization resulted 59% and 14%, respectively.

On the contrary, in the absence of H_2O_2, the photolysis of the MMTD did not result in any measurable mineralization of carbon, nitrogen, and sulfur but caused the formation of elemental colloidal sulfur. As expected, such results confirm that MMTD removal by both treatments implies the formation of some degradation by-products. Furthermore, taking into account the recorded formation of SO_4^{2-} and NO_3^{-} during the UV/H_2O_2 treatment, it is reasonable to assume that the end by-products should be preceded by some intermediates, which in turn should

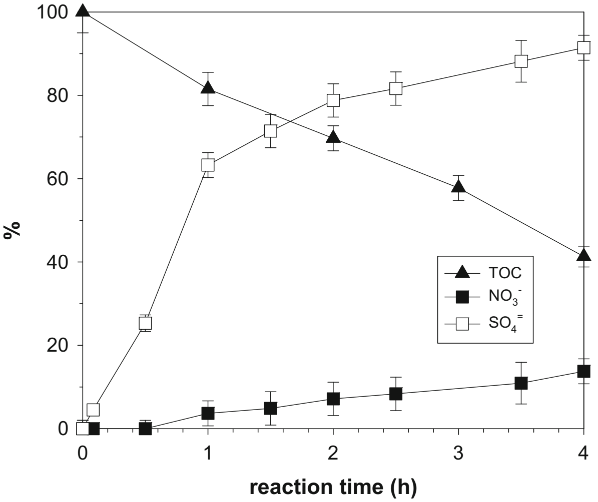

Fig. 6 TOC decrease, $SO_4^=$ and NO_3^- formation during MMTD degradation by UV/H_2O_2, all expressed as % with respect to the theoretical value. Experimental conditions: low-pressure mercury lamp, $[MMTD]_0 = 50$ mg/L, $[H_2O_2]_0 = 1.3$ g/L

Table 2 Mass spectral data for MMTD by-products analyzed by HPLC/MS

Derivative	MW	$[M+Na]^+$, $[M+H]^+$ and fragment ion masses (relative intensity)	$[M-H]^-$ and fragment ion masses (relative intensity)
MMTD	132		131(100), 90(13)
1	100	101(100), 74(12)	
2	116	117(52), 99(40), 87(100)	
3	180		179(100), 106(15), 58(30)
4	196		195(18), 58(100)
5	262	285(10), 263(100), 164(11), 158(10), 132(23), 59(7)	
6	230	253(14), 231(56), 190(13), 155(100), 132(18), 99(7), 59(23)	
7	294	317(30), 295(93), 231(99), 164(100)	

By-product identification numbers as reported for chemical structures in Fig. 7

undergo further degradation. In order to demonstrate such an assumption, the identification of the above degradation intermediates and/or end by-products was carried out by HPLC/MS as described in the experimental section.

In Table 2 the molecular weights (MW) of the identified compounds as well as the main fragment ion masses as appearing in the relative mass spectra are listed. Looking at Table 2 it is observed that by-products 1 and 2 have MW lower than that of MMTD. The MW of by-product 1 is consistent with a chemical structure resulting from MMTD after losing the thio group, whereas the MW of by-product 2 corresponds to the sulfinyl derivative of by-product 1. These structures also justify the fact that their mass spectrometric detection occurred only in positive ion mode.

By-products 3–7 have MW greater than MMTD suggesting that coupling and oxidation reactions took place. In particular, the MWs of by-products 3 and 4 are consistent with MMTD structures in which the SH group has been oxidized

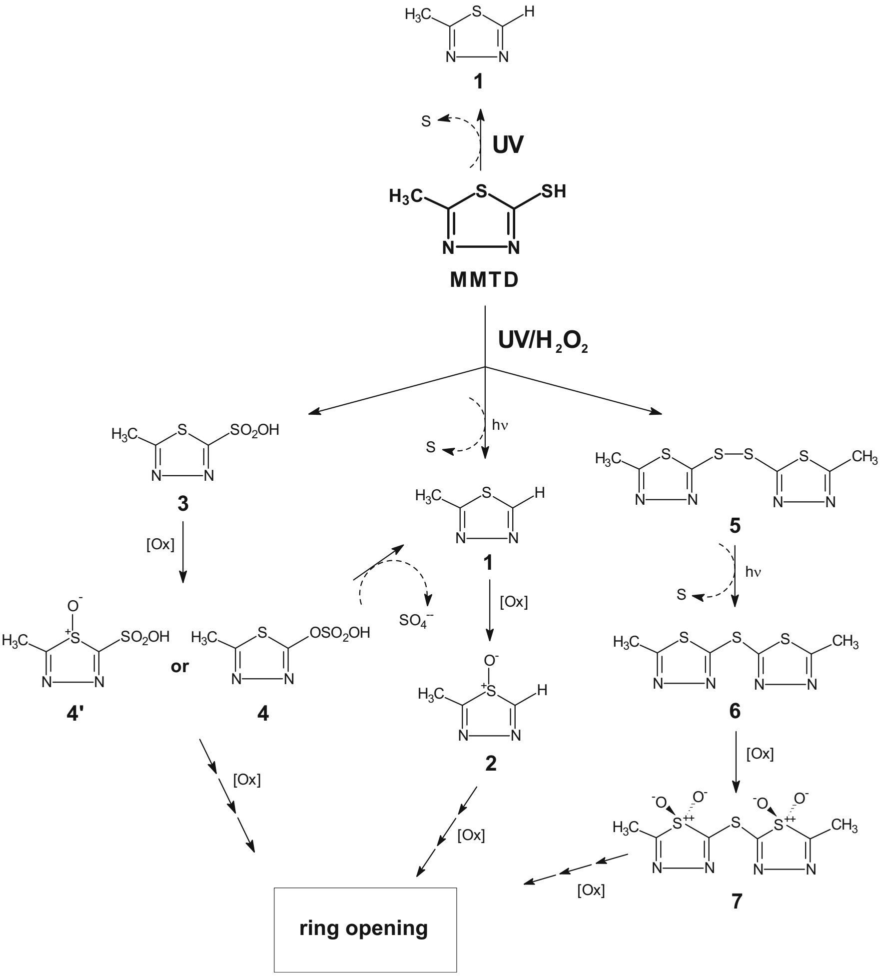

Fig. 7 Proposed pathway for MMTD degradation by UV and UV/H_2O_2

to $-SO_3H$ and $-OSO_3H$, respectively. The resulting compounds, being strong acids, are mass-spectrometrically detectable only in negative ion mode. By-products 5 and 6 have MWs corresponding to chemical structures derived by coupling reactions involving two MMTD molecules (by-product 5) or one MMTD and one by-product 1 molecule (by-product 6). Referring to by-product 7, it is the result of consecutive oxidations of by-product 6.

These structures were also confirmed by the interpretation of their mass spectra (data not showed). Based on the above results, the MMTD degradation pathway depicted in Fig. 7 has been proposed. This pathway accounts for both the UV degradation and the $^{\bullet}OH$ attack on different sites of MMTD.

Results confirm the effectiveness of the UV process for the transformation of the parent compound, alone or in combination with H_2O_2, that could be potentially harmful as it is well known from various works on the subject [47–49]. Such a 90% MMTD degradation requires a UV dose (170 kJ/m^2) much greater than that normally used to disinfect drinking water (250 J/m^2) so confirming that UV disinfection and UV contaminants degradation operate on very different fluence scales.

5 SBBGR: Sequencing Batch Biofilter Granular Reactor

5.1 Principle of Operation

In the last decade, a new technology (SBBGR: sequencing batch biofilter granular reactor), characterized by high treatment capability, high sludge retention times (higher than 6 months), and low sludge production (i.e., 80% lower than that of conventional activated sludge systems), has been proposed for the biological treatment of municipal and industrial wastewater [50].

SBBGR technology is based on a submerged biofilter working in a “fill and draw” mode. Biofilters are “attached biomass” systems in which organisms grow attached to a support material. This feature gives rise to higher biomass concentration in comparison to conventional suspended growth systems with consequent greater volumetric conversion capacities and reduction of the required reaction volumes. SBBGR operates in discontinuous sequential mode as the sequencing batch reactors, i.e., all the steps of the process take place, in sequence, in the same tank. Consequently, the SBBGR system combines the advantages of attached biomass systems (i.e., higher biomass concentrations and greater organic loads, absence of secondary settler) with those of periodic systems (i.e., greater flexibility and stability), and it is an unique system in virtue of the particular type of biomass growing in it [51]. In fact, the biomass consists of two different fractions: the biofilm attached to the carrier material and the granules entrapped in the pores produced by packing the filling material (see Fig. 8). Therefore, in SBBGR system the granules are not suspended (as in the granular biomass SBRs), but retained by the filling material. The whole biomass (i.e., biofilm and granules) is completely confined in a dedicated zone of the reactor (the bed), and a secondary settler is therefore no longer necessary. This feature gives a great advantage in terms of operating stability compared to granular biomass SBRs where a strong selective pressure (i.e., a very short sedimentation phase) is usually applied for sustaining the granulation. Such a high selective pressure may lead to the washout of the biomass from the reactor when a slight modification of the granule structure occurs. This drawback cannot occur in SBBGR since there is no sedimentation phase as the biomass is “entrapped” in the bed. Furthermore, this feature allows greater biomass retention in SBBGRs up to one magnitude order higher than that recorded in

Fig. 8 Photographs of the attached biomass in SBBGR system (on the *left*) and granules confined in the pores produced by packing the filling material (on the *right*)

conventional biological systems. As a result, a notable increase in sludge age is achieved, with consequent reduction in sludge production being the biomass decay rate comparable to the growth rate [52].

5.2 Potentialities and Realized Applications

SBBGR technology has been successfully applied for treating various wastewater types, such as municipal sewage, tannery effluents, municipal landfill leachates, and textile wastewater. For example, in sewage treatment, SBBGR was able to accomplish in a single stage the entire wastewater treatment train (i.e., primary and secondary treatment) carried out in the conventional plants and to assure removal efficiencies higher than 90% for COD, suspended solids, and nitrogen. Moreover, in addition to the low sludge production, the results obtained showed that the sludge produced does not longer require the aerobic/anaerobic stabilization.

In treating mature landfill leachate (influent COD of 24,400 mg/L and influent TSS of 1,540 mg/L), a SBBGR showed removal efficiencies of 78% for COD and 76% for TSS at an organic loading rate (OLR) of 1.1 $\mathrm{kg_{COD}/m^3 \cdot d}$ and 68% for COD and 60% for TSS at an OLR of 4.5 $\mathrm{kg_{COD}/m^3 \cdot d}$ (i.e., a fourfold increase in OLR produced only a slight reduction in COD removal efficiency). Sludge production values lower than 0.02 $\mathrm{kg_{TSS}/kg_{CODremoved}}$ were also recorded [53].

In the treatment of tannery wastewater (influent COD of 2,600–3,500 mg/L and influent TSS of 300–800 mg/L), constant high COD removal efficiencies (always higher than 90%) were obtained as the OLR was increased from 1.0 to 3.5 $\mathrm{kg_{COD}/m^3 \cdot d}$. TSS removal was higher than 80%, with effluent concentrations lower than 40 mg/L, and a sludge production of 0.1 $\mathrm{kg_{TSS}/kg_{CODremoved}}$ was measured [54].

Finally, during the treatment of textile dyeing wastewater, SBBGR showed good treatment efficiencies up to OLRs of 2.6 $\mathrm{kg_{COD}/m^3 \cdot d}$ with effluent concentrations suitable for discharge into the sewer system. Surfactant removal was also satisfactory, included in the range 40–90%, with an average value of 70%, and effluent concentrations around 3–4 mg/L. More than 50% removal (and even higher than 90%) was always obtained for TSS, with effluent concentrations below the discharge limits for the whole experimental period. The specific sludge production turned out to be lower than 0.1 $\mathrm{kg_{TSS}/kg_{CODremoved.}}$ [55].

5.3 Case Study: Removal of Endocrine Disruptors from Municipal Wastewater

In recent years the occurrence of endocrine disruptors in environmental compartments has become a matter of growing concern for their possible effects on both wildlife and humans [56]. In fact, due to their limited removal efficiency in conventional wastewater treatment plants, EDs end up in aquatic systems. It is suspected that many substances, belonging to different chemical classes (alkylphenols, PCBs, dioxins, pesticides, phytoestrogens, human and synthetic estrogens), may influence the hormonal system [57]. In particular, it is known that estrogens cause an estrogenic response in the reproductive apparatus and development of animals even at very low concentrations (ng/L) [58, 59], while other EDs are active at μg/L levels.

Natural steroids are excreted from the human body via biological fluids, mainly conjugated as glucuronides or sulfates, and are discharged into receiving waters after wastewater treatment [60]. In such forms they are less biologically active, but they can be activated by de-conjugation reactions, thus releasing free estrogens [61]. Fecal microorganisms present in sewage, such as *Escherichia coli*, can hydrolyze conjugated estrogens via glucuronidase and sulfatase enzymes [62]. Others sustain that most of the conjugated compounds, especially glucuronides, are degraded in WWTP and that residual conjugated sulfates and free estrogens are discharged into the environment [63].

Conventional municipal wastewater treatment plants usually show a low ability to remove EDs such as alkylphenols and steroid estrogens [63–65]. Therefore, the selection of the appropriate techniques for the efficient removal of EDs from wastewater is nowadays an issue of major interest.

SBBGR technology, operating under dynamic conditions and at high sludge age, enhances the metabolic activity of the biomass and then could allow the removal of pollutants present at very low concentrations, such as EDs. Therefore, a study was carried out at demonstrative scale for investigating the effectiveness of the SBBGR technology in removing EDs from municipal wastewater in comparison with a conventional activated sludge process. Among the EDs potentially occurring in municipal wastewater, the study focused on estrone (E1), 17β-estradiol (E2) (natural hormone derived from the biotransformation of cholesterol) [66], 17α-ethynylestradiol (EE2) (the synthetic hormone used as a contraceptive), 4-tert-octylphenol (4 t-OP) (a breakdown product of phenolic-based surfactants used in industrial applications) [67], and bisphenol A (BPA) (used in the production of polycarbonate epoxy resins, flame retardants, and many other products).

5.3.1 Experimental

The wastewater used in the study was the primary effluent of the wastewater treatment plant of Bari (350,000 PE), a Southern Italian city. Composite wastewater

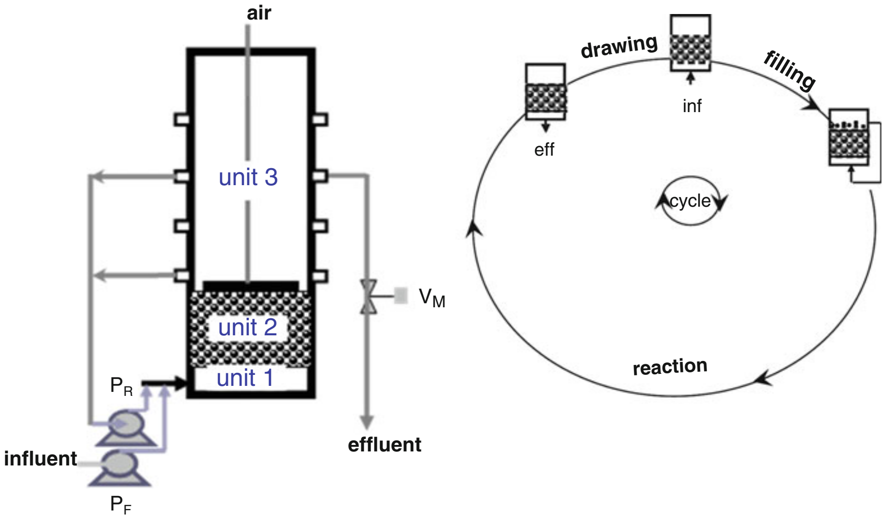

Fig. 9 Sketch of SBBGR system (on the *left*) and of its operation cycle (on the *right*)

samples were collected from the inlet and outlet of the biological stage (based on activated sludge process) of the plant. The inlet wastewater was also used for feeding the demonstrative SBBGR plant. Effluent samples were also collected from the SBBGR system. The demonstrative SBBGR plant consisted of a cylindrical zinc-plated steel reactor having a diameter and a height of 1 and 3.5 m, respectively. Looking at Fig. 9, which shows a sketch of SBBGR prototype, it is observed that it consisted of 3 cylindrical units laid one upon the other. In the lower unit (i.e., unit 1 in Fig. 9) the influent fed by volumetric pump P_F and/or the partially treated wastewater, taken from unit 3 by the recirculation pump P_R, is distributed by a reversed cone to unit 2. The central unit (i.e., unit 2 in Fig. 9) is the reactive zone containing the biomass. This unit is fully filled with biomass support material (KMT-k1 elements from Kaldness (Norway), 7 mm high, 8 mm diameter, specific area 690 m^2/m^3, density 0.95, and bed porosity 0.75). The upper unit (i.e., unit 3 in Fig. 9) acts as a storage aerated tank. Volumetric pump P_R takes the oxygenated liquid from unit 3 and feeds it to unit 1 at a flow rate of 2 m^3/h. The pump extracts the liquid at two different levels as shown in Fig. 9. Aeration was performed by a blower connected to diffusers (fine bubble disc system).

The operation of the SBBGR system was based on a succession of treatment cycles, each consisting of three consecutive phases: filling, reaction (under aerobic conditions), and drawing. During the filling phase, a fixed volume of wastewater to be treated was added (by the pump $P_{F,}$ see Fig. 9) to the liquid volume retained in the reactor from the previous treatment cycle. In the reaction phase, the filled wastewater was continuously aerated and recycled (by means of the pump P_R) through the biomass supporting material. Finally, the treated wastewater was discharged exploiting gravity by opening the motorized valve V_M, and then the plant was ready to start a new treatment cycle. The operative schedule (filling, recirculation, aeration, drawing, etc.) was completely automated, using a programmable logic controller (PLC).

A pressure meter set at the bottom of the bed reactor allowed online measurements of biofilter headloss due to biomass growth and captured suspended solids occurring during the operation of the reactor. When a fixed set value of headloss was reached, a washing step was carried out by compressed air until the headloss had decreased to a predefined value.

Samples (1 L) were concentrated using a previously published method [63]. ED determination was performed by HPLC/MS using a 1050-Ti chromatographic system (Agilent) interfaced to an API 165 mass spectrometer (Applied Biosystem/MSD Sciex) by means of a turboionspray interface. Alltima 5 μm C18 reversed-phase 250 × 3.2 mm column (Alltech) and a C18 4 × 2.0 mm precolumn (Phenomenex) were used with the following gradient: from 30/70 (acetonitrile/water) to 80/20 in 15 min, which was then held for 5 min. Chromatograms were acquired in selected ion monitoring (SIM) mode, with 300 or 500 ms dwelling time, using proper time windows. Quantitative determinations were performed by means of the standard addition technique using a three-level calibration up to 200 ng/L.

5.3.2 Results and Discussion

In order to verify whether the SBBGR system was more efficient than the conventional activated sludge process in removing EDs from municipal wastewater, the ED concentrations in the effluent of both full-scale WWTP and demonstrative SBBGR were monitored once a week for an operational period of five consecutive months and the output data compared. The results obtained are summarized in Table 3 in terms of mean value ± standard deviation. Considering that during the experimental period in most of the samples coming from both plants the EE2 concentration was below the quantification limit of the method, the EE2 data are not included in Table 3.

Data reported in Table 3 seem to indicate that SBBGR system was, in tendency, more efficient than the full-scale WWTP for all investigated EDs. In particular, as for BPA it was removed by both systems very efficiently, but the SBBGR system showed better performance over the whole experimental period. In fact, the average removal efficiencies were 74.2% and 88.9% for the full-scale WWTP and demonstrative SBBGR, respectively. Moreover, SBBGR system showed a larger stability in removing BPA as confirmed by the much smaller standard deviation. In the case of 17β-estradiol (E2) and 4-tert-octylphenol (4 t-OP), SBBGR showed removal efficiencies much higher than those of full-scale WWTP (72.0% and 84.7% for E2 and 4 t-OP, respectively, with respect to 39.6% and 61.2% obtained with the full-scale WWTP). Finally, regarding E1, although SBBGR plant showed the best performance, the removal efficiencies value obtained for this compound are only slightly higher than those of full-scale WWTP (58.5% against 51.2%).

Table 3 BPA, E2, E1, and 4 t-OP concentrations in influent and effluent, and their removal efficiencies, for full-scale WWTP and demonstrative SBBGR plant during a 5-month operation period (the results are reported in terms of mean value ± standard deviation – the standard deviation was calculated from all measurements)

ED		Full-scale WWTP	SBBGR
BPA	Influent (ng/L)	124.6 ± 31.6	
	Effluent (ng/L)	32.6 ± 35.0	12.2 ± 4.2
	Removal efficiency (%)	74.2 ± 23.9	88.9 ± 6.6
E1	Influent (ng/L)	46.8 ± 15.0	
	Effluent (ng/L)	24.4 ± 17.7	20.2 ± 15.1
	Removal efficiency (%)	51.2 ± 28.3	58.5 ± 30.0
E2	Influent (ng/L)	30.0 ± 4.9	
	Effluent (ng/L)	17.6 ± 3.0	8.3 ± 7.5
	Removal efficiency (%)	39.6 ± 15.2	72.0 ± 25.9
4 t-OP	Influent (ng/L)	52.4 ± 21.9	
	Effluent (ng/L)	18.8 ± 11.4	7.8 ± 8.9
	Removal efficiency (%)	61.2 ± 22.4	84.7 ± 17.9

The higher performances of the SBBGR system in removing the EDs can be explained considering its very high sludge age value (higher than 6 months) that offers a greater chance of removing endocrine disruptors. In fact, as it is known, the relatively high stability of these compounds in municipal effluents is mainly due to the insufficient sludge retention time of the conventional biological systems [67]. Moreover, as already mentioned, dynamic conditions in SBBGR enhance the metabolic activity of the biomass which in turn increases the chances of removing of "bioresistant" pollutants present at low concentrations.

6 Conclusion

Inexpensive commercial polymers, and even waste polymers, were demonstrated to be efficient sequestering phases in TPPBs for selected compounds, and a very small amount (5%, v/v) was sufficient to detoxify DCP at influent loads that were prohibitive for the conventional single-phase system. These findings open a new perspective to deal with xenobiotics in industrial WWTPs in order to produce effluents suitable for reuse being the proposed solution very flexible and modifiable to accomplish the requirements of the effluent standards. We can modify the solid partitioning phase as function of the pollutants, the bioreactor configuration, and the operating conditions and even use low-cost absorbent media (as tires) to face critical conditions related to xenobiotics.

As for the degradation processes based on UV and UV/H_2O_2, the results obtained in the described investigation confirm the effectiveness of UV-based processes, alone or in combination with H_2O_2, in degrading pharmaceutical intermediates potentially harmful for the environment. However, the processes used in this study require UV doses much greater than the ones used to disinfect water indicating that UV inactivation of microorganisms and UV degradation of organic chemicals operate on very different fluence scales.

As for the sequencing batch biofilter granular reactor, an innovative biological system developed in the last decade, the results obtained during an experimental campaign specifically addressed to the evaluation of the removal of endocrine disruptors compounds occurring in municipal wastewater have shown that SBBGR performs better than the conventional activated sludge system in removing E1, E2, BPA, and 4 t-OP. In fact, the average removal percentages of the above mentioned EDs, recorded during a 5-month operating period, were 58.5, 72.0, 88.9, and 84.7% and 51.2, 39.6, 74.2, and 61.2% for the SBBGR and activated sludge system, respectively.

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Conventional and New Processes for Urban Wastewater Disinfection: Effect on Emerging and Resistant Microorganisms

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Abstract The continuous release of chemical and microbiological pollutants into the environment and the increasing demand for safe water call for effective water and wastewater treatment processes. In particular, the detection of resistant microorganisms (e.g. antibiotic-resistant bacteria) in the effluents of urban wastewater treatment plants disposed into surface water or reused (e.g. in crop irrigation) shows that conventional treatments and disinfection processes do not effectively control the spread of pathogens into the environment. There is a need for new and more effective disinfection processes and technologies. The aim of this chapter is to briefly describe some of the emerging and antimicrobial-resistant microorganisms detected in wastewater, as well as the conventional and new advanced available technologies for wastewater disinfection, and to evaluate and discuss their effect on these microorganisms. Moreover, regulations and policies on wastewater reuse are also critically discussed and compared.

Keywords Antimicrobial-resistant bacteria, Nonconventional technologies, Wastewater disinfection, Waterborne pathogens

Contents

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Abbreviations

AOP	Advanced oxidation process
ARB	Antibiotic-resistant bacteria
ARG	Antibiotic-resistant gene
HAV	Hepatitis A virus
HEV	Hepatitis E virus
NDT	*N*-doped TiO_2
USEPA	US Environmental Protection Agency
WHO	World Health Organisation
WWTP	Urban wastewater treatment plant

1 Introduction

Effluent of urban wastewater treatment plants (WWTPs), if properly treated, can be reclaimed and reused for determined restricted uses, contributing in this way to the reduction of the pressure over the water scarcity worldwide.

Deep knowledge of the chemical and biological characteristics of this kind of water is required for adequate assessment of the limitations and risks associated to treated wastewater reuse. Various disinfection processes can be used to reduce the risk of diseases dissemination by pathogens present in WWTPs effluents; therefore, a great effort is being made through experimental research recently. Among the conventional disinfection practices, chlorination and application of UV-C and ozone are the most commonly used. However, other technologies are being actually under research in order to increase the efficiency of water disinfection and to overcome some limitations and drawbacks of the above-mentioned processes, reducing also the associated costs. In this sense, advanced oxidation processes (AOPs) have been proven to efficiently degrade a number of chemical and inactivate microbiological contaminants from wastewater.

Traditionally, research on water disinfection has been focused on coliforms (total/faecal, *Escherichia coli*), *Cryptosporidium* sp, *Giardia* cyst, *Legionella* sp, etc. Accordingly, policies and regulations on wastewater reuse set limits only for this kind of microorganisms for the different final reuse purposes. Nevertheless, new microbial detection techniques have revealed the presence of a wide range of other microorganisms in wastewater that represent new issues and concerns in the reuse of treated wastewater. These pathogens are being considered "emerging pathogens", as the concern of the society about their presence in treated water and water discharges to the environment is very recent [1]. This is the case of antibiotic-resistant bacteria (ARB). By them, genetic resistance material can be spread into the environment and finally result in a decrease of antibiotics' therapeutic efficacy against animal and human pathogens, especially when treated wastewater reuse strategies are in practice.

Different wastewater reuse guidelines and regulations currently available are based on similar chemical and microbiological parameters, although the maximum levels permitted for every rule vary. The most relevant guideline in this matter is the Water Reclamation and Reuse standard in the USA developed by Environmental Protection Agency [2]. The World Health Organization (WHO) in 1973 published the "Reuse of effluents: Methods of wastewater treatment and public health safeguards", a comprehensive guidance to protect public health and facilitate the rational use of wastewater and excreta in agriculture and aquaculture. A third edition of the WHO guidelines [3] for the safe use of wastewater, excreta and grey water was delivered, based on new health evidence, expanded to better reach key target audiences and reoriented to reflect contemporary thinking on risk management. At European level, there are several countries with national regulations for wastewater reuse. Many of them are based on the WHO guidelines. The most recent guide for water and wastewater reuse of Spain shows more restrictive criteria than those established in the wastewater WHO guidelines, including microbial load limits which depend on the type of microorganism and the type of final use and ultimate public access [4]. Other countries like Jordan, South Africa and Australia [5–7] have developed their own standards in this matter. Water quality requirements generally limit coliforms like total and faecal coliforms (TC and FC) or just *E. coli*. Other pathogens, such as viruses and protozoa, are seldom determined and are rarely required as control criteria [5–7]. A comparison of microbial water quality requirements for irrigation is shown in Table 1. Water quality can be achieved through conventional, widely practiced, secondary filtration and disinfection processes. However, as human contact increases, advanced treatment after secondary treatment may be required. Figure 1 shows a diagram of the main ways of wastewater treatments for different reuses according to USEPA recommendations [2].

Regarding wastewater reuse, there are two main concerns for human and environmental health risk: the potential risk of waterborne diseases for end users in contact with reclaimed wastewaters and/or the potential effects associated with

Table 1 Biological criteria of relevant international and national guidelines and recommendations in reclaimed water for irrigation

	Parameter				
WW reuse guidelines	Nematodes (eggs 10 L^{-1})	*Escherichia coli* (CFU 100 mL^{-1})	*Legionella* spp. (CFU L^{-1})	*Taenia saginata* *Taenia solium* (eggs L^{-1})	Enteroviruses, *Cryptosporidium* spp., *Giardia* spp.
WHO (2008)	Restricted ≤**10**	Unrestricted: ≤**10^{3}** (≤**10^{4}** for crops without root growing). Restricted ≤**10^{5}**. ≤**10^{4}** for 15-year-old users' exposure. **10^{6}** for mechanical irrigation	NR	NR	NR
	Unrestricted ≤**1**	Local irrigation: NR.			
USEPA (2012)	NR	Raw crops unprocessed: **no detectable**.	NR	NR	NR
		Raw crops processes; no raw crops: <**200**			
		Restricted areas: ≤**200**			
Australian (2006)	NR	Landscape irrigation (trees, shrubs, public gardens, etc.) <**10^{3}** (if not disinfected)	NR	NR	NR
		Commercial food crops consumed raw or unprocessed <**1**			
		Commercial food crops <**100**			
		Nonfood crops (trees, turf, woodlots, flowers) <**10^{4}**			

(continued)

Table 1 (continued)

	Parameter				
WW reuse guidelines	Nematodes (eggs 10 L^{-1})	*Escherichia coli* (CFU 100 mL^{-1})	*Legionella* spp. (CFU L^{-1})	*Taenia saginata* *Taenia solium* (eggs L^{-1})	Enteroviruses, *Cryptosporidium* spp., *Giardia* spp.
Spain (2007)	<**1**	Raw crops unprocessed <**100**	Raw crops unprocessed <**1,000**	Raw crops processes and irrigation for animals producers of milk and meat <**1**	NR
		Raw crops processes and irrigation for animals producers of milk and meat <**10^3**			
		Crops without water contact of products <**10^4**			
Italy[a] (2003)	NR	**10** (80% of samples)	NR	NR	NR
		Wetlands: **50** Stabilisation ponds: **100**			

[a]Reclaimed wastewater in Italy includes also the absence of *Salmonellae*
NR nonrecommended value

residual unregulated chemicals in the reclaimed wastewater persisting in the environment. The human groups more likely to be exposed to the health risks of wastewater reuse in agriculture are the farm workers, their families, crop handlers, consumers of crops and those living near wastewater-irrigated areas. Provision of adequate water supplies for consumption (to avoid consumption of wastewater) and for hygiene purposes (e.g. for handwashing) is important. Consumers can be protected by washing and cooking vegetables and by high standards of personal and food hygiene.

This chapter briefly describes some of the emerging and resistant microorganisms detected in wastewater and their implications for treated wastewater reuse and conventional and new advanced technologies for wastewater disinfection with regard to the effect on these microorganisms.

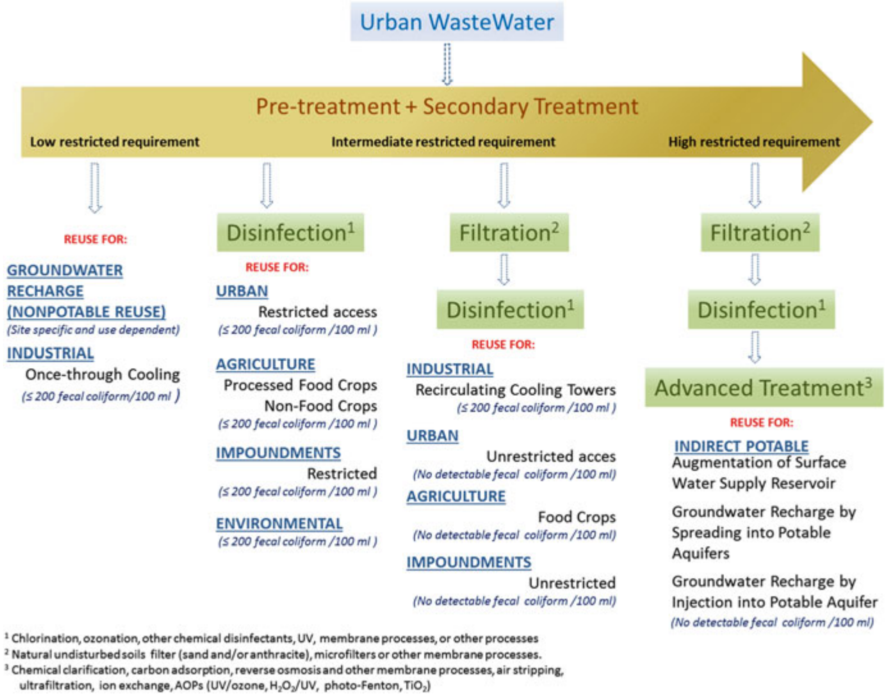

Fig. 1 Implementation stages for different water reuse practices according to EPA guidelines (adapted from USEPA [8])

2 Pathogenic and Antimicrobial-Resistant Microorganisms in Wastewater and Ecosystems

Waterborne pathogens and antimicrobial-resistant microorganisms (AMR) typically detected in wastewater and other aquatic environments are briefly introduced in this section. Relevant information about related human diseases and their occurrence in aquatic environments are summarised in Table 2.

2.1 *Enteric Viruses*

Many enteric viruses are very contagious due to their low infectious dose and disease transmission via different pathways, including contaminated food or water [34, 35]. These viruses can cause a wide range of illnesses including aseptic meningitis, myocarditis, respiratory and rash illnesses and acute gastroenteritis. They have been detected in various aquatic ecosystems (Table 2). Adenovirus is believed to be the second single largest cause of outbreaks (24%) after noroviruses

Table 2 Resistant microorganisms typically detected in aqueous ecosystems

Microorganism	Family	Human disease	Detected in
Adenovirus	Adenoviridae	Respiratory illness, gastrointestinal illness (occasionally), febrile illness in early childhood (bronchiolitis, pneumonia), conjunctivitis, tonsillitis, ear infection, croup, viral meningitis, encephalitis, haemorrhagic cystitis (rarely)	Bathing water and for recreational use [9], wastewater [10], river water [11]
Clostridium difficile	Clostridiaceae	Antibiotic-associated diarrhoea, pseudomembranous colitis, toxic megacolon, ileus, sepsis	Vegetables potentially exposed to contaminated water through irrigation [12], wastewater treatment plants [13]
Enterovirus	Picornaviridae	Mild respiratory illness, poliomyelitis, nonspecific febrile illness, aseptic meningitis (in children), Bornholm disease or epidemic pleurodynia, pericarditis and myocarditis, acute hemorrhagic conjunctivitis, herpangina, encephalitis (rarely), hand, foot and mouth disease	Coastal seawaters [14], drinking water [15], recreational water [16], wastewater [17]
Escherichia coli (0157)	Enterobacteriaceae	Gastrointestinal illness, hemorrhagic diarrhoea and kidney failure	Cattle [18], sheep, turkey and domestic animals (occasionally) and soil [19]
Helicobacter pylori	Helicobacteraceae	Acute gastritis, gastric cancer, gastric carcinoma, gastric mucosa-associated lymphoid tissue lymphoma and peptic ulcers	Coastal waters [20], water biofilms [21]
Hepatitis A virus	Picornaviridae	Hepatitis A, liver disease and jaundice	Marine waters [22], urban wastewater [23]
Hepatitis E virus	Hepeviridae	Hepatitis E (viral hepatitis, liver inflammation)	Urban wastewater [24, 25]
Klebsiella	Enterobacteriaceae	Pneumonia, urinary tract infections, septicaemia and soft tissue infections	Faeces of healthy animals and humans, drinking water [26]
Legionella pneumophila	Legionellaceae	Legionnaires' disease (atypical pneumonia), respiratory infections	Rivers [27], different water subsytems [28]
Salmonella enterica	Enterobacteriaceae	Mild self-limiting gastrointestinal illness, salmonellosis, typhoid fever	Contaminated irrigation water [29], river and seawater [30], urban wastewater [31]

(continued)

Table 2 (continued)

Microorganism	Family	Human disease	Detected in
Shigella sonnei	Enterobacteriaceae	Shigellosis, acute gastroenteritis, pneumonia and bloody diarrhoea	Recreational spray fountains, lakes, swimming pools and ground water sources [32, 33]

(45%) [36] and the second leading cause of viral gastroenteritis in children after rotavirus [37]. Hepatitis A virus (HAV) is responsible for approximately 1.5 million reported cases and tens of millions of infections each year, accounting for the most acute viral hepatitis worldwide [38]. HAV spreads by the faecal–oral route, either directly from person to person or via contaminated food or water, and infections often occur in conditions of poor sanitation and overcrowding [39]. Hepatitis E virus (HEV) infections typically occur in countries with poor sanitation systems, and for a long time, HEV was considered nonendemic in industrialised countries. However, in the last years, it has been more frequently detected in WWTP effluents from different European industrialised countries (Table 2).

2.2 *Enterobacteriaceae*

The Enterobacteriaceae is a large family of Gram-negative bacteria that includes, among others, many of the well-known/familiar pathogens, such as *Salmonella*, *E. coli*, *Klebsiella* and *Shigella*. There are only two species of *Salmonella*: *Salmonella bongori* and *Salmonella enterica*. All of the enteric pathogens are members of the species *S. enterica*. Salmonellosis is a disease associated with the consumption of raw vegetables, fruits and undercooked food, which are contaminated by *S. enterica*. Every year, approximately 40,000 cases of salmonellosis are reported in the USA [40]. *E. coli* is considered the most suitable index of faecal contamination. Most *E. coli* strains are harmless, but some of them are pathogenic and can cause different illnesses such as diarrhoea, urinary tract infections, bacteraemia and meningitis. *E. coli* O157:H7 is increasingly causing foodborne and waterborne illnesses [41]. This strain produces a powerful toxin and causes severe bloody diarrhoea and abdominal cramps. *Klebsiella* is a natural inhabitant of many water environments and may multiply to high numbers in waters rich in nutrients, such as pulp mill wastes, textile finishing plants and sugar-cane-processing operations [26]. *Klebsiella* can cause nosocomial infections and can lead to pneumonia, urinary tract infections, septicaemia and soft tissue infections. All *Shigella* species (*dysenteriae*, *flexneri*, *boydii* and *sonnei*) can produce severe disease, but illness due to *Shigella sonnei* is usually relatively mild and self-limiting. *Shigella* infection may be acquired by eating contaminated food or by drinking, swimming in or playing with the contaminated water [40].

2.3 Clostridium difficile

Clostridium difficile is a Gram-positive, anaerobic, endospore-forming bacterium, commonly considered as nosocomial pathogen that causes antibiotic-associated diarrhoea and pseudomembranous colitis [42]. *C. difficile* associated to diarrhoea can result in health-care-associated mortality, particularly among elderly people. Its main virulence factors are toxins. Toxigenic strains of *C. difficile* produce different toxins that directly mediate diarrhoea and colitis. Environment and animals are suspected to be important reservoirs/sources of exposure to *C. difficile*, but only a few studies have reported its isolation, particularly from water ecosystems [13, 43].

2.4 Legionella pneumophila

Legionella pneumophila is an aerobic, flagellated, non-spore-forming, Gram-negative bacterium. It is the major waterborne pathogenic bacterium which is the main cause of Legionnaires' disease or legionellosis [26]. *L. pneumophila* is a ubiquitous environmental microorganism found in freshwater [44] and has been isolated from various man-made water systems [45].

2.5 Antibiotic-Resistant Bacteria

In particular, urban wastewater treatment plants (WWTPs) [46] and hospital [47] effluents are among the anthropogenic sources of antibiotics and antibiotic-resistant bacteria (ARB) spread into aqueous ecosystems. Other potential sources of ABR are the manure and grey waters from treated cattle and other animals. Among the antimicrobial-resistant pathogens, methicillin-resistant *Staphylococcus aureus* (MRSA) [48, 49] and vancomycin-resistant *Enterococcus* spp. (VRE) [47, 50] are some of the most investigated. MRSA has also been found in different aqueous environments, such as WWTP effluents [51, 52], and marine water from temperate and warmer climates [53]. VRE is a leading cause of hospital-acquired infections, but a high prevalence of VRE has also been observed in WWTPs [50, 54].

3 Wastewater Disinfection by Conventional Processes: Effect on Emerging Microorganisms

Chlorination and UV radiation are typically used for urban wastewater disinfection, but application of ozone has also been attracting interest because of its capacity to simultaneously inactivate microorganisms and decrease the load of trace organic

Table 3 Effect of different water disinfection processes on the inactivation of resistant microorganisms

Microorganism	Disinfectant	Dose	Inactivation	Reference
Chloramphenicol-resistant bacteria	NaOCl	CT = 100 mg min L^{-1}	Increased ARB proportion	[56]
Chlorotetracycline-resistant heterotrophic bacteria	O_3	CT = 6 mg min L^{-1}	3-log reduction ($C_0 = 3.4 \times 10^5$ CFU mL^{-1})	[57]
Heterotrophic ARB (cephalexin, ciprofloxacin, erythromycin, gentamicin, vancomycin, sulfadiazine, rifampicin, tetracycline and chloramphenicol)	UV radiation	5 mJ cm^{-2}	1.0 ± 0.1 to 2.4 ± 0.1-log reduction	[58]
		50 mJ cm^{-2}	($C_0 = 10^3$ to 10^4 CFU mL^{-1})	
			Complete inactivation with the highest dose	
MDR (amoxicillin, ciprofloxacin and sulfamethoxazole) *E. coli* strains	NaOCl	CT = 120 mg min L^{-1}	99.999% ($C_0 = 10^6$ CFU mL^{-1})	[59]
	UV radiation	12.5 mJ cm^{-2}	99.999% (MDR1) ($C_0 = 1.5 \times 10^6$ CFU mL^{-1}). Not total inactivation (MDR2) ($C_0 = 1.5 \times 10^6$ CFU mL^{-1})	[60]
		25 mJ cm^{-2}		
MDR *E. coli* HB101 (plasmid DNA)	O_3	CT = 300 mg min L^{-1}	Total inactivation	[61]
Tetracycline-resistant *E. coli*	NaOCl	CT = 10 mg min L^{-1}	The average tetracycline resistance increased	[62]
	UV radiation	10 mJ cm^{-2}	4 log ($C_0 = 10^7$ CFU mL^{-1})	[62]
		80 mJ cm^{-2}	6 log ($C_0 = 10^7$ CFU mL^{-1})	

ARB antibiotic-resistant bacteria, *CT* disinfectant concentration × contact time, *CFU* colony-forming unit, *MDR* multidrug resistant chemicals [55]. In this section, the effect of these disinfection processes on the inactivation of resistant microorganisms is briefly reviewed, and the relevant data (disinfectant dose and inactivation rate) are summarised in Table 3.

3.1 Chlorination

Chlorination is one of the most commonly used disinfection processes because of its cost-effectiveness. As the final step in the wastewater treatment process, it involves adding chlorine gas (Cl_2), calcium hypochlorite ($Ca(OCl)_2$) or sodium hypochlorite (NaOCl), to water. These compounds form hypochlorous acid (HOCl), which is the active agent in chlorination besides Cl_2.

Chlorination has been proven to be effective against a range of waterborne pathogens. Different mechanisms can take place in the inactivation of microorganisms by chlorine, such as the oxidation of germ cells, the inhibition of enzyme activity and the damage of the cell wall membrane. Unfortunately, the chlorination process is not sufficiently effective in the inactivation of several pathogens, like viruses. For example, Katayama et al. [63] detected enteroviruses in 41 of 71 samples and adenoviruses in all samples collected after the chlorination process from six different WWTPs.

Early studies on the effect of chlorination process on ARB in wastewater date back to the 1970s [64]. More recently, Huang et al. [56] showed that the inactivation rates of ARB (namely, chloramphenicol-, rifampicin-, tetracycline-resistant bacteria) were not lower than that of total heterotrophic bacteria, even if the proportion of several ARB increased after chlorination. The same group also showed that the chlorination process increased the average tetracycline resistance of tetracycline-resistant *E. coli* [62]. Particularly, the inactivation rates of tetracycline-resistant *E. coli* were lower than those of antibiotic-sensitive *E. coli* when the initial concentration of chlorine was higher than 1.5-mg $Cl_2\ L^{-1}$. Accordingly, the chlorination process could select for tetracycline-resistant bacteria in drinking water and wastewater.

In contrast, Templeton et al. [65] did not observe any selection of chlorination process for ampicillin-resistant and trimethoprim-resistant *E. coli* strains, during water and wastewater treatment. Moreover, the chlorination process did not affect antibiotic resistance (measured as minimum inhibitory concentration, MIC) of indigenous multidrug-resistant *E. coli* strains under chlorine dose typical for wastewater disinfection [59]. Finally, Munir et al. [66] did not observe any significant ($p > 0.05$) contribution of the chlorination process to ARB and ARG reduction in five full-scale WWTPs in Michigan (USA). Therefore, the mechanism of how chlorination contributes to ARB and ARG selection in wastewater remains still unclear; more research in this matter is required.

3.2 Ozonation

The ozonation process is typically used for disinfection and oxidation of water and wastewater. Ozone can effectively inactivate protozoa, such as *Cryptosporidium* and *Giardia*, resistant to chlorination process [67, 68]. The required ozone exposure is quite high, and this may result in the formation of unwanted disinfection by-products, in particular bromates (in the presence of bromide), a potential human carcinogen [69]. On the other hand, low dosage may not effectively inactivate some cysts, protozoa, spores and viruses [70]. The effectiveness of the process depends on many factors, such as the concentration of ozone, the contact time, the target organisms and wastewater characteristics. Selma et al. [71] investigated the inactivation of *S. sonnei* (10^8 CFU mL^{-1} as initial concentration) by ozone and observed a 3.7- and 5.6-log unit reduction after 60 s with 1.6 and 2.2 mg L^{-1} as initial ozone doses, respectively.

The effect of ozonation on ARB has been addressed only in a few studies. Öncü et al. [61] investigated the effectiveness of chlorine and ozone disinfection on the reduction of the presence of antibiotic-resistant microorganisms compared with that of less commonly applied heterogeneous photocatalytic process. Chlorine did not affect plasmid DNA structure at the studied doses, while ozone (1–4.42 mg L^{-1}, 1-min contact time) and photocatalytic treatment resulted in conformational changes and the damage increased with increasing oxidant doses. Finally, Lee et al. [57] investigated the effect of ozonation process on the inactivation of chlortetracycline-resistant bacterial population in livestock wastewater and observed 3-log reduction of these bacteria concentration in 10-min treatment.

3.3 UV Radiation

UV radiation is another disinfection treatment that finds extended applications globally. UV (UV-C) radiation is absorbed by the microorganism's genetic material, such as DNA and RNA, resulting in the inhibition of cell replication and, in case of lethal doses, in a loss of reproducibility. The optimum wavelength range to effectively inactivate microorganisms is 250–270 nm. The UV dose is the key parameter to indicate how UV treatment was applied to a certain wastewater; it is defined as the product of the average UV intensity (typically expressed as mW cm^{-2}) and the average exposed time (s) of the fluid to be treated.

