Perspective

Advanced Technologies for Water Treatment and Reuse

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Introduction

One of the grand challenges for sustaining modern society is to secure adequate water resources of desirable quality for various designated uses. The social, economic, and environmental impact of past water resource development and the unavoidable prospects of water scarcity are driving a shift to a new paradigm in water resource management. New approaches incorporating the principles of sustainability motivate the search for technological solutions to provide society with ample water sources and to protect the existing ones at the same time. In this context, new technologies for alleviating water shortages, providing quality water and new designs, and re-engineering existing water facilities play a major role.[1,2]

In this article, we highlight the potential and future prospects of three technological options that will play a significant role in the sustainability of wastewater (WW) and drinking water treatment: (1) first, the large scope and use of membranes, both in the treatment of WW and in providing high-quality water from different sources and uses; (2) second, the shift of biological processes in the treatment of WW to allow the self-sufficient running of wastewater treatment plants (WWTPs) or the recovery of value-added products; and (3) the increasing use of advanced oxidation processes (AOPs) to provide efficient means to oxidize recalcitrant and harmful constituents that may be present at even very low concentrations (micropollutants).

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From WW Remediation to Water Desalination: The Increasing Role of Membranes

Membrane water treatment is expected to play an increasingly important role in areas such as drinking water, brackish and seawater desalination, and WW treatment and reuse because of the widely reported advantages of membranes; these include small process footprints, superior separation efficiency, and easy maintenance. The membranes used in water treatment are porous or nonporous water-permeable polymeric films or ceramic matrices that are designed to remove aquatic contaminants, primarily through size exclusion; in filtration operations, water permeation is facilitated by the differences in the hydraulic pressures between both sides of the membranes, namely, the transmembrane pressure (TMP). On the basis of the operating TMP membranes for water treatment, their uses can be broadly classified as low-pressure membranes (LPMs) and high-pressure membranes (HPMs). Figure 1 depicts conventional membrane filtration operations including both LPMs and HPMs.

LPMs (membranes in drinking water and WW treatment)

The application of LPMs in drinking water treatment and WW reuse has undergone accelerated development in the past decade with improvements in membrane quality and decreases in membrane costs. The total installed capacity of LPM systems reached nearly 16,000 million liters per day by the end of 2006.[3] Drinking water treatment and WW reuse accounted for 82% of the total capacity.

LPMs are operated at relatively low TMPs (typically <1-2 bar) and include microfiltration (MF) membranes and loose

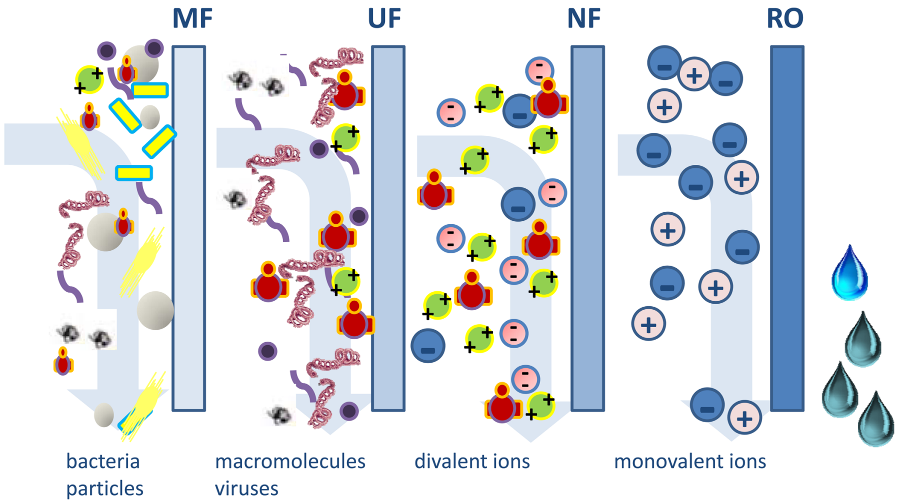

Figure 1. Membrane filtration operations.