According to the studies available in scientific literature, UV radiation treatment may be not effective in the inactivation of ARB and ARG reduction under commonly applied doses for wastewater disinfection (typically lower than 30 mJ cm^{-2}). Guo et al. [58] observed total inactivation of the ARB investigated only at high UV dose (50 mJ cm^{-2}). But they also observed an effect of UV radiation on ARB selectivity and ARG reduction [72]; in particular, the disinfection process decreased the proportion of erythromycin-resistant bacteria, increased that of tetracycline-resistant bacteria and reduced erythromycin- and tetracycline-resistant gene concentrations. According to the references found in the literature, damage of ARGs requires really high UV dose (200–400 mJ cm^{-2}) compared to that required for ARB inactivation (10–20 mJ cm^{-2}, 4–5-log reduction) [73]. Moreover, no statistically significant difference was observed in the inactivation of antibiotic-resistant and antibiotic-sensitive *E. coli* strains [62, 65]. Nevertheless, UV radiation has been found that may affect antibiotic resistance of bacteria surviving disinfection process [60].

When the effect of UV disinfection was evaluated at full scale, investigators did not observe any significant reduction of ARB and ARGs ($p > 0.05$) [66]. Also the statistical t-test between concentrations of ARGs in pre- and post-disinfected effluent did not show a significant difference between UV and chlorination disinfection process ($p > 0.05$). A similar result was observed in another study, in which UV disinfection did not cause a significant reduction of tet(G) or tet(Q) levels in wastewater effluents [74]. The investigators underline that although it was difficult to draw clear conclusions, UV disinfection may or may not reduce the abundance of some tetR gene types and does not reduce tetR genes diversity. In another full-scale study, Francy et al. [75] detected adenovirus in the effluent of UV disinfection process in percentages between 25% and 36%. These detection percentages were lower than those observed in post-chlorine disinfection (75%) in another WWTP. Particularly, UV after conventional secondary treatment provided lower log removals for adenovirus (median 0.24) than chlorine (median 0.81).

Therefore, UV and chlorination may not produce significant effect over ARB and ARG in wastewater, although the reasons remain still unclear. Some studies evidence a selection process for ARB and ARG produced by these treatments, but this is not always the case; it depends on the antibiotic and the bacteria.

4 Wastewater Disinfection by Nonconventional Processes

4.1 Advanced Oxidation Processes (AOPs)

AOPs are oxidative processes operated using different oxidative agents like O_3, H_2O_2 or even O_2, catalyst and/or UV radiation for treating wastewater containing hazardous organic compound and pathogens. They are based on generating oxidative hydroxyl radicals ($HO^{\bullet}$), which have very low selectivity and permit the degradation (total or partial) of a number of organic compounds. The most studied AOPs for water purification are Fenton, photo-Fenton, TiO_2 photocatalysis, UV/O_3 and UV/H_2O_2 [76]. Most of the studies are focused on the evaluation of the efficiency of AOPs using models of microorganisms like *E. coli* or *Bacillus* sp, *Cryptosporidium* and *Giardia* due to their high resistance to most of water disinfection treatments commonly used. However, when the research is addressed for recycling and reuse of treated wastewater for different end uses, the presence of other microorganisms becomes also relevant due to their importance for the specific end use of the treated water and their capability to spread not only human but also animal and plant diseases and antimicrobial resistances. This is the case of the ARB. Up to date, there are only few works evaluating the effect of AOPs on ARB.

The use of UV and H_2O_2 increases the efficiency of the UV treatment because $HO^{\bullet}$ radicals are generated by the photolysis of the H_2O_2 at short wavelengths (UV-C spectrum).

In contrast with UV disinfection, UV/H_2O_2 is based on two mechanisms: (1) absorption of UV photons (UV-C range) leading to excitation of molecules and bonds breaking in the DNA molecule and (2) reaction of some functional groups of organic molecules with the $HO^{\bullet}$ formed. When both water disinfection techniques are compared, the required doses to inactivate microorganisms vary a lot, clearly because of variability of water composition, optical properties and biological nature of the contamination. UV dose is directly related to the input energy, which is about 35 times higher for UV/H_2O_2 oxidation (500–750 mJ cm^{-2}) than for UV disinfection (20–70 mJ cm^{-2}). The higher the energy input, the easier molecular bonds are broken.

Several studies demonstrated the effectiveness of UV/H_2O_2 to remove *Bacillus* sp. from water. Zhang et al. [14] evaluated the efficiency of various combinations of UV and H_2O_2 adding to inactivate *Bacillus subtilis* spores. They proved the effect of sequential combinations including UV–H_2O_2, H_2O_2–UV and simultaneous (UV/H_2O_2) processes to reduce the presence of these microorganisms in water. They showed improved inactivation of *B. subtilis* spores in water (4.13-log reduction) using simultaneous UV/H_2O_2 with 0.60 mM of H_2O_2 and 113.0 μW cm^{-2} UV for 6 min; this was compared with UV followed by H_2O_2 (3.03 log) and H_2O_2 followed by UV (2.88-log reduction). Venieri et al. [77] investigated the efficacy of photocatalysis (UV-A/TiO_2), photolysis (UV-C) and sono-chemical treatments for the inactivation of *Bacillus anthracis*. These authors found that UV-C irradiation was by far more effective, as complete inactivation reduction from 10^6 CFU mL^{-1} to detection limit was achieved within 10 min. Moreover, after inactivation with UV-C, photo-reactivation of bacteria after the treatment did not occur until 72 h after the end of the treatment.

The efficiency of photo-Fenton process for water disinfection can be explained by the increased amount of $HO^{\bullet}$ generated through the catalytic cycle of iron ions (Fe^{2+} and Fe^{3+}) combined with H_2O_2 and UV–vis photons. High $HO^{\bullet}$ production is favoured by UV–vis irradiation up to a wavelength of 600 nm. After photo-dissociation of Fe^{3+} organic complexes, ferrous ions are regenerated and reinitiate the Fenton reaction, thus closing the photocatalytic cycle and generating more hydroxyl radicals and eliminating the need for further addition of iron.

Regarding ARB, Cengiz et al. [78] investigated the removal of tetM gene and its host *E. coli* HB101 from synthetically contaminated cow manure with Fenton and ozone oxidation processes. They observed a decrease of the tetM gene by increasing the Fenton reagent and the applied ozone dose.

Heterogeneous photocatalysis with the semiconductor TiO_2 has been used very efficiently to degrade hazardous pollutants and pathogens in water [76]. When the semiconductor particle is photoexcited by photons with energy above the semiconductor band-gap ($E_G = 3.2$ eV, $\lambda < 385$ nm for TiO_2), an electron from the valence band is promoted to the conduction band, leaving an electron vacancy ("hole") in the valence band, thus generating electron/hole pairs. This can lead to both reductive and oxidative processes at/or near the surface of the semiconductor particle. In the presence of oxygen, oxygen molecules are able to scavenge conduction band electrons to form superoxide ions ($O_2^{\bullet -}$), and photo-generated holes generate $HO^\bullet$ in the presence of adsorbed water molecules [79]. The efficacy of TiO_2/UV-A and the effect of UV-A irradiation on *Cryptosporidium parvum* oocyst inactivation were evaluated by Ryu et al. [80]; 1.3-, 2.6- and 3.3-log reduction of these oocysts was shown at UV-A doses of 2.7, 8.0 and 40 mJ cm^{-2}, respectively. The efficiency observed during UV-A (>315 nm)/TiO_2 photocatalytic treatment leads to only less than 0.28-log inactivation of oocysts, while the synergistic effect of germicidal UV-C (254 nm)/TiO_2 resulted in 2-log and 3-log oocyst inactivation with 4.0 and 11.0 mJ cm^{-2}, respectively.

4.2 Solar-Driven AOPs

It is well known that AOPs using natural sunlight have the advantage of lowering the treatment cost, although the availability of the photons is limited by night–day cycles and weather. The main AOPs conducted under natural sunlight for water disinfection are photocatalysis with TiO_2 and photo-Fenton.

Rincón and Pulgarin [81] investigated the photocatalytic efficiency of TiO_2 in a coaxial photocatalytic reactor for water contaminated by a mixture of *E. coli* and *Bacillus* sp. as well as wastewater containing a larger microbial community. *E. coli* was more sensitive to the treatment than *Enterococcus* sp., coliforms (other than *E. coli*) and Gram-negative (other than coliforms) and *Bacillus* sp. The inactivation rate of *B. subtilis* and *Bacillus cereus* with TiO_2 photocatalysis with monochromatic UV lamp (7 mW cm^{-2} at 365 nm) and sunlight (irradiation intensity at 365 nm of ~4 mW cm^{-2}) was investigated by Armon et al. [82], *B. subtilis* showed 4-log reduction at 0.25 g L^{-1} of TiO_2 after irradiation for 300 min in water, while *B. cereus* subjected to similar photocatalytic conditions was reduced by five orders of magnitude. In this study, a comparison between using artificial and natural (sunlight) UV irradiation was also investigated on both microorganisms. Better results with sunlight for *B. subtilis* were observed, while no difference between the two irradiation sources was found in the case of *B. cereus*.

The modification of the physicochemical characteristics of TiO_2 to increase the $HO^\bullet$ generation is currently under investigation. Several works could be found in literature on the use of modified TiO_2 for inactivation of microorganisms. *N*-doped TiO_2 (NDT) photocatalytic material was investigated to find out its disinfection capability when UV-A is irradiated against ARB isolated from WWTP [83]. The ARB used was *E. coli* resistant to vancomycin and tetracycline. The photocatalytic efficiency was compared with other commercially available TiO_2 powders

(Millennium PC50 and PC100) using solar simulator (250 W Lamp) and different catalyst load (0.025–0.5 g L^{-1}). This study showed that 0.2 g L^{-1} of NDT leads to the highest inactivation rate (8.5×10^5 CFU 100 mL^{-1} min^{-1}, after 10 min of irradiation) for the vancomycin- and tetracycline-resistant *E. coli* strain. Moreover, NDT did not significantly affect resistance of *E. coli* strain to tetracycline and vancomycin as irradiation time increased using an antibiotic-resistant test (Kirby–Bauer). Inactivation of *E. coli* cells and *B. subtilis* spores with composite nanostructured samples of Ag (0.5–20%)/(C, S)-TiO_2 has been also studied [84]. Ag/(C, S)-TiO_2 nanoparticles (crystallite size <10 nm) showed good antimicrobial properties against both *E. coli* (>8-log reduction) and *B. subtilis* spores (>5-log reduction) after 30-min exposure without light activation.

Recently, the efficiency of solar-driven photo-Fenton process for inactivation of antibiotic-resistant enterococci was investigated [85]. In this work, all enterococci including those resistant to ofloxacin and trimethoprim had been completely eliminated at the end of the treatment. Comparing the resistance rates against these two antibiotics led to the conclusion that ofloxacin resistance was almost double that of trimethoprim.

Agulló-Barceló et al. [86] investigated the efficiency of several solar treatments in a pilot solar CPC reactor (25 L): TiO_2 (100 mg L^{-1}), photo-Fenton (pH 3 – Fe, 10 mg L^{-1}; H_2O_2, 20 mg L^{-1}) and H_2O_2/Solar (H_2O_2 concentration of 20 and 50 mg L^{-1}) on the inactivation of 4 different wastewater pathogens from real wastewater effluent. Naturally present *E. coli*, spores of sulphite-reducing clostridia (SRC), somatic coliphages (SOMCPH) and F-specific RNA bacteriophages (FRNA) were tested. The inactivation efficiency order found for *E. coli* was photo-Fenton at pH 3 > H_2O_2 (20 mg L^{-1}) > TiO_2. For viral indicators, the ranking was photo-Fenton pH 3 > TiO_2 > H_2O_2 (20 mg L^{-1}), and SRC showed a higher resistance in all the evaluated processes. Therefore, photo-Fenton at pH 3 was the most effective treatment due to the extreme conditions of pH, which compromise the viability of most of waterborne microorganisms. Other solar AOPs used were more effective depending on the microorganism observed.

4.3 Sequential Disinfection Treatment

In this type of disinfection sequence, a strong primary disinfectant is firstly applied to achieve a portion of the target inactivation level followed by the secondary disinfectant to attain further inactivation and to provide residual disinfection for water distribution. When several disinfectants are applied consecutively, it is often found that the overall inactivation level achieved is higher than the sum of the inactivation levels achieved when each disinfectant is applied independently (as separate single-step disinfection process). For instance, the sequential application of ozone (or ozone/H_2O_2) followed by free chlorine was shown to achieve a higher level of inactivation of *B. subtilis* spores than the sum of the inactivation obtained with individual treatment by ozone (or ozone/H_2O_2) and free chlorine

[87]. This enhanced inactivation is referred to as synergism, which is beneficial since it leads to a reduction in the amount of disinfectant and reaction time.

There are few reports in the literature on the synergism of sequential disinfection processes with UV or UV/H_2O_2 followed by free chlorine. Some research groups did not observe any synergism in the sequential disinfection processes using UV alone in the primary step for MS-2 bacteriophage [88] and *B. subtilis* spores [87]. Nevertheless, a strong synergistic effect during the sequential application of the UV/H_2O_2 disinfection followed by free chlorine was observed in the inactivation of MS-2 phage and *B. subtilis* spores compared to UV irradiation (without H_2O_2) followed by free chlorine [87]. In another work [89], Fenton-like processes and UV-A/TiO_2 alone and coupled with free chlorine treatment in sequential mode for *B. subtilis* spore removal was evaluated. Fenton-like processes were more effective than suspended TiO_2 alone. Moreover, the authors demonstrated that the inactivation of *B. subtilis* spores using chlorine can be enhanced by primary treatment with photocatalysis.

5 Conclusions

The appearance and spread of resistant microorganisms (e.g. ARB and ARG) in the effluents of urban wastewater treatment plants disposed into surface water or reused wastewater is one of the biggest threats to the society related to domestic wastewater. This problem clearly demonstrates that conventional wastewater treatments and disinfection processes do not effectively control the spread of pathogens and antimicrobial resistance into the environment. Chlorination may not produce significant effect over ARB and ARG in wastewater, although the reasons remain still unclear. Some studies evidence a selection process for ARB and ARG produced by these treatments, but this is not always the case. Actually, few works investigate the effect of ozonation over antimicrobial-resistant microorganisms; although they show promising results, the problem of DBP formation in the presence of bromide remains still a big issue. On the other hand, UV radiation has been found to affect antibiotic resistance of bacteria and genes surviving disinfection process for very high dosage, compared with the common UV doses applied for disinfection of water with common bacterial strains. Advanced oxidation processes to control ARB and ARG have been investigated. For example, Fenton and ozonation lead to good results for removal of ARG; other ARB can be also effectively removed using *N*-modified titania as photocatalyst under UV-A irradiation. Although some research is being done to control ARB and ARG using AOPs, the mechanisms to effectively inactivate these microorganisms remain still unclear, and new research has to be carried out to accomplish this challenge.

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Impacts of Advanced Oxidation Processes on Microbiomes During Wastewater Treatment

Johannes Alexander, Popi Karaolia, Despo Fatta-Kassinos, and Thomas Schwartz

Abstract The increase of antibiotic resistance in clinical settings but also in wastewater treatment plants is of increasing concern to human health. The goal of this chapter is to investigate the potential of different tertiary wastewater treatment technologies as to the reduction of the amount of antibiotic-resistant bacteria and genes in wastewater effluents. Molecular- and cultivation-based techniques are reported in the current scientific literature for the analysis of bacterial communities and especially opportunistic pathogenically bacteria in wastewater and after different levels of disinfection processes. Additionally, the presence of antibiotic resistance genes (*van*A, *mec*A, *amp*C, *erm*B, *bla*VIM, *tet*M) and phenotypic resistance to ciprofloxacin, cefuroxime, trimethoprim, ofloxacin, and tetracycline were analyzed to characterize the impact of different wastewater treatments and advanced oxidation processes (AOPs) on the effluent antibiotic resistance patterns. The examination of the application of advanced oxidation and photo-driven technologies showed significant discrepancy among the removal of different bacterial families as well as bacterial species in wastewater.

Keywords Antibiotic-resistant bacteria, Ozone treatment, Photo-Fenton treatment, TiO_2 photocatalysis, UV-light, Wastewater reuse

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Contents

Abbreviations

·HO	Hydroxyl radical
AmpC	Ampicillin resistance gene
AOP	Advanced oxidation process
ARB	Antibiotic-resistant bacteria
ARG	Antibiotic resistance gene
blaVIM	Imipenem resistance gene
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
ermB	Erythromycin resistance
H_2O_2	Hydrogen peroxide
HGT	Horizontal gene transfer
intI1	Integron 1
mecA	Methicillin resistance gene
O_3	Ozone
recA	Gene coding for the bacterial DNA recombination protein
ROS	Reactive oxygen species
Sul1	Sulfonamide resistance
tetG	Tetracycline resistance gene G
tetM	Tetracycline resistance gene M
tetW	Tetracycline resistance gene W
tetX	Tetracycline resistance gene X
TiO_2	Titanium dioxide
UV	Ultraviolet radiation ranging from 400 to 100 nm
UV-C	Specific wavelength of 280–100 nm
vanA	Vancomycin resistance gene
WWTP	Wastewater treatment plant

1 Introduction

The reuse of treated wastewater, especially in agriculture, is an appealing and practical solution to address water scarcity as it significantly relieves pressure on water resources [1, 2]. However, quality standards are required to ensure safe use of wastewater and to avoid biological risks to human health. In this context, the dissemination of antibiotic-resistant bacteria (ARB) and antibiotic resistance genes (ARGs) from wastewater irrigation to natural soil and water environments is of public concern because it may contribute to local and global antibiotic resistance spreading. The use of treated wastewater in agricultural irrigation has also been found to have additional agronomic benefits associated with soil structure and fertility due to the residual nitrogen and phosphorus levels. Wastewater has a higher nutritive value compared to freshwater and may improve plant growth, reduce fertilizer application rates, and increase productivity of poor fertility soils [3].

The ongoing technological development of wastewater treatment processes has so far contributed to the significant reduction of waterborne diseases. Over the last decades, the occurrence of new chemical and microbiological contaminants in the aquatic environment has become an issue of increasing environmental concern. Wastewater is among the main sources of antimicrobial substances released into aquatic systems. Recent studies have identified increased abundance of clinically relevant ARB in the sediments nearby the effluents of wastewater treatment plants (WWTPs) and adjacent downstream aquatic habitats [4–6]. These systems play an important part in the distribution of pathogens and antibiotic resistance [7]. Current WWTPs are designed to remediate solids, degradable organic chemicals, and nutrients, but offer no specific removal mechanism for pathogenic bacteria. Advanced oxidation processes (AOP) offer a possibility to reduce or inactivate biologically and chemically potent agents through the in situ production of highly reactive hydroxyl radicals ($HO^\bullet$). $HO^\bullet$ can oxidize any biological target structure such as fatty acids (biomembranes), proteins (enzymes), nucleotides (DNA), etc., and would therefore be a suitable candidate for the reduction of the microbiological load of secondary treated wastewater. $HO^\bullet$ can be produced by one or more primary oxidants (e.g., ozone, hydrogen peroxide, and oxygen) in combination with ultraviolet light or catalysts (e.g., titanium dioxide). Chemical compounds present in industrial wastewater or household products can be transformed into intermediate products or become oxidized to stable inorganic compounds like carbon dioxide and salts in the case of complete mineralization. However, little is known about the effects of the treatment by AOPs on the structure of microbiomes of secondary treated wastewater.

Recent studies investigated the fate of clinical relevant ARGs and pathogenic microorganisms within the bacterial populations of wastewater [7]. The observed antibiotic resistance patterns are developed due to antibiotic treatment and represent a current threat to human health. Antibiotics are among the most successful drugs to treat a bacterial infection. Every year, large amounts of these pharmaceuticals are used in human and veterinary therapy. For example, Germany counted about 38 million prescriptions of antibiotics in human medicine in the year 2011 and used more than 1619 tons of antibiotics for veterinary purposes in 2012 [8]. Due to their incomplete metabolism in humans or due to disposal of unused antibiotics via lavatories, a large amount of antibiotics is released into municipal wastewater and thereafter into the aquatic environment. Low concentrations of antibiotics (9–244 ng/L) were found in the effluent of urban wastewater treatment plants [9–11]. These concentrations are unable to inhibit bacterial growth, but they modulate the transcription level of bacteria by at least 5% of the whole bacterial transcriptome [12, 13]. This transcriptome-modulation is responsible for relevant cell responses like virulence, sporulation, biofilm formation, and antibiotic production. In addition, low levels of antibiotics can increase the mutation ratio that can lead to antibiotic resistance development. Since mutations are known as spontaneously occurring processes promoted by several clinical but also environmental stimuli in bacteria, it is hard to specify critical hotspots. In contrast to clinical situations, mutated bacteria in wastewater system might be selected and proliferate due to their exposure to lower concentration of antibiotics. Experiments with wild-type *E. coli* treated with sublethal concentrations of antibiotics (i.e., below the MIC) resulted in significant increase in mutation rate relative to an untreated control [14]. It was demonstrated that these effects can lead to mutant strains that are sensitive to the applied antibiotic but resistant to other antibiotics or induce multidrug resistance. Therefore, ARGs can be acquired by a wide range of bacteria. With the molecular biological techniques specialized in the detection of ARGs in addition to cultivation methods, it is possible to overcome the problem related to the noncultivation of the majority of the bacterial population. The presence of transferable ARGs is not limited to cultivable bacteria, and therefore, their abundance in the total bacterial population is underestimated if only cultivation techniques are used. Despite this issue, cultivation techniques can provide useful information on the abundance of specific multiresistant opportunistic bacteria relevant for human health.

The removal of ARG from wastewater effluents needs to be studied systematically, in combination with treatment options which aim to make the wastewater effluents safe for wastewater reuse. This chapter provides information on existing studies on the removal of ARB and ARG from wastewater and tries to evaluate the efficiency of various advanced oxidation photo-driven technologies for their reduction in wastewater.

2 Conventional Wastewater Treatment

The use of safe and sustainable wastewater effluents requires complete and coherent knowledge of the risks of transmission of pathogenic bacteria to humans and to natural environments. The currently limited information and awareness of the patterns of antibiotic resistance in wastewater influents and effluents pose limitations to the beneficial use of reclaimed waters, as wastewater is among the main anthropogenic sources of release of subinhibitory concentrations of antibiotics in the range of ng/L [15, 16], ARB, and ARG [6] into the environment. As wastewater reclamation and reuse has gained increasing importance as a potential source of water for irrigation and agricultural purposes in water-deficient countries, the microbiological water quality standards have become more stringent to cope with the increasing demand of reclaimed wastewater [17].

Conventional WWTP effluents constitute a link between human activity and the environment through the discharge of treated wastewater, contributing in this way to the spread of antibiotic resistance determinants among a wide variety of microorganisms [18]. Biological and other conventional treatment processes in WWTP can result in changes in the abundances of specific phenotypes within the bacterial population of wastewater effluents [19]. As a consequence, WWTPs are considered important pools of ARB and ARG. Therefore, ARB and ARG can enter the soil, surface waters, groundwater, as well as produce through the discharge of treated wastewater or through wastewater reuse applications. It has been demonstrated that ARB can persist for many weeks on irrigated agricultural products [20, 21]. According to these studies, the isolated opportunistic bacteria were tested for antibiotic resistance, and this demonstrated the stability and activity of the respective ARGs.

The configuration of WWTPs may have an effect on the fate of ARB and ARG in wastewater. It has been shown that high bacterial cell densities in WWTPs favor the exchange of genetic material, even between different species through horizontal gene transfer. More specifically, the susceptibility of bacteria to selected antibiotics and antimicrobial drugs varies from activated sludge to the WWTP effluent [22]. The fate of tetracycline-resistant bacteria in the biological wastewater treatment process was studied by Kim et al. [22], showing an increase in the growth rate with an increasing organic loading, highlighting the effect of organic loading on the presence of such ARB. Moreover, Iwane et al. [23] reported an increase of tetracycline-resistant coliforms by 6.8% downstream of a WWTP in Tama River in Japan, indicating the inability of the WWTP treatment to fully remove tetracycline-resistant coliforms. In agreement with other studies, multiresistant coliform bacteria have been found at higher frequencies in treated sewage rather than in raw sewage [24] due to microbiological proliferation potential, indicating the inability of the conventional wastewater treatments to fully remove ARB and their associated genes. Also a higher percentage of amoxicillin and tetracycline-resistant *E. coli* was found in the treated effluent, compared to the inflow of the same WWTP [25].

Moreover, genes conferring resistance to a specific class of antimicrobials, e.g., tetracyclines, have been examined by various authors. Volkmann et al. [26] utilized real-time PCR assays for the detection and quantification of the ARG *van*A (vancomycin resistance) in enterococci, *amp*C (ampicillin resistance) in *Enterobacteriaceae,* and *mec*A (methicillin resistance) in staphylococci in various WWTPs indicating the presence of *van*A in 21% and *amp*C in 78% of the samples examined. Szczepanowski et al. [27] isolated and identified 140 and 123 different resistance genes in activated sludge and in the final effluents, respectively, in a German WWTP through a PCR and sequencing approach. Likewise, Du et al. [28] have also detected a number of clinically relevant ARGs in the effluents of five different WWTPs. An incomplete removal of ARGs was observed after various additional wastewater treatment processes (MBR, anaerobic/aerobic treatment). Noteworthy is the fact that treatment including an aeration step increased the total abundance of some ARGs.

Disinfection processes most frequently applied at WWTPs include UV radiation and chlorine treatment. The latter involves the oxidation of bacterial cells, alteration of cell permeability, and inhibition of enzymatic activity, while the treatment effectiveness depends on the type of microorganism, the wastewater characteristics, and chlorine dose [29]. Despite its effectiveness, chlorination can react with organic material to generate chlorinated organic compounds which can be highly carcinogenic and persistent. Moreover, it is known that some pathogens such as *Legionella* and *Cryptosporidium* are resistant to chlorination [30].

As a result of the inability of disinfection processes to effectively remove microorganisms completely from wastewater, alternative inactivation technologies can be utilized, which can potentially be more effective in the removal of resistant microorganisms without leading to the formation of toxic by-products (e.g., genotoxic or carcinogenic ones).

3 UV-Light Treatment

Ultraviolet (UV) irradiation for disinfection purposes uses energy-rich UV-C light at 200–260 nm. It has been successfully used in drinking water disinfection processes since decades. The inactivation effect is caused by UV-induced DNA alterations such as DNA-strand breaks, resulting in an inhibition of replication and finally in loss of proliferation [31, 32]. However, in wastewater applications, UV-disinfection application is limited due to the high amount of suspended particles and the overall turbidity of the wastewater, which significantly decrease the efficiency of the UV radiation. In addition, microorganisms possess several mechanisms to ensure cell survival after UV-light treatment. DNA damage can be tolerated by bacteria to a certain extent, until repair mechanisms are triggered [33, 34]. One of these mechanisms is called photoactivation. This mechanism involves a photon-absorbing enzyme called photolyase, which removes the nucleotide dimer bond. Apart from photoactivation, the *rec*A-dependent DNA repair mechanism is one of the major bacterial responses to DNA damage like excision gaps, daughter strand gaps, and double-strand breaks. Experiments have demonstrated the dark repair potential of opportunistic drinking water bacteria by *rec*A gene expression analyses which displayed a repair activity even after exposure to fluxes higher than 400 J/m^2 (German standard for drinking water disinfection). Regardless of the DNA repair mechanism, the survival and regrowth of bacteria can additionally reduce the efficiency of UV treatment [4].

UV fluxes of 400 and 600 J/m^2 were chosen to treat the effluent of a municipal WWTP in Germany [33, 35]. In both cases, exposure to 400 and 600 J/m^2 resulted in a 4-log reduction of cultivable bacteria. This reduction ratio was significantly lower compared to the 7-log reduction calculated based on the reference strains (*P. aeruginosa, Enterococcus faecium*). It is also known that UV-damaged bacteria, which survive the treatment, cannot be detected by conventional plating, as they lose reproducibility particularly during phases of intensive repair activities.

Additionally, different regeneration ratios of reference bacteria were observed by gene expression analysis of the *rec*A in *E. faecium* and *P. aeruginosa* [33]. As part of the bacterial SOS response which is one of the key regulator networks in DNA damage response systems, *rec*A coordinates the induction of over 20 genes. The gene product *rec*A is a multifunctional protein involved in a number of cellular processes, including homologous recombination, DNA repair, SOS response, and coordination of cell division [36]. SOS response in bacteria is activated by various DNA-damaging agents, including UV irradiation. *E. faecium* displayed a constitutive expression of *rec*A-specific mRNA, and a time-delayed regrowth was observed compared to *P. aeruginosa* after UV irradiation. Therefore, it was assumed that UV-light treated *E. faecium* cells entered a viable but not cultivable state (VBNC). In addition, Schwartz et al. [4] showed that enterococci were able to cross the UV-disinfection barrier and persist in biofilms of pipes commonly used for drinking water distribution systems, indicating that these organisms can develop mechanisms to overcome disinfection barriers. Generally, culture experiments with UV-light-treated wastewater bacteria exhibited a higher intrinsic resistance against UV irradiation than reference strains. Regrowth potential was observed between 24 and 39 h after irradiation (colony counts of wastewater bacteria exceeded the initial values). Furthermore, in agreement with cultivation experiments, molecular analysis revealed a lower degree of DNA damage in wastewater bacteria compared to the corresponding reference strains. Molecular analysis confirmed that after the initial inactivation, a strong regrowth of wastewater bacteria in the irradiated wastewater samples occurred. The number of amplifiable DNA targets increased continuously with time and exceeded the initial values at the end of the incubation period of 24 h.

4 Advanced Oxidation Processes (AOPs)

AOPs aim at improving the quality of secondary effluents, before they are discharged or reused. Unfortunately, despite the large number of studies dealing with bacterial inactivation by conventional treatments, there is still limited knowledge on the effect of AOPs on antibiotic resistance patterns and gene transfer [37].

The effect of AOPs on antibiotic resistance should be thoroughly evaluated, as they offer a promising alternative to conventional wastewater treatment which fails to remove ARB and ARG effectively. AOPs include, among other processes, Fenton and photo-Fenton oxidation, heterogeneous TiO_2 photocatalysis, and alkaline ozonation. These processes share the feature of the production of highly oxidizing nonselective hydroxyl radicals ($HO^•$), which have been proven to effectively remove a great variety of contaminants [15]. AOPs, however, are able to lead to the formation of oxidation transformation products, which may possess similar or even greater biological potency than the parent compounds, and hence, special attention should be paid to the oxidation time of the process.

4.1 Heterogeneous TiO_2-Photocatalysis

Heterogeneous TiO_2 semiconductor photocatalysis offers a promising alternative to the established disinfection processes and uses a stable, cheap, and reusable catalyst. The application of TiO_2 photocatalytic treatment compared to chlorination overcomes the obstacle of the formation of harmful chlorination by-products generated during chemical disinfection (e.g., trihalomethanes, *N*-nitrosdimethylamine) [38].

Semiconductor materials such as TiO_2 have an electronic structure which is characterized by a filled valence band and an empty conduction band. When a photon of higher energy than the band gap energy is absorbed by the semiconductor material, an electron/hole pair is formed (valence band holes are oxidants while conduction band electrons are reductants), which is trapped by available scavengers in the water matrix such as bacterial components and organic matter, preventing recombination of the electron/hole pair and leading to following redox reactions which produce $HO^•$. TiO_2 has been shown to be the most efficient catalyst tested for the decontamination of water and wastewater matrices. Solar UV-light ($\lambda < 400$ nm) can be utilized during TiO_2 photocatalysis [30], and therefore, the process can be considered as a green technology.

Photocatalytic inactivation of microorganisms is caused by the production of reactive oxygen species (ROS) such as $HO^•$ radicals generated at the TiO_2 surface, inducing oxidative stress to vital cellular components [39]. Despite the fact that the exact mechanism of cell death by photocatalysis has not been completely elucidated yet, many suggestions have been published regarding photocatalytic cell inactivation. The lipid peroxidation reaction in cell membranes causing malfunctioning of normal cell activities was reported by Maness et al. [40], while Sunada et al. [41] have suggested the initial damage of the outer membrane as the first step towards cell death.

A wide range of research has focused on the area of photocatalytic TiO_2 disinfection, from the inactivation of various bacteria including *Escherichia coli*, *Lactobacillus acidophilus,* and *Bacillus pumilus* to the effect of TiO_2 photocatalysis on multidrug-resistant bacteria in WWTPs. Herrera et al. [42] investigated the TiO_2-assisted disinfection of urban wastewater for two common microbial wastewater groups, coliforms and *Streptococcus faecalis*, comparing the action of artificially produced UV-C light and solar light. This study brought forward the issue of solution pH during the treatment, as at pH 5 the TiO_2 photocatalysis inactivation rate increased compared to the rate at the inherent TiO_2 solution with a pH of 7.8. At pH 5 without UV-light nor TiO_2, no bacterial inactivation was observed. This indicates that total coliforms and *S. faecalis* are not affected by the lower pH.

Improvements of the photocatalytic process have been suggested to resolve the issue of lack of proper electron acceptors in different aqueous matrices, with the use of (i) chemical oxidants, (ii) doped and modified TiO_2, (iii) coupling of TiO_2 with photosensitizers such as dyes, and (iv) coupling of TiO_2 photocatalysis with other AOPs [30]. These techniques may enhance the photocatalytic inactivation of ARB, as they target the increase of the availability of electron acceptors in wastewater effluents.

Rizzo et al. [6] investigated the effect of the N-doped TiO_2 photocatalyst under simulated solar radiation on the inactivation of multidrug-resistant *E. coli* which was isolated from biologically treated urban wastewater effluent. The inactivation of *E. coli* resistant to ciprofloxacin, cefuroxime, tetracycline, and vancomycin was examined with the use of the N-doped TiO_2 catalyst at various photocatalyst loadings. The results of this study have shown that the optimum catalyst loading was 0.2 g/L N-doped TiO_2, with complete inactivation taking place after 60 min of treatment. A Kirby-Bauer antibiotic testing on the surviving colonies indicated no effect of the photocatalysis on the *E. coli* resistance to vancomycin and tetracycline, but there was a decrease in resistance to ciprofloxacin and cefuroxime.

4.2 Photo-Fenton Treatment

Another promising AOP is the photo-Fenton treatment. It is a highly efficient homogeneous treatment, which involves the catalytic breakdown of hydrogen peroxide (H_2O_2) in reaction with ferrous iron ($Fe^{2+} + H_2O_2 + h\nu \rightarrow Fe^{3+} + HO^- + HO^{\cdot}$) in an acidic medium to form active transitory species such as hydroxyl radicals ($HO^{\bullet}$), in the presence of UV–vis sunlight [43].

During the photo-Fenton treatment, the catalytic regeneration of ferrous iron from ferric iron is a rate-limiting step in the cycle of photo-Fenton reactions, leading to the dependence of the treatment on the generated Fe^{3+} concentration in solution. In addition to this limitation, the low solubility of the ferrous iron leads to precipitation when the solution pH is not acidic, making the acidification of the aqueous solution necessary for the photo-Fenton treatment. In microbiological experimental settings, this challenge can also be troublesome since at pH around 3, the majority of investigated microorganisms are not viable, without the need for further Fenton treatment. In order to deal with this obstacle and examine the removal of microorganisms with the use of photo-Fenton, various studies have been conducted at a higher pH (pH >4), at which microorganisms are able to survive [44]. In complex water matrices such as wastewater, the present pollutants and dissolved iron kept in solution compete for the generated $HO^{\bullet}$ radicals, reducing the efficiency of the photo-Fenton process.

The microbial inactivation effect involves cellular damage through the production of reactive oxygen species (ROS), such as $HO^{\bullet}$ and superoxide radicals ($HOO^{\bullet}$). This effect on vital cellular constituents begins with the absorbance of photons from the source of illumination by the pathogens causing sublethal damage, followed by oxidative attack by $HO^{\bullet}$ on the cell membranes, leading to loss of cell membrane permeability control and deterioration of internal cellular mechanisms [45, 46]. This effect depends on the concentration of iron and $HO^{\bullet}$ which are generated during the photocatalytic process. The effect of photo-Fenton on the inactivation of wastewater inoculated with *Enterococcus faecalis* was investigated by Ortega-Gómez et al. [47] using photo-Fenton reaction at near-neutral pH. The results showed that there was a 5-log decrease of *E. faecalis* after 80 min of photocatalytic treatment, due to the strong attack of process-generated $HO^{\bullet}$ radicals which nonselectively attack cellular membranes and destroy bacterial protection mechanisms.

A study on the disinfection of *E. coli* K12 strain was examined by Rincón and Pulgarin [39]. After applying the photo-Fenton treatment, it became obvious that the photo-Fenton is a suitable method for water disinfection, with complete bacterial inactivation after 60 minutes of treatment. Moreover, Michael et al. [48] investigated the removal of antibiotic-resistant *E. faecalis* in an urban wastewater effluent in the presence of trimethoprim or ofloxacin by solar photo-Fenton (H_2O_2 75 mg L^{-1}, Fe^{2+} 5 mg L^{-1}). The results of the study indicated that the resistance pattern to ofloxacin was two times higher than the resistance shown to trimethoprim, in the presence of the Fenton reagents. Cengiz et al. [49] investigated the potential of photo-Fenton process in the removal of *tet*M resistance gene and its host *E. coli* HB101 in cow manure at various H_2O_2 concentrations. The results showed that at the examined doses of Fenton reagents (20–50 mM H_2O_2 and 5 mM Fe^{2+}), the *E. coli* inactivation rate increased with increasing dose of oxidant, in the presence of a steady concentration of the Fe^{2+} catalyst. The maximum final inactivation achieved was 56.6% of *E. coli* after 24 hours with the maximum dose of H_2O_2 (50 mM H_2O_2). Similarly, the *tet*M gene band intensity gradually decreased with increasing Fenton reagent's concentration. Moreover, Diao et al. [50] investigated the disinfection of artificial wastewater containing *E. coli* by photo-Fenton at pH 4, demonstrating its efficiency at a dose of 8.5 mg L^{-1} of H_2O_2 and 0.85 mg L^{-1} of Fe^{2+} and achieving complete disinfection after 5 min of treatment.

No studies have been conducted to compare the removal of ARB and selected resistance genes with the two discussed photocatalytic treatments, as each study so far has investigated different indicator bacteria and different selected resistance genes. As a result, no direct comparison can be made between the two treatments currently, but this is an area of study with great interest for the removal of ARB and ARG in wastewater effluents.

4.3 Ozonation

Ozone is one of the most powerful, commercially available oxidizing agents. The ozone molecule reacts with a wide variety of chemical compounds, either by direct contact of the ozone molecule with a target structure or indirectly by inducing $HO^{\bullet}$ formation. Its disinfection mechanism in drinking water applications includes destruction of the bacterial cell wall followed by leakage of cellular constituents outside of the cell, damage to nucleic acids through breakage of aromatic structures, and breakage of carbon-nitrogen bonds of proteins leading to depolymerization. The efficiency of disinfection depends on the susceptibility of the target organism, the contact time, and the concentration of the ozone. In wastewater applications, ozone treatment should be used at least after secondary treatment because of the high levels of suspended solids which can drastically reduce the ozone efficiency and reduce the amount of applied ozone which can otherwise lead to toxic by-product formation in the presence of, e.g., bromide ions. Additionally, ozone is produced in situ and consumes a higher amount of energy compared to conventional treatment systems, leading to increased treatment expenses.

Cengiz et al. [49] studied the destruction of antibiotic-resistant *E. coli* HB101 and the *tet*M gene. The results of ozonation have shown that an ozone dose of 3.125 mg g^{-1} of manure for 5 min is adequate to give 98.5% bacterial disinfection, hence almost a 2-log reduction of *E. coli*. The *tet*M agarose band intensity during PCR was also decreased with increased exposure to ozonation.

Due to the disinfection capabilities of ozonation in drinking water applications, an ozonation system was installed at a municipal WWTP in Germany. Ozone concentrations of 0.5 and 1.1 g O_3/g DOC were used to treat secondary treated wastewater. Four bacterial-specific phylogenetic markers for enterococci, staphylococci, enterobacteria, and *Pseudomonas aeruginosa* as well as ARGs coding for vancomycin, imipenem, ampicillin, and erythromycin resistance (*van*A, *bla*VIM, *amp*C, *erm*B) were used as clinical relevant parameters to characterize the effect of advanced wastewater treatments on the bacterial community. Molecular microbiological methods confirmed a several log decrease of the amount of phylogenetic markers in the overall bacterial community after ozone treatment. The species-specific bacterial markers decreased as well especially for enterococci and enterobacteria (Alexander et al., submitted). The effect on *P. aeruginosa* however was less significant. It became obvious that ozone treatment inactivated a high percentage of the microbial community present in the WTTP effluent. Nevertheless, fractions of the effluent population were robust against oxidative treatment and survived the ozone treatment. Interestingly, the surviving bacterial population demonstrated a high abundance of ARGs and mobile genetic elements. The high abundance of mobile genetic elements known to carry multiple ARGs is a potential indicator for horizontal gene transfer (HGT). In addition, an ozone system with recirculation reflux of 50% and 200% volume of treated wastewater resulted in a further decrease of all four bacterial markers, with species-dependent inactivation ratios, but still induced elevated levels of antibiotic resistance in the surviving bacterial population compared to the pretreatment bacterial community. So far, the exact molecular mechanism leading to the demonstrated ozone robustness of ARB is still unknown, but predispositions and adaptation processes to oxidative stress induced by low-level antibiotics at WWTPs are studied [51] which might be responsible for this effect.

Investigations were conducted regarding the correlation between ozone treatment and HGT. It is known that sublethal DNA damage introduced by various chemical and physical treatments is one of the trigger mechanisms of HGT. As mentioned before, a fraction of the effluent wastewater populations are not lethally affected by the oxidative treatment processes. Nevertheless, it is commonly known that damaged DNA induces bacterial repair mechanisms via the SOS response. In the case of ozonation, the highly conserved *rec*A system is the key regulator [33]. The *rec*A gene is also responsible for HGT and might contribute to the increased abundance of genetic mobile elements and ARGs in surviving ozone-treated populations. Consequently, recent gene expression analyses of natural wastewater populations may prove this hypothesis. In addition, bacterial wastewater communities represent a complex matrix due to turbidity and shielding-like properties of bacteria, e.g., aggregates or different species-dependent characteristics (cell wall composition, specific outer membranes with efflux pumps) that might impact the ozone treatment efficiency.

Ozone also inactivates enzymes by alteration of the catalytic center of the molecule. DNase enzymes are known to degrade the amount of free DNA molecules by hydrolytic cleaving of the DNA-associated phosphodiester linkages. Therefore, natural DNase activity is a useful wastewater component reducing the amount of free/liberated DNA molecules like ARGs or mobile genetic elements [52]. Analysis of ozone-treated wastewater confirmed an increase in DNase activity. This unexpected effect is possible due to the release of bacterial DNase enzymes from the loss of bacterial cell integrity caused by the ozone treatment. In contrast to drinking water, applications and efficiency of ozone treatment in wastewater are more challenging due to the increased turbidity, matrix composition, bacterial diversity, and aggregate formation. Besides their already established biocenosis, WWTPs are dealing with microorganisms from different sources such as clinical, municipal, or industrial wastewater. The characteristics and interactions of these bacteria in multispecies communities are more difficult to understand and to predict as regards stress response mechanisms, compared to single-species reference systems or drinking water habitats with low bacterial density. For example, *P. aeruginosa* demonstrated better tolerance against ozonation in comparison to enterococci or staphylococci (Alexander et al., submitted). Studies conducted confirm an increase of ARGs accumulated in bacteria in the sediment of receiving waters downstream of WWTPs [5]. This could be due to the accumulation of mobile genetic elements like resistant integrons and HGT events triggered by stress signals like DNA damage or due to effect of ARB, which are more likely to survive ozonation (increased robustness compared to nonresistant bacteria). Therefore, the effects of ozone on the effluent microbiomes seem to be advantageous when it comes to the application of combinations of different wastewater treatment technologies for the decrease of specific selections of subpopulations harboring ARGs. This would also contribute to the reduction of the potential of ARG transfer which is triggered by bacterial DNA repair mechanisms. Thus, more research on the molecular responses of microbiomes on applied wastewater treatment technologies is required, the aim being the optimization of the removal of pathogenic-opportunistic bacteria.

5 Conclusions

Recent studies that investigated the impact of AOPs and UV at full-scale wastewater treatment plants reveal reduced inactivation efficiency of natural wastewater bacteria compared to the findings of lab-scale studies. Wastewater communities are more robust to disinfection due to the bacterial diversity, biofilm, or aggregate formation and molecular predispositions due to the impacts of organic contaminants on bacteria, which, e.g., can trigger adaptation processes like ROS tolerance. Therefore, results from inactivation experiments with reference strains or free DNA in artificial wastewater are only partially comparable to naturally mixed populations in wastewater. Furthermore, recent studies with ozone-treated wastewater revealed a selection of ozone-robust bacterial subpopulations containing elevated levels of ARG and mobile genetic elements. More thorough investigation regarding the impact of AOPs and other treatments on natural wastewater bacteria is needed to reduce possible risks coming from discharged ARB into the aquatic environment. The integration of molecular biology analyses in combination with cultivation experiments is the first step for an extended microbial risk control. The selection of biological indicators (e.g., species, ARGs, mobile genetic elements) is helpful for the development of a novel advanced monitoring concept, because of the limitations of current monitoring systems based on cultivation of indicator bacteria. Finally, the fact that inactivation of specific bacteria or bacterial groups does not necessarily guarantee the removal of other waterborne microorganisms and only the minority of bacteria can be cultivated must be considered when planning a novel bacterial monitoring strategy.

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Advanced Technologies for Emerging Contaminants Removal in Urban Wastewater

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Abstract Human health can be adversely affected through lack of access to drinking water, inadequate sanitation, consumption of contaminated freshwater and seafood, and exposure to contaminated bathing water. For example, bioaccumulation of persistent organic contaminants may raise health concerns in vulnerable population groups. The wide range of "contaminants of emerging concern" present in European waters is a growing environmental and human concern. These substances are used in pharmaceuticals, personal care, and other consumer products, and their adverse effects have only recently become apparent. Understanding of their sources, emissions, levels, and effects in the aquatic environment is also limited. In this chapter, we review the advanced technologies recently investigated for the successful elimination of such contaminants present in urban municipal wastewater treatment plant effluents. An overview on the microcontaminants' behavior throughout conventional and advanced biological systems is also presented, stressing the important buffer effect of their adsorption on supported biofilm. It has been also stressed that combination of membrane filtration technologies and biological treatment avoids secondary clarification and tertiary steps. The use of membranes for wastewater treatment has rapidly increased in the last years due to the exceptional high-quality standards typically for reusing purposes given. Finally, advanced chemical and biological oxidation technologies must be efficient not only in removing microcontaminants but also pathogens and microorganisms from treated water for reusing applications. For instance, the elimination of antibiotics which may lead to proliferation of antibiotic resistance in pathogenic or nonpathogenic microorganisms must be a target jointly with contaminants of emerging concern removal from treated water.

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Contents

Abbreviations

AOPs	Advanced oxidation processes
APCAs	Aminopolycarboxylic acids
AR	Antibiotic resistance
ARB	Antibiotic-resistant bacteria
CAS	Conventional activated sludge
CEC	Contaminants of emerging concern
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
EDDS	Ethylenediamine-*N*,*N*′-disuccinic acid
EDTA	Ethylenediaminetetraacetic acid
EEA	European environment agency
EU	European union
FBBR	Fixed-bed biofilm reactor
HA	Humic acids
HS	Humic substances
LCA	Life cycle assessment
MBR	Membrane bioreactor
MDR	Multidrug resistant
MF	Microfiltration
MT	Membrane technology
MTBE	Methyl-*t*-butyl ether
MWWTP	Municipal wastewater treatment plant
NF	Nanofiltration
NOM	Natural dissolved organic matter
OPEX	Operating expenditures
PDBEs	Polybrominated diphenylethers

PPCPs	Personal care products
RO	Reverse osmosis
SBR	Sequential biomass reactor
TN	Total nitrogen
UF	Ultrafiltration
UWWTPs	Urban wastewater treatment plants
WTPs	Wastewater treatment plants

1 Introduction

Treatment of urban and industrial wastewaters must meet the requirements of increasingly stronger regulations. The Urban Wastewater Treatment Directive (Directive 91/271/EEC) is a cornerstone of European Union (EU) water legislation. Its objective is to protect the environment from the adverse effects of discharges of urban wastewater from settlement areas and biodegradable industrial wastewater from the agro-food sector, by requiring Member States to ensure that such water is collected and adequately treated. Full implementation of the Directive is also a prerequisite for meeting the environmental objectives set out in the EU Water Framework Directive (Directive 2000/60/EC) [1] as well as in the Marine Strategy Framework Directive (Directive 2008/56/EC) [2]. Wastewater generated by the population of the 27 Member States of the EU and by the industry is a major source of pollution of European waters including groundwater, rivers, lakes, and seas. Wastewater discharges can lead to excessive nutrient loads (eutrophication), accelerate biodiversity losses and affect drinking water supplies or bathing water sites, and thereby have important links to public health concerns. These impacts in turn may have serious negative consequences for economic sectors such as tourism (SEC (2011) 1561 final).

Around 80% of the population from countries from the north and south of Europe apply conventional systems for urban wastewater treatment. This percentage is even higher (around 90%) for those countries from the center of Europe. For east countries, nearly 67% of the population has access to wastewater treatment systems, while only 50% as medium percentage is detected for southeast European countries (Turkey, Bulgaria, and Romania). For the rest of European populations, the access to collecting systems without specific treatment is around 1.5% and 5.6%. In parallel, it is published by the European Environment Agency (EEA 2013) [3] that more than 85% of the inhabitants from the north and south of Europe have a municipal wastewater treatment plant (MWTP) including some kind of tertiary treatment for the elimination of nutrients or recalcitrant organic matter leaving the secondary biological treatment. Urban wastewater generated by almost half of the southern and eastern European population receives a tertiary treatment, which represents approximately 35% increase in the last 10 years. In the southeast of Europe, the percentage of population with access to tertiary treatment facilities is quite low (lower than 10%), compared to 22% of the population in this region

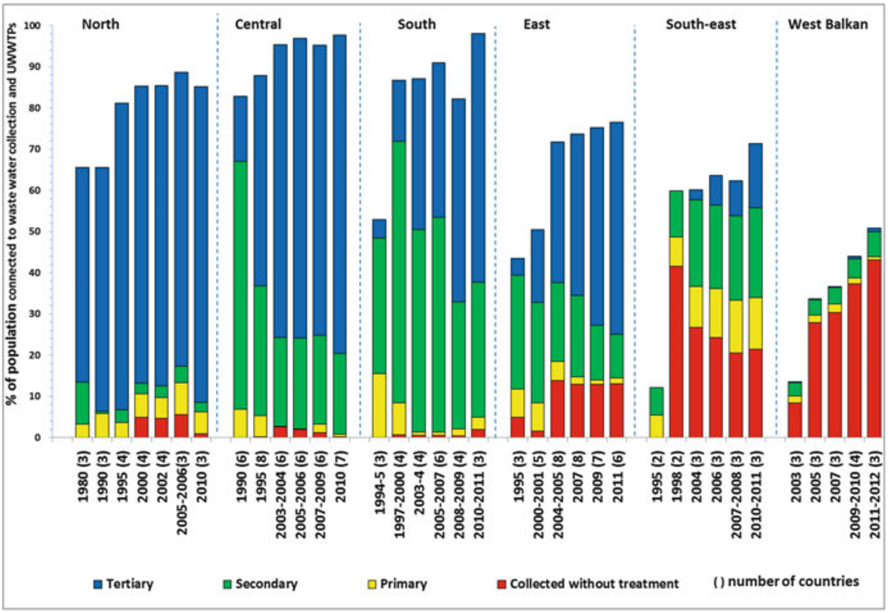

Fig. 1 Regional variation in wastewater treatment between 1980 and 2012 (Environmental Indicator Report 2013). *Primary* (mechanical) treatment removes part of the suspended solids. *Secondary* (biological) treatment uses aerobic or anaerobic microorganisms to decompose most of the organic matter and retain some of the nutrients (around 20–30%). *Tertiary* (advanced) treatment removes the organic matter even more efficiently. It generally includes phosphorus retention and in some cases nitrogen removal (*Source*: European Environment Agency [3])

having a secondary treatment. In Fig. 1, a summary of the percentage of population connected to wastewater collection systems and urban wastewater treatment plants (UWWTPs) in the different European regions is shown.

Different work areas (chemical, biological, and microbiological laboratories, industries, hospitals, and even the domestic/urban water) generate a wide variety of waste daily, which can be classified as hazardous because they are corrosive, reactive, explosive, toxic, flammable, and/or infectious. The discharge of hazardous wastes pollutes the water, soil, and air. This contamination may extend hundreds of kilometers from where the waste was initially discharged and is commonly found in the environment at concentrations in the μg L^{-1} range because these are not eliminated by conventional biological treatments [4–6]. Household activity mainly produces organic waste, but other kinds of substances are also discharged into the sewage system, such as those coming from the cars' emissions (hydrocarbon, plumb, and other metals), salts, acids, etc. The organic contamination charge of urban waste depends on the number of inhabitants, including seasonal population, and the contamination coming from the industrial sites connected to the urban sanitary system [7].

Apart from contaminants under regulation, there are "contaminants of emerging concern (CEC)" which have not been regulated yet including pharmaceuticals and personal care products (PPCPs), flame retardants, and many others. These have been found in surface water, groundwater, wastewater, and even in the drinking water [8], and their continuous occurrence in the aquatic environment is an issue of great importance nowadays. The presence in the environment of some of these substances has been linked to the pollution of groundwater and soil as well as the loss of biodiversity and some signs of their possible adverse effects on human health, such as neurotoxicity, endocrine disruption, and cancer [9–11]. CEC predominant pathway of entry to the environment is considered to be wastewater treatment plants (WTPs), which were not designed for their removal or sewage overflows. Several comprehensive research articles have been recently published on this issue both in EU [12] and in USA [13].

In the past, the focus was on detecting the severe, direct effects of individual contaminants and the short-term negative impact on ecosystems. But as scientific understanding has advanced, and the concentrated emissions have been lowered, environmental evaluation reveals a considerable number of chronic effects that can usually only be detected after a long period of time [14, 15]. Evaluation was focused mostly on the effect of individual substances, whereas we are now beginning to study and understand interactions in mixtures of these substances [16–18].

The full spectra of CEC which are released in MWTP effluents is currently not well established mainly because monitoring studies have been addressed till now through targeted compounds analysis (Table 1). However, during their use and subsequent release to the environment, CEC may be transformed by a variety of processes such as hydrolysis, photolysis, oxidative processes, or biotic ones by microorganisms in biological reactors yielding to the generation of numerous transformation products. Normally, it is assumed that transformation of parent compounds provokes a decrease in toxicity. However, in some cases, transformation leads to more active compounds. As a whole, there is a gap of knowledge on the identity/(eco)toxicity of CEC transformation products in MWTP effluents [19]. The risk of acute toxicity of CEC present in freshwaters at ng L^{-1} or μg L^{-1} range is thought to be negligible. However, there are substantial knowledge gaps in terms of chronic, long-term exposure or non-exposure of nontarget aquatic organisms and the effects on ecosystem functioning. Data are available to suggest that some compounds may display chronic effects at or close to the levels detected in the environment [20]. Moreover, the development of antibiotic-resistant bacteria due to the continuous release of antibiotic residues is also a major public health concern [21].

The presence of microcontaminants in MWTPs hampers the reuse of this water for other activities such as irrigation in agriculture, golf, and gardens. Direct reuse of biological treated wastewater cannot be contemplated due in part to the risk of microcontaminant accumulation in soils and plants with potential impact on food security and drinking water resources. Consequently, the potential economic value of this particular water is decreased. This situation strongly calls for the development of remediation techniques to limit the release of these substances in the

Table 1 Contaminants found in the environment and considered as CEC

Pharmaceuticals	Example
Veterinary and human antibiotics	Trimethoprim, erythromycin, lincomycin, sulfamethoxazole
Analgesics and anti-inflammatory drugs	Codeine, ibuprofen, acetaminophen, acetylsalicylic acid, diclofenac, Fenoprofen
Psychiatric drugs	Diazepam
Anticonvulsant drugs	Carbamazepine
Lipid regulators	Bezafibrate, clofibric acid, fenofibric acid
β-blockers	Metoprolol, propranolol, timolol
X-ray contrast agents	Iodobromide, iopamidol, diatrizoate
Steroids and hormones (contraceptives)	Estradiol, estrone, estriol, diethylstilbestrol
Personal care products	
Synthetic musk fragrances	Musk xylene, galaxolide, tonalide
Sunscreen agents	Benzophenone, methylbenzylidene camphor
Insect repellents	*N*,*N*-diethyltoluamide
Surfactants and metabolites	Alkylphenol ethoxylates, alkylphenols (octylphenol, nonylphenol), alkylphenol carboxylates
Flame retardants	Polybrominated diphenylethers (PBDEs), tetrabromo bisphenol-A, tris(2-chloroethyl)phosphate
Industrial additives and agents	Chelating agents (EDTA), aromatic sulfonates, benzotriazole, bisphenol, phthalates
Gasoline additives	Dialkyl ethers, methyl-*t*-butyl ether (MTBE)
Disinfection by-products	Bromo acids, iodo-THMs, bromoacetonitriles, cyanoformaldehyde, NDMA
Pesticides	Carbaryl, metolachlor, alachlor, 2,4-D, dieldrin, lindane, esfenvalerate, simazine, atrazine, isoproturon

environment. In this sense, in the last two decades, many researchers are establishing a methodology, known as life cycle assessment (LCA), for evaluating the environmental sustainability of new techniques proposed [22, 23], considering as general objective to further reduce the eco-toxicity, hormone effects, and pathogenic effects of the effluent [24].

In this chapter, various advanced technologies aimed at polishing the water (detoxification and disinfection) will be reviewed in order to show the progress made on this issue.

2 Microcontaminant Monitoring and Removal in Urban Wastewater Secondary Treatment by Conventional and Advanced Biological Systems

Conventional activated sludge (CAS) treatment is usually designed to remove or to decrease the concentrations of pathogens and the loads of the bulk organic and inorganic constituent that may otherwise pollute the receiving waters and lead to eutrophication. It is, generally, made up of a water treatment line (for removal of contaminants from the water phase with production of sediments with high water content) and a sludge line (for treatment of separated activated sludge produced in the water line, in order to make them compatible with the final disposal).

A water treatment line in CAS usually includes the following phases [25]: (1) mechanical preliminary treatments (or pretreatments); (2) mechanical treatments (or primary): primary settling, eventually after physical-chemical treatment of precipitation and flocculation; (3) biological treatment (or secondary): activated sludge (or attached biomass) necessarily followed by secondary settling. In general, CAS treatment is highly influenced by the season, being summer the one in which microcontaminant concentrations can be three times higher than in winter. This effect is attributed to eventual changes in the population due to tourism and normally major water consumption rates in summer. Nevertheless, it highlights that conventional MWTPs are not prepared to buffer changes in inlet wastewater characteristics. Therefore, this is a weak point of CAS against specific discharges, heavy rain, seasonal changes, and further unexpected events which could directly affect wastewater characteristics. The presence of PPCPs and endocrine-disrupting chemicals in urban and drinking water indicates that conventional and most commonly used water treatment technologies may not be sufficient to completely eliminate these compounds [26].

Many studies have reported monitoring of microcontaminants and CEC in water and different conventional biological wastewater treatment systems in the recent decade. For instance, Collado et al., showed the effect of the exposure to the antibiotic sulfamethoxazole on the microbial population genetics of a sequential biomass reactor (SBR) [27]. Although dissolved organic carbon (DOC) and nitrogen elimination was still successful in the SBR, changes in the adapted biomass were observed. Another example could be the work of Cruz-Morató et al., in which the pharmaceuticals elimination present in urban wastewater was proposed by means of a fluidized biological reactor. The complete elimination of seven of the ten pharmaceuticals detected was achieved [28].

2.1 Membrane Bioreactors

Membrane bioreactor (MBR) technology combines biological treatment with a membrane filtration process, replacing the gravitational sedimentation unit of

CAS systems. Since the biomass is filtered in a highly aerated tank, biological nutrient removal processes can be achieved in this compartment. The advantages of MBRs, such as their small footprint and high effluent quality, together with the decreasing cost of membranes, have made this technology a very attractive option for municipal applications, being one of the biological advanced processes most applied in last-generation MWTPs. For instance, Wijekoon et al., developed a methodology for the prediction of diverse microcontaminant elimination, according to their hydrophobicity, by means of a MBR [29].

As in conventional MWTPs, the removal potential of MBRs was also found dependent on the sludge retention time (SRT). Bernhard et al., reported better removals compared to CAS for investigated persistent polar microcontaminants, such as diclofenac, mecoprop, and sulfophenylcarboxylates [30]. Chen y Lee showed that MBR could remove bisphenol-A (BPA) slightly more effectively than CAS under equal conditions of sludge loadings ranging from 0.046 to 10.2 g kg^{-1} d^{-1} [31]. However, MBR could bear much higher volume loadings than CAS. Kim et al., found MBR system to be efficient for hormones (e.g., estriol, testosterone, androstenedione) and certain pharmaceuticals (e.g., acetaminophen, ibuprofen, and caffeine) with approximately 99% removal, but not efficient for erythromycin, TCEP, trimethoprim, naproxen, diclofenac, and carbamazepine [32]. Radjenovic et al., confirmed enhanced elimination of several pharmaceutical residues poorly removed by the CAS treatment (e.g., mefenamic acid, indomethacin, diclofenac, propyphenazone, pravastatin, gemfibrozil), whereas the antiepileptic drug carbamazepine and diuretic hydrochlorothiazide bypassed both the systems [33, 34]. In a review of the factors influencing the removal of microcontaminants from wastewater, Cirja et al., concluded that hydrophobic compounds are removed from the liquid phase via adsorption and possibly through biodegradation processes when the SRT is high enough [35, 36].

Nevertheless, in general, membrane biological systems are not a definitive technology for facing microcontaminant elimination, though they are considered a good pretreatment previously to the application of advanced oxidation processes (AOPs) on the concentrate stream, thanks to the high quality of their effluents. In addition, membrane-fouling control and energy efficiency are also key issues in MBR operation [37]. In this sense, operating expenditures (OPEX) are still one of the main factors affecting practical availability of this technology, mainly due to membrane aeration, permeability loss, and membrane replacements. Energy consumption in MBRs was reported to be three times higher than that in CAS combined with advanced tertiary treatment, but the gap has been narrowed significantly in recent years by the optimization of process settings and control [38–40].

2.2 Moving and Fixed-Bed Biofilm Reactors

More recently, some advanced biological treatments have been applied, operating under both aerobic conditions such as moving bed biofilm reactors [41]. Biofilm systems offer an interesting advantage for the treatment of wastewater with high concentration of readily biodegradable chemical oxidation demand (COD), thanks to their ability in oxidizing with high-rate soluble compounds diffusible into the biofilm. Among the biofilm systems, fixed-bed biofilm reactors (FBBR) are an alternative for the treatment of wastewater characterized by high organic loads and seasonal production. FBBR systems, where the biomass grows on plastic carriers with a high void ratio, offer some advantages such as (1) a decrease of the required volume with respect to the CAS systems; (2) the reduction of bulking problems, because the concentration of solids reaching the final settler is reduced, being made up only of biomass detached from the plastic elements; (3) the absence of return flow and backwashing due to the high void ratio of the filling media; and (4) an easier management with respect to the CAS plants [42]. In the recent years, huge amount of actual industrial wastewater have been partially treated by FBBR (sometimes also designated as immobilized biomass reactors) [43]. In this sense, there is also a growing interest in the scientific community for applying this kind of robust and highly stable advanced biological reactors to urban wastewater treatment as secondary step (substituting CAS), with the aim of having effluents with much lower variations in their characteristics for tackling final tertiary treatments.

FBBR can be operated in batch or continuous mode. Under batch-mode operation, the reactor is filled in by cycles with contaminated urban wastewater with the aim of determining the maximum treatment capacity of the system. Normally simulated or actual urban wastewater is spiked with higher concentrations of target contaminants (easily to follow), but in few occasions, actual MWPTs' influents are analyzed and treated as received. This case corresponds to the experimental series shown in Fig. 2, in which results of five cycles of FBBR batch operation are

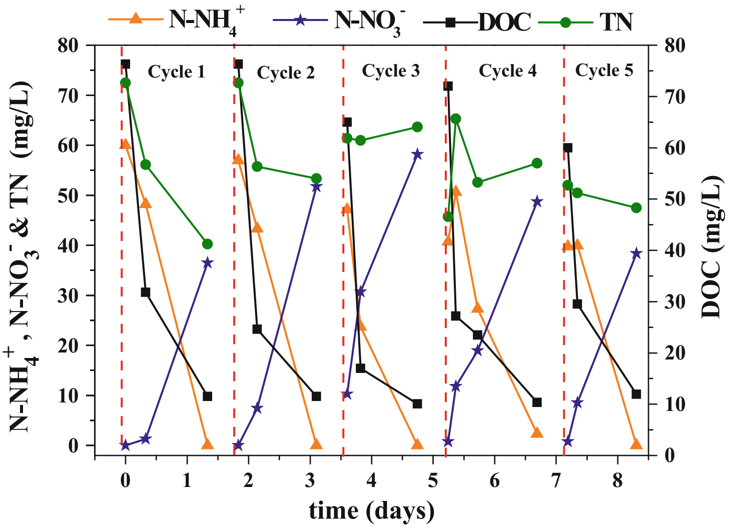

Fig. 2 DOC, TN concentration evolution, and nitrogen resulting from ammonia and nitrate monitoring during the batch operation of a FBBR

summarized. Firstly, it is possible to observe that the initial concentration of COD (in the range of 30–80 mg L^{-1}) is always degraded to 10 mg L^{-1}; this can be translated into a highly stable response of the system. In addition, the maximum biological DOC treatment capacity was found to be 9.2 and 5.8 mg L^{-1} h^{-1} from the side of ammonia conversion into nitrate species. In addition, nitrite was detected only at trace concentrations. It is important to highlight also how total nitrogen (TN) values increased during the third cycle probably due to an insufficient residence time stated in this system for nitrification process which normally requires higher treatment times. In the fourth cycle, a slight increase in batch operation time let nitrification activity got recovered and so TN decreased again.

In addition, the measurement by LC-MS/MS equipment of samples collected at the end of the first, second, and fifth cycles showed that total amount of microcontaminants detected in the effluent was less than 17 μg L^{-1}, much lower than the one detected in MWTP real effluents, which varied, depending on the day, between 40 and 80 μg L^{-1}. It must be also stressed that FBBR system also shows the capacity of retaining microcontaminants according to their chemical characteristics, until the system gets saturated once the adsorption equilibrium is overreached. At that moment, microcontaminants contained in the inlet flow would be not retained anymore and so part of the one already adsorbed would unpredictably leached when certain FBBR operating conditions change (temperature, pH, flow, inlet COD, etc.). In this sense, it is also crucial determining their concentration adsorbed on biofilm to get differentiated from true biodegradation. Regarding the operation of this fixed-bed bio-system, it was observed that around 65% of microcontaminant elimination was ascribable to adsorption and 35% of own biological degradation. However, these values change significantly depending on contaminants characteristics, e.g., more than 70% of the antibiotic ofloxacin was adsorbed on the biofilm, but not degraded, while 60% of sulfamethoxazole was degraded.

FBBR system presented higher fixed biomass resistance against significant changes in the target wastewater characteristics. In general, it has been observed a higher stability for FFBR effluents compared with CAS systems.

Despite the highly positive results obtained in the application of advanced biological treatments for microcontaminant removal, huge amount of studies have definitely demonstrated their final inefficiency in this task. Consequently, advanced treatment technologies such as activated carbon, reverse osmosis (RO), and AOPs may be viable for the removal of many trace contaminants contained even in the advanced biological systems effluents [44].

3 Solar Advanced Oxidation Processes as Tertiary Treatments for Emerging Contaminants Removal

The absence of specific treatments to guarantee the complete removal of all microcontaminants present in water resources due to their diverse physicochemical properties has been nowadays widely stated within the scientific community as an important problem. In this sense, optimal removal strategies for microcontaminants remain a challenge to researchers and engineers in order to minimize their adverse effects on the environment. As far as methods of CEC treatment and removal are concerned, the set of constraints to improve the surface water quality requires the development of new processing techniques such as AOPs, particularly suitable for persistent contaminants removal [4]. These technologies are based on the production of hydroxyl radicals ($HO^{\bullet}$) having the ability to unselectively oxidize a large variety of organic compounds. Criteria of operational and investment costs are of paramount significance in this field. The use of solar energy to achieve contaminants and CEC mineralization is probably a first answer to this issue [45]. Heterogeneous photocatalysis is based on the use of a wide-bandgap semiconductor, and homogeneous photocatalysis by photo-Fenton process is based on the addition of H_2O_2 to dissolved iron salts. In both processes, irradiation with UVA-visible light is required; therefore, the use of solar energy would be an attractive option for reducing operating costs [46]. Combined with the direct use of the solar energy, photochemical and photocatalytic processes are almost energy self-sufficient and allow the design of alternative water treatments which are basically simple, robust, and inexpensive to set up and run. Such processes, able to provide with useful water detoxification operation, would be fully in agreement with the framework of sustainable development and should integrate the concept of green chemistry. If the use of a renewable energy resource minimizes the operating costs, investment costs are largely dependent on technological choices that are to be incorporated as soon as the process design begins and more particularly at the full-scale reactor design step.

It appears that the link between solar energy and water treatment by AOPs is still presenting a real interest, as most of the published studies were in nonrealistic model waters at nonrealistic concentrations (mg L^{-1}). Very few studies use real MWTP effluents containing microcontaminants at μg L^{-1} range. The two main characteristics of such effluents are a very high flow rate combined with a very low CEC concentration levels (below μg L^{-1}) diluted in a high amount of dissolved organic matter (several tens of mg L^{-1}). Concerning this latter issue, the design of new treatment concepts is needed.

Some of the disadvantages associated with the application of AOPs are their high operating costs, depending on the specific process: (1) high electricity demand (e.g., O_3/H_2O_2 and UV-based AOPs), (2) the relatively large amounts of oxidants and/or catalysts consumed (e.g., O_3, H_2O_2, and iron-based AOPs), slow kinetics (photocatalysis with TiO_2), and (3) pH restrictions (e.g. Fenton and photo-Fenton treatments require optimum pH below 3). Nevertheless, by using solar energy as a

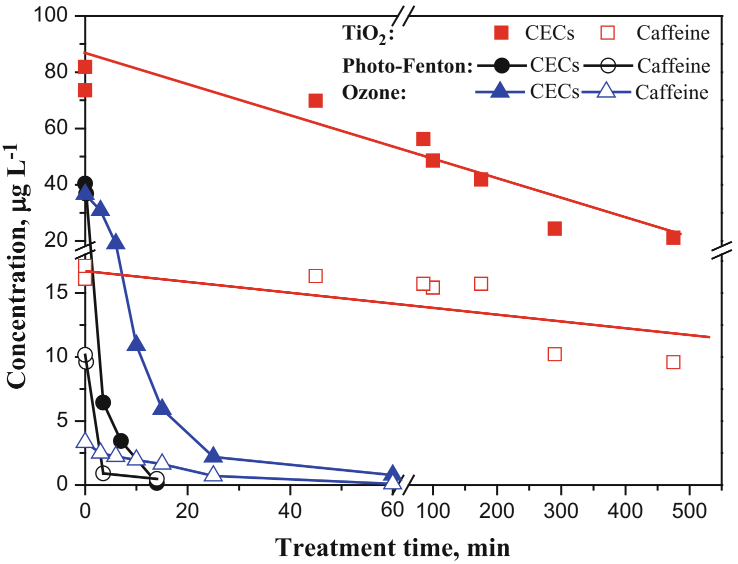

Fig. 3 Degradation of CEC by solar photocatalysis with TiO_2, solar photo-Fenton process, and ozonation. *Lines* are drawn for showing the trend of the results without any kinetic meaning

light source, optimizing the pH (by using iron complexing agents) and the amounts of oxidant/catalyst processes like photo-Fenton, may be used for commercial applications.

Heterogeneous photocatalysis with TiO_2 as catalyst has been widely tested for removal of CEC, mainly working with model compounds dissolved in demineralized water. Indeed, results applying this solar AOP are discouraging, perhaps due to the low photonic efficiency of the process, the scavenging of $HO^•$ by certain components of water (carbonates, chloride, etc.), and photocatalyst deactivation by adsorption of other components contained in MWTPs effluents [47]. It has been clearly demonstrated in the literature that heterogeneous photocatalysis with TiO_2 is not efficient for complete removal of microcontaminants, as the treatment time is in the range of several hours. Figure 3 shows an example of a real MWTP effluent (collected downstream of the secondary biological treatment) treated by this two different solar processes compared with ozonation. Initial concentrations of the microcontaminants detected were different depending on the day the wastewater was collected (40–80 μg L^{-1}) due to the inherent variability of real MWTP effluents. The concentration profile of each compound during degradation was determined by LC-MS analysis after applying solid-phase extraction. Figure 3 shows the degradation of the sum of all the microcontaminants and those found at higher concentrations (caffeine, for instance). Reaction rate of heterogeneous photocatalysis with TiO_2 is actually very low compared with the reaction rate showed by the other two advanced treatments.

Conventional solar photo-Fenton experiment with minimal concentration of iron (5 mg L^{-1}) and minimal initial concentration of H_2O_2 (50 mg L^{-1}) at neutral pH, produced, in general, slow degradation rates [48]. As iron precipitates at neutral pH, complexing agents, which are able to form photoactive species ($Fe^{3+}L$) [Eq. (1)], do not pollute the environment, increase toxicity, or reduce wastewater biodegradability, must be used for keeping iron in solution. As MWTP effluents do not normally contain these substances, since they are removed during drinking water treatment or consumed during the secondary biological treatment step (due to their biodegradable nature), they have to be added during the tertiary treatment:

$$\left[\mathrm{Fe}^{3+}\mathrm{L}\right] + h\nu \rightarrow \left[\mathrm{Fe}^{3+}\mathrm{L}\right]* \rightarrow \mathrm{Fe}^{2+} + \mathrm{L} \qquad (1)$$

Humic substances (HS) and in particular humic acids (HA) are naturally occurring organic substances which result from microbiological and chemical transformation of organic debris. Although HS differ depending on the source, some general properties are similar. They are the largest fraction of natural dissolved organic matter (NOM) showing strong light absorbance properties, and generating excited triplet states ($^3HS*$), various reactive oxygen species as singlet oxygen ($^1O_2$), and hydroxyl radicals. They behave like colloids and have absorptive qualities. They contain carboxylic acids; phenolic, alcoholic quinine; and amino and amido groups which enable them to support ion exchange and redox processes, to form stable complexes, and to stabilize free radicals [49–52].

Another type of complexing agents is aminopolycarboxylic acids (APCAs), which can form stable water-soluble complexes with metal ions and particularly with iron ions in a wide pH range. Therefore, they are used in a variety of domestic and industrial applications and for soil remediation. The most commonly used APCA is synthetically produced ethylenediaminetetraacetic acid (EDTA), but this substance is rather recalcitrant to biodegradation and has become a persistent organic contaminant [53]. Consequently, there is increasing interest to replace EDTA by another complexing agent like EDDS (ethylenediamine-*N*,*N′*-disuccinic acid), which has complexing properties similar to EDTA, but it is biodegradable, and it has been reported to be environmentally safe [54]. The useful chelating range for EDDS with Fe^{3+} is between pH 3 and 9 [55].

Results of MWTP effluents treatment with photo-Fenton modified by the addition of EDDS at neutral pH are promising, as the initial pH remained unmodified throughout the treatment, and therefore it is not necessary to be adjusted at the end of the oxidation process for water reuse. An illumination time of around 1 hour would be required to remove dozens of CEC, remaining at the end less than 5% of initial concentration. Indeed, tests conducted in the presence of carbonates [56] have shown that during photo-Fenton at neutral pH, inhibition of Fe^{2+} regeneration causes the stop of degradation after the initial Fenton phase due to the lack of photoactive ferric iron complexes and the high reactivity of $HO^{\bullet}$ with bicarbonate (rate constant 8.5×10^6 M^{-1} s^{-1}). This is the main reason why the effect of bicarbonate ions present in aqueous solution on organic compounds degradation by AOPs is usually so negative. However, experiments at neutral pH using EDDS showed that carbonates/bicarbonates did not significantly affect the CEC degradation rate [57]. The main drawback is the treatment cost, as EDDS is also degraded during the process and so it is not recoverable. Another drawback though is the increase in the DOC of the treated waters, as EDDS has to be added in at least the same molar concentration as iron to deliver good results.

4 Membrane Technologies Applied to Wastewater Concentration and Purification

Continuous improvements in existing technologies and development of new techniques for water treatment have resulted in breakthroughs in wastewater treatment and reclamation for water reuse. The membrane technology (MT) is included in this progress, which has emerged as a significant innovation for treatment and reclamation as well as a leading process in the upgrade and expansion of wastewater treatment plants.

The MT has proven to be a reliable technique with applications such as desalination, drinking water treatment, wastewater treatment (domestic, gray wastewater, industrial, municipal, leachate, and effluent reclamation), and reuse [58, 59]. During the last years, this technology has received much attention by researchers and manufactures, mainly because of the improvement of membrane materials and techniques, which provide higher fluxes, long lifetime and have partly solved the fouling problems, which can be considered as one of the most important costs of the process. This overall growth in the use of membranes can be attributed to, at least, the following factors: (1) increased legal pressure in the regulation of drinking water and wastewater; (2) increasing water demand, leading to its rational use; and (3) further development and commercialization of membrane technologies as well as sewage industries. Although the use of membranes for wastewater treatment appeared, approximately, 30 years ago, over the past decade, there has been a rapid increase in wastewater volume treated with membranes as it provides exceptionally high-quality standards, typically for reuse purposes [60–62].

Membranes are a feasible option because they enable the removal of contaminants that other conventional technologies cannot. They are also more economical than other alternatives, or require much less land area than competing technologies, since the combination of membrane filtration and biological treatment avoids secondary clarification and tertiary steps [63, 64]. For wastewater treatment applications, membranes are currently being used as a tertiary treatment for the removal of dissolved organic compounds, phosphorus, nitrogen species, colloidal and suspended solids, pathogens, and other microorganisms. Membrane systems for wastewater treatment include:

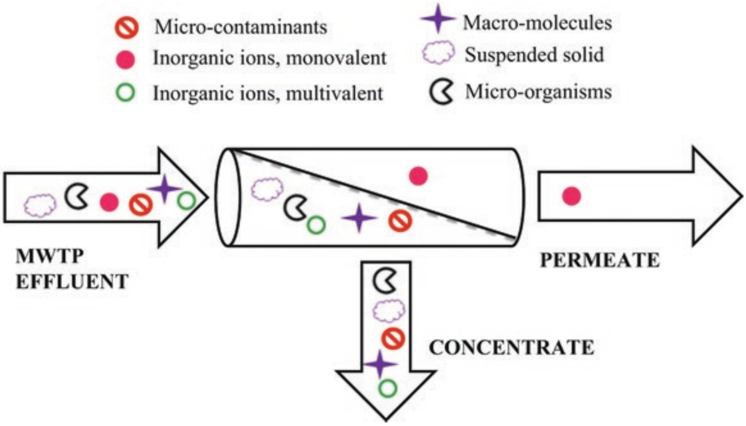

Fig. 4 Schematic diagram for a NF membrane. The RO has the same concept though inorganic monovalent ions are also retained

1. Membrane BioReactors (MBR): including usually microfiltration (MF) or ultrafiltration (UF) membranes immersed in aeration tanks (the most extended option), or implemented in external pressure-driven membrane units, as a replacement for secondary clarifiers and tertiary polishing filters [63]. Nowadays, the MBR are also using the external nanofiltration (NF) membrane [64] and submerged NF [65, 66], because this type (NF) is more efficient in the elimination of emerging contaminants.
2. Low-pressure membranes: usually MF or UF membranes, either as a pressure system or an immersed system. These technologies provide a higher degree of suspended solids removal following secondary clarification.
3. High-pressure membranes: NF or RO pressure systems for treatment and production of high-quality effluents that may be used for irrigation and industrial process water. Also, recent research has shown that CEC, such as PPCPs, can be removed by high-pressure membranes (see Fig. 4) [67–69].

Pressure-driven membrane processes (MF, UF, NF, RO) separate a feed stream into a purified permeate fraction, which is usually the desired product, and a concentrated fraction, the concentrate or retentate. MF membranes, which have pores ranging from 0.1 to 2 μm, operate at pressures below 5 bar, and bacteria/protozoa larger than the pore size can be removed from the feeding solution. UF membranes, additionally, remove macromolecules with a molecular weight above 5,000–100,000, depending on the membrane pore size. The operating pressure ranges from 2 to 8 bar. UF also acts as a disinfection barrier by removing bacteria as well as viruses. In NF, the rejection is extended to organic compounds with a molecular weight above 200–500 (depending on the pore size) and to multivalent ions (due to the membrane charge); the operating pressure is 5–15 bar. In RO, pressures range from 50 to 100 bar (seawater desalination as main application) or 15 to 50 bar (brackish water desalination and other applications). Membranes are dense and allow the retention of small organic compounds as well as ions; larger components may obviously also be removed but are usually removed in a MF/UF pretreatment as they may cause severe fouling problems in spiral wound NF or RO units [70].

The greatest technical defiance of the use of membranes for wastewater treatment is the fouling (scaling by means of inorganic ions, or biofouling by means of microorganisms) that affects system performance (reducing efficiency and shortening membrane life) and economic viability. Membrane fouling, which can be caused by colloids, soluble organic compounds, and microorganisms that are typically not well removed with conventional pretreatment methods, increases feeding pressure and requires frequent membrane cleaning [71, 72]. Other technical obstacles can include the complexity and expense of the concentrate treatment generated from membrane. In this sense, although in recent years MTs have been shown to be the most promising technologies for microcontaminant separation from wastewater [73], such systems are not destructives techniques. Most of the organics present in the NF and RO concentrates from MWTP effluents are mainly microcontaminants which are biorecalcitrant, since they have already been subjected to extensive biological treatment in the MWTP [74, 75]. Although NF/RO applied to microcontaminant separation has been also studied, some authors have focused rather on the separation mechanisms as a function of the physicochemical properties of the microcontaminants [71, 76]. Others studies have investigated how fouling affects the pharmaceuticals rejection [71, 73, 79, 80], and others authors centered their works in the membrane operation conditions (flux, pressure, temperature, pH, water characteristics, etc.) and their influence over microcontaminant separation [77, 78, 81, 82]. However, the main problem is the disposal of the generated concentrate which should be treated to minimize their environmental impact but normally is discharged into the ocean or surface water [58] or returned into the biologic system [83, 84]. Recent studies have demonstrated the impacts of NF concentrate recirculation (mainly in the fouling of the MBR, inorganic ions impact, and the different operations conditions) on membrane performance in an integrated MBR, during 364 days of system operation [85]. However, high salt content in wastewater is known to significantly reduce the treatment efficiency of conventional activated sludge, anaerobic, nitrification and denitrification processes [86–88]. Therefore, further research is still needed as one of the most important aspects of NF concentrate recirculation, the accumulation of the CEC on biomass and their chronic toxicity, has not been evaluated yet. These microcontaminants, in relatively low concentration (ng L^{-1} and μg L^{-1}), would be returned into a biological system which is not able to remove it and also may have a long-term negative impact. Further treatment is therefore necessary in the NF concentrate, and AOPs [60, 89] could be a good option.

On the other hand, the information available regarding the treatment of membrane concentrates containing microcontaminants by AOPs is very limited, especially when the main purpose is to evaluate microcontaminant removal in concentrates from MWTP effluents at low realistic concentrations (ng L^{-1} and μg L^{-1} range) [83, 90–92]. The most applied AOPs are ozonation (O_3, UV/O_3,

$UV/O_3/H_2O_2$, or O_3/H_2O_2) and electrochemical oxidation, but heterogeneous photocatalysis (UV/TiO_2, $UV/TiO_2/H_2O_2$, and iron oxides supported), photo-oxidation (UV/H_2O_2), ultrasound [59], and homogeneous photocatalysis ($UV/Fe^{2+}/H_2O_2$) [91] have been applied too. According to literature, DOC or model contaminants are usually monitored at mg L^{-1} concentrations, far from realistic conditions (in MWTP effluents) [74–76, 93–95].

5 Solar Advanced Disinfection Processes for Reusing Purposes

Untreated municipal wastewater contains a range of constituents, from dissolved metals and trace organic compounds to solids (rags, sticks, floating objects, grit, and grease) and a wide range of microorganisms. As widely stated in this chapter, treated wastewater for recovery requires a secondary treatment, which removes large suspended solids, dissolved organic matter, nutrients, and inorganic contents. Small particles may remain after a secondary treatment, including microorganisms and dissolved organic and inorganic matter; therefore, further treatment is a prerequisite for water recovery.

The main groups of pathogens found in wastewater are bacteria (e.g., *Escherichia coli*, *Salmonella* spp.), viruses (e.g., *Enteroviruses*, rotavirus, hepatitis A), protozoa (e.g., *Giardia lamblia*, *Cryptosporidium parvum*), and helminths (e.g., *Taenia* spp. (Tapeworm), *Ancylostoma* spp. (Hookworm)). While most microbes are harmless or beneficial for public health, others pose high health risk into the environment, including humans. Therefore, the main concern in treated wastewater reuse is decreasing the health risk associated with hazardous pathogens. International and national regulations and guidelines about wastewater restricted reuse establish limits for a number of biological parameters to control this biological risk.

In this chapter, new technologies highly efficient for the removal of chemicals contained in urban wastewater have been presented, but these must also be able to reduce levels of water pathogens although they cannot be considered as disinfection techniques. These processes include conventional and advanced secondary biological treatments. Table 2 presents the capability, in terms of log reduction, of the most commonly used treatments for pathogens removal in urban wastewater.

The challenge for future technologies which bring solutions for feasible wastewater reuse is to efficiently remove pathogens and chemical microcontaminants in the same processes. In this line, recent contributions explore the capability of AOPs to decrease emerging contaminants including antibiotics, pharmaceuticals, etc., and some enteric bacteria in real wastewater effluents. The photocatalytic treatment of TiO_2 in suspension and immobilized onto a fixed-bed reactor were used for the simultaneous *E. coli* inactivation and oxidation of pharmaceuticals in simulated wastewater treatment plant effluents [96]. The successful results obtained demonstrated that TiO_2 is an interesting technology for the treatment of wastewater,

Table 2 Log removals of microorganisms' indicators and enteric pathogens contained in urban treated wastewater with different water treatments

	E. coli (I)	*Clostridium perfringens* (I)	Phage (I)	Enteric bacteria	Enteric viruses	*Giardia lamblia*	*Cryptosporidium parvum*	Helminths
Secondary treatment	1–3	0.5–1	0.5–2.5	1–3	0.5–2	0.5–1.5	0.5–1	0–2
Membrane filtration	4 to >6	>6	2 to >6	>6	2 to >6	>6	4 to >6	>6
Reservoir storage	1–5	N/A	1–4	1–5	1–4	3–4	1–3.5	1.5 to >3
Ozonation	2–6	0–0.5	2–6	2–6	3–6	2–4	1–2	N/A
UV treatment	2 to >6	N/A	3 to >6	2 to >6	1 to >6	3 to >6	3 to >6	N/A
Advanced oxidation	>6	N/A	>6	>6	>6	>6	>6	N/A
Chlorination	2 to >6	1–2	0–2.5	2 to >6	1–3	0.5–1.5	0–0.5	0–1

Source: US Environmental Protection Agency 2012
(*I*) microorganisms' indicator, *N/A* not available

allowing the removal of CEC during the disinfection treatment. More recently, the same authors evaluated several photochemical technologies with the aim to simultaneously achieve bacterial inactivation and oxidation of pharmaceuticals. The technologies evaluated were UV-C and UV-C/H_2O_2, UV-A/TiO_2, and UV-A/TiO_2/H_2O_2. It was found that only UV-A/TiO_2 treatment achieved both completed *E. coli* inactivation and removal of pharmaceuticals along the process [97]. Gerrity et al., investigated the use of ozone for contaminant oxidation (trace organic contaminants) and disinfection (bacteriophage MS2, total and fecal coliforms, and *Bacillus* spores) for water reclamation in Reno, Nevada. The authors highlighted that this treatment could be an alternative to the standard indirect potable reuse configuration which includes membrane filtration, RO, UV/H_2O_2, and aquifer injection thanks to the high degree of microbial inactivation and contaminant destruction obtained [98].

Recently, some chemicals present in wastewater have acquired high interest by their impact on the environment. This is the case of antibiotics which may lead to proliferation of antibiotic resistance (AR) in pathogenic or nonpathogenic environmental microorganisms [99]. The efficiency of disinfection treatment to remove both antibiotics and antibiotic-resistant bacteria (ARB) from wastewater effluents has been investigated by Rizzo et al. These authors compared the effect of UV radiation and chlorination on the reduction of ARB (*E. coli* in this case) and three antibiotics (ciprofloxacin, amoxicillin, and sulfamethoxazole) concluding that conventional disinfection processes may not be effective in the inactivation of ARB [100]. A similar investigation using natural solar radiation and chlorine was done by these authors with a multidrug-resistant *E. coli* (MDR) strains selected from an urban wastewater. In this study, it was observed that chlorination achieved a higher inactivation compared to solar UV radiation. On the other hand, the solar photodegradation of antibiotics determined that the risk of the development of resistance to sulfamethoxazole in surface water was significantly higher compared to ciprofloxacin and amoxicillin [101].

6 Conclusions

The implementation of the Urban Wastewater Treatment Directive requires significant investments, probably the most substantial in the environmental sector, due to its requirement for providing wastewater treatment infrastructure for urban areas. Two alternative approaches are available for pollution abatement: “end-of-pipe” solutions, such as wastewater treatment, or “at source” measures, which aim to reduce the use and emission of polluting substances by economic sectors (e.g., through resource-efficiency measures or spatial legislative restrictions that limit the use of certain substances such as pesticides in designated areas). Regarding “end-of-pipe” approaches to cleaning up pollution, the implementation of the Urban Wastewater Treatment Directive has led to an increasing proportion of Europe’s population being connected to a municipal treatment works. The associated improvements in wastewater treatment have resulted in reduced discharges of nutrients, microbes, and some hazardous chemicals to receiving waters.

Recent literature shows widespread presence of different types of microcontaminants throughout the environment. It has been clearly found that their removal depends not only on their physicochemical properties but also on the source water characteristics, operational conditions, and treatment technologies used. Conventional and advanced biological treatments used as secondary step in MWTPs have been demonstrated to be inefficient in the elimination of microcontaminants present at so low concentrations (μg L^{-1} and ng L^{-1}). Even though, advanced biological processes have shown more stable behavior against changes in urban wastewater characteristics and adsorption equilibria responsible of a higher percentage of contaminants removed. Therefore, intelligent technical solutions with an appropriate treatment and an acceptable cost-efficiency should be maintained to solve the difficult situation between investment and environmental requirements. In this sense, AOPs are proposed as highly efficient tertiary treatments for the complete elimination of microcontaminants contained in the secondary treatment effluents. Several scientific works have been recently published, showing the successful elimination of specific microcontaminants contained in actual urban wastewater. In addition, the promising results obtained by using complexing agents for maintaining iron in solution at neutral pH for photo-Fenton applications are highly attractive. Furthermore, the use of NF membranes for concentrating microcontaminants and so reducing operating costs related to the reagents consumption and energy required for their complete elimination is also under study nowadays.

Membrane technologies are being also more and more used by MWTPs to polish the quality of the effluent and permitting its reuse. This fact reinforces the necessity of solving the environmental issue related with retentates that cannot be disposed to the water sources. Recirculating to the secondary biotreatment due to uncertainties in adsorption, bioaccumulation, and poising on activated sludge is not recommended.

Finally, combined advanced technologies applied for microcontaminant oxidation with high efficiency must be capable also to eliminate microorganisms contained in the treated effluents when water recovery and reuse is aimed.

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Immobilized Heterogeneous Photocatalysis for Reuse of Water Contaminated by Recalcitrant Organic Compounds: The Case of Antibiotics

Marie-Noëlle Pons, Amélie Le Frêche, Aurélie Cortyl, Jessica Van Deik, Marie Poret, and Orfan Zahraa

Abstract Photocatalysis has often being proposed to destroy micropollutants recalcitrant to biological treatment. However, the use of suspension of TiO_2 nanoparticles at an industrial scale is not easy. The chapter reports on the evaluation of the efficiency of two photocatalysts (P25 and PC500) immobilized on glass plates and cellulose fibers for the degradation of three antibiotics (amoxicilline, sulfamethoxazole and tylosin) used in human and animal medicine. Although the degradation rates of these antibiotics observed with the immobilized photocatalysts are lower than those reported in the literature with suspended photocatalysts for the same molecules, the feasibility of their degradation has been assessed.

Keywords Amoxicillin, Sulfamethoxazole, Titanium dioxide, Tylosin, UV light

Contents

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Abbreviations

[AB]	Antibiotic concentration
$[AB]_0$	Initial antibiotic concentration
e^{-}_{cb}	Electron in the conduction band
h^{+}_{vb}	Hole in the valence band
k_{deg}	Degradation constant
KLH	Adsorption constant
r	Rate of reaction
$r0$	Initial rate of degradation

1 Introduction

With 2,800 m^3 available per inhabitant and per year, France is not globally at risk of water shortage. About 3,000 million m^3 of water were used in 2010 for irrigation, 61% being withdrawn from rivers or reservoirs. About 5,500 million m^3 of water were used in the same year for potable water production, 71% being groundwater (http://www.statistiques.developpement-durable.gouv.fr/). But the water resource is not equally distributed over the country. The Mediterranean region is under a dry climate, and the southwest of France has high demand for irrigation. In Ile-de-France (i.e., the region around Paris) where about 12 million people are living, the demand excesses the resource. Therefore, the question of developing new water resources and directly reusing reclaimed wastewater is receiving a growing interest. In fact, indirect reuse is more widespread than many people think. Drinking water production from surface water is often impacted by the discharge upstream of the intake point of many wastewater treatment plants.