ultrafiltration (UF) membranes. With pore sizes ranging from approximately 10 to 100 nm, LPMs are effective in removing aquatic substances, such as turbidity and pathogens, but they are not effective for substances such as precursors of disinfection byproducts and organic micropollutants (OMPs). Upon filtration of natural waters or WW effluents, LPMs are subject to losses in the membrane permeability as a result of the accumulation of aquatic substances on or inside the membrane matrices. This phenomenon is known as *membrane fouling*. Contaminant removal effectiveness and fouling resistance comprise the most important aspects of LPM performance. The integration of pretreatment with LPM filtration has been widely used at full scale to reduce membrane fouling and/or to increase the removal of certain aquatic contaminants. Huang et al.[3] reported a review of the state of the art of pretreatment for LPMs, showing that compared to the well-demonstrated enhancement of contaminant removal, the impact of pretreatment on membrane fouling is often small or even negative. This is further complicated by variations in source water quality and membrane properties. They concluded that novel technologies are an immediate need for fouling control in a cost-effective and environmentally friendly (e.g., few or reusable chemicals, less secondary pollution) manner. This is important to the viability of LPMs used in municipal water treatment and water supply for individual households and small communities.

Recently, the forward osmosis (FO) process has gained much attention because of its versatile potential for low energy consumption in water-treatment processes, such as desalination or WW treatment.[4–7] Basically, FO exploits the advantage of naturally induced water diffusion across a semipermeable membrane from a low-concentration solution to a high-concentration solution, as shown in Figure 2. Ideally, the semipermeable membrane performs as a barrier that allows water to pass through but rejects salts or unwanted elements. The high-concentration solution acts as a draw solution, which has a higher osmotic pressure than the feed solution, to draw water from the feed across the membrane to itself.

For water reuse and desalination, FO requires much less energy to induce a net flow of water across the membrane compared to traditional pressure-driven membrane processes such as reverse osmosis (RO). However, in contrast to RO, the permeate of FO is not a water product that is ready for consumption but is instead a mixture of drawn water and draw solution. As a result, a second step of separation must be used to produce clean water and to regenerate the draw solution. The second step of separation might be energy-intensive if inappropriate draw solutes and recycle processes are used. Therefore, one must take both costs of the FO membranes and draw solute recycle into consideration to have a fair comparison of an FO technology with other water production technologies. Currently, the major challenges to be overcome include (1) the lack of an ideal draw solution that exhibits a high osmotic pressure and can be easily regenerated to produce pure water and (2) the lack of an optimized membrane that can produce a high water flux, is comparable to commercial RO membranes, with a low salt transmission, and possesses effective antifouling properties.[4,5]

Another potential application of the osmotic permeation of water consists of harvesting the energy released from the mixing of freshwater with saltwater with the pressure-retarded osmosis technology (PRO). In PRO, water from a low-salinity solution permeates through a membrane into a pressurized, high-salinity solution. Power is obtained by depressurization of the permeate through a hydroturbine. The combination of increased interest in renewable and sustainable sources of power production and recent progress in membrane science has led to a spike in PRO interest in the last decade. This

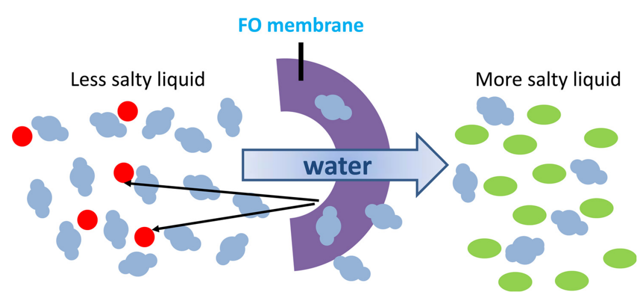

Figure 2. Water permeation through an FO membrane.

interest culminated in the first prototype installation of PRO, which opened in Norway in late 2009.[4,8]

HPMs

Seawater is no longer merely a marginal water resource but a commercial option for securing water supplies. HPMs, with nanofiltration (NF) and RO, is a prevalent desalination operation for various feed types and accounts for 55% (RO, 51%; NF, 4%) of the total water produced by desalination (44.1 Mm^3/day). The unique property of RO membranes to reject inorganic species while passing relatively pure water has led to its widespread use in the treatment and reclamation of high-salinity inland water sources since the late 1960s. Even though thermal and membrane desalination processes share equally the desalination production capacity, RO has emerged as the leader for future desalination installations. In addition, as per water desalination reports, the membrane market is estimated to have a healthily growth at an annual rate of 16%.

Achieving high product recovery (the ratio of the product volume to the feed volume) and minimizing the process cost are major challenges in RO operations. Different studies have shown that water product recovery for inland water reclamation by membrane desalination has to be sufficiently high, that is, greater than 70-80%, to be economically feasible.[9] Membranes are getting better, and nowadays, recent improvements in RO technology, including more efficient membranes made from carbon nanotubes and energy-recovery devices that boost output while cutting energy consumption and costs, have made it a feasible option for even small communities.

HPM operations constitute 38, 87, and 79% of the total water production from seawater, brackish water, and WW desalination processes, respectively. Brackish water RO is gaining more attention because of its low cost compared to SWRO.

Nonfiltration operations

Although filtration membranes, LPMs and HPMs, play a major role in water treatment and the latter in seawater desalination, different alternatives that improve water permeation e.g. by applying electric current such as Electrodialysis (ED) or promoting the liquid-vapor equilibrium at one side of the membrane such as membrane distillation (MD) contribute substantially to water desalination.

ED. ED is a mature membrane process in which ions are moved through a semipermeable membrane under the influence of an electrical current, as shown in Figure 3. ED processes were introduced in the mid-1950s, and there are currently more than 1000 installed plants worldwide, mainly for brackish water desalination. ED is economically most viable under low-salinity conditions; the current membranes in the market use too much energy at the high salinity levels of seawater. When applied to brackish and low-salinity waters, the advantages of ED are (1) high water recovery rates, (2) long membrane lifetimes, and (3) limited scaling and fouling. In ED reversal systems, the polarity and herewith the product and concentrate compartments are reversed periodically to prevent scale formation on the membranes. Additional alternatives are the design of hybrid membrane systems to reduce the energy consumption of ED and the manufacture of lower membrane and stack resistance with the maintenance of a high water recovery and operating conditions up to 50°C.[10]

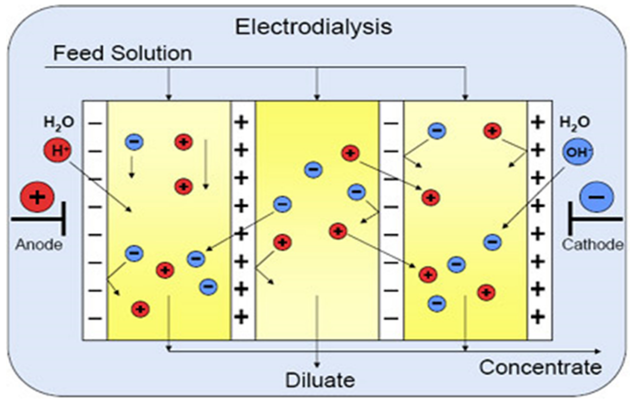

Figure 3. Fundamentals of the ED process.