If the efficiency of wastewater treatment plants with respect to major pollutants and nutrients is now under control, the question of micropollutants transported by wastewater and recalcitrant to classical (i.e., biological) treatment remains a very actual problem for stakeholders. These micropollutants result from human activities, and their origin is not only industrial but also domestic. Among the domestic micropollutants, pharmaceuticals have often been pointed out as a threat for the last 25 years not only in Europe [1–3] or the USA [4] but all over the world [5]. This question is critical in France, which in 2000 was the largest pharmaceuticals consumer in Europe [6]. Efforts have been made but France is still ranking first in Europe with regard to the antibiotics consumption (Fig. 1). Discharge of treated wastewater is not the only way for pharmaceuticals to enter into the aquatic environment. Run-off from fields after spreading of manure [7] or ill-stabilized wastewater sludge is another route. In France (which produces 20.4% and 19.3% of young and adult cattle, respectively, 13.6% of poultry, and 8.9% of pigs raised in Europe according to 2013 Eurostat data (ec.europa.eu/eurostat)), the exposition of animals to antibiotics in 2012 is similar to what it was in 1999, except for pigs: the total weight of treated pigs has been divided by a factor of 2 [8], although the

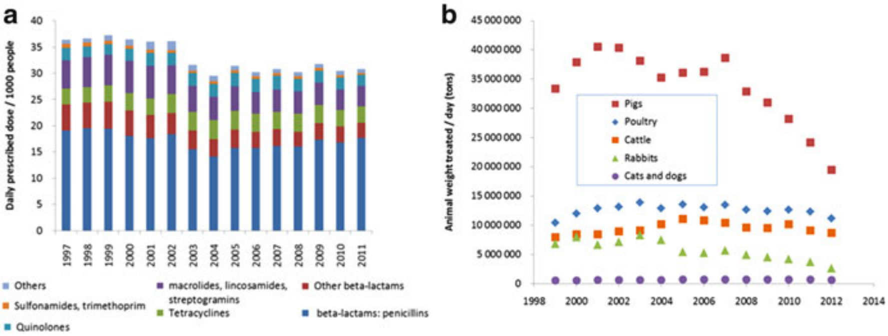


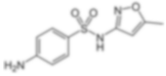
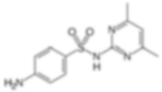
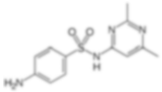
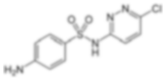
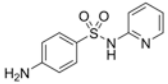
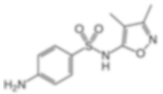
Fig. 1 Consumption of antibiotics in France: (**a**) humans; (**b**) animals. (Data from [8])

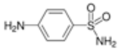
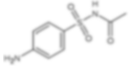
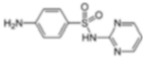
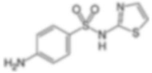
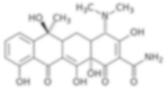
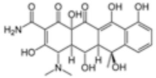
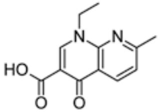
number of pigs has increased by 7% from 2000 to 2010 [9]. Another problem associated with the presence of antibiotics, either in or near wastewater treatment plants [10, 11] or in the aquatic environment [12–15] impacted by industrial discharges [7, 16–18], agriculture run-off [19], animal facilities [20, 21], or aquaculture [22–25], is the development and the spreading of antibiotic resistant bacteria [26, 27] and antibiotic resistance genes. If reclaimed wastewater reuse, for example, for irrigation [28], is one of the solutions to reduce water scarcity, public health should not be jeopardized [29–31].

Finding an advanced treatment to eliminate antibiotics residues from reclaimed wastewater has been a topic of research for several years. Among the proposed processes [32], photocatalysis appears environmentally friendly as it does not use reagents other than a catalyst which is basically reusable and can utilize solar light. In photocatalysis, absorption of a photon in the near-UV range promotes an electron, e^{-}_{cb}, to the conduction band, which produces a hole, h^{+}_{vb}, in the valence band. If separated, these two species can migrate to the catalyst surface and act as a reducer (oxygen reduction of a superoxide ion) and an oxidant (e.g., water oxidation of a hydroxyl radical or direct oxidation of the reactant), thus regenerating the catalyst electronic population. Highly reactive species such as hydroxyl radicals can react on adsorbed organic molecules and abstract a hydrogen atom and therefore induce oxidation. The ultimate goal is to transform the organic molecule into CO_2 and H_2O. The fate of nitrogen atoms present in the molecule depends upon the type of bonds, the end products being N_2 (as a gas), ammonium, and/or nitrate ions [33].

In Table 1, studies aiming at the photocatalytic degradation of various antibiotics are listed. Three families of antibiotics have been mostly investigated: sulfonamides (with nine different congeners of sulfamethoxazole), quinolones/fluoroquinolones, and penicillins/aminopenicillins. Macrolides have received much less interest in terms of number of molecules and number of reports on their photocatalytic degradation. Photocatalysis looks also promising with respect to antimicrobial resistance [94]. P25 titanium dioxide has been widely tested, mostly in suspension and under UV (365 nm) or solar/visible light. In most reports,

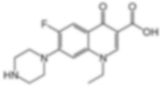
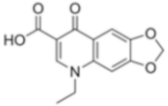
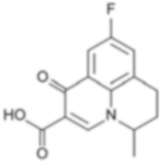
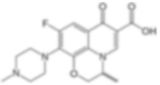
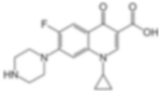
Table 1 Application of photocatalysis to antibiotics

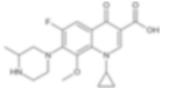
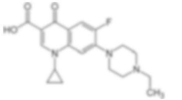
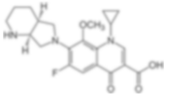
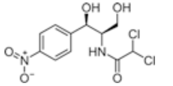
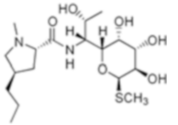
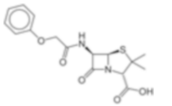
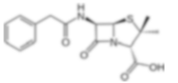
Antibiotic	Structure	Type	Photocatalyst	Light type	References
Sulfamethoxazole		Sulfonamide	TiO_2 (P25) (susp.)	LED (365 nm)	[34]
			TiO_2 (P25) (susp.) + H_2O_2	UV (300–400 nm)	[35]
			TiO_2 (P25) (susp.)	$\lambda > 290$ nm	[36, 37]
			TiO_2 (P25) (susp.)	UV (366 nm)	[38]
			TiO_2 (P25) (susp.)	UV (254 nm)	[39]
			TiO_2 (different kinds) (susp.)	UV (340–400 nm)	[40]
			TiO_2 (P25, SiO_x/TiO_2, Pt/TiO_2 susp.)	UV (254 and 365 nm)	[41]
			$H_3PW_{12}O_{40}/Ag–TiO_2$ (susp.)	$320 \text{ nm} < \lambda < 680$ nm	[42]
			$Bi_2O_3/Bi_2O_2CO_3/Sr_6Bi_2O_9$	$\lambda > 420$ nm (visible)	[43]
			TiO_2 (P25, Hombikat UV-100 (anatase; TiOxide (rutile)) (susp.)	324–400 nm	[44]
Sulfamethazine		Sulfonamide	Bi_2MoO_6(susp.)	Visible	[45]
			TiO_2 (P25) (susp.)	UV (365 nm)	[46]
			ZnO (susp.)	UV (365 nm)	[46]
Sulfisomidine		Sulfonamide	TiO_2 (P25) (susp.)	UV (200–436 nm)	[47]
Sulfachloropyridazine		Sulfonamide	TiO_2 (P25) (susp.)	UV (365 nm)	[48]
Sulfapyridine		Sulfonamide	TiO_2 (P25) (susp.)	UV (365 nm)	[48]
Sulfisoxazole		Sulfonamide	TiO_2 (P25) (susp.)	UV (365 nm)	[48]

Sulfanilamide		Sulfonamide	TiO_2 (P25) (susp.)	UV (366 nm)	[49]
Sulfacetamide		Sulfonamide	TiO_2 (P25) (susp.)	UV (366 nm)	[49]
Sulfadiazine		Sulfonamide	TiO_2 (P25) (susp.)	UV (366 nm)	[49]
Sulfathiazole		Sulfonamide	TiO_2 (P25) (susp.)	UV (366 nm)	[49]
Tetracycline		Tetracycline	Sr-Bi_2O_3 (susp.)	Visible	[50]
			TiO_2(susp.)	254 nm, 365 nm, solar light	[51]
			TiO_2 (P25) (susp.)	UV (365 nm)	[52]
			TiO_2 (P25 & Merck) (susp.)	UV (366 nm)	[53]
			TiO_2 (P25) (susp.)	Solar light	[54]
			Mesoporous BiOI microspheres (susp.)	Visible	[55]
			$Bi_{24}O_{31}Br_{10}$ nanoflakes	Visible	[56]
			ZnO (susp.)	Solar light	[54]
Oxytetracycline		Tetracycline	TiO_2 (P25) (susp.)	LED (365 nm)	[34]
			TiO_2 (P25) (susp.)	Solar light	[57, 58]
			TiO_2 + zeolites (susp.)	UV (254 nm)	[59]
			NF-TiO_2 (film)	$\lambda > 420$ nm	[60]
			La3+@POPD/TiO2/fly-ash cenospheres	Visible	[61]
Nalidixic acid		Quinolone	TiO_2 nanorod/silver nanoparticles (film)	$\lambda > 250$ nm	[62]
			TiO_2 nanorods (film)	$\lambda > 250$ nm	[62]
			TiO_2 (P25) (film)	$\lambda > 250$ nm	[62]

(continued)

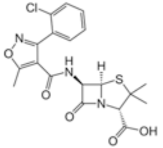
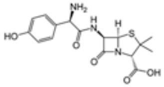
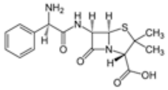
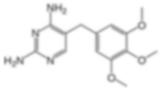
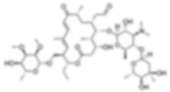
Table 1 (continued)

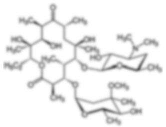
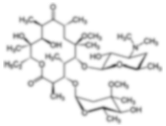
Norfloxacin		Quinolone	TiO_2 (Hombikat UV100 and P25) (susp.)	Visible and UV ($\lambda > 324$ nm)	[63]
Oxolinic acid		Quinolone	TiO_2 (P25) (susp.)	Visible	[68]
			TiO_2 (P25) (susp.)	UV (365 nm)	[64]
			TiO_2 (film)	UV (360 nm)	[65]
Flumequine		Quinolone	TiO_2 (P25) (susp.)	UV (254 nm)	[66]
			TiO_2 (P25) (susp.)	UV (300–400 nm)	[35]
			Doped (urea and thiourea) TiO2 (susp.)	Visible (simulated solar light)	[67]
Ofloxacin		Fluoroquinolone	TiO_2 (P25) (susp.)	UV (300–400 nm)	[35]
			TiO_2 (P25) (susp.)	UV (254–366 nm)	[68]
			TiO_2 (different kinds: P25, Hombikat, Tronox, Aldrich) (susp.)	UV (350–400 nm)	[69]
Ciprofloxacin		Fluoroquinolone	POPD/TiO_2/fly-ash cenospheres (susp.)	Visible	[70]
			TiO_2 (P25) (susp.)	UV (254 and 365 nm)	[71]
			TiO_2 (P25) (susp.)	UV (365 nm)	[72]
			TiO_2 (P25) (susp.)	UV (365 nm)	[73]
			TiO_2 (Hombikat UV100 and P25) (susp.)	Visible and UV ($\lambda > 324$ nm)	[63]
			TiO_2 (Hombikat UV100) (susp.)	Visible and UV ($\lambda > 324$ nm)	[74]
			TiO_2/fly ash (susp.)	Visible	[75]
			Fe^{2+}/Fe^{3+} on TiO_2/fly-ash cenospheres	Visible	[76]
			ZnS microspheres	UV (365 nm)	[2, 77]

Gatifloxacin		Fluoroquinolone	ZnS microspheres	UV (365 nm)	[2, 77]
Enrofloxacin		Fluoroquinolone	TiO_2 (Hombikat UV100 and P25) (susp.)	Visible and UV ($\lambda > 324$ nm)	[63]
Moxifloxacin		Fluoroquinolone	TiO_2 (P25) (susp.)	UV (365 nm)	[71, 78, 79]
Chloramphenicol			TiO_2(P25, Tronox, Merck) (susp.)	UV (365 nm)	[80]
			ZnO (susp.)	UV (365 nm)	[80]
			TiO_2 (100% anatase) (susp.)	UV ($\lambda > 300$ nm)	[81]
Lincomycin		Lincosamide	TiO_2 (P25) (susp.)	Solar light	[82]
			TiO_2 (P25 and Merck) (susp.)	UV (365 nm)	[53]
Penicillin V		Penicillin	ZnS (susp.)	Visible	[83]
Penicillin G		Penicillin	ZnS (susp.)	Visible	[83]

(continued)

Table 1 (continued)

Cloxacillin		Penicillin	TiO_2 (anatase)	UV (365 nm)	[84]
			ZnO	UV (365 nm)	[85]
			ZnS (susp.)	Visible	[83]
Amoxicillin		Aminopenicillin	TiO_2 (anatase) (susp.)	UV (365 nm)	[84]
			TiO_2 (P25) (susp.)	Solar light	[86]
			TiO_2 (P25, iron & carbon doped titania) (susp.)	UV (365 nm), artificial daylight	[87]
			TiO_2 (P25) (susp.)	UV (360 nm)	[88]
			TiO_2 (different kinds) (susp.)	UV (340–400 nm)	[89]
			ZnS (susp.)	Visible	[83]
			ZnO (susp.)	UV (365 nm)	[85]
Ampicillin		Aminopenicillin	TiO_2 (anatase) (susp.)	UV (365 nm)	[84]
			ZnO (susp.)	UV (365 nm)	[85]
			ZnS (susp.)	Visible	[83]
			ZnO/polyaniline nanocomposite	Solar light	[90]
Trimethoprim		Dihydrofolate reductase inhibitor	TiO_2 (P25) (susp.)	UV (λ > 280 nm)	[37]
Tylosin		Macrolide	TiO_2 (P25, PC105, PC500) (film)	UV (365 nm)	[91]

Erythromycin		Macrolide	TiO_2 (different kinds) (susp.)	UV (340–400 nm)	[92]
Clarithromycin		Macrolide	TiO_2 (P25) (susp.)	Solar	[93]

its high photocatalytic efficiency was pointed out. As titanium dioxide is less efficient under visible light than under UV light, photocatalysts able to work under visible light are being developed, either by modification of TiO_2 [61, 67, 75] or by using elements such as Zn [46, 54] or Bi [43, 45, 50]. It is however very difficult to compare the results obtained by the different research groups due to the various ways to report data (removal yield or rate, kinetic parameters) and to the large spectrum of operation conditions (such as light intensity, catalyst loading, and tested molecule concentration).

Experiments with suspensions of nanoparticles are easy to set up. But the separation of nanoparticles from the liquid phase after treatment is a critical step [95], especially in terms of industrial scale-up. Furthermore, there has been a growing concern about the toxicity of free nanoparticles [96]. Growth inhibition effects have been reported for bacteria and aquatic algae [97]. Primary endothelial human cells can be damaged by TiO_2 nanoparticles [98], for which genotoxic effect on human lymphocytes [99] and neuronal cells [100] has been reported. Endocrine and reproductive effects due to TiO_2 nanoparticles have been demonstrated on mammals (rats) [101]. Various processes have been developed to contain at best the nanoparticles within the processes: reactors with optimized settling units [102, 103], magnetic photocatalytic particles for easy recovery [104], and membrane reactors with microfiltration or ultrafiltration membranes of various chemical natures [105–112]. Among the problems listed with membranes are the possible reaction of their polymeric material under UV light and the abrasion by nanoparticles.

To limit the problem of working with nanoparticles in suspension, one solution is to immobilize them on a support. Many researchers have investigated the feasibility of coating the photocatalyst on inert surfaces such as glass beads [113] or plates [114, 115], activated carbon fibers [116], cotton material [117], cellulose fibers [118, 119], and cement surface [120]. One of the drawbacks of immobilization is that the activity of the photocatalyst is reduced.

It is not clear whether photocatalytic performance observed with photocatalysts in suspension slurries can be transposed easily when they are immobilized. The immobilization can change some properties such as crystallinity or crystallite size [121]. Immobilized photocatalysts have successfully degraded textile dyes [122, 123] or pesticides [124]. Our purpose has been to test the degradation of some antibiotics of three different families, i.e., sulfamethoxazole (sulfonamide), tylosin (macrolide), and amoxicillin (aminopenicillin), under UV light (365 nm), with TiO_2 immobilized either on glass plates (prepared in the laboratory) or on cellulose fibers (commercial support).

2 Materials and Methods

2.1 *Reactor*

The experimental setup which has been used for all experiments is shown in Fig. 2. The photocatalyst support (surface = 0.019 m^2, thickness = 0.003 m) is placed on the bottom of the glass tank (50.5 × 5.0 × 0.04 cm). The distance between the photocatalyst and the lamp is 6.3 cm. The lamp intensity has been measured with a VLX-3W radiometer (Vilber Lourmat Deutschland GmbH, Eberhardzell, Germany). The pump was operated at a flow rate of 0.22 L min^{-1}.

All experiments were conducted at 20°C, with the reservoir open to air, at the inherent pH solution (i.e., between 4 and 7). Irradiation of the photocatalysts was carried out either by a Phillips TL-D 18W UV fluorescent lamp (emission spectrum range, 315–400 nm; maximum emission wavelength, 365 nm) or an Osram L18W/640 lamp (emission spectrum range, 400–640 nm; maximum emission wavelength, 480 nm). The lamp was positioned parallel to the plate. The antibiotic solution (volume = 250 mL) was circulated for an hour in the dark prior to irradiation to evaluate for the antibiotic adsorption onto the photocatalysts.

2.2 *Immobilized Photocatalysts*

Two different titanium dioxide powders were tested. P25 (Evonik Industries, Essen, Germany) is mainly anatase (70% anatase, 30% rutile). According to the manufacturer's specifications [125], the elementary particle is quasi-spherical and its size is approximately 20 nm. The specific surface area, as measured from N_2 adsorption at

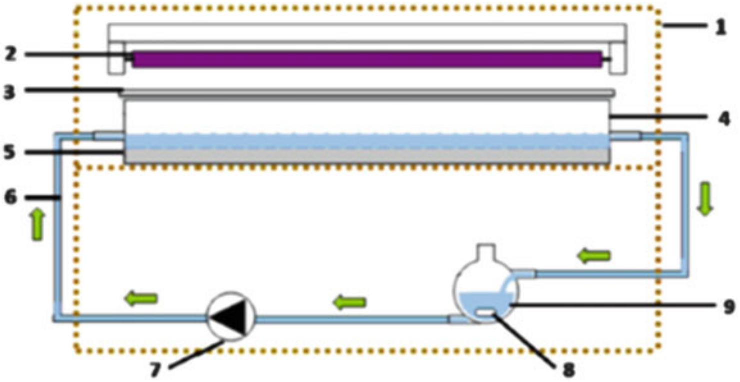


Fig. 2 Experimental setup: (1) protecting cover, (2) UV lamp, (3) protecting glass plate, (4) glass tank, (5) photocatalyst + support, (6) PTFE tubing, (7) peristaltic pump, (8) magnetic stirrer, (9) reservoir

77 K, is 44 m^2 g^{-1}, in agreement with the manufacturer's specifications. The other titanium dioxide powder was PC500 (100% anatase) (gift from Millennium Inorganic Chemicals, Paris, France). This catalyst has an average particle size of 5–10 nm and a specific surface area in the range 250–300 m^2 g^{-1} [126–128].

TiO_2 nanoparticles were fixed on glass plates by a heat attachment method [129]. A 4 g L^{-1} suspension of TiO_2 was prepared in deionized water. After pH adjustment with diluted HNO_3 to 3, the suspension was sonicated for 15 min (Bransonic 220, France). Then proper volume of suspension was carefully poured on the glass plate, previously pretreated by HF and washed with a NaOH solution, and allowed to dry out at room temperature for 12 h and at 100°C for 1 h. After drying, the plates were calcined at 475°C for 4 h. The procedure was repeated three times in order to get a homogenous coverage of the plate. The optical characteristics of the glass plates with immobilized photocatalysts were assessed with a Shimadzu LISR-2100 integrating sphere (Shimadzu, Duisburg, Germany). A nonwoven fabric made of cellulose fibers on which PC500 TiO_2 (18 g m^{-2}) has been fixed by compression was also used (gift from Ahlstrom, Pont-Evêque, France).

2.3 *Chemicals and Analysis*

Tylosin tartrate, amoxicillin, and sulfamethoxazole were purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France) and used without further purification. Methanol (HPLC grade), phosphoric acid, acetic acid, and formic acid and all other chemicals were of analytical reagent grade from FLUKA. Ultrapure water was used for the preparation of all solutions and titanium dioxide slurries and was obtained from a Milli-Q Gradient water system (Millipore, Molsheim, France).

The HPLC chromatography was carried out with a Shimadzu SPD-10A equipped with a UV–Vis spectrophotometric detector (set at 262 nm for sulfamethoxazole, 270 nm for amoxicillin, and 290 nm for tylosin). A Lichrosorb C18 250 × 4.6 mm column or a Grace Smart RP 18 5 μ–250 × 2.1 mm column was used. The solvent is a mixture of water (50%), methanol (0.2%), and formic acid (50%). For some experiments, sulfate, nitrate, and ammonium ions were monitored by ion chromatography.

3 Results and Discussion

3.1 *General*

Figure 3 compares the absorbance spectra of P25 and PC500 immobilized on glass and the UV–Vis spectra of the three antibiotics. At 365 nm (the wavelength of the maximal emission of the UV lamp), the absorbance of the immobilized P25 is

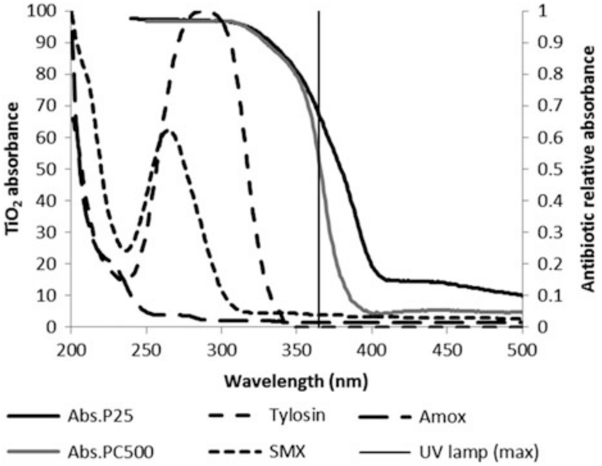


Fig. 3 Absorbance spectra of photocatalysts immobilized on glass plates and normalized UV–Vis spectra of antibiotics in aqueous solution

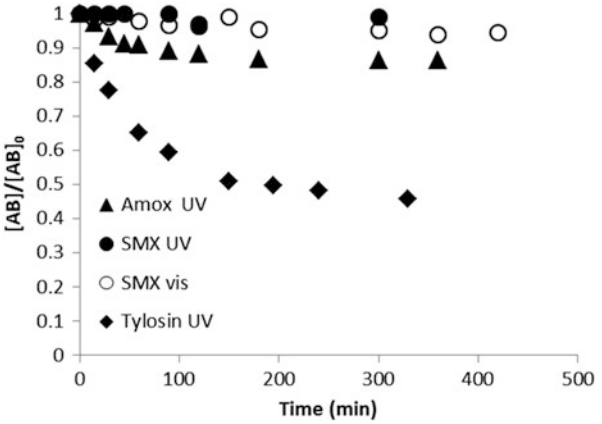


Fig. 4 Photolysis of the amoxicillin under UV light, sulfamethoxazole (under UV and visible light), and tylosin (under UV light)

slightly larger than the absorbance of the immobilized PC500 (67% and 53%, respectively). Photolysis and adsorption of antibiotics onto the photocatalysts were first studied. No significant degradation by photolysis under UV or visible light was observed for sulfamethoxazole (Fig. 4). This is in agreement with the results of Baran et al. [49] at a similar irradiation wavelength but a higher radiation intensity (2.9 mW cm^{-2} against 1.4 mW cm^{-2} in our experimental setup), Xekoukoulotakis et al. [40] (10% degradation after 2 h of irradiation), and Hu et al. [44] ($\approx$10% after 1 h of irradiation). These findings contrast those of Abellán et al. [36] who observed a degradation of 39% of sulfamethoxazole after 6 h with an irradiation wavelength longer than 290 nm. Sulfamethoxazole is indeed absorbing some light (5% of the absorbance spectrum) between 290 and 315 nm. A slight photolysis effect was observed for amoxicillin (15% degradation after 5 h) which is larger than the degradation reported by Rizzo et al. [88] (no significant degradation after 2 h), Elmolla et al. [84] (2.9% after 6 h), or Pereira et al. [86] (<2% under solar light after 0.5 h). Photolysis was significant for tylosin (55% degradation after 5 h), for which 9% of its absorbance spectrum corresponds to the UV lamp range (315–400 nm). Ten percent degradation was reported for another macrolide, erythromycin, after 2 h under UV light by Xekoukoulotakis et al. [92]. But erythromycin is a 14-member ring macrolide and tylosin a 16-member ring macrolide: the structural difference (Table 1) can induce a difference in photolytic reactivity. Less than 10% adsorption in the dark was observed for all antibiotics and all immobilized photocatalysts.

3.2 *Photocatalytic Results*

Figure 5 compares the kinetics obtained for the different antibiotics at the same concentration of 25 mg L^{-1} with the different immobilized photocatalysts. Tylosin was degraded much faster than the amoxicillin and sulfamethoxazole, but part of this degradation is imputable to direct photolysis.

Several tests were run to assess the experimental reproducibility. Figure 6 presents the case of sulfamethoxazole for P25 and PC500 immobilized on glass plates. Although the reproducibility was slightly lower for PC500, it was of the order of 5% for the whole set of experimental conditions.

Rarely will a single pollutant in a wastewater be treated. The presence of several molecules in a solution to be photocatalyzed can induce competition between them. Zahraa et al. [130] reported such competition with immobilized P25 in the case of salicylic acid and atrazine with slower degradation observed for salicylic acid in the presence of atrazine than in the absence of this pesticide. Binary mixtures with

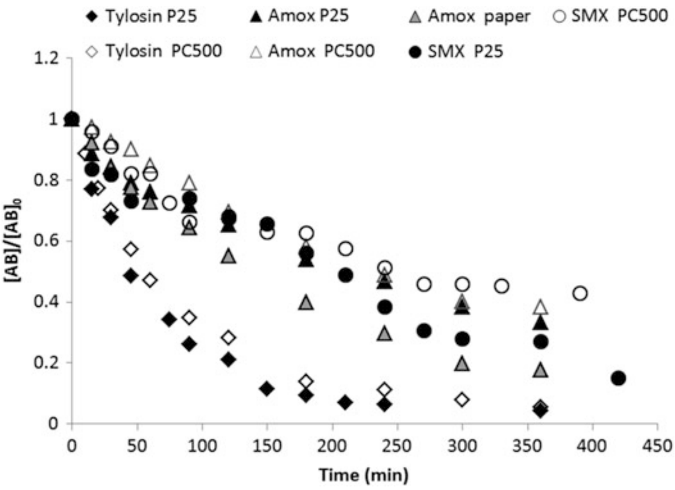


Fig. 5 Comparison of the degradation kinetics for the different antibiotics and photocatalysts. $[AB]_0 = 25$ mg L^{-1}

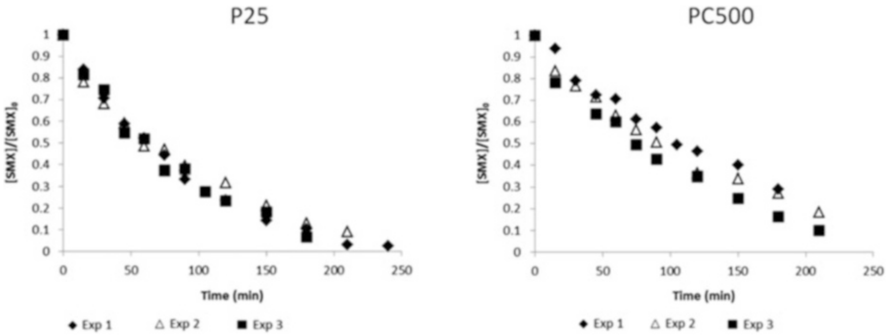


Fig. 6 Experimental reproducibility test for sulfamethoxazole, with catalysts immobilized on glass plate. $[SMX]_0 = 1.25$ mg L^{-1}

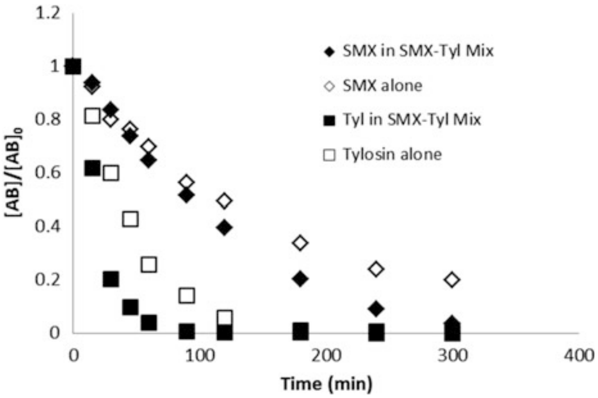


Fig. 7 Comparison of the degradation kinetics of tylosin and sulfamethoxazole (25 mg L^{-1})

different ratios of tylosin and sulfamethoxazole have been treated and the kinetics compared to those of the single antibiotic for the three immobilized photocatalysts. No competition was observed for any photocatalyst, and Fig. 7 presents the case of PC500 immobilized on cellulose fibers.

3.3 *Transformation Products*

The efficiency of photocatalytic process is generally assessed by monitoring the disappearance of the parent molecule. But little is known about the degradation pathways and the fate of transformation products [131]. Dissolved organic carbon degradation, which takes into account the parent molecule and the organic transformation products, is usually slower than the degradation of the parent molecule.

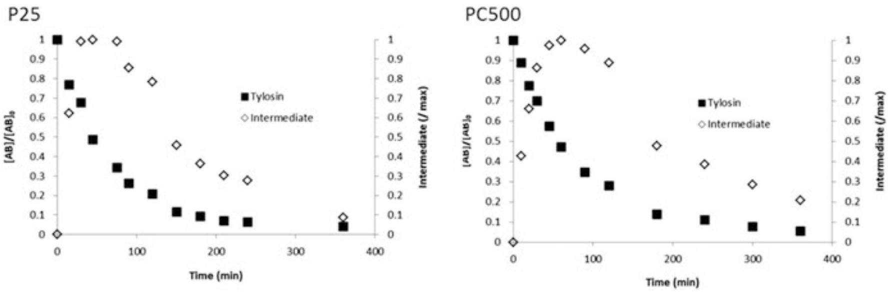


Fig. 8 Parent molecule and intermediate degradation kinetics during 25 mg L^{-1} tylosin photocatalysis with TiO_2 immobilized on glass plates.

Vasquez et al. [68] noticed that ofloxacin was fully degraded after 32 min with a removal yield of only 32% for dissolved organic carbon: several intermediates were indeed detected by mass spectrometry, some of them being visible on HPLC spectra. In the case of clarithromycin, Calza et al. [132] monitored the formation of 29 species by high-resolution mass spectrometry coupled to HPLC. During our experiments, no intermediates were detected by HPLC for sulfamethoxazole and amoxicillin, although Abellán et al. [36] and Baran et al. [49] for sulfamethoxazole and Klauson et al. [88] and Hu et al. [44] described the photocatalytic reaction pathways of both antibiotics with several intermediates characterized by mass spectrometry. According to Baran et al. [38], sulfamethoxazole intermediate products are less toxic than the parent molecule. Similar results were reported by Sirtori et al. [133] for flumequine and nalidixic acid. Sulfate and ammonium ions were detected as end products for sulfamethoxazole photocatalysis (data not shown). For tylosin, an intermediate was detected on HPLC spectra, as shown in Fig. 8 for P25 and PC500 immobilized on glass plates. Its kinetics are similar to those observed by Hu et al. for sulfamethoxazole [47].

3.4 Modeling

A simple Langmuir–Hinshelwood model is often used to describe the kinetics of photocatalytic degradation [95, 134]. The rate of reaction is given by

$$r = k_{\text{deg}} \frac{K_{\text{LH}} \cdot [\text{AB}]}{1 + K_{\text{LH}} \cdot [\text{AB}]}, \tag{1}$$

where K_{LH} is the adsorption constant, [AB] is the antibiotic concentration in the aqueous phase, and k_{deg} is the degradation constant, which depends on various physicochemical parameters including the irradiation conditions. This equation can be rewritten in a linear form as

Table 2 Kinetic constants for amoxicillin

Photocatalyst	PC500 immobilized on cellulose fibers	P25 immobilized on glass plate	PC500 immobilized on glass plate
K_{deg}(mg L^{-1} min^{-1})	0.523	0.715	0.234
K_{LH} (L mg^{-1})	0.0558	0.00752	0.0512
Photocatalyst surface loading (g m^{-2})	20	2.4	2.4
Photocatalyst volume loading (g L^{-1})	1.5	0.2	0.2

$$\frac{1}{r_0} = \frac{1}{K_{\text{LH}} \cdot k_{\text{deg}}} \cdot \frac{1}{[\text{AB}]_0} + \frac{1}{k_{\text{deg}}}, \tag{2}$$

where r_0 is the initial rate of degradation and $[\text{AB}]_0$ is the initial antibiotic concentration, which was varied between 1 and 100 mg L^{-1} for the different antibiotics. The model parameters were then estimated by plotting $1/r_0$ versus $1/[\text{AB}]_0$.

For amoxicillin the degradation constant is higher for P25 than for PC500, immobilized either on cellulose fibers or on a glass plate (Table 2). This can be explained by the larger amount of hydroxyl radicals that can be produced by the mixture of rutile and anatase of P25. The adsorption constant of P25 is lower than the one of PC500, which has a much larger specific area. Dimitrakopoulou et al. [89] obtained for k_{deg} and K_{LH} 2.28 mg L^{-1} min^{-1} and 0.09 L mn^{-1}, respectively, for P25 in suspension at a loading of 0.5 g L^{-1}. These values are higher than those obtained for immobilized P25.

For sulfamethoxazole, the degradation and adsorption constants obtained for immobilized P25 ($K_{\text{deg}} = 0.357$ mg L^{-1} min^{-1} and $K_{\text{LH}} = 0.032$ L mg^{-1}) are also lower than those found in literature for P25 in suspension: $K_{\text{deg}} = 1.91$ mg L^{-1} min^{-1} and $K_{\text{LH}} = 0.166$ L mg^{-1} with 0.1 g L^{-1} TiO_2 at pH 3 [44], $K_{\text{deg}} = 1.91$ mg L^{-1} min^{-1} and $K_{\text{LH}} = 0.166$ L mg^{-1} with 0.5 g L^{-1} TiO_2 at pH 4 [40], and $K_{\text{deg}} = 0.91$ mg L^{-1} min^{-1} and $K_{\text{LH}} = 0.0.062$ L mg^{-1} at pH 4.8 [46]. If, in our experiments, k_{deg} is higher for immobilized P25 than for immobilized PC500 (0.127 mg L^{-1} min^{-1}), the adsorption constants are similar as $K_{\text{LH}} = 0.036$ L mg^{-1} for PC500. For tylosin (Table 3), a much higher degradation constant was obtained for PC500 than for P25, for which the adsorption constant was higher than the one of PC500.

The effect of pH changes during the photocatalysis experiments, which were not strictly investigated in the present work, results from the difference between the photocatalyst (isoelectric point (IEP) which defines the type of charges carried by the photocatalyst) and the micropollutant properties (acid–base speciation). pH was checked prior and after experiment and no large variation (<0.5 pH unit) was observed. The IEP of PC500 is slightly lower than the IEP of P25: 6.2 versus 7 [121]. TiO_2 will be positively charged at pH < IEP and negatively charged at pH > IEP. Hu et al. [44] did not observe a significant effect of pH for the

Table 3 Tylosin

Photocatalyst	P25	PC500
K_{deg}(mg L^{-1} min^{-1})	8.25	18.35
K_{LH} (L mg^{-1})	0.022	0.001

Photocatalyst loading on glass plate: 2.4 g m^{-2}

photocatalysis of sulfamethoxazole with P25. Sulfamethoxazole has two pK_a: 1.85 and 5.6 [135]. A slight pH effect (i.e., a 5% increase between pH 5 and 8) was reported by Elmolla and Chaudhuri for the photocatalysis of amoxicillin with anatase (IEP = 6.4) [84]. Different dissociation behaviors can be found in literature for this antibiotic: p$Ka_1 = 3.39$, p$Ka_2 = 6.71$, and p$Ka_3 = 9.41$ for Babić et al. [135]; p$Ka_1 = 2.68$, p$Ka_2 = 7.49$, and p$Ka_3 = 8.94$ for Pereira et al. [86]; and p$Ka_1 = 2.6$ and p$Ka_2 = 9$ for Elmolla and Chaudhuri [84]. Although macrolide should normally have only one pK_a near 9 (p$K_a = 8.8$ for erythromycin [92]), tylosin tartrate has two pK_a: p$Ka_1 = 3.31$ (tartrate moiety) and p$Ka_2 = 7.5$ [135]. Applications involving immobilized photocatalysts at near-neutral pH would be preferred by operators as it corresponds to the pH range of most urban secondary effluents.

4 Conclusions

Strict comparison of the performance of suspended and immobilized photocatalysts is not easy as operation conditions often differ between reports in terms of the amount and type of photocatalysts and the operational conditions (type of reactor, light, pH, liquid phase composition). The immobilization of the photocatalyst reduces the degradation rate, but it is still a valid option for the treatment of effluents containing antibiotics as it performs better than photolysis and facilitates the manipulation of nanoparticles. Secondary effluent contains other organic compounds, among which are other pharmaceuticals other than antibiotics, and many ions susceptible to hinder further photocatalytic process. There is therefore place for more research to develop immobilized photocatalysis, to optimize the reactor design, and to select the proper photocatalyst and light type to effectively reduce the effluent toxicity due to organic micropollutants [88, 131].

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Constructed Wetlands Integrated with Advanced Oxidation Processes in Wastewater Treatment for Reuse

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Abstract The development of integrated systems for wastewater treatment has been investigated in recent years not only for the improvement of control parameters but also to allow the routine reuse of wastewater to be effectively implemented. Several studies also seek to add processes that may reuse by-products, energy, and unit operations in a single integrated remediation unit. Considering the sustainability scenario, all these processes should be designed and controlled with description of scope, mass inventory, and energy demand in order to establish indexes of environmental pressure. Classical publications of books and articles for wastewater treatment have already described to more than 10 years several procedures and standards for reuse (direct or indirect), segregation at source, required treatment levels, groundwater recharge, combination of remediation processes, logistics, and sanitation. In this case, further investigation to decentralized systems, such as reed bed filters, with reduced costs of implementation and operation is required, as well as the simplicity of units to be installed. This tendency of integrated phytoremediation systems supports the growing interest for the combination of a system already considered classic in wastewater treatment, the constructed wetlands (CWs), with advanced oxidation processes (AOPs), particularly the photocatalysis with direct or indirect use of solar energy. Because of its already reported disinfection and detoxification potentials which might enable the reuse of urban wastewaters for some specific purposes, the photocatalytic treatment was selected for a study of case. So, this chapter covers the phenological aspects of

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a macrophyte still little used in phytoremediation, the *Hymenachne grumosa*; the evolution of the combined use of Upflow Anaerobic Sludge Blanket systems (UASB) + CWs; and the integration of the processes UASB + CWs + UV $/TiO_2/O_3$ with indirect use of solar energy in photoreactors designed for these studies.

Keywords Advanced oxidation, Constructed wetlands, Hymenachne grumosa, Integrated treatment, Wastewater reuse

Contents

1 Introduction

The integration of wastewater treatment process advances on the focus of energy and nutrient recovery as well as on the reuse of water. Another important aspect that must be considered is that the integration may not only establish complementary unit operations and chemical conversions for the efficiency of the process but also could combine the reuse of materials, complements of phase separation steps, and the degradation/disinfection of the dissolved pollutant load.

The literature establishes divisions concerning the processes by stages and principle of methods to classify the wastewater treatment processes [1–4]. In this knowledge organization aspect, the biological methods have always been the center of the processes, especially because the mechanisms of biodegradation have better thermodynamic efficiency (more favorable ΔG), more friendly material balance, and sustainability of the systems for reuse of the output materials as well as maintenance.

Concerning the reuse of water, technical standards will require even more of the control references, especially due to the different reuse purposes of the water, since the occurrence of thousands of contaminants and pollutants with characteristics of ecotoxicity and genotoxicity requires replacements and minimization in pollutant sources, phase separation, and degradation in the remediation processes.

The water reuse can be carried out in different ways: indirect planned or unplanned, direct planned and with water recycling. Usually, examples for the reuse of water include activities such as landscape irrigation, irrigation of crops fields, industrial uses, aquifer recharge, non-potable urban uses, among others [5].

The comparison parameters for the indirect reuse of wastewater allow the comparison with the Guidelines for Water Reuse EPA /600/R-12/618 [6] (R2 Hawaii Water) establishing initial parameters as boosters for the application of the treatment system.

Several European countries, including France, Italy, and Spain, have developed legislation for the reuse of treated effluent. In the USA, the Environmental Protection Agency (EPA) has established reference contact with 50 regulatory agencies beyond the District of Columbia. The information regarding the reuse of wastewater show that 22 states adopted regulations and 11 states have guidelines or standards of design concerning the reuse of water as the main intention. The others states, due to different constitutions, make or have just completed revisions of its current reuse regulations or of new guidelines.

Through State Regulatory Programs for Water Reuse, the EPA (2012) [6] divided the reuse in different categories: urban reuse (direct and indirect), agricultural reuse (processed food crops and nonfood crops), impoundments (unrestricted and restricted), environmental reuse, industrial reuse, and ground water recharge – no potable reuse and potable reuse (indirect and direct). There are no references of US states regarding the case of direct potable reuse without prior equalization storage. Usual patterns to control the reuse can be exemplified with the required parameters for restricted use in Hawaii (R2 Water) [6]: BOD_5 30 mg L^{-1} or 60 mg L^{-1} depending on design flow, chlorine residual > 5 mg L^{-1}, actual modal contact time of 10 min, TSS 30 mg L^{-1} or 60 mg L^{-1} depending on design flow, and fecal coliform up to 23/100 mL (7-day median) or up to 200/100 mL (not more than one sample exceeds this value in 30 days).

With a more complex control of contaminants and pollutants over the past decades, the determination of more specific parameters increased. Along the last year, the speciation, selectivity, and limit of detection of the analytical methods have been improved and consequently implemented in the main control standards of wastewater in the world. Global references include the EPA (2012) [6] and the EU-wide monitoring survey on wastewater treatment plant effluents [7]. The introduction of new technologies, e.g., solid-phase extraction (SPE), liquid-liquid extraction-liquid chromatography-tandem mass spectrometry (LLE-LC-MS-MS), high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS-MS), and gas chromatography-high-resolution mass spectrometry (GC-HRMS) allowed the determination of organic compounds at trace levels. Regarding the inorganic priority pollutants, the use of inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma-atomic emission spectrometry (ICP-AES) provides amplitude of control with special focus to gadolinium (Gd) and trace elements in addition to the heavy metals.

The bioassays also refer the increasing control to the ecotoxicity and genotoxicity parameters, among which can be exemplified the acute toxicity test with *Daphnia magna*, the dioxin-like activity, the antimicrobial activity, and the estrogenicity test [8].

With the increasing number of analytical requirements and a wide range of control parameters, recognized efficient processes for the wastewater treatment, whether from agricultural, industrial, services, or residential sources, require now a pre- or posttreatment. Several integrated systems have been investigated or applied, especially units that may combine degradation associated with phase separations: AOPs with hybrid systems [9, 10], UV/TiO_2 + biological flow system [11], integrated process of photo-Fenton plus *Solanum nigrum L.* weed plants [12], and heterogeneous catalytic wet hydrogen peroxide oxidation combined with rotating biological contactors [13].

The application of integrated systems has also been researched for both compact units of multifunction systems as well as for single systems that involve several mechanisms, especially nitrification, denitrification, adsorption, and storage in accumulating organic matter [14]. This is the case of the natural and constructed wetlands, which have been applied and researched worldwide since the late 1950s [15]. Natural systems include lakes, marginal wetlands, extensive marshes, and lowland swamps, where, for example, *Typha* spp. and *Scirpus* spp. are often present. The constructed wetlands (CWs) usually consist of single cells in parallel or in series with alternate arrangements, surrounded by clay, stone, cement, or high-density polyethylene (HDPE), configuring wetlands of free water on the surface or subsurface [16].

In addition to configuring multiple processes, depending on the hydrodynamic of the unit (vertical and/or horizontal fluxes and surface or subsurface horizontal flows, also with the possibility of alternate arrangements), the CWs may allow the control of extent of anaerobic, anoxic, and aerobic areas to generate redox potential (E_H). Results obtained indicated that the maximum redox gradient was between the surface and the bottom of the bed for continuous planted wetlands (25 cm: -407.7 ± 73.8 mV) and, to a lesser extent, between the surface and the middle part of the wetland (15 cm: -356.5 ± 76.7 mV). Finally, the maximum redox gradients obtained for planted wetlands operated under continuous flow regime would lead to a power production of about 16 mW/m^2 [17].

Figure 1 shows a unit of UASB + BF + CWs + AOPs photocatalyzed as one example of integrated processes. This example presents a wide range of opportunities for studies and applications for wastewater treatment plant (WWTP) with higher potential for disinfection and detoxification of wastewaters.

With the operationality of a decentralized system, a suitable phenology for each climate reality, as a main or integrated process, and adding detoxification processes to control ecotoxicity and genotoxicity, the CWs are of interest to the researches and applications worldwide to configure new treatment stations for the reuse of wastewaters.