MD. The MD process is driven by a temperature gradient created across a microporous membrane that separates vapor-liquid/liquid-liquid phases in equilibrium. In the MD process, the feed water is heated to increase its vapor pressure; this generates the difference between the partial pressure at both sides of the membrane. Hot water evaporates through nonwetted pores of hydrophobic membranes, which cannot be wetted by liquid water. MD advantages include its ability to produce drinking water with very low salinity. In addition, seawater can be distilled in a range of temperatures from 323 to 363 K; this reduces the amount of heat typically needed for desalination. It requires a steady, inexpensive source of heat to prevent the temperatures of the water on either side of the membrane from equalizing because this would impede the vaporization/condensation process. Recently, interest in using the MD process for desalination has been increasing worldwide because of these attractive features, especially when coupled with solar energy or the use of a low-grade heat source.[11]

MD has significantly lower requirements concerning the pretreatment of feed water, and therefore, it enables the production of pure water from water sources, the quality of which prevents the direct application of the RO for this purpose. However, the feed usually contains various impurities, which in turn, lead to the formation of deposits. Deposits both pollute surfaces of membranes and make it easier for water to penetrate membrane pores. Consequently, membranes lose their separation properties, and the MD process stops. This is why it is essential to prevent the formation of deposits on the membrane surface.[11]

Future perspectives

Despite the healthy situation of membrane technology in water treatment, there is still a very large research requirement to cover some of the following gaps.

New Membrane Materials and Fouling Control. Existing membranes for water treatment, typically polymeric in nature, are still restricted by several challenges; these include the trade-off between the permeability and selectivity (also called the *Robeson upper boundary* in membrane gas separation) and the low resistance to fouling. Nanocomposite membranes, a new class of membranes fabricated by the combination of polymeric materials with nanomaterials, are emerging as a promising solution to these challenges. Researchers could design advanced nanocomposite membranes to meet specific water-treatment applications by tuning their structure and physicochemical properties (e.g., hydrophilicity, porosity, charge density, thermal and mechanical stability) and introducing unique functionalities (e.g., antibacterial, photocatalytic, or adsorptive capabilities). The potential applications of nanocomposite membranes could cover the whole filtration spectrum, including MF, UF, NF, RO, and FO. However, the practical application of nanocomposite membranes for water treatment is still in its infancy. There have been many laboratory-based studies on the application of nanocomposite membranes, but very few reports exist on large-scale production and industrial applications. Among future challenges, the simultaneous improvement of antimicrobial and antifouling properties is highly desirable, where the accumulation of live/dead bacteria cells, extracellular biomaterials, and other foulants on the membrane surface will be mitigated. A method to effectively attach biocidal agents onto the membrane and control their release should be further examined. For commercial applications, there is a need to consider attaching biocidal agents onto the membrane and recharging them as needed in a cost-effective way.[12]

Cellulose nanomaterials are naturally occurring with unique structural, mechanical, and optical properties. A recent review[13] suggests that they have great untapped potential in water-treatment technologies because of their high surface-area–to–volume ratio, low environmental impact, high strength, functionality, and sustainability in water-treatment technologies.

Membrane fouling is a serious problem, which results in permeate flux decline or increased TMP. Membrane fouling is viewed as an accumulation of rejected constituents on the membrane surface; it comprises two components: the external/surface and internal fouling. The nature of fouling is strongly dependent on the feed water source. Antony et al.[9] reported a review on the mechanisms of scale formation and the properties of alkaline, nonalkaline, and silica-based scales that are encountered when RO is used in desalination and brackish water and WW recycling applications.

Sustainable Management of RO Brines. At present, RO is the most energy-efficient technology for seawater desalination and is the benchmark for comparison for any new desalination technology. Although the most prevalent use is to produce potable water from saline water for domestic or municipal purposes, the use of desalination and desalination technologies for industrial applications is growing, especially in sectors such as the oil and gas industry and in food and beverages. The European brewery industry, which produces about 40 million L^3/year, requires an average value of 4.7 L of water/L of beer, accounts for an important percentage of this water produced by RO technology. Operating with water recoveries from 35 to 85%, RO plants generate huge volumes of concentrates that contain all of the retained compounds that are commonly discharged to water bodies and constitute a potentially serious threat to marine ecosystems.[14] The evidence for salinity, thermal, and contaminant impacts of desalination brines upon receiving water quality is relatively clear; local salt increases can have an irreversible impact on sensible coastal habitats. In inland plants, the traditional option consists of reducing the concentrate volume before disposal. Evaporation techniques have been widely applied for this purpose, and among the emerging technologies, MD, alone or coupled with crystallization; ED with ionic and bipolar membranes; and FO are still promising technologies for volume reduction.[15,16]