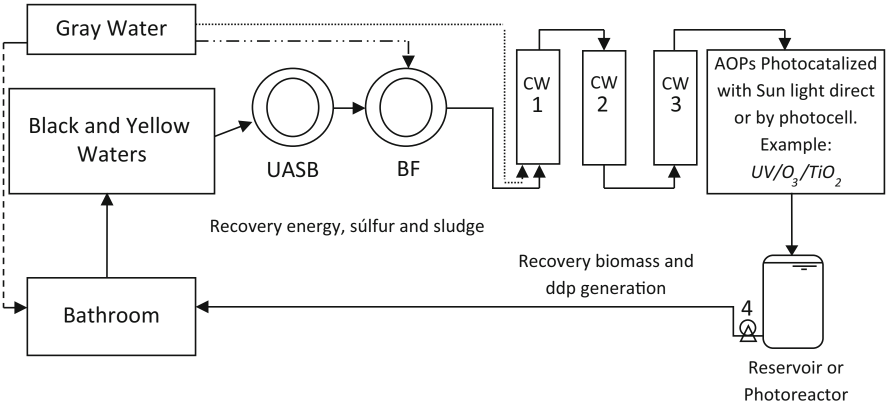

Fig. 1 Example of sustainability for obtaining water for reuse with the UASB + BF + CWs + $UV/O_3/TiO_2$ system. *UASB* upflow anaerobic sludge blanket; *BF* anaerobic biofilter; *1-CW* subsurface flow constructed wetlands (SSFCW); *2-CW* vertical flow constructed wetlands (VFCW); *3-CW* SSFCW; *4* pump using solar energy from photovoltaic cell for wastewater reuse

2 Systematization of Phenological Aspects for Implementation of Constructed Wetlands with Macrophytes Still Little Studied

The study of phenological patterns of aquatic macrophytes is very important for understanding the biology of this group and, in this way, contributes for its best application in wastewater treatment units with the CWs. The phenology studies the phases of the biological cycles of plants or animals, as well as its occurrence throughout the year, contributing to a better comprehension of the regeneration and reproduction of plants. Recently, Vymazal [18] published a paper which highlights the important role that emergent macrophytes have in reducing the speed of the wind on the water surface of the CWs and the consequences of preventing resuspension of settled material, providing more uniform substrates to *Periphyton* and bacteria, which contributes to a better denitrification process involved in the decomposition of the biomass [18].

In the same work, the author also refers to more than 600 investigations involving free-water surface constructed wetlands (FWSCWs) in 43 countries, where the macrophytes with higher frequency of citations were *Typha, Scirpus (Schoenoplectus), Phragmites, Juncus,* and *Eleocharis*. In terms of species, the most frequently used species were *Typha latifolia*, *Phragmites australis*, *Typha angustifolia*, *Juncus effusus*, *Scirpus lacustris*, *Scirpus californicus,* and *Phalaris arundinacea*. Finally, regarding the application and distribution of the macrophytes over the continents, the author refers to *P. australis* in Europe and Asia, *T. latifolia* in North America, *Cyperus papyrus* in Africa, *P. australis* and *Typha domingensis* in Central and South Americas, and *Scirpus validus* (*S. tabernaemontani*) in Oceania.

Kadlec and Knight [19] report the chosen species for the general configuration of the CWs as mainly belonging to the families *Typhaceae, Juncaceae,* and *Gramineae* [19].

In a work carried out by Silveira [20], *Hymenachne grumosa* (Fig. 2) was used in a novel way in subsurface flow constructed wetlands (SSFCWs) for the treatment of urban wastewaters. This species is a very common forage of the Brazilian southern fields and used as animal food [20].

The systematization of treatment assays with more appropriate macrophytes for certain regions can be exemplified through the work performed on *H. grumosa* [20]. By the collection of 50 individuals, including young, sprouts, and adults, to morphologically characterize the populations age, the structure of individuals, number of shoots, and the maximum height were determined. For the establishment of aquatic macrophytes in wetlands, whole seedlings were used. The planting occurred concomitant with the application of the wastewater and involved the equivalent of 23 seedlings m^{-2}, measuring about 0.15 m. It is important to highlight the need of fertile collections, i.e., with the presence of inflorescence, so that the plants provide appropriate characteristics to confirm its taxon.

The phenological analyses are important for the control of the constructed wetlands performance. Such analyses must be carried out at each flowering cycle and include the determination of the root size, the number of shoots, dry and wet biomass, as well as plant tissue analysis. Usually, analysis of plant tissue samples includes the determination of total organic carbon, total Kjeldahl nitrogen (TKN), total phosphorus, and, if necessary or relevant, heavy metals.

Silveira [20] reported values of phenological analysis for the treatment of wastewaters from university campus using subsurface flow constructed wetlands (SSFCWs). The treated wastewaters have characteristics of black and yellow waters with load factor proportions of COD:TKN: P total of 30.1:4.9:1. Usual load factors of secondary wastewaters for CWs work with proportions of 36.1:8.5:1. This deficit of carbonaceous material can reduce the remediation efficiency of the CWs. However, the registered production rate of dry biomass was 2.12 kg m^{-2} over a period of 4 months. This value can be considered very satisfactory, since data found in the literature for *Typha* sp. registered dry biomass values of 0.7 kg m^{-2} [21].

Aside from the weather conditions, the pollutant and volumetric loads are also important factors in these comparisons. In the work carried out by Silveira [20], the applied volumetric loads varied between 0.09 and 0.045 m day^{-1} with load factors of 30.2 g of COD m^{-2} day^{-1} and 4.0 g of TKN m^{-2} day^{-1}. These values are close to those reported by Brasil et al. [21], however, for *Typha* sp. In comparison to other species used on the CWs, *H. grumosa* was more effective on the production of biomass. Concerning the root lengths (Fig. 2g), it developed to 40 cm in 4 months of operation. Comparatively, the results obtained with similar hydrodynamic systems were 30 cm for a grass species – Tifton 85 (*Cynodon dactylon Pers.*) – and 20 cm for the elephant grass (*Pennisetum purpureum Schum*) [22]). The root depth of *Typha* sp. obtained by Brasil et al. [21] was 30 cm, whereas Freitas [23] obtained an average value of 27 cm for *Zizaniopsis bonariensis* [23].

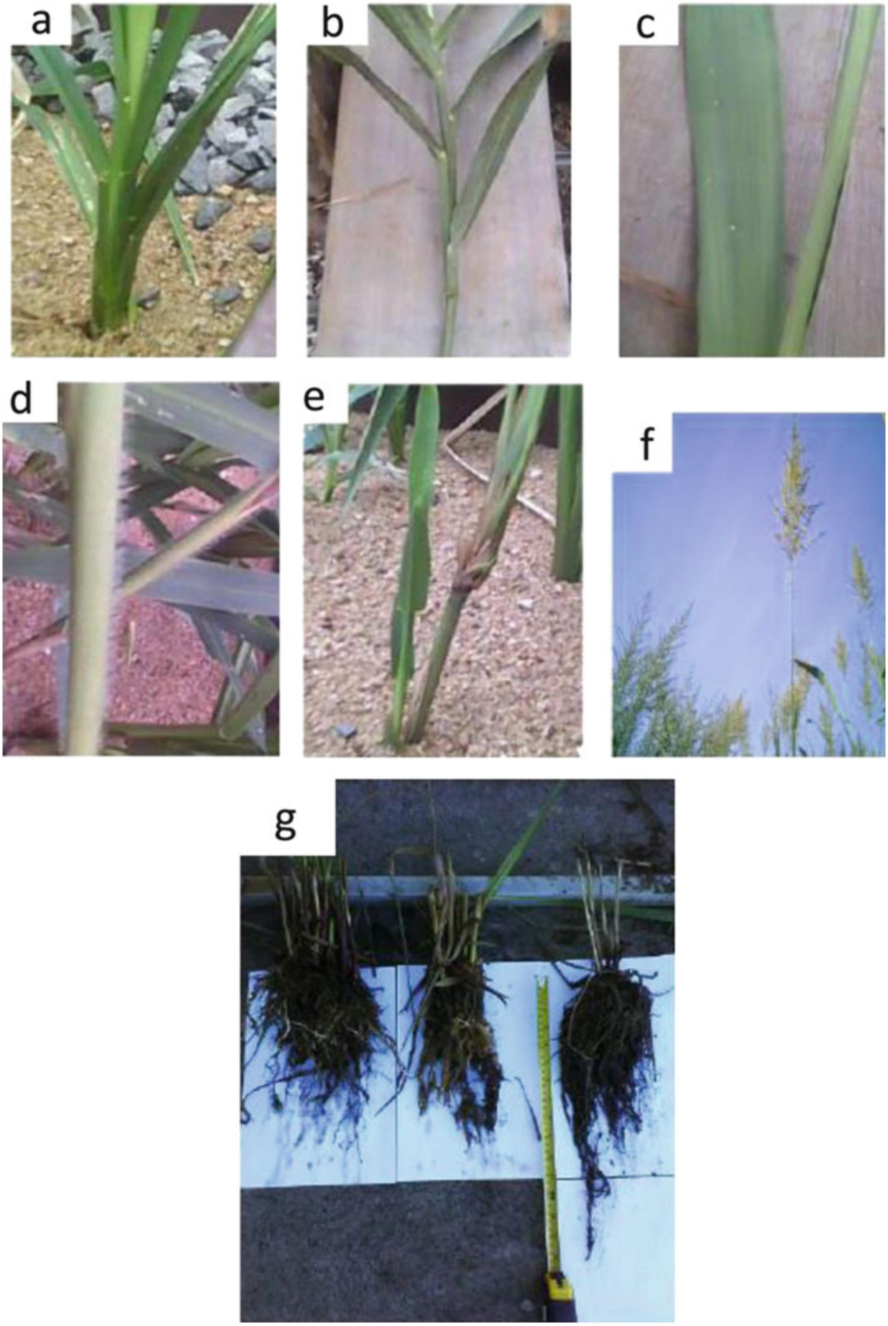

Fig. 2 Structural features of *Hymenachne grumosa:* (**a**) and (**b**) stem-type thatch (with nodes and internodes), (**c**) leaves with parallel nervation, (**d**) stem hair, (**e**) shoots nodes, (**f**) inflorescence, and (**g**) measuring of the roots length (source: Silveira [20])

Regarding the different seasons, it was possible to observe the growth and flowering of *H. grumosa* during the summer months, with an average height of the flowering individuals between 100 and 130 cm. This demonstrates the adaptation ability of the plants to abrupt climate variations, with temperatures ranging more than 30°C, between the periods of winter and summer.

In terms of the ion recovery from biomass production, the use of *H. grumosa* in the SSFCWs presented contribution to the ion sodium, with values between 40,000 and 80,000 mg kg^{-1} compared with 8,000 mg kg^{-1} of *Typha* sp. [21] and proved to be an interesting alternative to retain and/or remove the alkali metal.

These data demonstrate, especially for the conditions of subtropical and temperate climates, the potentiality of *H. grumos*a as a reference macrophyte for phytoremediation, polishing, and/or integrated system to recover nutrients and maximize the reuse of treated wastewaters. Items of the integrated systems will address this aspect.

The application of CWs for the elimination of veterinary drugs from a pig farm wastewater doped with 100 μg L^{-1} of the drugs for 12 weeks operating in a free-water surface showed removal rates of 94% and 98% for enrofloxacin and tetracycline, respectively [14].

Hijosa-Valsero et al. [24] observed the degradation of pharmaceuticals and personal care products (PPCPs) in constructed wetlands, relating the linear correlation between removal of contaminants with the temperature and the redox potential [24].

A research performed by de la Varga et al. [25] investigated the removal of heavy metals from municipal wastewater by using the integration of UASB + SFCW + SSFCW. The results indicated removals of the metals in the following order: Sn > Cr > Cu > Pb > Zn > Fe (63–94%) [25]. Furthermore, according to the authors, medium removal efficiencies were achieved for Ni (49%) and Hg (42%).

3 Wastewater Treatment Systems Integrated with Constructed Wetlands

The integration of different wastewater treatment methods has been studied to minimize the limitations of the processes and add potential for improving the efficiency. An example of this integration is the ozonation/flotation system, where the coagulation associated from ozone (reducing the negative zeta potential) is integrated with the degradation of organic compounds and at same time with the flotation, which is provided by microbubble necessary for gas-liquid transfer. Therefore, it seems to be an alternative for the remediation of environmental impacts in a more cleanly way.

In this sense, the integration of different treatments methods with CWs appears as an interesting alternative. The ability of hybrid CWs systems has as reference the integration of different configurations (vertical flow, horizontal flow, and free-water surface sequential) already investigated for the treatment of wastewaters with the so-called contaminants of emerging concern. These investigations involve contaminants such as drugs, surfactants, personal care products, plasticizers, and herbicides. Avila et al. [8] applied the alternating combination of two vertical flow constructed wetlands (VFCWs) disposed in parallel (volumetric ratios of 0.06, 0.13, and 0.18 day m^{-1}) sequentially with a subsurface flow constructed wetland (SSFCW) and subsequently with a free-water surface constructed wetland (FWSCW), each with 2 m^2 [8]. The compounds ibuprofen, diclofenac, tonalide, acetaminophen, oxybenzone, bisphenol, triclosan, and 17α-ethinylestradiol were added to control the elimination. The obtained results showed that the hybrid system was, with exception of the antibiotics, efficient to eliminate the target pollutants. Considering a volumetric loading of 0.18 m^{-1} day, $87 \pm 10\%$ elimination was achieved, while for the antibiotics, the registered elimination was only of $43 \pm 32\%$. The initial aerobic condition of the VFCWs ($E_H = +110 \pm 19$ mV) played a key role in providing this best condition.

Other integrations are also presented as definitions of sequential, combined, or hybrid systems. Along with other processes, these integrations may involve the CWs with conventional processes, such as the anaerobic sludge blanket upstream reactors (UASB) + CWs [26, 27] as well as with advanced process of reverse osmosis [28] and the so-called advanced oxidation processes [29–31].

For more classical references of combinations, the CWs are used in secondary and tertiary treatment, especially concerning domestic wastewaters with complex composition. However, it must be pointed out the need of a primary treatment in order to prevent accumulations of solids and avoiding in this way the clogging of the beds of the constructed wetlands.

For the domestic wastewaters, about 90% of the COD elimination occurs on a seven-day period of detention in the CWs with surface flow. The reduction of nutrients, nitrogen and phosphorus compounds, requires a higher retention time of the wastewater. A nutrient removal of approximately 90% demands a retention period in the surface flow between 7 and 14 days [19].

The UASB reactor has great potential for wastewater treatment in tropical regions. However, the effluent arising from this reactor, as well as from other anaerobic treatments, requires a posttreatment to remove the insoluble organic matter and nutrients, particularly phosphorus and nitrogen, since they tend to not meet the legal requirements of wastewater disposal. Several studies have been performed to posttreat the anaerobic wastewaters, and among them, the ones carried out with the CWs can be highlighted for its ability to remove the pollution load, maintain the conservation of the terrestrial and aquatic ecosystems, reduce the global warming, fix the carbon from the environment maintaining the balance of CO_2, and conserve biodiversity [32]. In this sense, many countries worldwide have conducted researches using UASB + CWs for the treatment of wastewaters with high levels of oxygen depletion and eutrophying potential in the past decades [33].

3.1 Integrated System UASB + CWs

Sousa et al. [26] evaluating the efficiency of posttreatment of UASB reactor wastewaters with SSFCWs verified COD reductions of 70–86% in systems vegetated with *Juncus* sp., but without a significant difference in comparison to the non-vegetated system (control). On the other side, the TKN reductions showed significant differences in the vegetated systems (80–90%). For phosphorus, the authors observed an efficiency of 82–90% reduction, followed by a decay in the subsequent years. The authors attributed this decay to the saturation of the substrate with precipitated phosphorus compounds. Nevertheless, the highest differences were registered for removal of fecal coliforms, with 4 more logarithmic units in the vegetated CWs. Furthermore, this study also presents characteristic operational values for integrations of UASB + CWs: **UASB** – specific organic load, kg COD m^{-1} day^{-1} = 2.2–2.8; hydraulic retention time (h) = 6.0; – **SSFCWs**: hydraulic detention time = 10.2 h, COD applied load = 6–9 g m^{-2} day^{-1}; TKN applied load = 1.2–1.7 g m^{-2} day^{-1}; total phosphorus applied load = 0.15–0.22 g m^{-2} day^{-1}.

Figure 3 demonstrates the possibilities for the development of integrated treatments, as a function of the electrical potential difference (EPD) provided in the bed of CWs and with several simultaneous mechanisms of the system in the different CWs configurations.

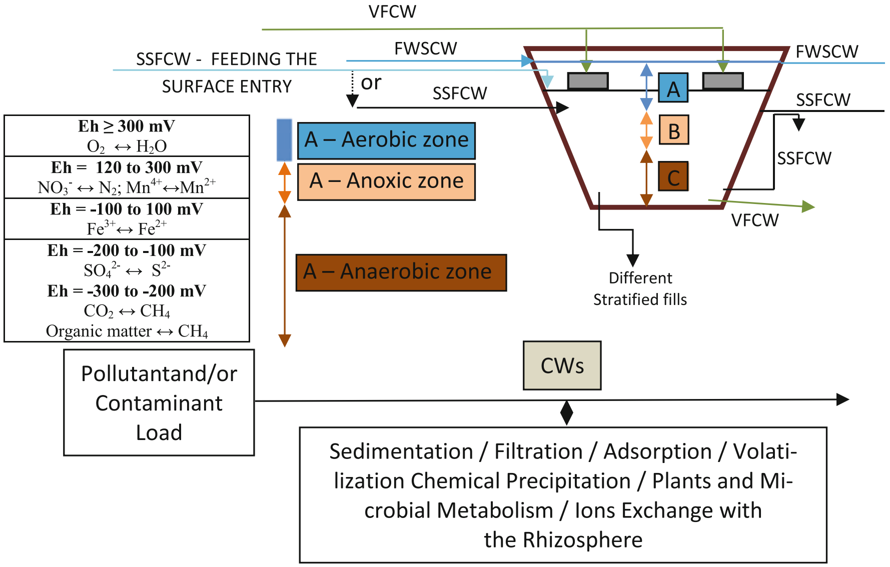

Fig. 3 Configuration changes to the CWs with the involved mechanisms and stratification characteristics of the electrochemical potential in the systems [34]. *VFCW* vertical flow constructed wetland; *SSFCW* subsurface flow constructed wetland; *FWSCW* free-water surface constructed wetland

Besides the physical, chemical, and physicochemical processes, the microbial metabolism also presents a great diversity of reactions. In a work published by Samsó and García [35], the stratification of bacterial groups was determined by measurements of electron acceptors and donors (O_2, NO_3^-, SO_4^{2-}, and NH_3, H_2S, respectively). Additional parameters, such as CH_4, CH_3SCH_3, and NO_x, were also determined in order to associate the metabolic activities of the different bacterial groups in SSFCW. The determination of the microbial stratification in SSFCW was the presence of fermentative bacteria in the input stage of the CW; followed by heterotrophic and sulfate-reducing bacteria, with a distribution of methanogenic and nitrifying bacteria in the midstream of the CW; and finally, in the oxic region, a predominant presence of sulfide-oxidizing bacteria among the nitrifying bacteria, with significant reduction of methanogenic and sulfate-reducing bacteria in the anaerobic region. The stability of the microbial community was determined as been reached between 400 and 700 days of operation (urban wastewater previously treated with Imhoff tank studies during 3 years, with a coefficient of conductivity of 50 m day^{-1}; COD of raw wastewater = 260 mg L^{-1} was used).

Considering the mechanisms for nitrogen removal in CWs, especially for SSFCWs, the most cited pathways in the literature involve biological processes: ammonification, nitrification, denitrification, plant uptake, biomass assimilation, and dissimilatory nitrate reduction [18, 36, 37]. Physical (volatilization) and physicochemical (adsorption) processes are also cited, both for the fraction of organic compounds containing nitrogen (proteins, amino acids, urea, and uric acid) and inorganic (NH_4^+, NO_2^-, NO_3^-, N_2O, NO_2, NH_3, and N_2). Other reaction pathways involve Anammox and Canon processes. Table 1 summarizes the main reactions of both processes.

When the total nitrogen (TN) removal rates obtained with SSFCW are compared (2.8–5.7 g m^{-2} day^{-1}), the Anammox process demonstrates an increase from 5 to 10 times when an inoculation of biomass occurs in the SSFCW. Removal efficiencies of TN higher than 95% with SSFCW and involving the Anammox process have been obtained even with relations of $BOD_5/TN = 0.5$. This highlights the polishing

Table 1 Anammox and Canon processes with transformations that may occur in SSFCW [37]

Anaerobic ammonium oxidation – Anammox	Completely autotrophic nitrite removal over nitrate – Canon
$NH_4^+ \rightarrow N_2H_4$	
$N_2H_4 \rightarrow N_2H_2$	
$N_2H_2 \rightarrow N_2$	
	$NH_4^+ + 0.85O_2 \rightarrow 0.43\ N_2 + 0.13NO_3^- + 1.3H_2O + 1.4\ H^+$
$NO_2^- \rightarrow NH_2OH$ *reducing equivalents* (NAD/NADH and FAD/FADH2)	
$NO_2^- \rightarrow NO_3^-$	

potentiality of COD/TN = 1.0 to reduce the eutrophication by pretreated wastewaters through anaerobic processes, which mainly reduce the carbon source [37].

The Canon process was observed in studies conducted by Sun and Austin [38] for VFCWs, considering the need of the coexistence of oxidants of the ammonium ion in aerobic conditions and the bacteria group *Planctomycete* in limited oxygen conditions [38]. These are necessary requirements to obtain conditions for nitrification. Load factors of NH_4-N 0.12 kg m^{-3} day^{-1} are required to the operational conditions of the Canon process in the CWs.

Dornelas [39] evaluated the efficiency of CWs with horizontal subsurface flow as posttreatment of wastewaters arising from a UASB reactor, comparing the performance of a planted unit and other non-planted ones (control) [39]. The mean concentration values of the wastewaters for the planted and unplanted CWs were, respectively, BOD_5, 15 and 17 mg L^{-1}; COD, 43 and 52 mg L^{-1}; TSS, 6 and 4 mg L^{-1}; TN, 29 and 32 mg L^{-1}; P total, 1.9 and 1.9 mg L^{-1}; and *E. coli*, 1.5×10^5 and 5.1×10^5 NPM/100 mL. The planted system presented removal efficiencies significantly better in comparison to the unplanted for the parameters of COD, TN, and *E. coli*. According the authors, these results show the potential of the CWs to effectively treat wastewaters from anaerobic reactors. In terms of global efficiency, the UASB + CW planted system reached removals of 91% and 90% for, respectively, COD and BOD_5, whereas the UASB + CW unplanted system removed 90 and 88% of these parameters. The same situation occurred for TSS, producing final wastewaters with 97% and 6 mg L^{-1} in the planted system and 98% and 4 mg L^{-1} in the unplanted system. Regarding the nutrients (N, P), the removal was less pronounced (TN: 14% in the planted system and 6% in the unplanted, while a reduction of 35% phosphor was registered in both systems). Removals of 1–2 log units were obtained for *E. coli*, with a better performance of the planted unit. The authors emphasize the considerable loss of water by evapotranspiration on the planted CW and evaporation on the unplanted CW, with average values of, respectively, 42% and 22% for exit flows of the treated wastewaters.

Bevilacqua et al. [27] evaluated the application of CWs as posttreatment of wastewaters from an UASB reactor, in terms of removal of the helminth eggs. The authors tested different configurations, including flow variations (surface and subsurface) and cultivated macrophytes (*Brachiaria arrecta* and *Typha* sp.) [27]. The results indicated reductions in both configurations; however, they are not sufficient to fulfill the requirements set by the World Health Organization (WHO) for irrigation with wastewaters (<1 helminth egg/L). The removal efficiencies ranged from 79% in subsurface flow and 84% in the surface flow, whereas the percentages of samples with undetectable levels of helminth eggs in wastewater were 50% in the surface flow and 40% in subsurface flow.

Pereira et al. [40] tested the efficiency of CWs as posttreatment for wastewaters arising from UASB reactor aiming to use the produced biomass as animal feed [40]. The author tested configurations with surface and subsurface flows and vegetated with two types of macrophytes (*Brachiaria arrecta* and *Typha* sp.). The wastewater of the UASB reactor remained, showing high concentrations for all the analyzed parameters, resulting in contamination of macrophytes. In the worst-case scenario, the following results were registered: 10^4 *E. coli*, 228 cysts of *Giardia* sp., 321.4 oocysts of *Cryptosporidium* sp., and 147.2 helminth eggs per 100 g (wet weight). The surface flow unit showed the highest average value for *E. coli* (2.7×10^4 NMP/100 g). The contamination of the vegetation cover was lower in the subsurface flow unit, but the constructed wetlands do not seem to protect against the contamination of the aerial part of the macrophytes, leading to a potential risk to human (operators) and animal (eventual consumer of biomass) health.

Calijuri et al. [41] evaluated the efficiency of the posttreatment of domestic wastewaters in CWs with subsurface flow, pretreated anaerobically in decanto-digester system [41]. The treatment system showed removals of 85% COD, 86% BOD_5, and 90% TSS, whereas the obtained values for nutrients, ammonia nitrogen, and total soluble phosphates were of 25%, 36%, and 40%, respectively. An evapotranspiration of around 34% of the input flow from the CWs was measured. The organic matter, firstly removed in a decanto-digester, presented a mean removal efficiency of approximately 68% for COD and BOD_5 and an overall system efficiency of $86 \pm 8\%$ for COD and $85 \pm 11\%$ for BOD_5. The overall efficiency of solid removal was $90\% \pm 38$ for TSS, with a minimum undetectable value and a maximum value of 28 mg L^{-1}. The global efficiency of the phosphorus removal was $36 \pm 25\%$ for total phosphorus and $40 \pm 43\%$ for total soluble phosphorus. The two wetlands showed low removal efficiency of *E. coli* (2log units), being lower than the efficiency of the decanto-digester.

3.2 Integrated Systems Involving UASB + CWs + AOPs: Applications in the Disinfection of Secondary Wastewaters

The integration of CWs with AOPs is one of the most studied configurations for wastewater treatment aiming its disinfection and detoxification, mainly by the combined use of phytoremediation and advanced oxidation processes and normally integrating the approach of Sect. 3.1 with the UASB reactor.

The most investigated AOPs, seeking the integration of systems, involve photochemical and electrochemical processes [31]. Lourenço [42] developed a comparative study of the photocatalytic ozonation ($UV/TiO_2/O_3$) in a column-type reactor, with the photoirradiation being applied in a tubular reactor and aiming the disinfection of a campus secondary wastewaters pretreated by a UASB + CWs (Fig. 4) system [42]. The additional operational conditions for the UASB + CWs system and the column-type photoreactor (CTP) are presented on Tables 2 and 3.

Initially, comparative studies based on the work conducted by Hur et al. [43] were carried out, also directed to the development of a photocatalytic reactor for the $UV/TiO_2/O_3$ process (Table 4) [43]. In these studies, methylene blue was used as a target molecule for comparative conditions also applied by Hur et al. [43].

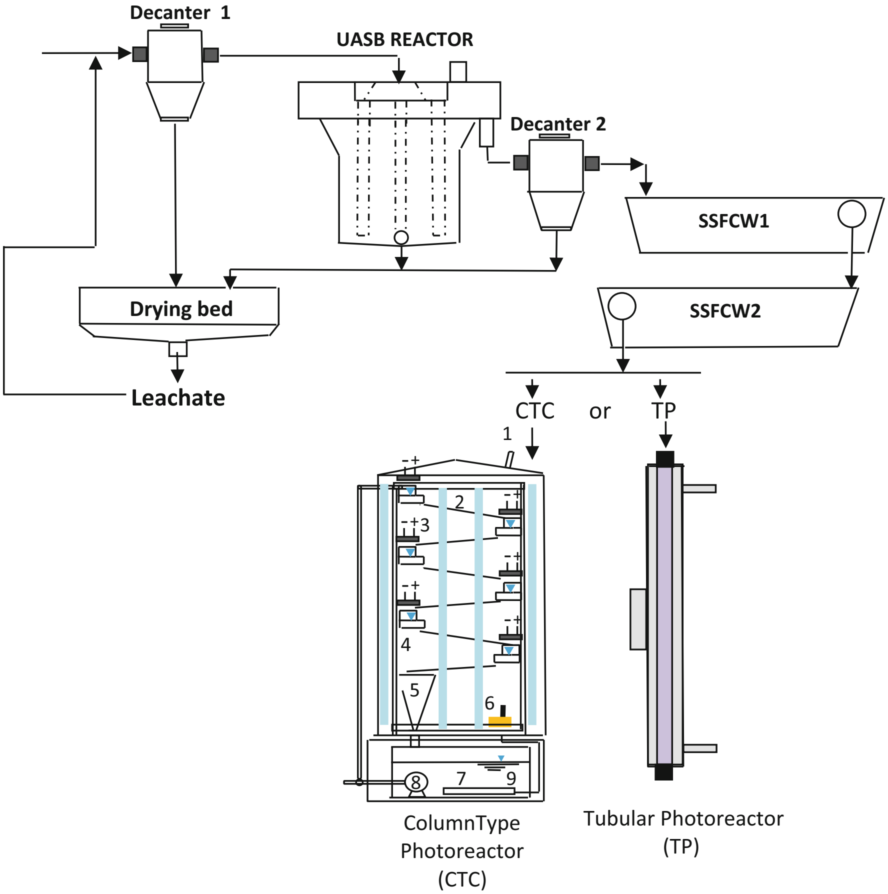

Fig. 4 Decanters + UASB + SSFCWs + or tubular photoreactor or column-type photoreactor system (*1* air input, *2* ramps, *3* ventilators, *4* gutters, *5* collector funnel, *6* aeration pump, *7* equalizer tank, *8* recirculation pump, *9* aeration device)

Table 2 Overview of the operational conditions of the UASB + SSFCWs system

Parameters	Values
UASB	
HDT (d)	1.5
Specific organic load kg COD m^{-1} day^{-1}	0.17
SSFCWs	
Volumetric coefficient (VC) m^{-2} day^{-1}	0.54
g COD m^{-2} day^{-1}	91.8
g TKN $m^{-2}day^{-1}$	28.1
g P $m^{-2}day^{-1}$	4.1

Table 3 Operational conditions for catalytic photoozonization of the effluent from UASB + SSFCWs using CTP reactor

Parameters	Values
Useful volume (L)	10
Concentration of O_3 in the wastewater (mg L^{-1})	0.37
Energy consumption (W)	25.8
Lamp (W *Daylight F 3078 GL*)	30
Treatment time (min)	60
Capacity of O_3 generation (mg O_3 h^{-1})	1.8
Total energy consumption (WL^{-1*})	25.8
UV radiation dosage cm^{-2} (254 nm)	30
Useful volume of the photocatalytic ramp (L)	0.78
Treatment capacity (L h^{-1})	10
Recirculation rate (L h^{-1})	180
Hydraulic detention time on the wastewater disposal ramps (min)	0.26 × 18 cicles (4,68 min)
Treatment time (min)	60

Table 4 Performance comparison of the catalytic ozonization photoreactors with literature data for the degradation of methylene blue (5 mg L^{-1}, pH = 7.5)

Process	Regression equation	Representativeness
$UV/TiO_2/O_3$ [43]	$\log y = 0.13–0.02910x$	0.995
UV/TiO_2 [43]	$\log y = -0.15–0.00236x$	0.988
$UV/TiO_2/O_3$ – column-type photoreactor	$\log y = -0.72–0.0065x$	0.970

As can be observed on Table 4, the slopes demonstrate a better efficiency of the reactor proposed by Hur et al. [43], with values regarding the decolorizing rate 4.5 times higher [43]. This indicates a greater generation of oxidizing radicals able for the disinfection. However, it must be pointed out that the referred study presents a configuration of the photochemical reactor with immersed lamps that are externally surrounded by Al_2O_3 beads adsorbed with TiO_2 and the ozone applied on the treatment is generated through electrical discharges from a commercial generator. So, it appears as a more complex and costly system.

On the other side in the same study, a comparison of the slope of the UV/TiO_2 process shows that the $UV/TiO_2/O_3$ process, proposed in this work, is 2.5 times more efficient due to the aggregation of the ozone generated photochemically.

The studies performed by Lourenço [42] were associated with disinfection assays using a catalytic photoreactor (column type) [42]. The researches involved advanced oxidation methods in the combination with TiO_2 (photocatalyst) and oxidation precursors of hydroxyl radicals, O_2 and O_3, adsorbed on the photocatalyst (mechanisms on the Fig. 5). Considering these combinations, the disinfection efficiency of the $UV/TiO_2/O_3$ method was studied.

This disinfection assay was carried out with 10 L of the wastewater, which was recirculated during 60 min by a submersed pump. Starting from time point 0, samples were collected at regular intervals and stored in suitable bottles, which were

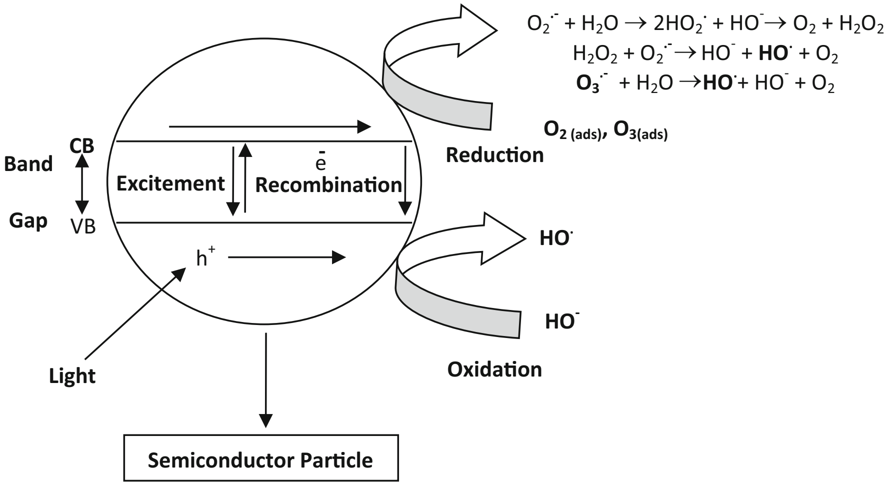

Fig. 5 Reactions of oxidant radical formation in photocatalytic advanced oxidative processes (UV/TiO_2/O_3) (adapted from Litter [44] and Machado et al. [45])

Table 5 Results of disinfection for the tubular and photo column-type reactors

Time (min)	Coliformes termotolerantes (NMP/100 mL) – TP	Coliformes termotolerantes (NMP/100 mL) – CTP
0	22,000	90,000
4	40	2,600
6	<20	1,100
10	<20	220
12	<20	20
20	<20	20
30	<20	20
40	<20	<20
50	<20	<20
60	<20	<20

Table 6 Correlation coefficients of the tubular- and column-type photoreactors for disinfection assays of secondary wastewaters from SSFCWs

Process	Linear regression equation	Representativeness
Tubular reactor UV	$\log y = 3.38386 - 0.22123x$	0.85
Column type reactor UV/TiO_2/O_3	$\log y = 4.78877 - 0.27825x$	0.98

subsequently sent for analysis of alkalinity, turbidity, pH, and fecal coliforms. At the same time, pH, BOD_5, TOC, NH_4^+, TSS, temperature, and turbidity were determined through the employment of a multiparameter sensor.

Table 5 shows the variations of thermotolerant coliform-forming units over 60 min of disinfection.

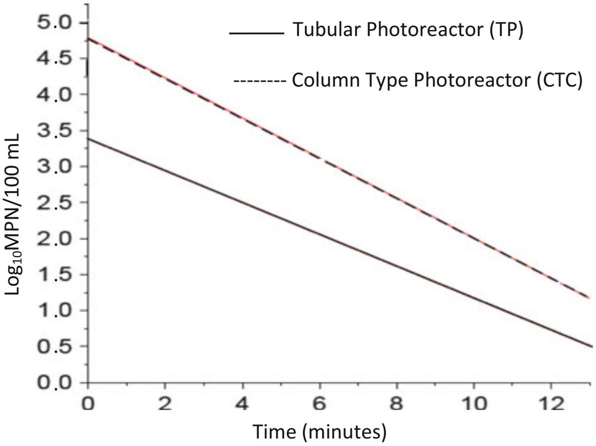

Fig. 6 Graph of disinfection curves for comparative determination of slopes

Following, Table 6 and Fig. 6 demonstrate the data of linear regression curves and the disinfection curves for the determination of the slopes.

In terms of disinfecting performance, the tubular reactor presents a higher rate per unit time, since the ratio between the slopes shown in Fig. 6 indicates a value 16% higher for UV/TiO_2/O_3 than the UV method. The configuration of the tubular photoreactor has the advantage of allowing the diffusion of radiation without diminishing the transmittance, since the diameter of 10 cm ensures the effectiveness of the irradiated power density. However, the reduction of the turbidity, variation of the pH, and the alkalinity are higher for the column-type photoreactor, reinforcing that the new configuration of the column-type photoreactor establishes disinfection by advanced oxidation processes.

Table 7 presents the characterization data of the general parameters of the pollutant load before and after disinfection in the photoreactor column.

The pH range was kept neutral, since it is more favorable to the generation of hydroxyl radicals, either by photoirradiation or by radical decomposition of the dissolved ozone [44].

The treatment of wastewater from SSFCW with a column-type photoreactor presented a decrease of 41.3% in the alkalinity. This result demonstrates greater oxidation capacity to the reduction of observed total alkalinity, indicating good possibilities for the application of the column-type photoreactor due to the generation of hydroxyl radicals, mainly associated with the reduction of the HCO_3^- ion.

Table 7 Characterization of the general parameters of the pollutant load before and after disinfection with the column-type photoreactor (UV/TiO_2/O_3)

Parameters	Wastewater – UASB + SSFCW	Wastewater – UV/TiO_2/O_3	NBR – 13969/1997 classes 1*/3	Guidelines for water reuse – EPA/600/R-12/618 – Hawaii (R2 Water)	Resolution – CONSEMA/RS-128/06 e 129/06
					$100 \leq Q < 200$ m^3 day^{-1}
BOD_5 (mg L^{-1})	70.2	67.2	–	30–60	≤120
TOC (mg L^{-1})	191.0	184.0	–	–	–
pH	7.0	7.0	6–8/–		
T SS (mg L^{-1})	184.0	176.0	–		–
Turbidity (NTU)	145.0	138.0	<5/<10		–
Temperature (°C)	26.3	35.4			–
Thermotolerant coliforms (MPN/100 mL)	90,000	<20	<200/<500	2.2/100 mL (7-day med) – 23/100 mL (not more than one sample exceeds this value in 30 days) – 200/100 mL (max)	–
Total alkalinity $CaCO_3$ (mg L^{-1})	202.6	119.0			–

[a]Residual chlorine = 0.5–1.5 mg L^{-1}. NBR = Brazilian Association of Technical Standards. CONSEMA = State Board of environment from Rio Grande do Sul, Brazil

4 Integrated Systems Involving CWs + AOPs Applied to the Detoxification of Secondary Wastewaters

The wastewaters detoxification history by the application of the integrated treatment systems CWs + AOPs is recent, with papers published more frequently only some years ago. Antoniadis et al. [30], studying the integration of the photo-Fenton + CW methods for the treatment of synthetic urban wastewaters, observed significant reduction of dissolved organic carbon (DOC) and COD, with ranges higher than of 80% [30]. Nevertheless, the N-$NH_4{}^{+}$ and $NO_3{}^{-}$ values measured after treatment were elevated both for photo-Fenton as for the CW, increasing from 77.5 to 92.3 mg L^{-1} and from 2 to 34 mg L^{-1}, respectively. Phosphorus reductions averaged 73% in the photo-Fenton treatment, and further reduction of 17.9% was observed after passing through the CWs. The precipitation of $FePO_4{}^{3-}$ is the first cause associated with better performance of photo-Fenton treatment for the phosphorus reductions.

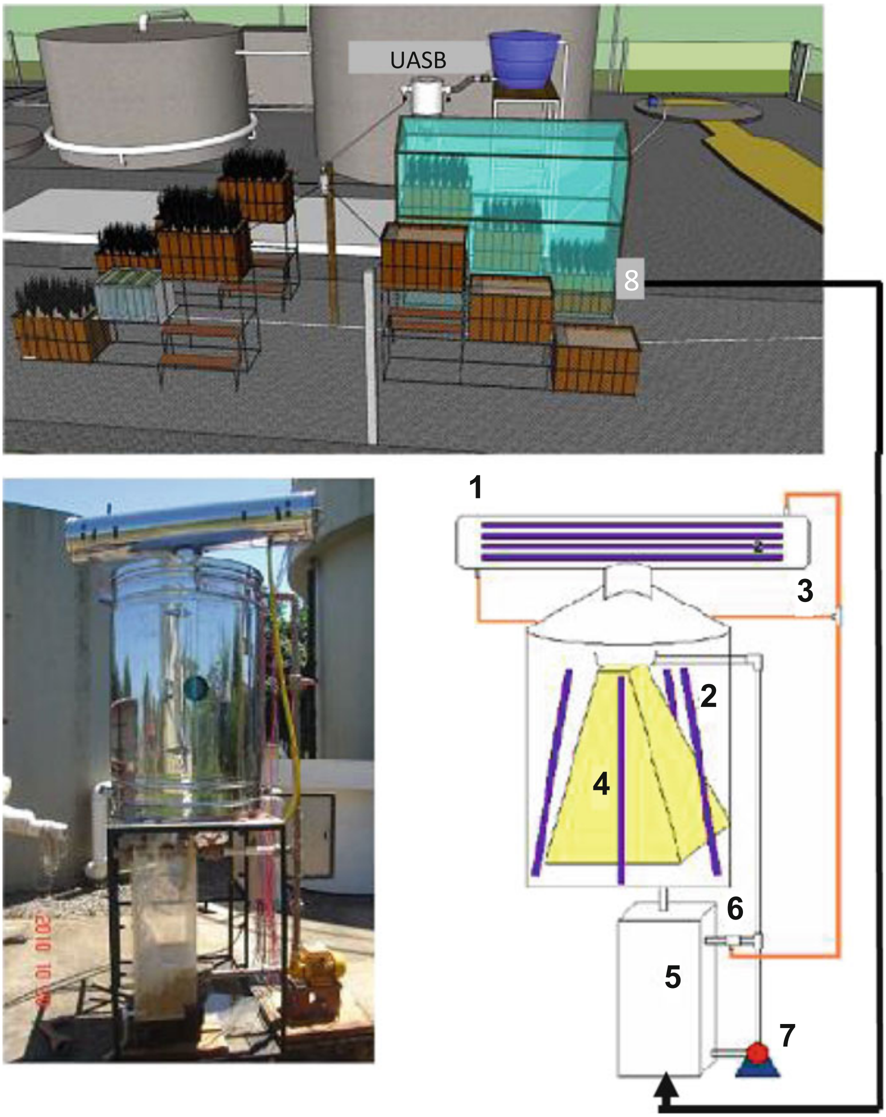

Fig. 7 FTC catalytic photoozonator. *1* Collimator with support for the germicidal lamps (30 W, $\lambda = 254$ nm) containing inlet and outlet. *2* Monochromatic mercury low-pressure lamps (30 W, $\lambda = 254$ nm). *3* Silicone tubes for air suction on the collimator and photoreactor. PVC pipes (diameter = 2,54 cm) for recirculation of wastewaters. *4* Cone-type ramp, in acrylic (5 mm) with or without TiO_2. *5* Handler equalizer tank with 30 L useful volume, in acrylic, fitted with PVC fittings with flanges sealing. *6* Tube-type Pitot-Venturi. *7* Centrifugal pump 0.5 HP. *8* Wastewaters of the SSFCWs for the $UV/TiO_2/O_3$ assays

Araña et al. [29] studied the integration of the photocatalysis (TiO_2/UV) + CW for the treatment of commercial pesticides and fungicides [29]. The authors monitored the evolution of compounds generated during different application times of the TiO_2/UV method by gas chromatography (GC), mass spectrometry (MS), and high-performance liquid chromatography (HPLC) and tried to associate the chronic toxicity to certain compounds generated in the elimination of pesticides. When comparing the efficiency for the reduction of the toxicity to *Lemna minor* (three different systems of CWs were tested: one vegetated with *Phragmites australis*, the other vegetated with another *Papyrus* sp., and the last one with non-vegetated substrate), the authors conclude that the presence of the species used in these CWs did not influence the elimination of the compounds and consequently the toxicity reduction. Higher toxicity reductions of the pesticides were obtained by the application of the TiO_2/UV (applied for 1 h) + CWs integration.

Grafias et al. [31] described the inefficiency of an AOP system to detoxify the wastewater of a processing olive agro industry. The EC_{50} registered extremely toxic values for *Vibrio fischeri* with 3.8% in the raw wastewater, and this value remained as 3.4% after treatment with the electrooxidation. When combining the electrooxidation with CWs as posttreatment, the toxicity decreased ($EC_{50} = 26\%$). Nevertheless, the best results were achieved when the electrooxidation was applied as a posttreatment of CWs, with the average EC_{50} values reaching 45.0%.

Horn [46] published a work integrating UASB + SSFCW + UV/TiO_2/O_3 in batch mode, establishing the use of the macrophyte *H. grumosa* in optimized conditions inside a greenhouse [46]. The temperature was kept around 24°C with a hydraulic detention time (HDT) of 7 days. During the batch flow mode, the average loads applied to the CWs systems were 19.2 g COD m^2 day^{-1}, 3.5 g TKN m^2 day^{-1}, and 0.45 g P_{total} m^2 day^{-1}. In this situation, the reactor was designed with a different configuration from the CTP (mentioned in Sect. 3.2). The new configuration can be seen in Fig. 7.

The FTC was composed by an emerged irradiation system with a tapered acrylic support covered with TiO_2 (P25 Degussa). The applied UVC radiation was generated from a photovoltaic cell of 1kVh, and the wastewater recirculation was done with the help of gas-liquid transfer Pitot-Venturi system. Production rates of photogenerated ozone of 160 mg h^{-1} were applied in up to 4 h of treatment. The general and specific parameters for the qualification of the final effluent of the integrated system are shown in Table 8.

The batch configuration of the CW (in greenhouse) + FTC (point 8 in Fig. 7) afforded COD and BOD_5 average reductions of 62% and 88%, respectively. Additionally, the measured reductions of TKN, N-NH_3, and Ptotal were 27.4%, 27.1%, and 63.3%, respectively. One of the obstacles for the operational implementation of FTC was the saturation of the cone ramp observed after 4 h of operation. The photocatalytic activity was controlled by the degradation of a reference standard solution of methylene blue (5 mg L^{-1}), which reduces approximately 80% after 4 h operation, due to formation of Fe_2O_3 layer. The Fe_2O_3 was generated from steel 1040 because the load compartment of the centrifugal pump

Table 8 Control parameters for influent/effluent from system UASB + SSFCWs + UV/TiO_2/O_3-type cone. Photoreactor (FTC)

Parameters	Wastewater – UASB + SSFCWs	Wastewater – UV/TiO_2/O_3	NBR – 13969/1997	Guidelines for water reuse – EPA/600/R-12/618 – Hawaii (R2 water)	Resolution – CONSEMA/RS-128/06 e 129/06
					$100 \leq Q < 200$ m^3 d^{-1}
COD (mg L^{-1})	71.5	50.0	-		≤330
BOD_5 (mg L^{-1})	21.3	20	-	30–60	≤120
TKN (mg L^{-1})	41.8	30.5			–
NH_3 (mg L^{-1})	24.8	15	-		≤20
NO_3^- (mg L^{-1})	0.8	1.5			–
Ptotal (mg L^{-1})	2.5	1.2			–
Conductivity (μScm^{-1})	832.7	1119.1			–
pH	7.9	8.0	6–8/–		–
Turbidity (TU)	11.6	38.0	<5/<10		-
Color (λ = 420 nm)	0.21	0.12	–		Do not change the receiver body
$CE(I)_{50}$	71.3	48	–		FT = 1 acute toxicity * $CE(I)_{50} = 100\%$
$CI(I)_{50}$	17.6	20.0	–		-
Total coliforms CFU/100 mL	$1{,}2 \cdot 10^6$	<100	<200/<500-	2.2/100 mL (7-day med) -23/100 mL (not more than one sample exceeds this value in 30 days) –200/100 mL (max)	-
Escherichia coli CFU/100 mL	$8{,}2 \cdot 10^5$	<100			-

$CE(I)_{50}$ 48 h e $CI(I)_{50}$ em %. Brazilian Association of Technical Standards. CONSEMA = State Board of environment from Rio Grande do Sul, Brazil was exposed to anodization conditions (increase in turbidity) and consequently contamination on the photocatalytic support. Since the radiation has the barrier of the ferric oxide layer, washings with HCl 1% v/v are needed. The replacement of the centrifugal pump by an inert pumping box will be necessary for future studies.

Lobo et al. [47] proposed a classification of wastewaters, based on their toxicity, in four ranges: $< 25\%$ extremely toxic, 25–50% highly toxic, 50–75% moderately toxic, and $> 75\%$ slightly toxic [47].

Regarding the acute toxicity (with *Daphnia magna)*, the raw wastewaters evolve from a condition of moderately toxic (EC_{50} between 50 and 75%) to a slightly toxic (EC_{50} between 75 and 100%) after the treatment. The chronic detoxification (with *Ceriodaphnia dúbia*) was inefficient, keeping the wastewaters in the ranges of extremely toxic as $IC_{50} = 17.6\%$. Concerning the disinfection, the effectiveness is attributed especially to $UV/TiO_2/O_3$ combination, reducing the total coliforms load (CFU/100 mL) of 1.4×10^5 to 100 CFU/100 mL. The condition for reuse of treated wastewaters is close to the framework of the Class 1 of the NBR 13969/1997 [48] (Brazilian Association of Technical Standards – NBR 13969), especially considering the microbial load. Adjustments for the reduction of the turbidity must also involve a better phase separation of the particulate matter detached from the TiO_2 ramp.

Aspects of the greatest difficulties for the treatment of effluents with toxic compounds in CWs are the concern in further research on mechanisms and by-products that occur in the system of phytoremediation (organics and inorganics, including biomass generated). Even with accurate analytical procedures, for the control of removal of contaminants or pollutants, further studies of the mechanisms of degradation will still be required [49]. Moreover, toxicity studies involving mainly chronic ecotoxic and genotoxic indicators should also continue to be investigated. These parameters may be decisive for choosing the application of the CWs as an alternative for pre- or posttreatment of wastewaters in integrated systems along with other treatment methods such as aerobic or anaerobic treatments, mixed biological systems, and advanced oxidation processes.

For systems with a relation $COD/BOD_5 = 2$, the possibility of a pretreatment with CWs, using, for example, AOPs for a final polishing of eventual residual pollutants, can be the more adequate option.

5 Conclusions

The combination of CWs with other processes might enable an improvement of the sustainability in wastewater treatments.

First there is a possibility of increasing the potentialities of phytoremediation of load factors, especially the COD, total nitrogen, and total phosphorus. In this case, the use of anaerobes methods seems to be an interesting alternative, which allows for the reduction of COD load parameter. Regarding nitrogen and phosphorus, there is the potential for pretreatment with aerated biofilter and algae, which are removed prior to entry into CWs or filtered in VFCWs.

In another line of research, the CWs may allow decentralized treatment systems for detoxification of organic compounds, especially if associated with advanced oxidation processes, such as electrooxidation, ozonation by photochemical generation, (UVC and vacuum ultraviolet (VUV)), and photocatalytic ramps.

The possibility of recovering energy and nutrients also provides another line of research for the CWs in integrated systems, especially when considering the preliminary results obtained with fuel cells.

Another point where the CWs deserve attention is in the context of life-cycle assessment, particularly concerning the design of the systems, reducing the high environmental impact associated to some materials such as waterproof blankets and to the emission control of greenhouse gases, such as methane.

Therefore, because of the possibility to develop a more sustainable system, which may allow the recovery of energy, water, nutrients, and biomass, the continuity of the researches of CWs in integrated systems should be highly encouraged.

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Membrane Bioreactors (MBRs) for Water Reuse in the USA

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Abstract Water scarcity is a global problem, and the production of wastewater is growing correspondingly along with the ever-increasing water consumption. Wastewater can be used as an alternative water resource. Technological developments in treating municipal wastewater, such as membrane bioreactors (MBRs), provide high-quality effluents appropriate for water reuse. In this chapter, we review water reuse issues and standards, features and challenges of membrane bioreactor systems, and status of MBR applications in the USA. It can be concluded that MBRs are a superior wastewater treatment technology compared to conventional activated sludge systems, and they can help fulfill the growing water reuse demand.

Keywords Membrane bioreactor, Membrane fouling, Pollutant removal, Wastewater reuse

Contents

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Abbreviations

BOD	Biochemical oxygen demand
CAS	Conventional activated sludge
COD	Chemical oxygen demand
EBPR	Enhanced biological phosphorus removal
EPS	Extracellular polymeric substances
FAO	Food and Agriculture Organization
GE	General Electric
HAdV	Human adenovirus
HRT	Hydraulic retention time
IWMI	International Water Management Institute
MBR	Membrane bioreactor
MLSS	Mixed liquor suspended solids
NRC	National Research Council
NTU	Nephelometric turbidity unit
PVDF	Polyvinylidene fluoride
SEM	Scanning electron microscope
SMP	Soluble microbial products
SNdN	Simultaneous nitrification and denitrification
SRT	Solids retention time
TKN	Total Kjeldahl nitrogen
TMP	Transmembrane pressure
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphate
TSS	Total suspended solids
USEPA	US Environmental Protection Agency
UV	Ultraviolet
WHO	World Health Organization
WRF	Water Reclamation Facility
WWTP	Wastewater treatment plant

1 Water Reuse in the USA

Generally, the USA is not considered as a country with severe water scarcity [1]. However, it has been reported that precipitation is not able to satisfy the withdrawals of freshwater in many regions across the USA, especially in the areas with fast-growing population [2]. The value of reclaimed water, as an alternative to freshwater sources, has been recognized in many countries. China, Mexico, and the USA are the top three countries regarding to total volume of reused water, but in China and Mexico, around half of the reused water is untreated wastewater.

The USA ranks first for the reuse of treated water, and the volume is approximately four times higher than in Saudi Arabia, who takes the second place [3]. Approximately 9.84 million m^3 of water is reused/reclaimed per day in the USA, but that only accounts to 7.4% of the total volume of wastewater generated [4, 5]. The volume of reused water is increasing at an annual rate of 15% [4]. In the USA, reclaimed water may serve for many purposes, including urban reuse, industrial reuse, agriculture reuse, environmental reuse, groundwater recharge, and potable reuse [5]. Agricultural reuse takes the largest portion of 29% of reclaimed water across the country, while landscape/golf course irrigation and recreational impoundment occupy a total of 25% [5, 6]. The remaining categories of reuses include commercial and industrial reuse, groundwater recharge, geothermal/energy production, natural system restoration, and discharge to wetlands and wildlife habitat.

California is the most populous state in the USA has the largest surface and groundwater withdrawals and is facing an unprecedented water crisis" [7]. The history of water reuse in California can be traced back to the 1890s. In 2009, the recycled water in California has reached 0.8 km^3, but it is still only a small portion when compared to the state's annual water use, 53 km^3 [8]. According to the California State Water Resources Control Board [9], agricultural irrigation takes the largest portion (37%) of the reclaimed water. The percentages for landscape irrigation and golf course irrigation are 17% and 7%, respectively. Aquifer recharge, as an indirect potable reuse, has been implemented in California since the 1960s [10], and now its share is 12%. The National Water Research Institute [11] proposed the possibility of direct water reuse in southern California, but this has not been applied so far. It has been estimated that the annual water reuse could reach 2.5 km^3 by 2020 and 3.7 km^3 by 2030 [12].

Florida is a leading state in water reuse, where 49% of treated water is reused [13]. The total amount of reused water increased from 0.285 km^3 in 1986 to 1 km^3 in 2012, and the per capita reuse flow was 0.14 million m^3 per day in average [14]. A percentage of 55% of reclaimed water is used in public access areas, such as parks and schools. Ten percent of reclaimed water is used to irrigate farmland. Industrial reuse and groundwater recharge take 17% and 13% of reclaimed water, respectively. The rapid growing population has been suggested as the major driving force for the high level of water reuse [15]. Economic merits may be another driving force. A total of 74 water reuse utilities in Florida claimed that they provided reclaimed water to their customers for free [14].

As the public is a major stakeholder involved in the decision-making of water management [16], social factors play a key role in water reuse [17]. Water reuse projects may fail due to social resistance, even though the treated water can meet certain standards. For example, several indirect potable water reuse projects in the USA were strongly opposed by the public. Also, notions like "toilet to tap" made people uncomfortable, and the social acceptance for water reuse was fairly low. Social awareness of water reuse is rising in the USA and a survey conducted by the WateReuse Research Foundation indicated that people in cities where water reuse projects had been applied were aware of reclaimed water [18]. However, the levels of water reuse across the USA are quite diverse, and it appears that public trust on agencies and confidence on the ability of technologies in pollutant removal were low [19]. To conclude, water reuse may still be a controversial topic in the US public.

2 Water Reuse Standards

Water reuse generally refers to "the use of treated wastewater (reclaimed water) for a beneficial purpose" [20]. It has been considered as an alternative water source in addition to natural water sources. Water reuse can be classified to direct reuse and indirect reuse. Applications of reclaimed water coming out from treatment facilities directly to target fields, such as agricultural or landscape irrigation, are referred to as direct reuse. Indirect reuse, on the other hand, is the discharge of treated water to water bodies (e.g., streams, groundwater aquifer) or storage in a reservoir (e.g., impoundment) before reuse [21]. Water reuse can also be categorized into direct potable reuse, indirect potable reuse, and non-potable reuse, in terms of drinking water supply. Non-potable reuse, like agricultural irrigation, has been widely accepted by scientific communities and the general public, whereas potable reuse is still far to reach a consensus [17, 22].

In 1989, the World Health Organization (WHO) published a health guideline for the use of wastewater in agriculture and aquaculture. The water quality standards are mainly focused on microbial pathogens [23]. After 3 years, Food and Agriculture Organization (FAO) released its guideline for wastewater treatment and use in agriculture and recommended standards for pH, fecal coliforms, and trace elements [24]. Several countries, to name a few, Germany, Japan, China, and Australia, have established their own standards for water reuse [25]. The latest water reuse guideline in the USA was published by EPA in 2012. Based on different reuse applications, water quality criteria are set, and the key parameters include pH, biochemical oxygen demand (BOD), total organic carbon (TOC), turbidity or total suspended solids (TSS), fecal coliform, and Cl_2 residual, as shown in Table 1. Nitrogen and phosphorus are not included in the EPA water reuse criteria, but they are considered as water quality monitoring parameters, of which the treatment goals in reclaimed water are 1–30 and 1–20 mg/L, respectively [21]. State and local authorities may have additional and stricter standards, depending on the types of reuses. For example, California includes total nitrogen (10 mg/L) for indirect potable reuse and it requires that the level of both *Clostridium* and coliphage should not exceed 5/100 mL (monthly mean) and 25/100 mL (daily maximum) in agricultural reuse water [5].

Table 1 Water quality criteria of EPA guideline for water reuse [5]

	Non-potable reuse I	Non-potable reuse II	Indirect potable reuse
Reuse category	Urban reuse (restricted), processed food corps, nonfood corps, impoundments (restricted), environmental reuse, industrial reuse	Urban reuse (unrestricted), impoundments (unrestricted), food corps	Groundwater recharge into potable aquifers, augmentation of surface water supply reservoirs
pH	6.0–9.0	6.0–9.0	6.5–8.5
Organic matter	$\leq$30 mg/L BOD	$\leq$10 mg/L BOD	$\leq$2 mg/L TOC of wastewater origin
Turbidity or TSS	$\leq$30 mg/L TSS	$\leq$2 NTU	$\leq$2 NTU
Fecal coliforms	$\leq$200 fecal coliform/100 mL	No detectable fecal coliform/100 mL	No detectable fecal coliform/100 mL
Cl_2 residual	1 mg/L Cl_2 (min)	1 mg/L Cl_2 (min)	1 mg/L Cl_2 (min)

3 Membrane Bioreactor Technology for Water Reuse

Membrane bioreactors, a combination of activated sludge process with biomass separation by membrane filtration, have become a state-of-the-art technology for municipal and industrial wastewater treatment. Generally there are two ways of integrating the membrane modules into activated sludge process [26]: (1) the submerged configuration, in which the membranes are immersed in the mixed liquor, and permeate is pumped mechanically or by gravity flow, and (2) the sidestream configuration, in which the activated sludge is pumped through membrane module and then recycled, in order to maintain a constant sludge concentration. Comparatively, submerged (immersed) MBR systems are more cost-effective and less energy consuming than sidestream systems [27, 28]. Three membrane modules are available for MBRs: hollow fiber, flat sheet, and tubular, of which hollow fiber and flat sheet are more prevalent [29]. Compared to traditional activated sludge reactors, advantages of MBR include smaller footprint and better effluent quality. Operation of MBR systems is easier since the performance variability is less, and it significantly reduces the overall area of treatment plant [30]. MBRs have become a particularly attractive treatment choice for water reuse. In fact, the global MBR market is expanding rapidly.

Membrane bioreactors have been considered as a feasible and promising tool for water reuse [25, 31–33]. Atasoy et al. [34] suggested that MBRs cannot only reclaim the grey water but also support the reuse of black water, which is more difficult to be recycled due to its high contamination level. MBR technology is able to treat industrial wastewater and match the requirements for water reuse [35, 36] as well. Cicek [37] suggested that MBR technology is capable to remove agricultural wastes, such as pesticides, nitrates, and endocrine-disrupting compounds, and therefore it can be applied for agricultural wastewater treatment. Cote et al. [38] described ultrafiltration as “the best available technology” for water reuse, and

MBR is a technological option where ultrafiltration can be applied. The fast descending cost of MBR facilities [39] makes it further more competitive. Howell [40] concluded four incentives that promote MBR applications for waste treatment: (1) MBR plants are more compact; (2) expansion of plant capacity is simple; (3) the effluent quality is high; and (4) the value of reusing is widely recognized.

4 Membrane Fouling

When membrane filtration is carried out in activated sludge, biosolids, colloidal species, and macromolecular species will deposit and accumulate on membrane surface and lead to a flux and permeability decline. This process is called membrane fouling, and it has been considered as the major obstacle and challenge of the development and application of MBRs, as it increases the maintenance and operational costs [26, 41]. Ji et al. [42] published a scanning electron microscope (SEM) photograph of fouled membrane surface, which indicates that biofilm consists of two layers: an inner gel layer and an outer cake layer. The gel layer is thin and compact, and it is strongly attached on the membrane surface. Shin and Kang [43] suggested that the formation of gel layer is caused by membrane pore blocking and biomass colonization. In contrast, cake layer is thick, porous, and highly compressible [44], and it has been suggested that the formation of the cake layer is mainly due to the floc deposition [45]. Transmembrane pressure (TMP) is widely used to indicate the extent of membrane fouling [46–48]. Higher TMP generally means severe membrane fouling. Membrane fouling could be reversible or irreversible. Reversible fouling is defined as fouling on the membrane surface that can be removed by physical washing, while irreversible fouling, on the other hand, refers to internal fouling into the membrane pores, which can only be removed by chemical clean [49]. Fouling control is one of the most important issues in MBR operation.

Mixed liquor suspended solids (MLSS) can largely affect the membrane filtration performance [48]. High MLSS concentrations can accelerate membrane fouling due to large amounts of foulant and rapid deposition of sludge particles on the membrane surface [50, 51], and it has a direct impact upon cake layer formation [52]. However, Hong et al. [53] observed MLSS exhibited very little influence on permeate flux for the range of 3,600–8,400 mg/L, and they suggested fouling was independent of MLSS concentration until a very high value was reached. Additionally, Li et al. [54] even reported a negative correlation between MLSS and membrane fouling resistance.

Extracellular polymeric substances (EPS) in activated sludge are composed of multiple classes of macromolecules such as carbohydrates, proteins, nucleic acids, phospholipids, and other polymeric compounds found at or outside the cell surface and in the intercellular space of microbial aggregates [55]. High concentration of

EPS could affect membrane fouling by increasing viscosity of the mixed liquor [56] and filamentous bacteria growth [57]. In addition, components of soluble microbial products (SMP) such as humic and fulvic acids, polysaccharide, proteins, nucleic acid, organic acids, amino acids, antibiotics, steroids, enzymes, structural components of cells, and products of energy metabolism affect fouling [58]. Carbohydrate component of the SMP was found to be negatively correlated with membrane permeability [59].

A positive correlation between food to microorganisms (F/M) ratio and membrane fouling has been found in previous studies. No evidence indicated that F/M ratio had direct impact on membrane fouling, but it could increase the EPS concentrations [60] and in turn cause membrane fouling. Additionally, low F/M ratio equals little substrate per unit biomass, which leads to competition among the microorganisms and results in reduction of the net sludge production [61]. At steady state, low net sludge production leads to higher solids retention time (SRT) and less membrane fouling.

Positive correlations have been found between the presence of filamentous bacteria and membrane fouling. Choi et al. [30] observed that membrane fouling was most serious under filamentous sludge bulking conditions. It has been reported that filamentous bacteria could change the floc morphology [54] and lead to irregular shape of the bulking sludge [62]; the overgrowth of filamentous bacteria in sludge suspension could form a thick and non-porous cake layer and cause severe membrane fouling [63]; and excessive growth of filamentous bacteria could indirectly cause membrane fouling by significantly increasing the extracellular polymeric substances (EPS) concentration and sludge viscosity [57].

Hydraulic retention time (HRT) indicates the average time that wastewater stays in activated sludge reactor. It has been suggested that HRT only has an indirect effect on membrane fouling [49, 64] by affecting other factors, such as MLSS. SRT indicates the average time that suspended solids stay in the activated sludge reactor. SRT is suggested as one of the critical factors controlling SMP concentration in the reactor [65]. With prolonged SRT, concentrations of suspended solids and volatile suspended solids in the bioreactor increase [66], and membrane fouling tends to increase due to deposition on the membrane surface [51]. Nevertheless, similar to HRT, SRT can only indirectly influence membrane fouling [49], but the effect of changes in SRT on fouling potential is more intense than that of HRT [67].

Membrane backwash and chemical clean are the two major ways to mitigate membrane fouling in MBR systems. Membrane backwash is a physical process that removes the loosely attached cake layer. Membrane permeate is commonly used for backwash. The backwash duration varies from seconds to minutes. Chemical clean, on the other hand, is a process that can remove most of the fouling substances from the membrane and recover the membrane permeability to a large extent.

5 Removal of Suspended Particles and Chemical Pollutants in MBRs

In order to achieve high removal of pollutants, such as nitrogen and phosphate reduction, MBR systems usually consist of multiple stages, (Table 2). For example, the wastewater treatment plant (WWTP) in Traverse City, MI, is equipped with MBR, and it has a total of six stages: one anaerobic stage, one anoxic stage, three aerobic stages, and one aerobic/membrane stage [75]. The operational parameters (MLSS, SRT, recycle ratio, etc.) may be different among stages. Anaerobic treatment is used at the front end of some MBR systems.

As shown in Table 2, MBR systems are able to achieve high removal for suspended solids and turbidity, due to small membrane pore sizes. It has been suggested that membranes can act as a near-absolute barrier for suspended solids [76]. This allows MBRs to be operated at high MLSS levels [77, 78] that leads to higher removal for pollutants, such as organic substances. Full-scale MBRs can achieve high removals (usually $>95\%$) for organic substances (Table 2).

The major removal mechanisms of organic matter in conventional activated sludge systems are adsorption and biodegradation. These two mechanisms are also applied in MBR systems [79], and it has been reported that MBRs can remove organic matter more efficiently compared to conventional activated sludge systems [80]. Also, Huang et al. [81] reported high removals of organic matter in a submerged MBR.

As discussed above, MBR systems can be operated at a high level of MLSS, and this may enhance the bio-processes, such as nitrification and EBPR. Also, membranes can effectively remove nitrogen and phosphate associated with large particles. Compared to other pollutants, however, removal of nitrogen and phosphate in MBR systems appears to be less stable. Extra attention needs to be paid to the removal of nitrogen and phosphate when designing new MBR systems. Chemical precipitation is a traditional method for phosphate removal. This method is reliable, but costs of chemicals and chemical feed systems may be considerable. An alternative method is “enhanced biological phosphorus removal (EBPR).” This process consists of an anaerobic stage, where P is released, and an aerobic stage, where P is consumed [82, 83]. This process is widely used in wastewater treatment plants with lower costs, but it is less stable than chemical treatment [84]. Conventional methods and technologies may be employed and integrated to the MBRs. For instance, the SymBio® technology, which promotes the simultaneous nitrification and denitrification (SNdN), is applied in an MBR plant at Delphos (OH, USA) [85].

Table 2 Pollutant removal in selected full-scale MBR plants in the USA

Plant configuration and MBR module	Pollutant removal (influent/effluent)[a]		Reference
Leoni Twp WWTP, MI	TSS	~170/2	[68]
Anoxic + pre-aeration + membrane tanks	BOD	~170/2	
Kubota$^{®}$ immersed flat sheet membrane	NH_3–N	23/0.07	
UV disinfection	TP	5/0.24	
The Hamptons WWTP, GA	TSS	200/<2	[69]
Anoxic + aerobic stages	Turbidity	NA/<0.5	
Kubota$^{®}$ flat sheet membrane	BOD	200/<3	
Chemical disinfection	TN	40/<10	
	TP	10/<0.13	
Ken's Foods WWTP, MA (food industry)	TSS	12,000/<2	[27]
Anaerobic Kubota systems	BOD	18,000/16	
Kubota$^{®}$ immersed flat sheet membrane	COD	34,000/200	
No disinfection unit reported			
Traverse City WWTP, MI	TSS	248 < 1	[27, 70];
Anaerobic + anoxic + aerobic stages	BOD	280/<2	
ZeeWeed$^{®}$ immersed hollow fiber membrane	NH_3–N	27.9/<0.08	
UV disinfection	TP	6.9/0.7	
Cauley Creek WRF, GA	TSS	174/3.2	[70, 71]
Anaerobic + swing zone +2 aerobic stages + membrane tanks	BOD	182/2	
ZeeWeed$^{®}$ immersed hollow fiber membrane	COD	398/12	
UV disinfection	TKN	33/1.9	
	NH_3–N	24.8/0.21	
	TP	5/0.1	
Calls Creek WWTP, GA	TSS	248/1	[70, 72]
Anoxic + aerobic + membrane tanks	Turbidity	NA/0.3	
Siemens/US Filter Systems Orbal$^{®}$ system	BOD	145/1	
UV disinfection	NH_3–N	14.8/0.21	
	TP	0.88/0.28	
Redlands WWTP, CA	TSS	130/<5	[73]
Anoxic + aerobic + membrane tanks	Turbidity	NA/<0.2	
ZeeWeed$^{®}$ reinforced hollow fiber UF membrane	BOD	160/<5	
Chlorine disinfection	TN	24/<10	
Santa Paula WWTP, CA	TSS	210/<5	[74]
Anoxic + aerobic + membrane tanks	BOD	320/<5	
PURON$^{®}$ membrane filtration modules	TKN	53/<7	
UV disinfection	TDS	1,300/<1,000	

[a] Concentrations of some pollutants in the influent are extrapolated based on the concentrations in the effluent and removal efficiencies. Units for turbidity are NTU and for other parameters mg/L

6 Removal of Pathogens in MBRs

Removing microbial pathogens is critical for water reuse safety. The water reuse guidelines set microbial requirements in terms of fecal coliform. Bacteria removal in full-scale MBR systems is summarized in Table 3. It can be seen that most full-scale MBRs can achieve high removal efficiency for bacteria, and membrane pore size appears to be an important factor. Aidan et al. [92] reported that an MBR equipped with 0.8 μm ceramic membrane could only remove 39% coliform bacteria, while high or complete removal was reached by using membranes with smaller pore sizes [77, 93, 94]. Compared to bacterial indicators, investigations for the removal of specific pathogens in MBRs are relatively rare. Tests for some pathogenic bacteria (e.g., *Salmonella* spp., *Campylobacter* spp., *Cryptosporidium*, etc.) were applied in several MBR studies, but no concentrations in the influent (raw wastewater) were detected [95, 96].

It has been reported that more than 100 types of enteric viruses are excreted in human feces and are present in contaminated waters [97, 98]. Enteric viruses pose a considerable threat to human health due to their low infectious dose and long survival in the environment. Table 4 shows the removal of bacterial viruses (coliphages) and human viruses, such as adenovirus, enteroviruses, and noroviruses in full-scale MBRs. In a bench-scale MBR with hydrophobic polyvinylidene fluoride membrane (pore size = 0.22 μm) could remove 99% of poliovirus, while ultrafiltration could achieve a complete rejection due to smaller pore size [103]. Presence of biomass, low transmembrane pressure, and stirring could enhance the removal [103]. MBR systems with higher HRT and lower SRT seemed to be more efficient in removing viruses [104].

Gallas-Lindemann et al. [105] reported high removal efficiencies for *Giardia* (99.4%) and *Cryptosporidium* (94.2%) in a full-scale MBR. Herrera-Robledo et al. [106] reported high removal of helminth eggs in a bench-scale anaerobic MBR with ultrafiltration membranes. By using a pilot-scale anaerobic MBR, Saddoud et al. [107, 108] obtained complete removal for helminth ova and protozoan cysts. Abdel-Shafy [109] investigated the removal of protozoan cysts, helminth eggs, and nematodes in a pilot submerged MBR, and the results indicated that the MBR was able to reject all of these microorganisms.

MBR treatment is usually followed by disinfection. Chlorine disinfection is the most commonly used method in conventional activated sludge plants. It is cost-effective and well established, but the residual and forms of chorine could be toxic, and further dechlorination may be required [110]. Ozone is more effective than chlorine for disinfection, without any residual left in effluent; however, it is very reactive and corrosive, and costs for the method could be considerable [111]. UV disinfection leaves no residual in the effluent, but high water turbidity may cause it to be less effective [112]. As described above, high TSS removal can be achieved in

Table 3 Bacteria removal in full-scale MBRs

MBR type (membrane pore size)	Bacterial indicators	Removal efficiency		Reference
		Before disinfection	After disinfection	
Submerged hollow fiber MBR (0.035 μm)	Total coliform	NA	Up to 4 logs	[86]
Submerged hollow sheet (0.2 μm)	Total viable count	3.6 logs	4.6 logs	[87]
	E. coli	4.7 logs	Complete removal	
	Total coliform	4.1 logs	Complete removal	
Submerged MBR (0.4 μm)	*E. coli*	>98%	NA	[88]
Submerged flat sheet MBR (0.4 μm)	*E. coli*	6.35–6.68 logs	NA	[89]
	Enterococci	5.64–5.84 logs	NA	
Parallel-panel submerged MBR (0.45 μm)	*E. coli*	1.7–5.7 logs	NA	[90]
Submerged flat sheet MBR (0.4 μm)	Total coliforms	6.02 logs	6.93 logs	[33]
	Thermotolerant coliforms	6.72 logs	7.32 logs	
	Fecal coliforms	6.98 logs	Complete removal	
	E. coli	6.77 logs	Complete removal	
	Enterococci	5.77 logs	Complete removal	
Microfiltration MBR (<0.4 μm)	*E. coli*	5.37 to >6.85 logs	Not enhanced	[91]
	Enterococci	4.82–7.49 logs	Not enhanced	
	Fecal coliforms	5.34–7.23 logs	Removal enhanced by >0.30 log	

Table 4 Virus removal in full-scale MBRs

MBR type (membrane pore size)	Virus	Removal efficiency		Reference
		Before disinfection	After disinfection	
Submerged flat sheet MBR (0.4 μm)	F-specific coliphage	5.82 logs	Complete removal	[33]
	Somatic coliphage	4.44 logs	5.98 logs	
	Bacteriophages infecting *Bacteroides fragilis*	Complete removal	Complete removal	
Submerged hollow fiber MBR (0.1 μm)	HAdV	4.1–5.6 logs	NA	[99]
Submerged MBR (0.4 μm)	Norovirus I	NA	0–5.3 logs[a]	[100]
	Norovirus II	NA	0–5.5 logs[a]	
Submerged hollow fiber MBR (0.1 μm)	HAdV	3.4–4.5 logs[a]	Removal enhanced by ~0.8 log[a]	[101]
	Enterovirus	2.9–4.6 logs[a]	Removal enhanced by ~0.4 log[a]	
Submerged hollow fiber MBR (0.1 μm)	HAdV	4.1–6.3 logs	NA	[102]
	Enterovirus	4.1–6.8 logs	NA	
	Norovirus II	3.5–4.8 logs	NA	
Microfiltration MBR (<0.4 μm)	F-specific coliphage	>4.58–6 logs	Not enhanced	[91]
	Somatic coliphage	2.67–4.04 logs	Removal enhanced by >2.18 logs[b]	
	Adenovirus	2.38 to >4.86 logs	Not enhanced	
	Enterovirus	>2.2–4.74 logs	Not enhanced	
	Norovirus I	>1.51–3.32 logs	Not enhanced	
	Culturable viruses	>1.99–3.61 logs	Not enhanced	
Flat sheet submerged MBR (0.4 μm)	Somatic coliphage	4.43–4.44 logs	NA	[89]
	F-specific coliphage	5.81–5.83 logs	NA	
Parallel-panel submerged MBR (0.45 μm)	Norovirus	0.9–6.8 logs	NA	[90]
	Sapovirus	1.7–4.1 logs	NA	

[a] Read from graphs

[b] Median value

MBRs, which makes UV become a feasible and preferable disinfection process in MBR plants. In fact many MBR plants in the USA use UV for disinfection, to name a few: Duvall WWTP (WA), Nantucket WWTP (MA), and Cauley Creek WWTP (GA).

7 Comparison Between Conventional Activated Sludge (CAS) Systems and MBR

Similar to conventional treatment, pretreatment to remove large objects and separate solids and grease from wastewater is required before raw wastewater enters MBR systems. Typical components of pretreatment include coarse screen, grit, grease trap, fine screen, equalization, and primary sedimentation. Activated sludge is a component in both CAS and MBR, but different microbial community structures have been observed between the two systems in many previous studies [113–117]. Furthermore, sludge floc size in MBR is smaller compared to CAS systems [118, 119], which implies higher oxygen transfer rate [120].

It has been widely accepted that in general MBRs have superior and stable performance in pollutant removal compared to conventional activated sludge. Soriano et al. [121] obtained higher carbon and nitrogen removal in an MBR system. Munz et al. [117] attributed more efficient COD removal and nitrification in MBR due to different microbial community compositions and distributions. Cirja et al. [79] concluded that sorption and biodegradation were the major mechanisms of organic micropollutant removal in both CAS and MBR. Although no substantial difference was found between these two systems, the potential capability of MBR for high organic load was suggested. Gonzalez et al. [80] showed that concentrations of COD, $NH^{+}{}_{4}$, and total suspended solids (TSS) in MBR effluent were consistently lower than CAS, and were independent from influent concentrations. Bernhard et al. [122] suggested that MBR provided better removals for non-adsorbing persistent polar pollutants, such as sulfophenylcarboxylates. Holbrook et al. [119] concluded that accumulation of nondegradable chemical oxygen demand in MBR was responsible for smaller average floc size and higher observed biological yield coefficient compared to CAS. Wei et al. [123] reported that worm growth was much faster in CAS reactor, which might affect effluent quality. Pauwels et al. [124] found that MBR offered similar removal for ammonium nitrogen and ethinyl estradiol when treating hospital water but had better performance in rejecting indicator microorganisms, such as fecal coliforms. Simmons and Xagoraraki [101] found higher reduction of human adenoviruses and enteroviruses in an MBR plant as compared to CAS plants.

8 Applications of MBRs for Water Reuse in the USA

So far, more than 6,000 MBR plants have been installed worldwide, and over 600 of them are in the USA [68]. Table 5 shows MBR plants in the USA with water reuse applications. Many MBR facilities provide no information in sight of water reuse.

As shown in Table 5, most MBR plants in the USA began their service after 2004. In fact, a lot of these plants served as conventional WWTPs for decades and were upgraded to MBRs in the twenty-first century. For example, the Union Rome WWTP was initially built in 1986 and commissioned as an MBR in 2009. The maximum capacities of most MBR plants are below 38,000 m^3/day (10 mgd), but they could reach 95,000 m^3/day (25 mgd). Construction of an MBR typically takes 1–3 years, depending on the size. Additionally, the capacities of MBRs are usually expandable. Kubota and GE appear to be the most prevalent membrane suppliers for MBR facilities across the USA, and they are also the major membrane suppliers in Europe [32]. GE is known for its ZeeWeed membranes, which are a type of ultrafiltration hollow fiber membrane, while Kubota generally provides flat-plate microfiltration membranes.

Reclaimed water from MBR systems with reuse programs in the USA is mostly used for non-potable purposes, among which land irrigation appears to be one of the most common applications (e.g., Upper Sweetwater WWTP, GA; Corona WWTP, CA). Other non-potable reuse applications include industrial reuse (e.g., Redlands WWTP, CA) and fire protection (e.g., Red Hawk Casino WWTP, CA). Some MBR plants in the USA have injected their treated water to underground aquifers, as a type of indirect potable reuse (e.g., Shelton WWTP, WA; Upper Wallkill WWTP, NJ). Although direct potable reuse has been proposed by Water Reuse Association [8, 10], no evidence shows that treated water from MBRs is to be applied for such purpose in the USA. It is notable that many MBR WWTPs discharged their effluent directly to the river without any reuse (e.g., Crooked Creek WRF, GA; Nantucket WWTP, MA), even though the water quality meets the standard for water reuse. In addition, the wastewater treatment facilities with water reuse applications may also discharge a portion of their reclaimed water, depending on the demands. For example, the demand of reclaimed water for agricultural irrigation may be low in winter, while treated wastewater is produced all year around.

Table 5 Selected MBR wastewater treatment facilities in the USA with water reuse[a]

Name	Location	Commission year	Peak capacity (m^3/day)	Membrane manufacturer	Water reuse
Carnation WWTP	King County, WA	2008	1,817	GE	Irrigation
Brightwater WWTP	King County, WA	2011	117,348	GE (ZeeWeed)	Irrigation, industrial reuse
Cauley Creek WRF	Fulton County, GA	2004	18,927	GE (ZeeWeed)	Land irrigation, lawn watering, discharge
Fowler WRF	Forsyth County, GA	2004	9,464	GE (Zenon)	Land irrigation
Spokane County WRF	Spokane County, WA	2011	30,283	GE	Industrial, urban irrigation, wetlands restoration, aquifer recharge
Yellow River WRF	Gwinnett County, GA	2012	69,273	GE (ZeeWeed) (GE)	Non-potable purpose or direct discharge to the river
James Creek WRF	Forsyth County, GA	2006	3,785	Kubota (Enviroquip)	Land irrigation
Johns Creek Environmental Campus	Fulton County, GA	2009	56,781	GE (Zenon)	Irrigation, toilet water, fire protection
Pooler WWTP	Chatham County, GA	2004	9,464	GE (ZeeWeed)	Irrigation to golf course
Upper Sweetwater WWTP	Paulding County, GA	Before 2009	3,785	Kubota	Irrigation to golf course
Yakama Nation Legends Casino WWTP	Yakima County, WA	2008	1,363	Kubota (Enviroquip)	Lawn irrigation, discharge
Shelton WWTP	Mason County, WA	2012	15,142	Kubota (Ovivo)	Regional plan participants, ground water recharge
Red Hawk Casino WWTP	CA	2008	2,650	Kubota	Toilet flushing, fire protection, landscaping
American Canyon WWTP	Napa County, CA	2002	14,195	GE (ZeeWeed)	Vineyard and golf course irrigation, discharge

(continued)

Table 5 (continued)

Name	Location	Commission year	Peak capacity (m^3/day)	Membrane manufacturer	Water reuse
Corona WWTP	Riverside County, CA	2001	3,785	GE (ZeeWeed)	Landscape irrigation, discharge
Marco Island WWTP	Collier County, FL	2007	11,356	GE (ZeeWeed)	Land irrigation
Ironhouse Sanitary District WWTP	Contra Costa County, CA	2011	32,555	GE (ZeeWeed)	Irrigation, discharge
Fallingwater Conservancy WWTP	Fayette County, PA	2003	3,331	GE (ZeeWeed)	Flush water, garden irrigation
Redlands WWTP	San Bernardino County, CA	2004	24,984	GE (ZeeWeed)	Industrial reuse
The Hamptons WRF	Forsyth County, GA	2003	1,041	Kubota	Land irrigation
Santa Paula WWTP	Ventura County, CA	2010	27,255	Koch membrane	Irrigation
Upper Wallkill WWTP	Sussex County, NJ	2010	1,003	Kubota	Groundwater discharge

[a]Many MBR facilities in the USA are not included in this table due to lack of information regarding water reuse.

MGD million gallons per day, *WWTP* wastewater treatment plant, *WRF* water reclamation facility, *Discharge* discharge to the environment (rivers, creeks, canals, etc.)

9 Conclusions

Due to the ever-growing water demand and fierce water crisis all over the world, water reuse and water reclamation, as alternatives to natural water resources, are drawing more and more attention. In the USA, the levels of water reuse are low in general but are increasing fast. Agricultural irrigation is generally the most common application of reused water across the country; other reuses include land irrigation, aquifer recharge, commercial and industrial reuse, and discharge to wetlands and wildlife habitats. The US Environmental Protection Agency (USEPA) has established guidelines and criteria for water reuse in 2012. Membrane bioreactor (MBR) technology has been proven as an effective method in wastewater treatment and provides effluent that meets EPA water reuse criteria. In the USA, a number of conventional WWTPs have been upgraded to MBR plants, and effluent water is being reused. Previous studies have demonstrated that MBRs have smaller footprints, less land occupancy, and higher removal efficiencies for pollutants, especially organic micropollutants and pathogens in contrast to conventional activated sludge systems. It has been shown that removal of bacterial indicators and pathogenic viruses is superior in MBR systems as compared to conventional activated sludge systems. Membrane fouling is considered as the main obstacle in MBRs, and fouling control is one of the key issues in MBR operation. In the USA, treated water from MBR plants is more likely to be reused for land irrigation, such as in lawns and golf courses. Although membrane technology has been studied for decades and MBR facilities are widely installed in the USA, the reuse level of reclaimed water from MBRs appears to be low. However, great potential of water reuse is expected when social, economical, and environmental drivers are activated.

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Treatment of RO Concentrate for Enhanced Water Recovery from Wastewater Treatment Plant Effluent

Teik-Thye Lim and Pow-Seng Yap

Abstract Due to continual deterioration of surface water quality and increased water scarcity, water reclamation of the treated effluent has become a widely accepted strategy for sustainable water supply in urban areas. Reverse osmosis (RO) is a reliable and essential water reclamation technology for producing high-quality water for reuse. The RO concentrate, which is the waste stream produced from the RO process, is volumetrically substantial and contains environmentally harmful substances and therefore can cause severe environmental impacts if disposed of to receiving water bodies. Several technologies are available for further treatment of RO concentrate to reduce its volume, remove its total dissolved solids (TDS) and total organic carbon (TOC) and reclaim it for additional water recovery. This chapter presents a review of RO concentrate quality and various technologies for treating RO concentrate originated from municipal wastewater treatment plant. The technologies discussed include mineral recovery, electrochemical desalting and removal of TOC through adsorption, coagulation and oxidative degradation. Other alternative strategies including the emerging technologies for increasing water recovery rate from water reclamation plant are also proposed.

Keywords Advanced chemical oxidation, Municipal wastewater, Reverse osmosis, RO concentrate, Water reclamation

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Contents

Abbreviations

AC	Activated carbon
AOP	Advanced oxidation process
BAC	Biological activated carbon
BDD	Boron-doped diamond
CDI	Capacitive deionisation
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
EO	Electrochemical oxidation
GAC	Granular activated carbon
MBR	Membrane bioreactor
MF	Microfiltration
MW	Molecular weight
MWWTP	Municipal wastewater treatment plant
NF	Nanofiltration
NOM	Natural organic matter
PAC	Powdered activated carbon
RO	Reverse osmosis
SHE	Standard hydrogen electrode
SMP	Soluble microbial product
TDS	Total dissolved solids
THM	Trihalomethane
TiO_2	Titanium dioxide
TOC	Total organic carbon
TSS	Total suspended solids
UF	Ultrafiltration
UV	Ultraviolet

1 Introduction

In recent years, the issue of global water scarcity and water shortage is receiving more attention than ever. The supply of freshwater in the world is diminishing rapidly, and therefore other sources of water must be made available to augment the conventional water resources. In this context, water reclamation and reuse emerges as a sustainable practice to mitigate the water stress and improve the water security. Through water reclamation, each drop of water can be used multiple times in close loops, and thus it reduces excessive exploitation of and reliance on the natural water sources. Reclaimed water can be reused for various applications, as indirect (and direct) potable reuse and non-potable reuse. Currently, the majority of reclaimed water in the world is for non-potable reuse applications such as urban reuse, industrial reuse, irrigation, residential reuse, recreational reuse, groundwater recharge and environmental enhancement [1, 2].

Reclamation of high-quality water from unconventional sources and waste streams requires multiple-barrier water reclamation process and use of reliable water production technologies. Membrane technologies including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are reliable technologies most suitable for high-quality water reclamation. They are widely used as integral treatment units for seawater desalination, brackish groundwater and surface water desalination and water reclamation of treated municipal and industrial effluents [3].

In Singapore, the secondary effluents from most of the municipal wastewater treatment plants (MWWTPs) are reclaimed through a multiple-barrier reclamation process to produce high-purity reclaimed water known as NEWater. The water reclamation process uses advanced dual-membrane (MF/UF and RO) processes and ultraviolet (UV) disinfection [4]. The NEWater is used mainly for wafer fabrication and electronic industries as well as for air-conditioning purposes at commercial buildings [5]. It is worth to note that NEWater is a good feedwater for steam boiler, ultrapure water production and some manufacturing processes that require high-purity water. Up to 2.5% of NEWater is being mixed with water in reservoirs for indirect potable reuse. In 2003, the first NEWater plants were opened in Bedok and Kranji, respectively [5]. At present, there are four NEWater plants in Singapore. The NEWater plant at Changi is the latest and largest, with a capacity of 190,000 $m^3\ d^{-1}$. NEWater now meets 30% of Singapore's total water demand. It is also anticipated that by 2060, the NEWater can serve up to 55% of the country's water demand [5].

The RO concentrate, which is the waste stream produced from the RO process, contains environmentally harmful substances and can cause severe environmental impacts if improperly disposed of. There are several options to reduce the impact of RO concentrate disposal. These generally include modification of water reclamation process, volume reduction of RO concentrate and RO concentrate treatment. This chapter focuses on the treatment of RO concentrate produced from the water reclamation of the effluents of MWWTPs. While the content presented herein can be applicable to certain types of industrial RO concentrates, the industrial effluents are vastly diverse in quality and composition and should be addressed individually which is beyond the scope of this chapter. RO concentrates produced from groundwater, surface water and seawater desalination plants and their treatment are also not discussed here, but these topics have been extensively reviewed in earlier publications [6, 7].

2 Production and Quality of RO Concentrate

Generally, to produce high-quality reclaimed water from the treated effluent, a RO membrane is needed. Figure 1a shows several examples of process flows for high-quality water reclamation of treated effluents and production of RO concentrate (sometimes also referred as RO reject, RO retentate or RO brine). Often, a pretreatment system is also installed which should remove total suspended solids (TSS) and a small fraction of total organic carbon (TOC) (e.g. macromolecules) to ensure optimal operation of RO with low membrane fouling propensity. Disinfection of feedwater (chlorination) may be also carried out to prevent biofouling of the pretreatment system and RO membrane. RO concentrates generally contain dissolved constituents which are similar to the RO feed. Except for the monovalent ions of small solvated ionic radii, the concentrations of the constituents present in the RO feed are magnified in the concentrate according to a factor of $1/(1–R)$, where R is the water recovery rate:

$$R = \frac{\text{Permeate flow rate}}{\text{Feed flow rate}} \tag{1}$$

and, correspondingly,

$$\text{Concentration factor } = \frac{\mathrm{C_{concentrate}}}{\mathrm{C_{feed}}} \approx \frac{1}{1 - R} \tag{2}$$

where $\mathrm{C_{concentrate}}$ and $\mathrm{C_{feed}}$ are the concentrations of the solute in the RO concentrate and RO feed, respectively. Most municipal water reclamation plants typically operate with recoveries of 70–85% for RO systems and 80–85% for NF systems [8]. Figure 1b shows a two-stage RO process which allows water recovery of 75% or more from RO feed.

The composition of TSS in RO concentrate depends on the pretreatment process, which should aim to effectively remove most TSS. The quality of RO concentrates originated from the effluents of MWWTPs at different locations worldwide is compared in Table 1. Generally, the RO concentrates have a low turbidity due to effective TSS removal by the pretreatment systems. Silica concentrations, which are not commonly reported, range from several tenths of mg L^{-1} to slightly above 100 mg L^{-1}.