Hybrid Membrane Processes. Hybrid membrane processes have emerged over the last decade as alternative treatment technologies for upgrading or improving conventional treatment processes and meeting the tightening of water quality regulations. LPMs can effectively remove particulate contaminants, including protozoa parasites such as *Cryptosporidium*. However, membranes cannot effectively remove dissolved natural organic matter, synthetic organic compounds, and trace organic compounds. Consequently, to improve the treatment performance, LPMs have been coupled with other processes, mainly coagulation, ozonation, or adsorption. Among these alternatives, the combination of activated carbon with LPMs has received increasing attention over the last 2 decades. Stoquart et al.[17] reported the current state of scientific knowledge regarding the use of hybrid membrane processes for the production of drinking water and reviewed the different configurations and their performance.

Photocatalytic membranes have shown great potential for use in energy-efficient water purification and WW treatment because they combine the physical separation of membrane filtration and the organic degradation and antibacterial properties achieved by photocatalysis in a single unit. Titanium dioxide (TiO_2) is the most commonly used material for the fabrication of photocatalytic membranes because of its low cost, nontoxicity, and high chemical stability. Photocatalytic membranes generally outperform conventional membranes in terms of reducing membrane fouling and improving membrane quality. Several review articles have been published on photocatalytic membrane reactors. Ollis[18] reviewed and discussed different methods for integrating the photocatalyst with membranes for water treatment. Mozia[19] reviewed the general configurations of photocatalytic membrane reactors and the advantages and drawbacks of photocatalytic membranes in terms of permeate flux, membrane fouling, and permeate quality. More recently, Leong et al.[20] reviewed the developments in the fabrication and characterization of TiO_2 photocatalytic membranes and their performances in WW treatment; they highlighted the stability of polymer membranes under ultraviolet (UV) irradiation, a concern that needs further investigation. Furthermore, to implement TiO_2 photocatalytic membranes in industry, the configuration of the membrane reactor needs to be better designed so that the exposure of the membrane surface to the UV lamp is optimized. Coupling membrane filtration with advanced oxidation of RO brines has been reported as a highly effective tertiary treatment of WW with almost complete mineralization of the brine organic constituents.[21]

A New and Sustainable Concept of WWTPs: Recovery of Energy and Value-Added Products

WWTPs were originally conceived to protect natural resources from the negative impact of the direct discharge to water bodies of urban (and various industrial) WW by the removal or a decrease in the presence of major water

Table 1. Unit Operations and Processes Used to Remove Constituents Found in WWs

Constituent	Unit operation or process
Suspended solids	Screening
	Grit removal
	Sedimentation
	High-rate clarification
	Flotation
	Chemical precipitation
	Depth filtration
	Surface filtration
Biodegradable organics	Aerobic suspended-growth variations
	Aerobic attached-growth variations
	Anaerobic suspended-growth variations
	Anaerobic attached-growth variations
	Lagoon variations
	Physical-chemical processes
	Chemical oxidation
	Advanced oxidation
	Membrane filtration
Nutrients	
Nitrogen	Chemical oxidation
	Suspended-growth nitrification and denitrification variations
	Fixed-film nitrification and denitrification variations
	Air stripping
	Ion exchange
Phosphorous	Chemical treatment
	Biological phosphorous removal
Nitrogen and phosphorous	Biological nutrient removal variations
Pathogens	Chlorine compounds
	Chlorine dioxide
	Ozone
	UV radiation
Colloidal and dissolved solids	Membranes
	Chemical treatment
	Carbon adsorption
	Ion exchange
VOCs	Air stripping
	Carbon adsorption
	Advanced oxidation
Odors	Chemical scrubbers
	Carbon adsorption
	Biofilters
	Compost filters