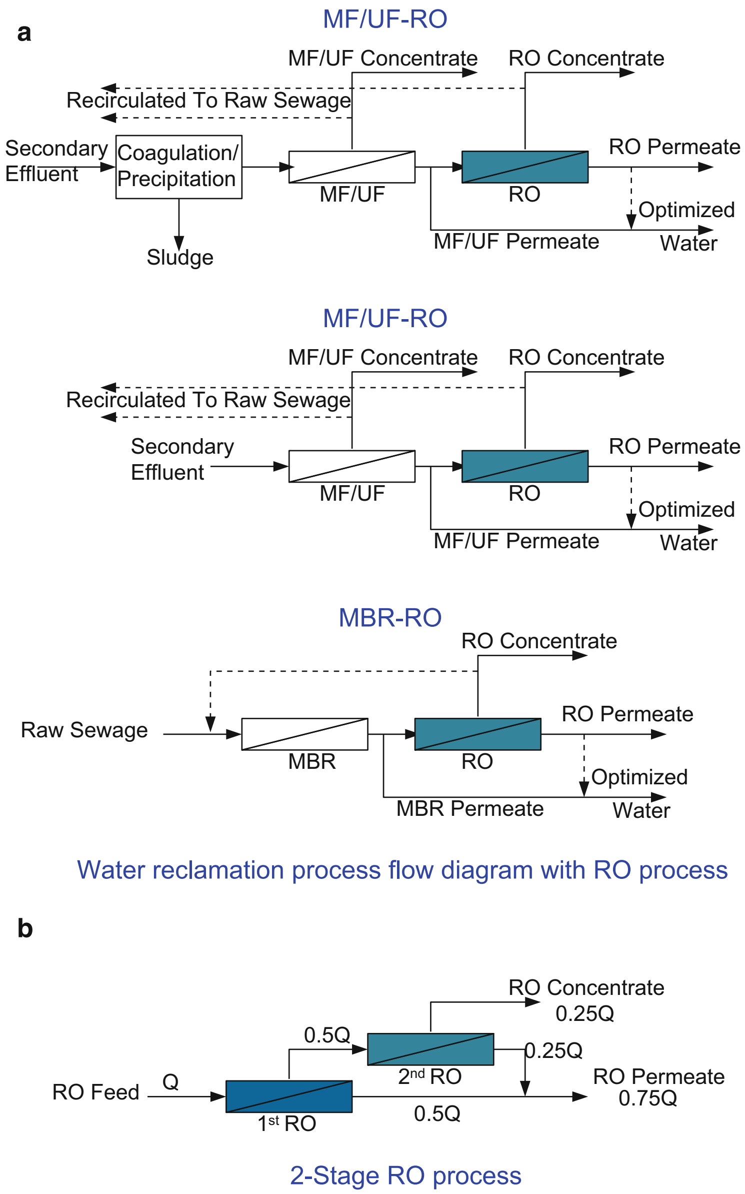

Fig. 1 (**a**) Flow diagrams of several water reclamation processes involving MF/UF–RO membrane processes and generation of RO concentrate stream and (**b**) two-stage RO with 75% water recovery (adopted in Singapore)

Table 1 Characteristics of RO concentrates (modified from Pérez-González et al. [25])

Parameters	Tao et al. [4]	Ersever et al. [26]	Zhou et al. [18]	Westerhoff et al. [24]	Van Hege et al. [23]	Van Hege et al. [27]	Pérez et al. [22]	Radjenovic et al. [28]	Chaplin et al. [29]	Lee et al. [17]	Lee et al. [30]	Badruzzaman et al. [15]	Kumar et al. [14]
pH	–	–	6.9	7	8.2	8.3	7.8	7.6	–	7.2	7.5	–	–
Turbidity, NTU	–	–	3.2	–	–	–	2	–	–	–	–	–	–
DOC, mg L^{-1}	–	–	–	40	–	–	23.3	57.2	19.2	–	–	–	–
COD, mg L^{-1}	–	–	60	138	158	184	–	–	–	64.6	–	–	–
TOC, mg L^{-1}	31.1	40	18	–	–	–	–	–	–	18.4	24.5	25	–
TKN, mg L^{-1}	–	–	10	–	–	–	–	–	–	–	–	–	–
TAN, mg L^{-1}	–	–	–	–	37.5	34	–	–	–	–	–	–	–
NH_4^+, mg L^{-1}	–	80	–	–	–	–	121.8	–	–	–	–	–	–
TDS, mg L^{-1}	1,275	3,965	1,129	5,560	–	–	–	–	–	1,218	1,276	2,950	2,750
Conductivity, μScm^{-1}	2,060	–	1,705	10,000	3,990	4,340	3,250	4,110	4,450	1,972	1,990	3,600	–
Alkalinity, mg L^{-1} as $CaCO_3$	–	1,006	–	1,110	–	–	1,233	–	289	–	–	520	–
SiO_2, mg L^{-1}	41.1	–	–	–	–	–	–	–	–	–	–	120	120
Cations													
Na^+, mg L^{-1}	305	–	203	–	–	–	–	–	435	240.9	226.9	580	910
Mg^{2+}, mg L^{-1}	14	–	7	–	–	32	–	–	122	7.1	11.5	9.7	5
K^+, mg L^{-1}	54	–	62	–	–	–	–	–	22.6	65.3	38.4	88	24
Ca^{2+}, mg L^{-1}	83	–	65	–	–	159	–	–	306	110.1	110.1	96	5
Fe^{2+}, mg L^{-1}	–	–	–	–	–	–	–	0.3	–	–	–	0.1	–
Mn^{2+}, mg L^{-1}	–	–	–	–	–	–	–	230.5	–	–	–	54	–
Anions													

Cl^-, mg L^{-1}	389	900	256	–	592.9	700	479	1.4	220.1	267.1	333.2	684	2,811
SO_4^{2-}, mg L^{-1}	197	1,240	217	–	–	–	443	240	1,584	218.4	159.1	468	1,437
NO_3^-, mg L^{-1}	69	–	91	–	–	–	–	–	3.1	88.5	60.2	296	269
NO_2^-, mg L^{-1}	–	–	2	–	–	–	–	–	–	8.3	–	–	–
PO_4^{3-}, mg L^{-1}	19	20	39	–	–	–	–	–	–	34.7	21.3	10	–
HCO_3^-, mg L^{-1}	–	–	–	–	–	–	–	–	–	–	–	–	–
F^-, mg L^{-1}	1.52	–	–	–	–	–	–	–	–	–	–	–	–

Table 2 Size fractions of organic compounds in RO concentrates from two water reclamation plants as reported by Bagastyo et al. [13]

	RO concentrate (LP)				RO concentrate (BD)			
Parameters (kDa)	DOC	COD	Colour	DON	DOC	COD	Colour	DON
>10	14	6	6	6	16	15	32	11
5–10	12	8	8	6	12	11	19	15
3–5	14	11	11	10	20	18	22	16
1–3	13	11	11	10	14	8	10	17
0.5–1	21	28	28	15	25	17	12	29
<0.5	25	35	5	53	14	31	5	12

LP: Luggage point water reclamation plant produces 8.8 ML day^{-1} of recycled water from a secondary effluent of biological nutrient removal treatment using MF/RO processes. The RO recovery ratio is ~70% when operating at full capacity

BD: Bundamba advanced water treatment plant has two parallel MF/RO treatment trains which can deliver up to 66 ML day^{-1} of recycled water using a mixture of biological nutrient removal effluents from four wastewater treatment plants

It is worth noting that the low solubility of silica in water (~150 mg L^{-1}) could limit the water recovery rates of RO systems. The precipitation and deposition of amorphous silica and silicates will result in consequential RO membrane fouling. Once formed, silica scale is very difficult and costly to remove.

The TOC (approximately COD/3) levels of RO concentrates are less than ~60 mg L^{-1}. The total dissolved solid (TDS) levels of RO concentrates are in the order of 10^3 mg L^{-1}. The organics in the effluent of MWWTP mainly comprise biopolymers and humic-like substances which are resistant to further biological treatment after extensive biodegradation processes [9–11]. They are primarily humic substances and soluble microbial products (SMPs). In addition, the soluble biorefractory organics of low molecular weight (MW) including petrochemicals, personal care products, pharmaceutical products, pesticides and endocrine disruptors are present. Microorganisms especially bacteria, pathogens or cell debris are also present. They form the main organic constituents in RO concentrate [12]. Bagastyo et al. [13] reported that 50% of the organics in RO concentrate of MWWTP effluents were less than 1 kDa and they were SMPs and smaller humic and fulvic acids. Table 2 shows the fractionation of organic substances in two RO concentrates which were from the RO system treating secondary effluent of biological nutrient removal. The dissolved organic nitrogen (DON) was primarily found in the fraction of smallest size (<0.5 kDa). It was associated with SMPs which are hydrophilic [13]. The colour-causing substances were mostly distributed in the medium to high size ranges of organics (>0.5 kDa).

Besides the constituents present in the RO feed which are originated from the treated effluent, the RO concentrate also contains substances/chemicals added during pretreatment process as well as substances used during periodic cleaning of the membranes. They include antiscalants, disinfectants, coagulants and flocculants and alkalis. Antiscalants can inhibit carbonate, phosphate, sulphate and fluoride scales and disperse colloids and metal oxides within plant equipment and membranes. They are not so effective to inhibit formation of polymerised silica which forms a persistent scale. Antiscalants can control acid-soluble scales at a fraction of the dosage required to control the same scale using sulphuric acid. The typical antiscalant dose ranges from 0.5 to 2.0 mg L^{-1} [6]. In the context of municipal water reclamation, antiscalants added are to inhibit formation of carbonate and phosphate scales. The major chemicals used as antiscalants are organic, carboxylic-rich polymers such as polyacrylic acid and polymaleic acid, sodium hexametaphosphate, organophosphate, citric acid, sulphuric acid and proprietary chemicals. Recently, many new proprietary antiscalants have been introduced into the market to prevent silica fouling by a combination of anti-precipitation, anti-agglomeration and dispersion processes.

Coagulants such as aluminium sulphate, ferric chloride and ferric sulphate are sometimes used in the pretreatment process to remove TSS. Coagulant aids such as proprietary cationic or anionic polyelectrolytes may also be added in some cases to enhance the flocculation process and floc sedimentation. The flocs formed may be drawn out and combined with the RO concentrate for discharge. Hypochlorite and chloramines are the most commonly used biocides in water reclamation plants to control membrane biofouling. It is anticipated that RO concentrate should contain trace concentrations of disinfection by-products such as trihalomethanes (THMs) and haloacetic acids, haloacetonitriles, haloketones and nitrosamines.

The current best practices to prevent RO membrane fouling include use of MF or UF membranes to remove colloidal particles, maintaining a chlorine residual to prevent biofouling of membrane, application of suitable antiscalant and optimisation of RO operation such as limiting RO recovery rates (to prevent membrane scaling) and utilisation of suitable membranes which minimises organic fouling.

For the water reclamation facilities located in coastal regions, the common practice for RO concentrate management is disposal through sewage ocean outfall [6, 7]. Alternative disposal practices are through sewer systems and into inland receiving water bodies. The main environmental impacts arising from disposal of RO concentrate from water reclamation plants are associated with nutrients and anthropogenic pollutants such as endocrine disruptors, carcinogenic chemicals and metals, as well as ion imbalance [6]. The chemicals added such as antiscalants, polyelectrolytes and coagulants could also cause aesthetic problems. Disposal into sewer systems is a convenient approach but can cause detrimental effects to the operation of downstream MWWTP because the high TDS of the RO concentrate will inhibit biological treatment processes [6].

3 RO Concentrate Treatment

The strategy for treating RO concentrate is through removal of inorganic species (which could be inorganic foulant) and chemical oxygen demand (COD) (organic foulant). The treated RO concentrate should have a lower scale formation potential, lower organic fouling propensity and lower osmotic pressure, so that it can be recirculated back to improve water recovery. The more proactive strategy is to make the RO concentrate a valuable resource for producing useful chemicals from the solutes.

3.1 Recovery of Minerals

High levels of calcium, silica, phosphate, carbonate and other ions can result in formation of scales or inorganic foulants. Calcite and phosphate minerals are among the commonly reported scales in RO system during water reclamation of MWWTP effluents. Other sparingly soluble minerals such as calcium sulphate, silica complexes, barium sulphate, strontium sulphate and calcium fluoride could also be formed. Some of the scales can be easily removed with cleaning, while others are persistent scales. Among the frequently reported problematic scales in RO concentrate of MWWTP effluents are calcium phosphate and silica precipitate. Because $Ca_3(PO_4)_2$ and CaF_2 are valuable resources, the best practice to control the scale formation potential of RO concentrate is to recover the minerals for reuse.

Kumar et al. [14] demonstrated phosphate removal from RO concentrate generated from two wastewater treatment plants using phosphate-selective polymeric exchange resin. In one of the plants, the phosphate concentration was 10 mg L^{-1} as P. The phosphate-loaded resin could be regenerated with NaCl solution, and the regenerant stream was then treated with adding sufficient dose of Mg^{2+} and NH_4^+, to precipitate phosphate from the regenerant as struvite:

$$Mg^{2+} + NH_4^{+} + PO_4^{3+} + 6\,H_2O \leftrightarrow MgNH_4PO_4 \bullet 6H_2O \qquad (3)$$

In their study, the optimum condition for struvite precipitation occurred at Mg^{2+}:NH_4^+:P molar ratio of 1.5:1:1 and pH 9.0. Struvite can be directly used as a slow release fertiliser.

It should be noted that since antiscalants are often added to RO feedwater to reduce scale formation potential and increase water recovery, the antiscalants present in the RO concentrate may prevent precipitation of problematic constituents. This limits the potential of mineral recovery and removal of scale-forming ions from the RO concentrate.

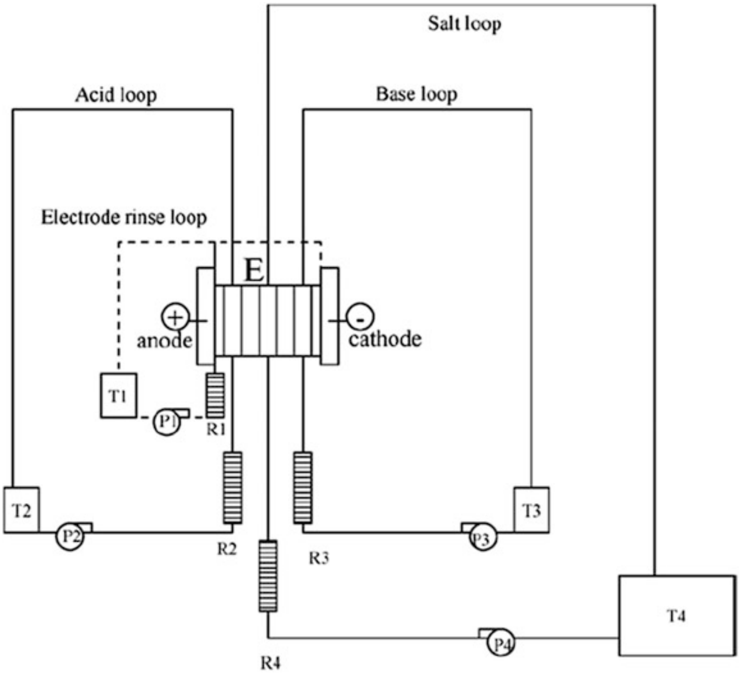

Fig. 2 Schematic of the bipolar membrane electrodialysis setup used in the bench-scale test conducted by Badruzzaman et al. [15] (E, electrodialysis stack; P1, pump 1 for electrode rinse; T1, tank for electrode rinse; R1, rotameter for electrode rinse; P2, pump for acid loop; T2, tank for acid recirculation; R2, rotameter for acid recirculation; P3, pump 3 for base loop; T3, tank for base recirculation; R3, rotameter for base recirculation; P4, pump 4 for salt loop; T4, tank for salt recirculation; R4, rotameter for salt recirculation). *Source*: Badruzzaman et al. [15]

3.2 Electrochemical Separation of Dissolved Solids

Salinity of the RO concentrate can be reduced using electrodialysis. Membrane electrodialysis has been applied to remove NaCl from a RO concentrate from a MWWTP incorporating membrane bioreactor (MBR) coupled with RO water reclamation process train and meanwhile produce HCl and NaOH solutions for beneficial use [15]. The system setup is shown in Fig. 2. The bipolar membrane electrodialysis cell (110 mm × 110 mm, 3 chambers) was the PCCell ED 64–4 Cell (PCCell GmbH, Germany). There were four streams passing through the electrodialysis cell, namely, the feed stream, the acid and base streams (the product streams) and electrode rinse stream. A constant DC current was maintained across the cathode and anode. The produced acid and base by the membrane electrodialysis process after 10 h of operation were of the quality comparable with the technical grade and the NF (US National Formulary) grade acids and bases. In order to prevent precipitation and scaling of divalent metals on the membrane, the RO concentrate needs to be pretreated to remove divalent metals (or hardness).

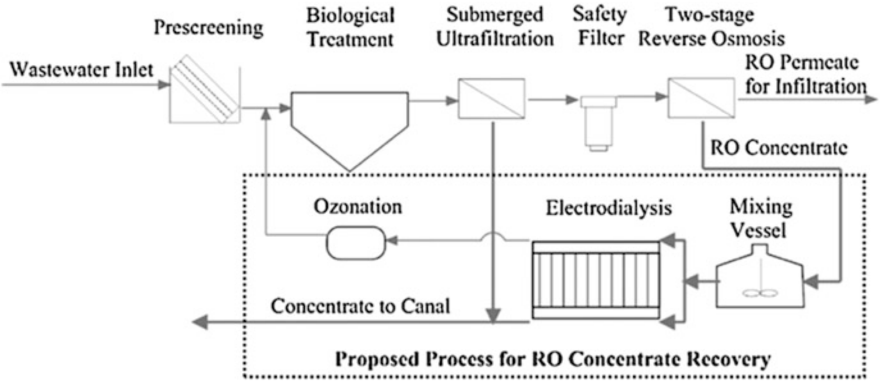

Fig. 3 Schematic diagram of inter-municipal water company of the Veurne region (Wulpen, Belgium) wastewater treatment process. *Source*: Zhang et al. [16]

While the experiment of Badruzzaman et al. [15] used Na^+-based cation exchange resin to remove the divalent metals, lime-softening treatment is favourable for practical application since it can simultaneously remove other membrane foulants such as organics and silica and it is an established, cost-effective technology in water and wastewater treatment.

Another resource which can be reclaimed from RO concentrate is hypochlorite, through electrochlorination process. Working on the RO concentrate with its quality as shown in Table 1, Badruzzaman et al. [15] achieved a production of 6,000 mg L^{-1} of free chlorine (hypochlorite). Comparing with membrane electrodialysis, the electrochlorination would require a significantly higher operational cost but generate much valuable product (hypochlorite).

A pilot-scale electrodialysis of RO concentrate (Fig. 3) was reported by Zhang et al. [16]. The RO concentrate was produced from a water reclamation plant operating UF–RO process for reclamation of effluent from biological treatment in a MWWTP. HCl was added to remove carbonate in the feed and the concentrate stream of the electrodialysis and thus reduce the scale formation during the electrodialysis treatment. Ozonation was introduced to improve the biodegradability of the TOC of electrodialysis effluent and the ozonated water recirculated back to the biological treatment tank. The electrodialysis effluent quality was similar to that of the MWWTP effluent except a higher TOC level. Through incorporation of the RO–electrodialysis system, an overall 95% water recovery from the sewage influent could be achieved by the MWWTP.

Tao et al. [4] applied capacitive deionisation (CDI) as an integral treatment to reclaim RO concentrate. The pretreatment system for the CDI feed comprised a biological activated carbon (BAC) filter with an optional MF/UF. The CDI consisted of two oppositely charged electrodes (with or without cationic and anionic selective membranes) which were made of a carbonaceous material. There were three process steps occurring in each cycle of CDI operation: purification, regeneration and purging. In the purification step, a low DC current was applied through water which caused charge differential to form between the electrodes; thereby ions were attracted by highly conductive porous electrodes of opposite charges while the desalted water passed through the CDI cell. In the regeneration step, the electrodes were regenerated by reversing the electrode polarity, whereby the ions were repelled from the electrodes. In the purging step, the CDI concentrate (reject) was flushed out from the cell. The CDI was operated at a low voltage (1–1.5 V) and could only provide marginal energy recovery during the regeneration step. The CDI process was able to achieve >88% TDS removal, while $PO_4^{3-}$and TOC removals were at 52–81% and 50–63%, respectively [17]. The BAC–MF/UF–CDI–RO treatment could achieve 70% water recovery from the RO concentrate at a total energy of ~1.2 kWh m^{-3}. However, fouling of the carbonaceous electrodes due to electrosorption of TOC was observed, and they were difficult to clean.

3.3 Removal of Organics Using Adsorption

Adsorption using activated carbon (AC) is the widely applied water and wastewater treatment technology to remove dissolved organic carbon (DOC). AC can adsorb almost all kinds of organic compounds, and it has especially high affinity for hydrophobic compounds. Zhou et al. [18] applied granular activated carbon (GAC) and powdered activated carbon (PAC) to remove DOC in a RO concentrate from a NEWater plant in Singapore. With 5 g L^{-1} of dosing in the batch adsorption system, GAC and PAC could remove 88% and 95% of DOC in the RO concentrate, respectively. However, the organics remaining in the RO concentrate would be hardly adsorbable even with a higher AC dose, indicating the presence of a small fraction of organics which had a rather low affinity for the AC. Generally, this fraction is associated with the hydrophilic organics of large MW [19]. Dialynas et al. [20] applied GAC to treat the concentrate produced from the RO treatment of an effluent from MBR operated in a MWWTP in Greece. DOC removal was fast during the first hour and then slowed down (owing to intraparticle diffusion-control mechanism). The highest DOC removal was 91% for the GAC dose of 5 g L^{-1}. This was higher than DOC removal via coagulation with ferric chloride and aluminium sulphate, photocatalysis, electrolytic oxidation (17.8A, 30 min, boron-doped diamond electrode) and sonolysis (135 W, 80 kHz, 60 min). Gur-Reznik et al. [19] also reported that GAC could remove 80–90% of natural organic matter (NOM) present in MBR effluent.

Lee et al. [17] applied BAC to remove the organic substances present in the RO concentrate which was originated from water reclamation plant treating municipal wastewater. The TOC removal was 23.5%, through simultaneous adsorption and biodegradation in the BAC column. The BAC followed by UF was installed to pretreat the RO concentrate before it was treated by a CDI unit.

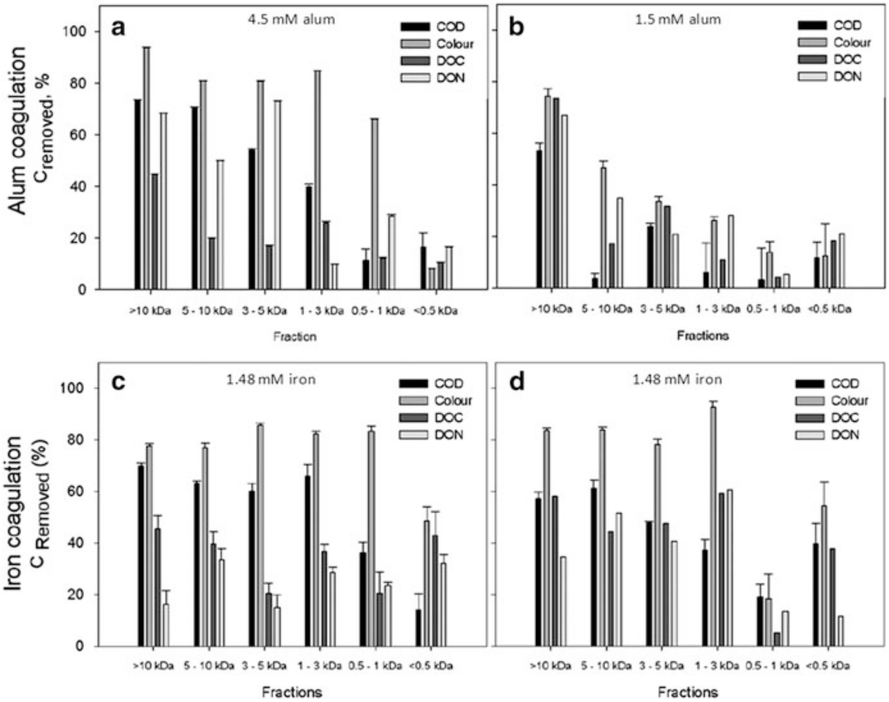

Fig. 4 Fractions of removed organics and colour with alum and iron coagulants in RO concentrate originated from Luggage point water reclamation plant (**a**, **c**) and RO concentrate originated from Bundamba advanced water treatment plant (**b**, **d**), South East Queensland (Australia). The error bars represent 95% confidence interval of three replicate samples. *Source*: Bagastyo et al. [13]

3.4 Removal of Organics Using Coagulation

Coagulation/flocculation is conventional water treatment process which can effectively remove colloidal particles and bulk organics including NOM and other organics contributing to DOC. In the study reported by Bagastyo et al. [13], coagulation using iron could remove organics of a wider size range, while alum preferentially removed COD corresponding to >10 kDa molecular sizes and overall not as effective as iron coagulant (Fig. 4). Their optimum dose was 1.5 mM, beyond which their coagulation effect only increased marginally. Colour-causing compounds, especially those >0.5 kDa, were more readily removed by alum and iron coagulation. DON, which was represented predominantly by the fraction of <1 kDa (Table 2), was the most difficult to remove with coagulation compared to COD and colour.

Dialynas et al. [20] applied coagulation treatment of RO concentrate from MBR effluent with alum and $FeCl_3$. Coagulation with alum at 2 mM achieved 42% DOC removal, while $FeCl_3$ at a dose of only 0.4 mM could achieve 52% DOC removal. In the study conducted by Zhou et al. [18], coagulation with $FeCl_3$ was carried out as pretreatment of RO concentrate from a NEWater plant, prior to its treatment with oxidation processes. The optimal coagulant dose was 1.0 mM at which 26% of DOC present in the RO concentrate was removed. Their coagulation treatment mainly removed hydrophobic organics of high MW (>10 kDa) and was inefficient in removing soluble organics of low MW. The largely varying removal efficiencies among these studies with respect to organics removal might be attributed to the different characteristics of RO concentrates investigated.

3.5 Removal of Organics Using Advanced Oxidation Processes (AOPs)

Oxidative degradation is a proven advanced treatment technology for removing recalcitrant organics. In the last decades, numerous oxidative treatments of RO concentrate were carried out for the removal of TOC. Table 3 summarises the investigations on removals of the bulk organics (represented by TOC, COD or DOC) or specific organic pollutants in RO concentrates of municipal sources using different AOPs. Some general observations are discussed below.

Among the various oxidation technologies for RO concentrate treatment, electrochemical oxidation (EO) is the most commonly investigated. Other treatment technologies are ozonation, photocatalysis, ultrasonication, UV/H_2O_2, Fenton/Fenton-like processes and their combinations. EO treatment involves both direct anodic and indirect oxidation process. It is believed that the direct anodic oxidation is less significant compared to indirect oxidation processes [21]. The oxidative species can be electrogenerated by anodic process, and sometimes by cathodic process too. Boron-doped diamond (BDD) electrode is the most commonly used electrode materials for EO treatment of RO concentrate [20, 22, 23]. BDD exhibits an extremely wide potential window of greater than 3.0 V, which is higher than O_2 evolution [2.3 V vs standard hydrogen electrode (SHE)], and thus is able to produce $HO^{\bullet}$, a non-selective, second most powerful oxidising species (E^{o} ($HO^{\bullet}/H_2O$) = 2.80 V vs SHE) after fluorine. BDD is also electrochemically stable. Its inert surface has low organic adsorption, and thus it has a high resistance against organic fouling. EO can completely remove many pharmaceuticals or pesticides spiked into RO concentrates. During EO treatment, simultaneous electrogenerated $ClO^{-}/ClO_3^{\bullet}$ would contribute to the organics removal and meanwhile also lead to the formation of chlorinated/brominated organics and thus increase the toxicity of the treated RO concentrate.

Simple ozonation could selectively degrade certain organic substances present in RO concentrate, especially pharmaceuticals (e.g. beta-blockers). Molecular O_3 is effective in oxidation of certain groups of organics, especially those that contain nucleophiles and unsaturated bonds. However, ozonation could only remove a small fraction of DOC present in the RO concentrate, suggesting that a large fraction of organics are O_3 resistant. The effectiveness of ozonation increases

Table 3 Applications of advanced oxidation processes for degradation of organics in RO concentrates originated from MWWTP effluents

References	Sources of RO concentrate	Water characteristics	Target organics	AOP features	Experimental conditions	Finding remarks
Zhou et al. [18]	WWTP second effluent (Singapore)	DOC 18 mg L^{-1}; COD 60 mg L^{-1}; TDS 1,129 mg L^{-1}; conductivity 1,705 μScm^{-1}; pH 6.9	DOC, COD	PCO; US; O_3; H_2O_2 and all combinations of the four AOPs	9 W UVC (254 nm) or UVA (360 nm); P25 2 gL^{-1}; US 220 W, 20 kHz; O_3 10 mg L^{-1}; H_2O_2 5 mM; pH~6.9 or 5 (after coagulation with 1 mM $FeCl_3$)	These AOPs only removed small fraction of DOC (1 h). O_3-based AOPs exhibited better DOC removal due to decomposition of organic with large MW; $FeCl_3$ coagulation pretreatment plus the AOPs could synergistically improve DOC removal, biodegradability and decreased ecotoxicity, MW and aromaticity
Bagastyo et al. [13]	WWTP second effluent, (Bundamba, Australia)	DOC 42–62 mg L^{-1}; conductivity 7,300–12,760 μScm^{-1}; pH 7.8–8.1; DON 5.3–7.8 mg L^{-1}	DOC, COD	UV/H_2O_2	60 W UVC at 254 nm; 200–800 mg L^{-1} H_2O_2	UV/H_2O_2 achieved 50–55% COD removal at pH 7 after 210 min. The organics were broken down to small size fractions (<0.5 kDa)

Westerhoff et al. [24]	WWTP second effluent (Scottsdale, AZ, USA)	DOC 40 mg L^{-1}; COD 138 mg L^{-1}; TDS 5,560 mg L^{-1}; conductivity 10,000 μScm^{-1}; pH 7.0	DOC	PCO (UVC/TiO_2); UV/H_2O_2; O_3/H_2O_2; Fenton (Fe^{2+}/H_2O_2); Fenton-like (Fe^{3+}/H_2O_2)	PCO, 450 W UVC (254 nm), P25 2 gL^{-1}, pH 5 or 7; UV/H_2O_2, 10 mMH_2O_2, pH 4 or 7; O_3/H_2O_2, 0.7 mol H_2O_2/mol O_3, 1 g L^{-1},O_3, pH 7; Fenton, 10 mM Fe^{2+},10 mM H_2O_2, pH~3.3	PCO achieved up to 95% DOC removal at pH 5 (~3 h); the efficiency was independent of P25 dose from 1–5 g L^{-1}. O_3/H_2O_2 removed ~50% DOC. Other AOPs removed DOC <10% at pH 7, while 40–50% at pH 3–4. EE/O (PCO operation) 9.6 kWh m^{-3} ($ 0.62 m^{-3}) at pH 5
Lee et al. [17]	WWTP second effluent (Singapore)	DOC 16 mg L^{-1}; BOD <2 mg L^{-1}; pH 6.9	DOC	O_3 (followed by biological activated carbon)	O_3 doses: 3, 6 and 10 mg L^{-1}; reaction = 10/20 min	O_3 pretreatment of RO concentrate achieved DOC removal of 5.3–24.5% with biodegradability increased by 1.8–3.5 times
Benner et al. [31]	WWTP effluent	DOC 46 mg L^{-1}; selected pharmaceuticals ~1–4 μg L^{-1}	4 beta-blockers (acebutolol, atenolol, metoprolol, propranolol)	O_3	Continuous quenching flow system; pH 2–9; O_3 5–10 mg L^{-1}	Second-order reaction; moderate O_3 efficiently removed beta-blockers with elevated DOC at pH ≥ 7

(continued)

Table 3 (continued)

References	Sources of RO concentrate	Water characteristics	Target organics	AOP features	Experimental conditions	Finding remarks
Dialynas et al. [20]	Pilot MBR effluent from municipal wastewater (Chania, Greece)	DOC: ~8–13 mg L^{-1}	DOC	PCO; US; and EO	9 W UVA, P25 0.5 or 1 gL^{-1}; US 150 W 80 kHz; electrodes, boron-doped diamond (BDD) on silicon; current intensity 17.8 A	Three AOPs showed similar behaviour in DOC removal at 1 h: moderate removal of DOC in the first few minutes followed by further oxidation at a very slow rate
Van Hege et al. [23]	Effluent from a mixed domestic and textile WWTP	COD 4.9 mM O_2; conductivity 3,990 μScm^{-1}; pH 8.2; total ammonia nitrogen 2.7 mM N	COD, TAN, Cl^- and ClO_3^-	EO	Inner circulating cell; anode, BDD on niobium; cathode, Ti/RuO_2; current density (J), 16.7 $mAcm^{-2}$	Organics and total ammonia nitrogen were readily oxidised by electrogenerated hypochlorite. As compared to RuO_2, BDD anode showed higher efficiency due to high selectivity towards the evolution of hypochlorite
Van Hege et al. [27]	Same as above	COD 151–218 mg L^{-1}; conductivity 3,990–5,290 μScm^{-1}; pH 8.0–8.7; TAN 31–38 mg N L^{-1}	COD, TAN, Cl^- and ClO_3^-	EO	Same as above; plus two electrodes—PbO_2 and SnO_2	PbO_2 and SnO_2 anodes showed low stability and gave rise to high pH values and subsequent precipitation of calcium and magnesium compounds

Radjenovic et al. [28]	WWTP second effluent, Bundamba, Australia	DOC 57 mg L^{-1}; conductivity 4,100 μScm^{-1}; pH 7.5–7.7 (spiked with 28 pharmaceuticals and pesticides)	DOC, trace organic contaminants	EO	Cell: $20 \times 5 \times 1.2$ cm Anode: $Ti/Ru_{0.7}Ir_{0.3}O_2$ Cathode: stainless steel $J = 1$–250 A m^{-2}; reaction time = 75 min; in continuous/batch mode	Twenty of the pharmaceuticals and pesticides were completely removed at $J \geq 150$ Am^{-2} and 437 Am^{-2} for continuous and batch mode. Compounds with electrophilic groups on the aromatic ring or without stronger nucleophilic substituents would be resistant to electro-oxidation. The increase in toxicity was due to formation of chlorinated/brominated organics
Pérez et al. [22]	WWTP second effluent, UF–RO pilot plant, ~3 m^3 h^{-1}	DOC 20–27 mg L^{-1}; conductivity 1,700–4,800 μScm^{-1}; pH 7.6–7.9	DOC, COD, NH^{4+}, Cl^-, THMs; 4 pharmaceuticals: caffeine, 4-AAA, naproxen, gemfibrozil	EO	Labscale DiaCell system; anode, BDD on silicon; cathode, stainless steel; $J = 20$–200 Am^{-2}	Removal kinetics was strongly influenced by current density; THMs formed during the reaction; pharmaceuticals were almost removed (2 h)

PCO photocatalytic oxidation, *US* ultrasonication with pH, since indirect attack of organics by $HO^{\bullet}$ generated through ozonation increases at higher pH. In addition, ozonation treatment could increase the low MW fraction of organics as well as the biodegradability of TOC in the RO concentrate. For this reason, posttreatment of ozonated RO concentrate with BAC was carried out by Lee et al. [17]. They reported that their ozone–BAC treatment at an ozone dosage of 6.0 mg L^{-1} and 20-min contact time was able to achieve 3 times higher TOC removal compared to using BAC alone.

The other oxidative treatments are AOPs, such as photocatalysis, ultrasonication, UV/H_2O_2 and Fenton processes. They rely on generation of $HO^{\bullet}$ to oxidise DOC in RO concentrate. However, the presence of high concentrations of inorganic anions, especially Cl^- and HCO_3^-, would strongly scavenge the produced $HO^{\bullet}$ and thus inhibit the DOC removal efficiencies. As a result, most of these AOPs could only remove small fractions (generally <30%) of DOC from the raw RO concentrates within a reasonable treatment time [18, 24]. Increasing the intensities of AOPs could slightly improve the removal efficiencies but would not be able to completely remove the organics from RO concentrate [13]. O_3-based AOPs, such as photocatalytic ozonation ($O_3/UV/TiO_2$), could synergistically remove DOC at higher efficiencies (~50–60%). It was attributed to faster decomposition of the large MW organics of up to 100 kDa. All these AOPs were not effective in removing the fraction of organics with larger MW (>100 kDa) [18].

Proper pretreatment of RO concentrate could enhance the DOC removal efficiency achieved by the AOPs. For instance, many AOPs achieved 40–50% of DOC removal at an acidic RO concentrate (pH 3–4) while removed less than 10% of the organics from the raw RO concentrate (pH~7) [24]. $FeCl_3$ coagulation can be an effective pretreatment method to significantly improve the AOPs treatment efficiencies, since it could remove the organic fractions of MW >100 kDa as well as decrease the pH value of the raw RO concentrate [18]. AC adsorption could remove a large fraction of DOC from RO concentrate [18–20]. However, AC adsorption was not an appropriate pretreatment method for subsequent AOPs treatment, since it removed the organic fractions with MW <100 kDa and left behind the AOP-resistant organic fractions in the RO concentrate [18].

4 Conclusion and Future Perspectives

Besides treatment of RO concentrate for TDS and TOC removal, there are other strategies to enhance the overall water recovery rate by MWWTPs, including:

- Effective pretreatment of RO feed which will reduce its osmotic pressure and membrane foulants and thus allow a higher water recovery rate from the RO process
- Use of novel RO membranes with good antifouling and high water permeability properties to recover more water with less energy, less fouling and easy cleaning

- Use of novel process configurations for water reclamation (e.g. closed circuit desalination)
- Use of heat-based membrane technologies (e.g. membrane distillation) and tapping waste heat from heat-generating facilities such as power plants through facilities' co-location.

RO concentrate is a challenging and yet important source of water to reclaim. Strategy to deal with RO concentrate has to be sustainable in the long run. The cost-benefit analysis of recovery of water and minerals from RO concentrate should be weighed against the option of water extraction and transportation from natural sources. The overall carbon footprint and environmental impacts associated with water supply and disposal should be considered in a broader context. Local constraints including land space, hydro-geographical setting and availability of low-grade energy such as waste heat (with facilities' co-location) should be considered too.

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Recent Developments in Potable Water Reuse

Jörg E. Drewes and Nils Horstmeyer

Abstract Potable water reuse through the use of treated wastewater effluents has been practiced for more than 50 years. The majority of projects worldwide are characterized as indirect potable water reuse, where an environmental buffer (groundwater aquifer or surface water reservoir) provided retention, additional attenuation, and blending prior to use as drinking water. In order to protect public health, these projects have utilized different treatment processes and combinations to establish multiple barriers against microbial and chemical contaminants. Due to the advancements in environmental analytical chemistry and the recognition of contaminants of emerging concern occurring in reclaimed water that might exhibit adverse health effects, additional advanced treatment processes (including ozone, advanced oxidation, activated carbon) were implemented. With increasing reliability of advanced water treatment processes and operational experience over several decades, the role of the environmental buffer to provide treatment and retention time has been revisited in projects that came online during the last 10 years. Recent trends are favoring direct potable water reuse applications in particular in the USA and Southern Africa that might evolve as the new paradigm for drinking water augmentation using impaired source water. However, questions remain regarding proper protection of public health, reliability and degree of treatment, appropriateness and design of monitoring strategies, maintenance requirements, and cost.

Keywords Contaminants of emerging concern, Environmental buffer, Multiple barriers, Pathogens, Potable water reuse

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Contents

Abbreviations

ADD	Acceptable daily dose
AOP	Advanced oxidation processes
BAC	Biologically active activated carbon
BNR	Biological nutrient removal
CA	California
CAS	Conventional activated sludge
CDPH	California Department of Public Health
CEC	Contaminants of emerging concern
DAF	Dissolved air flotation
DALY	Disability-adjusted life years
DEET	*N*,*N*-Diethyl-meta-toluamide
DPR	Direct potable water reuse
EPA	Environmental Protection Agency
EQS	Environmental Quality Standard
EU	European Union
GAC	Granular activated carbon
H_2O_2	Hydrogen peroxide
HAA	Haloacetic acid
IMS	Integrated membrane system
IPR	Indirect potable water reuse
LOD	Limit of detection
MCL	Maximum contaminant level
MF	Microfiltration
NA	Not available
NDMA	*N*-Nitrosodimethylamine
NRC	National Research Council
O_3	Ozonation

PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PNEC	Predicted no-effect concentration
RBAL	Risk-based action level
RBF	Riverbank filtration
RfD	Reference dose
RO	Reverse osmosis
SAT	Soil-aquifer treatment
spp.	Species pluralis
TCEP	Tris(2-chloroethyl) phosphate
TCPP	Tris(1-chloro-2-propyl) phosphate
TDCP	Tris(1,3-dichloro-2-propyl) phosphate
THM	Trihalomethane
TTC	Thresholds of toxicological concern
UF	Ultrafiltration
UncFactor	Uncertainty factor
USA	United States of America
UV	Ultraviolet light
WTP	Water treatment plant
WWTP	Wastewater treatment plant

1 Introduction

Reuse of municipal wastewater – untreated or treated – has been practiced for many centuries with the objective of diverting human waste outside of urban settlements [1]. However, water reuse as a *planned* activity started about one century ago with the use of treated effluent to irrigate Golden Gate Park in San Francisco, California, in 1912 [2]. Non-potable water reuse applications have grown substantially since then from urban landscape irrigation to irrigation of food crops, cooling water, car wash facilities, firefighting, public fountains, stream flow augmentation, to seawater intrusion barriers [3]. With better effluent qualities and scarcity of locally available freshwater supplies, water reuse using treated municipal wastewater effluents has also been considered to augment drinking water supplies as early as the 1960s with pioneering applications in the United States of America (USA) and Namibia. Today, planned potable water reuse is recognized worldwide as an increasingly important component of regional water resource management with a growing number of established projects [4, 5].

Planned potable water reuse projects are characterized as indirect or direct (Fig. 1). Indirect potable water reuse (IPR) is referred to as the purposeful addition of highly treated wastewater (i.e., reclaimed or recycled water) via an environmental buffer that is subsequently used to augment a drinking water supply [5]. The environmental buffers can comprise a groundwater aquifer or a surface water reservoir with the intent to provide retention, additional attenuation of contaminants,

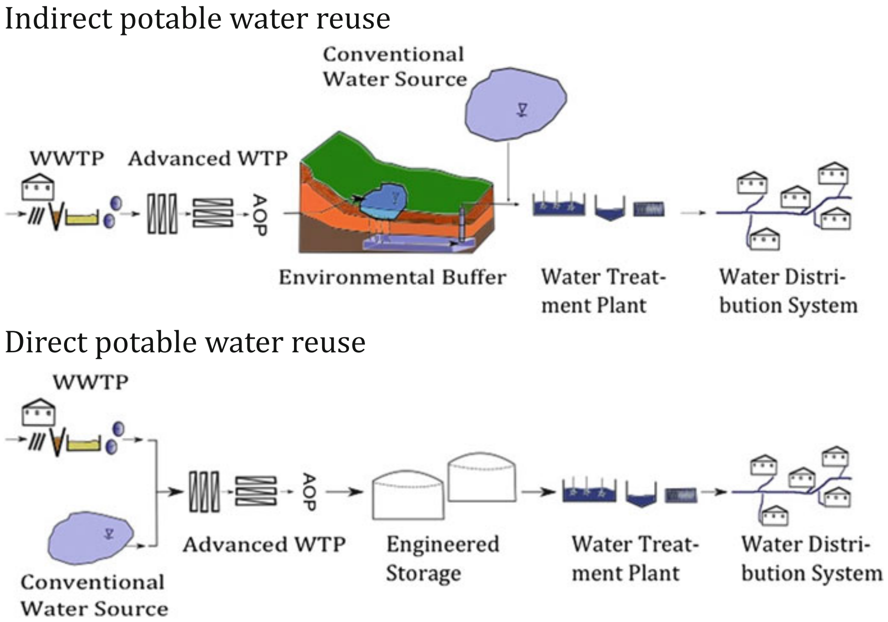


Fig. 1 Conceptual design of indirect and direct potable water reuse applications

and blending prior to use as drinking water. Direct potable water reuse (DPR) is defined as the immediate addition of reclaimed water to a drinking water distribution system or the raw water supply directly upstream of a drinking water treatment facility. In order to provide time to react to any process upset conditions in DPR projects, an engineered storage facility can provide the desired retention time prior to release of the treated water into a distribution system.

In particular during the last 10 years, there is increasing interest worldwide in establishing drinking water augmentation projects using reclaimed water. These initiatives in potable water reuse are driven by population growth; lack of conventional freshwater supplies; competing environmental, industrial, and agricultural needs for water; more frequent and severe drought conditions stressing the availability of conventional freshwater resources; and a higher level of confidence in the efficiency of treatment processes involved.

This chapter describes the current state of potable water reuse practices worldwide including recent advances and trends regarding design and operation of potable water reuse schemes, risk mitigation strategies including water treatment performance goals regarding health risks, the assessment of system reliability, and monitoring strategies for process performance and compliance.

2 The Current State of Potable Water Reuse Applications

2.1 The Evolution of Indirect Potable Water Reuse

Indirect potable water reuse has been practiced in the USA for more than 50 years. In 1962, the pioneering IPR project was established in the Montebello Forebay in Southern California to augment local groundwater supplies with a blend of reclaimed water, stormwater, and imported surface water via surface spreading operation. Severe water scarcity and a lack of alternatives led to the establishment of the first direct potable water reuse project by the City of Windhoek in 1968, which has been replaced by the new Goreangab Water Reclamation Plant in 2002.

In 1976, the Orange County Water District, California, established the Water Factory 21, which was the first IPR facility employing advanced water treatment processes including integrated membrane systems (microfiltration/reverse osmosis) for direct injection projects. Further process evolutions and program expansions in Orange County have resulted in the Groundwater Replenishment System established in 2008, which after completion of a plant expansion in 2015 represents the largest IPR project worldwide with a capacity of 348,000 m^3/day. Potable water reuse projects located in coastal areas in the USA, Singapore, and Australia have favored the use of integrated membrane systems (IMS), in same cases coupled with advanced oxidation processes using ultraviolet light irradiation with hydrogen peroxide (UV/H_2O_2) addition. For inland projects, however, high-pressure membrane filtration is favored less due to the lack of suitable and cost-effective waste stream disposal options. Instead, IPR projects in these locations have employed various combinations of low-pressure membranes (e.g., ultrafiltration), granular activated carbon (GAC) filtration, chemical oxidation (e.g., ozone), and natural treatment systems (e.g., soil-aquifer treatment (SAT), riverbank filtration, wetland treatment) [5, 6]. Table 1 summarizes established potable water reuse projects worldwide.

A range of multiple treatment options and combinations exist, including engineered and natural treatment processes, to design IPR schemes. While these schemes are unified in the goal to lower the risk from microbial and chemical constituents of concern, their individual process treatment efficiency for various contaminants and reliability can vary widely. A similar degree of variability exists regarding the functions of the environmental buffer, including (1) the provision of time to respond to process upsets, (2) attenuation of contaminants, and (3) blending or dilution. While there is ample evidence that an environmental buffer such as soil-aquifer treatment can be very effective regarding these three functions [7, 8], in cases where advanced treatment such as reverse osmosis is employed, additional water quality improvements in a subsequent environmental buffer are marginal at best [9]. Previous studies could not demonstrate that natural barriers provide any public health protection that is not also available by other engineered (above-ground) processes. Thus, the National Research Council (NRC) of the USA

Table 1 Established potable water reuse projects worldwide (adopted from Drewes and Khan [5])

Year	Project	Capacity (m^3/day)	Country	Advanced treatment sequence	Potable water reuse type
1962	Montebello Forebay Spreading Grounds, Los Angeles County Sanitation Districts/ Water Replenishment District, California	165,000	USA	Media filtration-SAT	IPR/groundwater recharge
1968	(Old) Goreangab Water Reclamation Plant, Windhoek	7,000	Namibia	DAF-media filtration-GAC	DPR
1976	Water Factory 21, Orange County Water District, California	60,000	USA	Lime clarification-air stripping-RO-UV/AOP	IPR/seawater intrusion barrier
1978	Upper Occoquan Service Authority, Virginia	204,000	USA	Lime clarification-media filtration-GAC-ion exchange	IPR/surface water augmentation
1985	Hueco Bolson Recharge Project, El Paso, Texas	38,000	USA	Lime clarification-media filtration-ozone-GAC-ozone	IPR/groundwater recharge
1985	Clayton County, Georgia	66,000	USA	UV-wetland	IPR/surface water augmentation
1993	West Basin Water Recycling Plant, California	47,000	USA	Microfiltration-RO-UV/AOP	IPR/seawater intrusion barrier
1999	Gwinnett County, Georgia	227,000	USA	Ultrafiltration-ozone-GAC	IPR/surface water augmentation
1999	Scottsdale Water Campus, Arizona	53,000	USA	Media filtration-microfiltration-RO-UV/AOP	IPR/groundwater recharge
2002	New Goreangab Water Reclamation Plant, Windhoek	21,000	Namibia	Ozone-clarification-DAF-media filtration-ozone-BAC/GAC-ultrafiltration	DPR
2002	Torreele Reuse Plant	7,000	Belgium	Ultrafiltration-RO-UV	IPR/groundwater recharge
2003	NEWater, Bedok	86,000	Singapore	Ultrafiltration-RO-UV	IPR/surface water augmentation

(continued)

Table 1 (continued)

Year	Project	Capacity (m^3/day)	Country	Advanced treatment sequence	Potable water reuse type
2003	NEWater, Kranji	55,000	Singapore	Ultrafiltration-RO-UV	IPR/surface water augmentation
2005	Alamitos Barrier, California	10,000	USA	Ultrafiltration-RO-UV	IPR/seawater intrusion barrier
2007	Chino Basin Recharge Project, California	69,000	USA	Media filtration-SAT	IPR/groundwater recharge
2008	Groundwater Replenishment Project, California	265,000	USA	Microfiltration-RO-UV/AOP	IPR/groundwater recharge/seawater intrusion barrier
2008	Western Corridor Project, Southeast Queensland	232,000	Australia	Microfiltration-RO-UV/AOP	IPR/surface water augmentation (not operational)
2008	Loudon County, Virginia	42,000	USA	Microfiltration-GAC	IPR/surface water augmentation
2009	Arapahoe/Cottonwood, Colorado	34,000	USA	Riverbank filtration-RO-UV/AOP	IPR/groundwater recharge
2010	NEWater, Changi	230,000	Singapore	Ultrafiltration-RO-UV	IPR/surface water augmentation
2010	Prairie Waters Project, Colorado	190,000	USA	Riverbank filtration-softening-UV/AOP-BAC-GAC	IPR/groundwater recharge
2010	Groundwater Replenishment Trial, Perth, Western Australia	5,000	Australia	Ultrafiltration-RO-UV	IPR/groundwater recharge
2011	Cloudcroft, New Mexico	100	USA	Microfiltration-RO-UV/AOP-ultrafiltration-GAC	DPR (not operational)
2012	Dominguez Gap Barrier	10,000	USA	Microfiltration-RO	IPR/groundwater recharge
2012	Beaufort West	1,000	South Africa	Media filtration-ultrafiltration-RO-UV/AOP	DPR

(continued)

Table 1 (continued)

Year	Project	Capacity (m^3/day)	Country	Advanced treatment sequence	Potable water reuse type
2013	Raw Water Production Facility, Big Springs, Texas	7,000	USA	Microfiltration-RO-UV/AOP	DPR
2014	Groundwater Replenishment Project, California (expansion)	348,000	USA	Microfiltration-RO-UV/AOP	IPR/groundwater recharge/seawater intrusion barrier

IPR indirect potable water reuse, *DPR* direct potable water reuse, *DAF* dissolved air flotation, *RO* reverse osmosis, *GAC* granular activated carbon, *BAC* biologically active activated carbon, *AOP* advanced oxidation processes, *UV* ultraviolet light, *SAT* soil-aquifer treatment

concluded that environmental buffers are not essential elements to achieve quality assurance in water reuse projects [10]. As a consequence, the NRC suggested that the classification of potable water reuse projects as indirect (i.e., includes an environmental buffer) and direct (i.e., does not include an environmental buffer) is not meaningful from a technical perspective because the terms are not linked to product water quality [10].

2.2 Trends Toward Direct Potable Water Reuse

Significant technological improvements, operational experience over many decades, and advancements in microbiology, chemistry, and toxicology have resulted in a high degree of confidence in the practice of drinking water augmentation using reclaimed water in the USA [5]. In the early 2010, this confidence level and the impacts from severe droughts, rising energy prices, and requirements for environmental restoration have resulted in a number of initiatives to explore the viability of direct potable water reuse [11]. While some smaller scale DPR projects were recently established in South Africa and the USA primarily driven by severe drought conditions and a lack of alternative supplies (see Table 1), a large initiative was launched in 2010 to advance DPR as a future water supply option for California [6, 12]. In September 2010, reflecting the increased interest in DPR, the Governor of the State of California signed into law Senate Bill 918. This bill mandates the California Department of Public Health (CDPH) to investigate the feasibility of developing regulatory criteria for DPR and to provide a final report on that investigation to the legislature by the end of 2016.

California's Water Recycling Policy has set ambitious goals to increase the total amount of recycled water of currently 802 million m^3/year by a factor of four by 2030. However, especially in Southern California, it has been recognized that further growth of non-potable water reuse in urban settings has reached its limit in many locations and the goal to significantly grow water recycling in the state cannot be met by non-potable water reuse activities. The main limitations of non-potable water reuse are the cost-prohibitive expansion of dedicated dual distribution systems in built-out urban environments and the lack of additional large customers that could be served for non-potable water reuse applications (i.e., public parks, golf courses). Southern California has also relied on imported water from the Colorado River and the State Water Project, which availability has been significantly reduced due to competing environmental needs and declining supplies as a consequence of climate change impacts. Thus, DPR has been recognized in California as a locally sourced, sustainable water supply for the future since it does not require a dedicated dual distribution system and provides cost savings compared to the development and importation of conventional supplies [11, 12]. Nevertheless, there is still a significant gap of knowledge regarding requirements of a fail-safe operation, real-time monitoring, appropriateness of treatment barriers against new contaminants and transformation products, blending options with conventional supplies, and regulatory and public acceptance before DPR can be implemented at a large scale [12].

These trends and developments point to the need to develop better guidance and standardization for the design and operation of potable water reuse schemes including best management practices that can assist the regulatory community and water industry in developing high confidence in fail-safe potable water reuse applications that are protective of public health.

3 Managing Health Risks in Potable Water Reuse

Health risks in potable water reuse applications are associated with microbial and chemical contaminants that can have adverse effects on human health [5]. In addition, aesthetic issues related to taste and odor are also an important consideration for public acceptance of potable water reuse projects [13]. While conventional wastewater treatment in many countries provides an effluent quality that is suitable to be discharged to surface water, treated effluents are still composed of a wide range of naturally occurring and anthropogenic trace organic and inorganic contaminants residual nutrients, total dissolved solids, residual heavy metals, and pathogens [5]. Microbial contaminants including bacteria, viruses, and protozoan parasites are acknowledged as the most critical constituent in reclaimed water due to potential acute human health impacts in public water supplies. Chemical contaminants, of which a large number can still be present in reclaimed water, can be of concern due to potential adverse acute and chronic health effects [10].

In the USA, there are no federal water quality standards for potable water reuse that go beyond drinking water standards under the Safe Drinking Water Act. Four states have developed state-specific regulations or guidelines specifically pertaining to IPR, which differ widely [14]. In 2008, Australia has published the first country national guidelines for the augmentation of drinking water supplies with recycled water, which follow a risk-based approach individual states and territories can adopt [15].

In the European Union (EU), the basis for European water policy is the Water Framework Directive 2000/60/EC [16]. The Directive divides chemical contaminants into priority substances (significant risk to or via aquatic environment) and priority hazardous substances (subset of priority substances, considered to be extremely harmful). While no specific guidelines for potable water reuse currently exist in the EU, water quality standards will likely consider requirements set forth in the Drinking Water Directive (1998/83/EC) [17], the Groundwater Directive (2006/118/EC) [18], and the Environmental Quality Standards Directive (2008/105/EC) [19]. Environmental quality standards (EQS) are currently identified for 45 priority (hazardous) substances with the aim to achieve good chemical status of groundwater and surface waters [19, 20].

As a baseline requirement in any country practicing potable water reuse using reclaimed water, the water quality has to meet drinking water standards. In Europe and the USA, maximum quality standards for drinking water can be used as performance standards for treatment trains; however, they currently only cover less than 100 contaminants potentially also present in reclaimed water. While these include a range of pesticides and industrial contaminants, they do not comprise contaminants that are typically associated with discharges from municipal wastewater effluents, including pharmaceutical residues, personal care products, household chemicals, hormones, or emerging disinfection by-products. Thus, given the origin of reclaimed water, additional water quality requirements acknowledging the impaired quality of the source should be defined where potable water reuse is practiced.

3.1 Setting Water Quality Performance Requirements in Potable Water Reuse

In order to quantify the potential for human health effects as a result of exposure to microbial and chemical contaminants, regulatory agencies have adopted the concept of a “tolerable level of risk” to assist in setting water quality guidelines or standards. In the regulatory realm, *de minimis* risk is defined as a level of risk characterized by the risk being virtually nonexistent to describe risks that are “below regulatory concerns.” Traditionally, for drinking water supplies, *de minimis* risk levels are related to health criteria (i.e., toxicity of the constituent, characteristics of the population, exposure). Different risk levels are commonly used, depending on the specific situation and type of contaminant. The United States Environmental Protection Agency, Office of Drinking Water, uses a “regulatory window” of 10^{-6} to 10^{-4} for the evaluation of risk where 10^{-4} is the baseline risk for all regulations and

10^{-6} is the *de minimis* risk level [21]. Microbial contaminants are regulated at a *de minimis* level of 10^{-4} (where 10^{-4} is the annual individual risk of infection by a given pathogen).

In order to mitigate the acute risk from microbial contaminants, the Australian Water Recycling Guidelines have adopted a numerical definition of safety using disability-adjusted life years (DALYs) to convert the likelihood of infection or illness into burdens of disease, setting a tolerable risk as 10^{-6} DALYs per person per year [6]. Considering a concentration of selected pathogens in raw sewage and an average daily consumption of two liters per person per year, the log reduction required to achieve compliance with 10^{-6} DALYs per person per year can be calculated using Eq. (1). Removal criteria for pathogenic microorganisms are listed in Table 2.

$$\text{Log reduction} = \log((\text{source concentration} \times 2\,\text{L} \times 365\,\text{days})/\text{DALYd}), \qquad (1)$$

where DALYd (the dose equivalent to 10^{-6} DALYs) for *Cryptosporidium* is 1.6×10^{-2}, for enteric viruses is 2.5×10^{-3}, and for *Campylobacter* is 3.8×10^{-2} [6].

Performance goals for potable water reuse projects in California have been proposed that are based on a low tolerable or *de minimis* risk level of 10^{-4} annual risk of infection and occurrence data of pathogens in raw wastewater [22].

In order to meet these requirements, a given potable water reuse treatment train has to demonstrate that the additive removal efficiencies for microbial contaminants provided by individual treatment processes can meet the desired overall log removal criteria. Meeting this goal would ensure that the reclaimed water is free of pathogenic microorganisms with a large margin of safety and could be safely used for potable purposes. The reason for this rather high degree of conservatism is the lack of comprehensive occurrence data for pathogenic microorganisms in raw sewage.

Table 2 Removal criteria for pathogenic microorganisms for the evaluation of potable water reuse schemes (adopted from [6, 22])

Microbial group	Criterion ($\log_{10}$ removal) California	Criterion ($\log_{10}$ removal) Australia	Possible surrogates	Notes
Enteric virus	12	9.4	MS-2 bacteriophage	
Cryptosporidium spp.	10	8	Inactivated *Cryptosporidium oocysts*, aerobic spores	Addresses also *Giardia* and other protozoa
Total coliform bacteria	10	NA	NA	Addresses also enteric pathogenic bacteria
Campylobacter	NA	8.1		

For the evaluation of potable water reuse treatment schemes regarding chemical contaminants, the following factors need to be considered:

- The contaminant chosen to assess treatment performance must occur frequently enough and at a concentration significantly above the analytical method detection limit.
- Appropriate and commercially available analytical methods exist for the quantification of target contaminants in reclaimed water.
- Targeted contaminants for monitoring programs should be broadly representative of both the varying types of contaminants of health concern ("indicator contaminants with health relevance") and the wide range of physicochemical and biological properties that affect their removal of various unit processes within a potable water reuse treatment train ("performance indicator contaminants to assess treatment efficacy").
- The establishment of multiple treatment barriers with different removal mechanisms (i.e., chemical oxidation, biological treatment, physical separation) provides robustness against a wide range of currently not yet identified contaminants.

Performance goals for chemical contaminants for a proposed potable water reuse scheme will include contaminants of recognized health concern that have published guideline values or standards. These include regulated contaminants with an acceptable health risk specified, for example, as drinking water standards in the EU Water Framework Directive, the EPA maximum contaminant levels (MCLs) in the USA, chemical guideline values in the Australian Water Recycling Guidelines, WHO Drinking Water Goals, or EPA health advisories or health reference levels. For unregulated contaminants with known toxicological information, the *de minimis* risk approach can be used. In order to specify *de minimis* benchmarks for these contaminants, a reference dose (RfD), acceptable daily dose (ADD), or predicted no-effect concentration (PNEC) information expressing their toxicological relevance can be adopted [6, 23–26]. These benchmarks are considered in a risk-based action level (RBAL) following a framework proposed by the WHO [27] and the USA National Research Council [19] for chemical exposure via drinking water (considering a relative source contribution of 0.2):

$$\text{RBAL, }\mu\text{g/L} = \frac{\left(\text{Benchmark, }\frac{\mu\text{g}}{\text{kg}\times d}\right)\times 60\,\text{kg}\times 0.2}{2\,\text{L}/d\times\text{UncFactor}}, \tag{2}$$

where neither existing guideline values nor relevant toxicological data to develop benchmark values are available; a quantitative structure-activity relationship approach can be used as a method for deriving thresholds of toxicological concern (TTCs) [6]. The TTC approach is based upon the statistical evaluation of a large group of chemicals with similar structure and functional groups. It allows to identify a 95 percent lower confidence level for chronic no adverse effect level and then apply uncertainty factors similar to noncancer risk assessments. The use of TTCs is well established internationally and has been used by the USA Food and

Table 3 Health-based indicator contaminants of interest proposed for monitoring programs of potable water reuse projects (adopted from [22, 29, 30])

Chemical	Criterion	Note
N-Nitrosodimethylamine (NDMA)	10 ng/L	California reporting level
Trihalomethanes (THMs)	60 μg/L	MCL of USA EPA
Haloacetic acids (HAAs)	80 μg/L	MCL of USA EPA
Bromate	10 μg/L	MCL of USA EPA; EU
Chlorate	700 μg/L	WHO
Perfluorooctanoic acid (PFOA)	0.4 μg/L	Provisional EPA Health Advisory
Perfluorooctanesulfonic acid (PFOS)	0.2 μg/L	Provisional EPA Health Advisory
Perchlorate	15 μg/L	EPA Health Advisory
1,4-Dioxane	1 μg/L	California notification level
Simazine	4 μg/L	MCL of USA EPA
2,3-Dichlorophenoxyacetic acid (2,4-D)	70 μg/L	MCL of USA EPA
17β-Estradiol	0.9 ng/L	Monitoring trigger level
Triclosan	350 ng/L	Monitoring trigger level

Drug Administration and the WHO for setting guidelines for minor contaminants. A similar approach has been proposed by the German EPA (Umweltbundesamt) to derive public health advisory values and precautionary values for contaminants of emerging concern [28]. Precautionary values for unregulated contaminants with insufficient toxicological data usually are assigned a blanket value of 0.1 μgL^{-1}.

Given the large number of contaminants, deviations in published RfD or PNEC values for individual contaminants, and differences in expert opinion regarding appropriate uncertainty factors (UncFactor) for carcinogenic contaminants, a uniform list of contaminants that should be monitored in potable water reuse schemes does not yet exist. Nevertheless, several scientific groups and panels have proposed contaminants with human health relevance to be used in monitoring programs of potable water reuse projects [22, 29, 30]. Table 3 lists proposed health-based indicator contaminants for potable water reuse projects.

Performance validation and verification of established and alternative treatment trains can occur through direct measurements of indicator contaminants representing a variety of structures and physicochemical properties that correlate with the core removal mechanisms (i.e., biotransformation, adsorption, size exclusion, chemical oxidation) of individual unit processes [31–33]. In addition, the removal of specific performance-based indicator contaminants or families of contaminants with closely related properties may be correlated with the removal of other routinely measured compounds or operational parameters that can be monitored continuously as a surrogate parameter (e.g., electrical conductivity, UV absorbance) [31, 34, 35]. These approaches have the advantage that they can be established as real-time monitoring strategies where a high resolution of system performance control is desired. Table 4 summarizes proposed maximum concentrations of performance-based indicator contaminants and expected removal percentages for monitoring of treatment train efficacy of potable water reuse projects.

Table 4 Performance-based indicator contaminants proposed for monitoring programs of potable water reuse projects (adopted from [22, 26, 30])

Chemical	Criterion (max. concentration or minimum percent removal)	Note
Atenolol	4 μg/L	[26]
Caffeine	350 ng/L 90%	Monitoring trigger level [30] Removal by SAT or RO/AOP treatment [30]
Carbamazepine	100 μg/L	[26]
DEET	200 μg/L 90%	[26] Removal by SAT or RO/AOP treatment [30]
Dilantin	50 μg/L	[26]
Gemfibrozil	90%	Removal by SAT [30]
Iopromide	90%	Removal by SAT [30]
Meprobamate	200 μg/L	[26]
Primidone	375 μg/L	[26]
Sucralose	None 25% 90%	Approved for use as a sweetener in food Removal by SAT [30] Removal by RO/AOP treatment [30]
TCEP	5 μg/L	Monitoring trigger level, State of Minnesota guidance value [26, 30]

4 Design Principles of Potable Water Reuse

The core design elements of potable water reuse treatment trains involve a thorough understanding of source water characteristics, the establishment of reliable treatment systems, storage and blending considerations, and an overarching monitoring program for performance and compliance (Fig. 2). These elements are further discussed in the sections below.

4.1 Monitoring Program for Performance and Compliance

Monitoring programs for potable water reuse projects need to be considered and designed to address source control and treatment performance assessments, assuring that specified finished water quality criteria are met. Assessing treatment train performance and compliance and finished water quality criteria have been discussed in previous sections. Source control requirements are being addressed in the next section. Additional information can be found in Drewes and Khan [5].

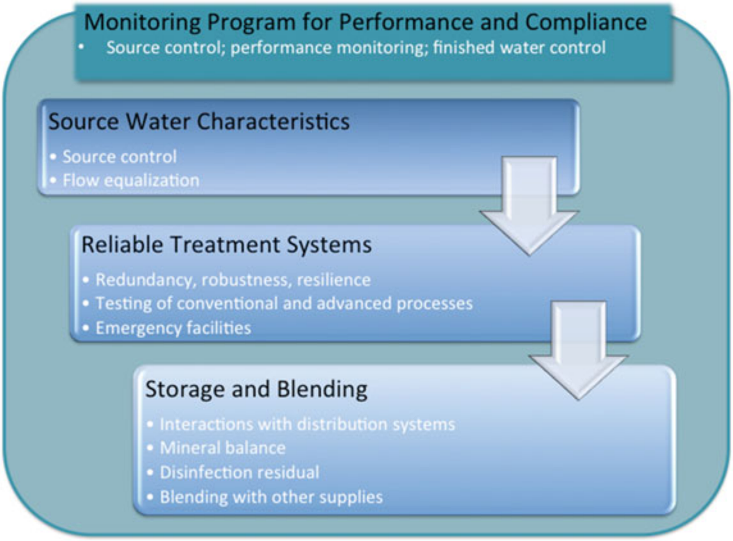


Fig. 2 Key design elements of potable water reuse schemes

4.2 *Source Water Characteristics*

Understanding the variability of source water quality is a prerequisite to properly design efficient processes for a potable water reuse treatment train. Besides treatment processes, flow equalization measures can be effective in mitigating and eliminating significant differences in source water quality and quantity. In particular for DPR project, flow equalization is an important design feature that can result in both a more consistent source water quality and a more homogeneous load to downstream treatment processes, in general contributing to a more consistent finished water quality.

In addition, source control through monitoring and compliance assessments of point discharges to the sewer system is a critical element to maintain a consistent reclaimed water quality [5, 6]. These programs are conducted with the goal of reducing treatment costs, targeting inorganic and organic contaminants of concern that are not primarily removed during conventional wastewater treatment (i.e., heavy metals, trace organic contaminants), and therefore improving the reliability of the final water quality.

4.3 *Reliable Treatment Systems*

Any potable water reuse scheme should be designed to reliably supply a finished water quality that is safe for human consumption at all times. System reliability of a potable water reuse project is defined as the probability of adequate performance for a specified period of time under predefined conditions. Reliability in potable water reuse systems can be achieved by a number of supporting concepts including redundancy, robustness, and resilience.

The concept of redundancy describes the use of multiple barriers to control acute risks. Robustness is defined as the capacity to remove a wide range of particular chemical contaminants. In addition, potable water reuse facilities must also be resilient to ensure reliability even under rare failure events. A resilient system in this respect is not a system that never fails, but a system that fails safely, meaning that failures are mitigated through well-designed response plans including the prevention of distributing water that does not meet specified requirements. System reliability requirements may include standby power supplies, provisions for alarms, readily available replacement equipment, online monitoring of system performance and water quality, redundant process components that are critical for the protection of public health, flexible piping and pumping configurations, trained personnel, and emergency storage or disposal options.

Combining water treatment processes that are capable of providing effective, reliable, and redundant barriers to pathogens and contaminants are referred to as the *multiple-barrier approach* to water treatment. For potable water reuse projects, although the multiple barriers do tend to be relied on to provide cumulative steps toward the achievement of overall treatment goals, there is generally an expectation that they will accommodate a degree of treatment redundancy for pathogens. That is, the protection of public safety will be maintained even if a single treatment barrier fails. The independence of multiple barriers is a key aspect of system reliability and safety. In order to mitigate the acute risk from microbial contaminants and to meet overall removal criteria as discussed earlier (see Table 2), various unit processes can be combined in a meaningful fashion considering conservative expected log removal efficiency of individual unit processes for pathogenic microorganisms as specified in Table 5 [36].

Table 5 Log removal efficiencies of various unit processes to remove target microbial contaminants (adopted from [36])

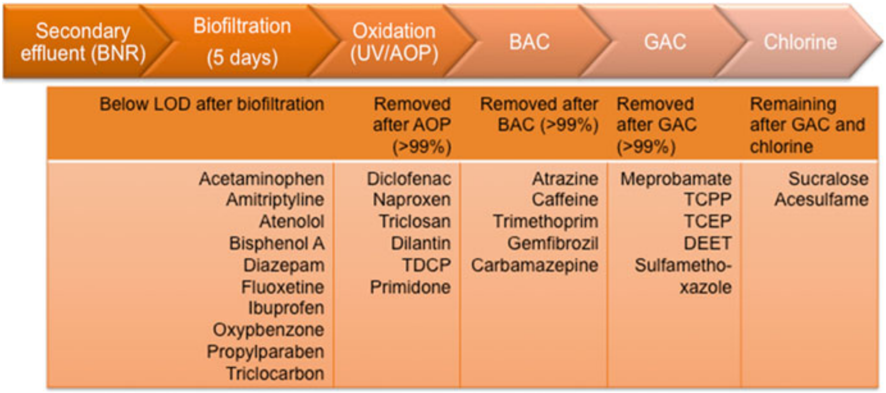
Unit process	Enteric viruses	*Cryptosporidium*	Total coliform bacteria
Conventional activated sludge (CAS)	1	0	2
Microfiltration (MF)	0	4	4
Ultrafiltration (UF)	1	4	4
Reverse osmosis (RO)	2	2	2
Ozonation (O_3)	6	1	4
Biologically active activated carbon (BAC)	0	0	0
Ultraviolet light (UV)	6	6	6
UV light with hydrogen peroxide (UV/AOP)	6	6	6
Free chlorine	3	0	4

For an IPR scheme typically designed for direct injection into a potable aquifer, accumulative virus log removal efficiencies for enteric viruses would total 22 (Fig. 3). An IPR treatment train with very short retention in an environmental buffer consisting of biofiltration via subsurface treatment, advanced oxidation, and activated carbon treatment followed by final disinfection prior to blending with conventional supply would achieve an overall virus log removal efficiency of 12 (Fig. 4). Both treatment combinations would also exceed the required log removal criteria for cryptosporidium and total coliform bacteria (data not shown). Given that the proposed log removal criteria are already very conservative (Table 2), the margin of safety that potable water reuse projects utilizing treatment combinations as illustrated in Figures 3 and 4 can provide against pathogenic contaminants will likely exceed conventional drinking water supplies that are using source water receiving small amounts of wastewater discharge (exceeding a contribution of 5%) by several orders of magnitude [10].

Given the wide range of different contaminants present in reclaimed water, robust multiple barriers should be designed to consider a sequence of diverse processes that are capable of targeting the wide range of physicochemical properties represented by various classes of contaminants. The requirement for redundancy normally associated with pathogen removal is not applied to multiple barriers for chemicals. This is because exposure to chemicals is more of a chronic risk, relating to long-term exposure, as compared with the acute risks associated with pathogens, for which even short-term exposure may have significant impacts on human health. Thus, for the removal of chemical contaminants, diversity in treatment rather than redundancy can result in highly efficient overall removal of trace organic contaminants generating a finished water quality that is indistinguishable to conventional supplies (Fig. 5).

Fig. 3 Virus log removal efficiency by a potable water reuse treatment train consisting of integrated membrane systems followed by advanced oxidation processes and an environmental buffer

Fig. 4 Virus log removal efficiency by a potable water reuse treatment train consisting of biofiltration via subsurface treatment, advanced oxidation, and activated carbon treatment followed by final disinfection prior to blending with conventional supply



Below LOD after biofiltration	Removed after AOP (>99%)	Removed after BAC (>99%)	Removed after GAC (>99%)	Remaining after GAC and chlorine
Acetaminophen	Diclofenac	Atrazine	Meprobamate	Sucralose
Amitriptyline	Naproxen	Caffeine	TCPP	Acesulfame
Atenolol	Triclosan	Trimethoprim	TCEP	
Bisphenol A	Dilantin	Gemfibrozil	DEET	
Diazepam	TDCP	Carbamazepine	Sulfamethoxazole	
Fluoxetine	Primidone			
Ibuprofen				
Oxypbenzone				
Propylparaben				
Triclocarbon				

Fig. 5 CEC removal efficiency by a potable water reuse treatment train consisting of biofiltration via subsurface treatment, advanced oxidation, and activated carbon treatment followed by final disinfection prior to blending with conventional supply (Note: concentrations for the artificial sweetener sucralose and acesulfame in the finished water where in the elevated ng/L range were well below any health relevance level)

4.4 Storage and Blending

The water quality after advanced treatment requires adjustments in particular where different source waters are blended regarding compatibility with the drinking water distribution system (i.e., saturation index, corrosivity) and aesthetics (i.e., mineral balance, color). In IPR systems, storage and blending can occur by passing water through an environmental buffer. In many potable water reuse systems, however, the primary benefit of environmental buffers is to provide time to respond to an inadequate water quality associated with inappropriate treatment or other factors [5]. Thus, in the context of DPR projects, an engineered storage unit or adequate (real-time) monitoring systems (or both) might be able to fulfill the function of the environmental buffer. However, additional research is needed to develop specific storage and blending requirements for DPR projects.

5 Energy Requirements

An important consideration besides water quality aspects for the implementation of potable water reuse schemes is the energy footprint associated with different supply options including reuse. While the energy footprint of potable water reuse schemes mainly depends on the type and sequence of individual unit processes, the energy requirements of alternative water supply options are much dependent upon local conditions, in particular when it comes to reliance on imported water.

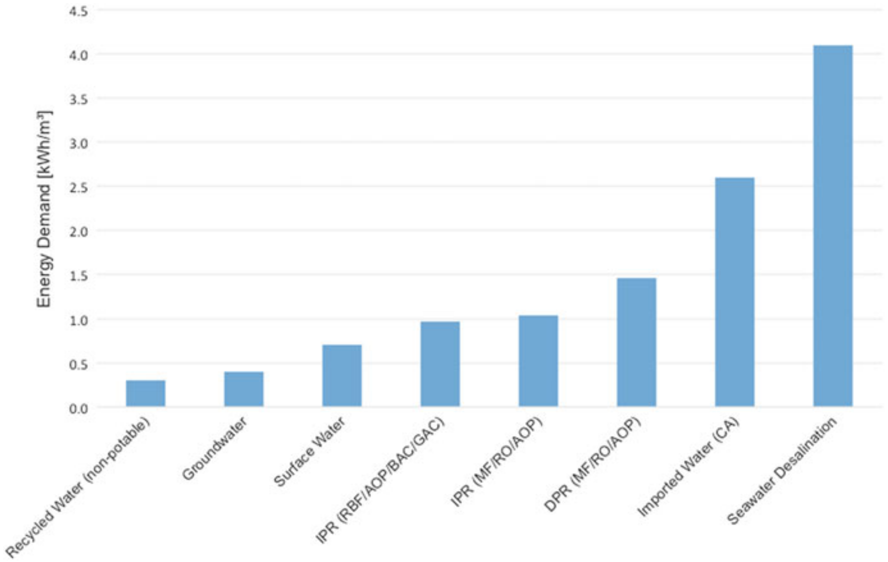


Fig. 6 Specific energy requirements for conventional and alternative water supply options based on the estimates for California (adopted from [10, 12])

Specific energy data for various supply options for California summarized in Fig. 6 illustrates that potable water reuse either indirect or direct can represent very cost-effective supply alternatives to ocean desalination and use of imported water. Different treatment train configurations for potable water reuse schemes should be investigated to further decrease the energy footprint, in particular where energy-intense processes are employed (i.e., high-pressure membranes, advanced oxidation processes).

6 Conclusions

The practice of potable water reuse has evolved over the last 50 years into a viable option for an integrated water resource management to safely augment drinking water supplies with recycled water. Today, potable water reuse is also practiced in locations that are not characterized by arid or semiarid climate conditions, but regions that experience seasonal water shortage or have a desire to diversify their water resource portfolio for future climate change impacts.

While there is also increasing recognition that unplanned or de facto potable water reuse is occurring where treated wastewater effluents are discharged to surface water that subsequently serves as a source of drinking water, proper safeguards to mitigate the risks associated with microbial and chemical contaminants is not always appropriately addressed [10, 37]. Thus, best management practices and risk management frameworks developed for potable water reuse projects as described in this chapter might also provide guidance for de facto potable water reuse situations.

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Long-Term Strategies for Tackling Micropollutants

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Abstract Nowadays, more than 30,000 chemicals (including pharmaceuticals, biocides and pesticides) are estimated to be of relevance for the aquatic environment. Wastewater has to be treated to meet the required quality for its reuse. Many approaches for the assessment of water quality are used or are under development. It is now widely accepted that none of these approaches is suitable to assess all the (micro)biological and chemical contaminants. Many processes for water and wastewater treatment have been proposed and researched, and some of them are already applied in routine treatment. Unfortunately, these are not able to completely remove most of the contaminants. In contrast, most often, each of them removes only a minor percentage. Some processes may even result in the formation of transformation products of widely unknown fate and effects. This clearly demonstrates the serious limitations of such end-of-pipe approaches like effluent treatment. Therefore, in the future, more attention has to be paid on the prevention of the

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introduction of such contaminants into the water cycle, i.e., by measures that have to be taken at the beginning of the pipe. Approaches helpful in this direction are presented here.

Keywords Aquatic cycle, Beginning of the pipe, Contaminant, End of the pipe, Input, Micropollutant, Prevention

Contents

1 Introduction

Discussions in the context of the climate change mostly focus on the quantity of available water resources for all mankind. The water's quality, though, is receiving far less attention, although a high purity of water (chemically as well as microbiologically) is as important as the available quantity for mankind. This doesn't only apply for its use as drinking water or for irrigation purposes but also for its industrial use in the context of the production of high-technology products for which high-purity water is often needed.

2 Micropollutants in the Aquatic Environment

Micropollutants are chemicals in the aquatic utilization cycle in concentrations of μg/L or below [1, 2]. Currently in this context organic chemicals are basically considered as such. This includes ingredients of detergents and cleaning materials, paints, flame retardants and other chemicals being washed out from textiles, pharmaceuticals, disinfectants, biocides, corrosion inhibitors, complexing agents, softening agents, and preservatives, to name but a few of the most common ones [3, 4]. However, beyond these organic micropollutants, inorganic chemical species such as phoshporous, arsenic, heavy metals and increasingly rare earth metals are of interest. Depending on their usage, these originate from households, trades, industry, healthcare, agriculture, and other sources. About 30,000 of the chemicals on the EU market are considered to be environmentally relevant. A further increase in the diversity of chemicals and the used amounts is expected [5]. At the same time, the reuse of purified sewage gains more and more importance due to an alarming water shortage, e.g., for food production [6].

A lot of these materials are released into the environment as an “unwanted” side effect by their intended use. Improved chemical analysis helped to make that concentration level accessible during the last two decades. Not just the detection limits were improved but also the list of principally accessible chemicals was expanded. Notably polar compounds may nowadays be determined in a much better and extensive way than 20 years ago.

At best, micropollutants are unwanted substances in the water. However, there are cases in which such substances already have negative impacts on environmental organisms at quite low concentrations. Regarding human beings, there is hardly any data available on this issue. On the one hand, this is due to the fact that the concentrations are so low, and on the other hand, it is due to the great time scales and different life conditions which hardly allow an establishment of an exact cause-and-effect relationship for chronic and sub-chronic effects or for causing cancer. However, the properties of some of these substances, as, for example, those directly interacting with the DNA (e.g., several cytostatic drugs) or endocrines, cause to take notice. For the time being all risk assessment is based on isolated considerations of single substances. The fate and effects of substance mixtures still is very vague [7].

In terms of preventative healthcare as well as of sustainable development, micropollutants represent a major obstacle to a sustainable water management. This doesn’t only apply to the usage of water as drinking water and for irrigation for food production and the protection of the environment but also to the industrial usage of water. The increasing progress in some fields requires increasingly more pure water. Such a purification of water, though, demands energetic and technical efforts, thus also financial investments. All these points suggest preventative measures to be taken into consideration as well.

3 Limits of (Advanced) Wastewater and Drinking Water Treatment

The processing of water to drinking water and the purification of wastewater represent one of the major advances during the past 100 years, to which we probably much more owe the higher life expectancy than to all other medical progress – apart from the development of disinfectants and soap maybe.

The various effective processes applied in the water and wastewater treatment along with the very much improved handling of waste and chemical products as a whole result in quite low concentration of chemical substances in the aquatic environment and the urban water cycle in developed countries, hence the term micropollutants that indicates these “trace substances.” Nowadays, however, their presence has been reported to a considerable extent in most parts of the world. For this reason, attempts are being made to further improve the water quality in order to completely eliminate trace substances – mostly with the focus on wastewater purification and drinking water treatment, so to say at the end of the pipe. However, it has also been revealed in the past few years that due to the high amount and number as well as ever increasing diversity of chemical substances with totally different properties and areas of application, the removal capacity of the technologies has been reached. With regard to the standard wastewater treatment, for instance, a prolonged sludge age doesn't lead or only for some chemicals leads to an improved elimination of the micropollutants. In some cases, the elimination of the precursors (i.e., parent chemicals) is improved. However, if the elimination isn't based on sorption (i.e., accumulation in activated sludge or on activated charcoal) or complete mineralization, new, mostly unknown substances, i.e., unknown products of incomplete biodegradation or non biotic chemical transformation (so-called transformation products), are created. In other words, new chemical entities will be generated by microbiological and/or inorganic reactions within treatment processes or in nature [4, 8–10]. These transformation products have different physicochemical properties resulting in a different environmental behavior and different effects.

As a consequence of the very unsatisfactory elimination of chemical substances in wastewater, the research on technologies for advanced wastewater treatment has been intensified considerably over the past years and has partially (e.g., Switzerland) been implemented on a large scale. Numerous investigations, mostly on pharmaceuticals, have revealed, though, that neither the single techniques (e.g., sorption on activated carbon, membrane and other filtration processes, oxidation processes with strong oxidants like, for example, ozone and/or hydrogen peroxide or photolysis (treatment with UV radiation)) nor their possible combinations eliminate all those micropollutants with respect to number and concentration, let alone that additional energy and chemicals are needed, costs are resulting, a and that such treatment will not be available in most countries and regions. In general a combination of processes may eliminate a few substances by 80–100% (and probably only a minor part will then also be fully mineralized) and another amount at about 50 or 60%, and depending on the process and the substance combination, a more or less bigger part will not be eliminated at all. This is easily comprehensible. Different chemical substances also have different chemical properties such as polarity, different functional groups that can interact with a specific sorbent or can react with a specific reagent such as ozone or a biological target. Otherwise they wouldn't be different chemicals with different (application) properties in the first place. This also applies for substances within a comparatively closely related substance group as, for example, certain nonionic surfactants or flame retardants or even subgroups of pharmaceuticals, for example, antibiotics, and again subgroups within the group of antibiotics. Even substances within the group of the ß-lactam antibiotics, of which the molecules are quite similar, may have different properties and fate behavior. Especially as far as oxidative processes are concerned, a variety of transformation products with unknown properties is often created [11] – depending on the process up to ten or more from one parent substance. These and their individual relative share may differ a lot depending on the chosen reaction conditions and treatment duration and may be subject to temporal dynamics. As these compounds are often not available as pure substances, it cannot be assessed whether a high peak in UV–Vis detection or mass spectrometry corresponds also to a high concentration and vice versa – let alone their toxicity. Furthermore, their relative share is dependent of the time of treatment [12]. Therefore, the appropriate treatment as well as the optimal conditions and duration is different for each substance. It is therefore not surprising that in the literature [13] there had already been described 38 transformation products for single antibiotic ciprofloxacin up until May 2012 alone. It has to be noticed that this doesn't mean that all those created new molecules could be identified as it cannot be said which are accessible to those analytical methods and which are not, which is due to a lack of reference substances. Moreover, the establishment of an unequivocal chemical structure is associated with high uncertainty. It has also been revealed that there might be an increase in toxicity resulting from such a treatment [12, 14], including drinking water treatment [15, 16]. Latest research suggests that the ozonation of wastewater may even lead to a selection or accumulation of resistance material in the effluent.

In the literature, the unproven assumption can be found that transformation products being created in oxidative treatments, for example, generally have a better biodegradability because of the introduction of hydroxyl groups into the parent molecule. However, a higher polarity doesn't necessarily imply a better biodegradability. Biodegradability is determined by the fact that a molecule fits into the corresponding enzyme's "pocket" of its active center and may interact with it (not too weakly, not too strongly, fitting spatial arrangement). Accordingly, in literature more and more cases are being reported in which transformation products being created in oxidative treatments are not found to be biodegradable. It might be that those transformation products are neither better eliminated from the water phase by adsorption. Activated carbon, for example, is rather a good sorbent for less-polar substances, however, transformation products are often more polar than their parent compounds. If a biofilm is formed on the activated carbon after a certain time, this is slightly more polar and some substances may absorb there. To which extent this will occur, though, is yet uncertain. Highly polar transformation products resulting from oxidative treatment are expected to stay in the water phase and not enter into the less polar biofilms. What does this really mean for a potential evolution of resistance if also antibiotics and resistant bacteria are accumulated in such biofilms? And what's the use of activated carbon as a sorbent in the case of biofilm cultivation? Wouldn't the slow sand filter be just as suitable? Some investigations show at least that slow sand filters reach the best elimination capacities and that in comparison they have the best life cycle assessment [17].

Given the fact that several thousands to ten thousands different parent substances are considered to be environmentally relevant, complete elimination and identification and assessment of the transformation products at the end of the pipe de facto represents an insoluble task, even though this might not appear to be the case at first glance since certain substances can in fact be eliminated by the (advanced) wastewater treatment. In fact, for most substances, we don't have any data regarding their elimination and degradation behavior or even their effect (with up to 100 possible endpoints using often several different tests for each of them that would have to be measured). Let alone the tests and endpoints that will be of interest in the future. For example, endocrine activity was not considered 30 years ago. Nowadays, however, it is seen as one of the most important ones. Neurotoxicity, for example, will probably be among the next wave of endpoints to be considered in the near future.

The same could be true for the assessment of the impact on behavior of individual organisms and its consequences on population and ecosystem level [18, 19]. These examples also demonstrate that we will probably never be able to assess all possible effects in advance.

Furthermore, in the age of impact-driven science as well as of technology driven by economics, often the quality of the investigations is too low [20]. Considering the variety of parent compounds and all potential transformation products, a complete or even satisfying risk assessment will probably never be possible to take place in a cost-effective manner, if at all.

Moreover, we neither know yet which new substances might appear on the market in the future and which will be released into the aquatic cycle, nor how these will behave during the application of the different cleaning technologies and which unknown transformation products will be formed within the different treatment processes nor how to assess them. Engineered nanoparticles may serve here as a recent example. The example of pharmaceuticals shows that up to now most investigations have been made on so-called "traditional" substances which partially don't have such a great significance any more or which have meanwhile been replaced or are about to be replaced by new ones. As far as brand new substance groups such a nanoparticles are concerned, we are facing enormous methodological challenges. Assessments for pharmaceuticals and nanoparticles are often based on the application of classical, standardized tests that have been developed for plain chemicals. Moreover, it is completely uncertain which new chemical entities we will have to expect in future. The same applies to all other chemical substance classes and application areas, although the dynamics might not be as high as in the case of nanoparticles. As a result of the increasing usage of high-technology metals as, for example, those from the rare earth group, for products for the turnaround in energy policy (*Energiewende*) or medical application, it can be expected that these will also be increasingly released into the water cycle. First indications (e.g., gadolinium or dysprosium) already exist [21]. Gadolinium is meanwhile being used as a hydrological tracer for anthropogenic influences [22]. It is yet unknown whether highly toxic substances such as gadolinium (III) or chromium (VI) arise or nitroso dimethyl amine (NDMA) in oxidative methods of the water purification and the wastewater treatment [15, 16]. At any rate they are not completely eliminated in sewage plants. This is why trace substances and their transformation products are considered to be a worldwide issue. However, they cannot be quantified [23, 24].

4 Long-Term Strategies

Undoubtedly the conventional wastewater treatment has highly contributed to the progress in health and environmental protection. As outlined above though, it cannot offer a solution to the problems to such an extent as it would be needed (including the advanced treatment; fourth stage). New approaches are necessary which not only focus on the end of the pipe but also consider the use patterns and fate of chemical substances in the aquatic cycle in an interdisciplinary context. Such an approach at the beginning of the pipe, i.e., focusing on the chemical substances and the reason for their usage, has the charm that the focus is on prevention rather than on (incomplete) treatment that needs additional resources and may create follow-up problems. Hence, with regard to substances, a much more sustainable water management becomes possible also where the different preconditions for purely technical approaches do not exist and may not be established, e.g., in developing and/or arid countries and regions. There will be no “one and only” strategy or even technology but (partly) rather a variety of appropriate measures or set of measures depending on the nature, the type, as well as the reasons for the use of chemical substances i.e. their characteristics and functionalities.

The measures listed below may be considered as possible approaches – they are by no means exhaustive. Some may rather be implemented on an operational basis, others rather on local or regional catchment areas, while some even require political and social rethinking and will therefore take more time:

- Improvement of separation of wastewater streams and application of a better-targeted treatment and/or retain pollutants.
- Applying more substances in closed systems, e.g., within production, especially problematic ones, i.e., those that are not mineralized quickly and completely after being released into the aquatic utilization cycle or the aquatic environment.
- Using chemical substances that are easily mineralized, i.e., quickly and completely, in conventional sewage plants and in the aquatic environment.
- Development of substances with an improved/optimized biodegradation level (“Benign by Design” [25–27]) for products that may be released in the wastewater for unintended or even intended use (e.g., personal care products and cosmetics; household chemicals; biocides including pesticides, disinfectants, and pharmaceuticals).
- Considering the elimination of pollutants in drinking water treatments as a “police filter” rather than as a routine, i.e., it should only be used as a safety barrier in case such a pollutant really gets there.
- Considering the entire material flows for the same substance in different applications, e.g., within one industrial state or commercial area and not just a single company.
- Going beyond individual applications, i.e., focus on the entire material flows (local, regional, national level) and depending on their level and not just on individual companies or branches as well as their temporal variations and dynamics.
- Reducing the variety of substances and their temporal dynamics in different applications.
- Keeping an eye on the entire flows (as well as on all sources of a substance, creating balance sheets) and creating them as homogenous as possible as well as keeping any impacts to a minimum.
- Attaining a better knowledge about the specific reasons for the usage of certain substances in industry, commerce, agriculture, households, healthcare facilities, etc.

- Subsequently achieving the overall objective: a better knowledge about the functionality certain substances offer for their application.
- Clarification of nonmaterial alternatives (e.g., different production methods, different products, different values) which makes application of certain substances redundant, along with savings potential for producers and end users.
- Development of new business models: for instance, in the case of disinfectants, the objective would not be the highest possible consumption of disinfectants but rather the maintenance of certain standards of hygiene – a disinfectant manufacturer can deliver both; in the latter case, manufacturers would have an interest in applying disinfectants only where actually necessary and/or if training measures are not successful. If they need less disinfectants at equally high standards of hygiene, they save costs and generate a higher share of the financial turnover by nonmaterial resources, for example, by user trainings and consultation [28, 29].
- In macroeconomic terms (economically and financially), a slight improvement within the production process may cause significant extra costs for the wastewater and drinking water management (higher costs, higher toxicity); possibly with allocation of external costs and in the worst case, it is better to stick to the "old" substance not being subject to such hygienic and monetary consequences or which allows a much better estimation of risks, thanks to data being available ("substitute problem").
- Adequate consideration of the precautionary approach: "If there is nothing to be seen, it doesn't mean there is nothing/that nothing happens." An adequate dealing with agnosia or impossible knowledge (e.g., primary elimination doesn't necessarily imply full mineralization or improvement of the situation), long-term risks are beyond a classical cause-effect analysis.

As already outlined above, this list is not exhaustive and some facts aren't new, for example, that avoidance is better than a reduction only or even treatment of substances being released in the urban water cycle or the aquatic environment. It is important, though, not to consider only one approach but rather all options. On the one hand, a situation-specific application is essential; on the other hand, it should not be too restrictive.

According to the principle of "Ockham's Razor," the solution should finally be as simple as possible and as complex as needed only. If the entry of chemical substances regarding their nature, amount, and spatiotemporal dynamics is considerably reduced, the wastewater treatment – as one building block of several – can better fulfill the requirements. This view may indeed not be new, but it holds a still buried treasure!

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Index

D. Fatta-Kassinos et al. (eds.), *Advanced Treatment Technologies for Urban Wastewater Reuse,* Hdb Env Chem (2016) 45: 301–306, DOI 10.1007/698_2015