constituents. The conventional WWTP generally consists of a primary, secondary, and sometimes a tertiary stage, with different biological and physicochemical processes available for each stage of the treatment. Primary treatment intends to reduce the solid content of the WW (oils and fats, grease, sand, grit and settleable solids). This step is performed entirely by means of filtration and sedimentation and is common in all WWTPs. However, the secondary treatment, which typically relies on a biological process to remove organic matter and/or nutrients with aerobic or anaerobic systems, can differ substantially. Several biological treatments are being used in modern municipal WWTPs, but the most common method is conventional activated sludge (AS). Membrane bioreactors (MBR), moving bed biofilm reactors, or fixed bed bioreactors are less common. AS plants use dissolved oxygen to promote the growth of a biological floc that substantially removes the organic material and nitrogen under given conditions. In the final step, tertiary WW treatment processes can be applied to remove phosphorus by precipitation, particles on a filter, and other minor constituents. In some WWTPs, the effluent is also disinfected before it is released into the environment, typically by chlorination or UV irradiation. Table 1 lists the unit operations and processes currently used to remove the major constituents found in WW. A detailed description and the operational conditions can be found elsewhere.[22]

Most of the listed operations imply the transfer of water constituents to a secondary phase; this results in the formation of significant volumes of sludge, which is further treated in a specific treatment line. However, new regulations and energy prices, together with the increasing concern related to the environment and human health protection, has motivated the development of innovative technologies that are able not only to remove major constituents from WW but also to recover energy, valuable products, and clean water for further reuse. Figure 4 depicts the upgrading options for WWTPs, some of which are discussed in more detail in the following sections.

Technologies to reduce energy consumption

The WW equivalent energy content is evaluated on average to be 3.856 kWh/kg of oxidized chemical oxygen demand

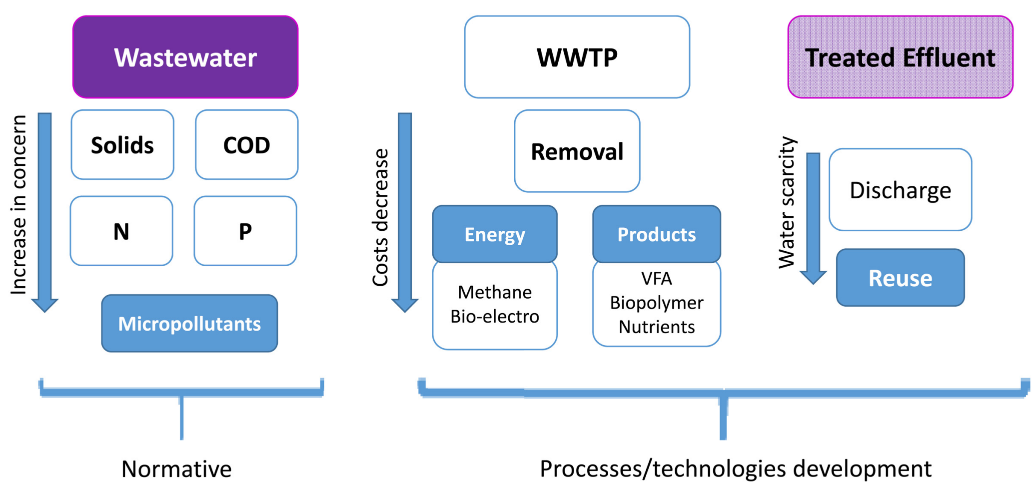

Figure 4. Upgrading options of WWTPs in terms of WW composition, treatment technologies, and quality of produced effluent-identifying driving forces.

(COD).[23] On the basis of this number, the self-sufficient operation of a WWTP is possible but requires implementation of new processes or innovative technologies. First, the efficient separation/concentration of the organic matter has to be performed through an improvement in the primary sedimentation and maximization of dissolved organic carbon, treated by anaerobic digestion together with the application of the combined partial nitrification-anaerobic ammonium oxidation (anammox) in the water line of the WWTP.[24] In addition, new technologies based on aerobic granular biomass, microalgae, or psychrophilic anaerobic digestion can provide important advantages.[25] In the case of the sludge line, the application of the partial nitrification-anammox process is also a promising alternative.

Anaerobic Treatment of the Main Stream. Anaerobic treatment of sewage has a number of potential advantages, which are mostly related to the very favorable energy balance. However, it has only been extensively applied in some countries, such as Brazil and to a lesser extent Colombia, because of the warm temperature of their sewage. The three main drawbacks that hinder further development of the direct anaerobic treatment are related to (1) the slow kinetics of the process at temperatures below 20-25°C, which imply a low biomass growth rate; (2) the unbalanced C/N ratio of the effluent leaving the digester for a proper denitrification; and (3) the methane dissolved in the effluent that is further released to the atmosphere, which increases greenhouse gas (GHG) emissions. Some promising solutions for these three issues are now available, and therefore, anaerobic digestion (AD) appears now as the key process in new conceptions of WWTP. The anaerobic MBR concept allows a suitable retention of active biomass, and its major operational problem (clogging) seems to have been successfully solved.[24] Coupling anaerobic MBR with the anammox treatment is a very promising solution for autotrophic nitrogen removal, and currently, different approaches seem feasible for operating anammox in the mainstream at low temperatures. This combined action would provide answers simultaneously to the two first drawbacks mentioned previously.[26] The combination of upflow an anaerobic sludge blanket with an anoxic moving bed reactor and an aerobic chamber provided with a membrane is a very interesting proposal for solving the aforementioned drawbacks. Here, the dissolved methane from the upflow anaerobic sludge blanket is sufficient to denitrify in the anoxic chamber the nitrate produced in the aerobic one.[26] The conception of WWTPs based on AD units will contribute greatly to the economic, environmental, and energetic sustainability of sewage treatment.

Aerobic Granular Reactors. Aerobic granular reactors are a sequence of batch reactors that operate in cycles and are designed for the development of granular biomass under aerobic conditions. When applied in the substitution of AS systems, they have proven to fulfill organic matter and nitrogen removal requirements. Compared to AS, these systems perform similarly or better in terms of process stability, sludge production, and effluent quality. Furthermore, they require 25% less surface for implantation and consume 65–75% less energy.[27–30]

With regard to application, although several patents owned by different companies of the water sector have been granted, only the Nereda technology has been realized on a full scale. This technology is based on the formation of aerobic granules in the operation of the biological phosphorous removal process by means of the imposition of alternating anaerobic/aerobic conditions. Since 2005, over 21 full-scale aerobic granular sludge technology (AGS) systems have been implemented in The Netherlands, Portugal, and South Africa for the treatment of mainly municipal WW or a mixture of municipal-industrial WW with the Nereda process. The most frequent sizes of these plants range from 20,000 to 100,000 population equivalents. With respect to the operational conditions, these plants can cope with organic loading rates as high as 2.8 kg of COD/$m^3 \cdot d$ at hydraulic retention times as short as 0.2 days.

Some of these treatment plants have been built to upgrade existing WWTPs. However, most of them are new construction. About 20 new plants are scheduled to be built in different countries, including Australia, China, Brazil, India, the Middle East, Belgium, the United Kingdom, Poland, Ireland, and the United States.

Codigestion. The concept of codigestion is being extensively developed in some European countries, such as Denmark, Austria, and Germany, to produce energy from wastes and energetic crops at farms.[31] Anaerobic codigestion has also a great opportunity for the combined treatment of municipal and industrial wastes and sludge, and at the same time, it provides the opportunity for the cogeneration of electricity and heat. The main concerns about this approach consist of the reluctance of operators against a possible overload and consequent acidification of the digester with dramatic consequences. Several monitoring, fault-detection, and control systems have been developed for increased efficiency and the safe operation of anaerobic digesters,[32] although few of them consider codigestion. In a recent article, an integrated system for optimizing the blending of several substrates and monitoring and controlling the efficiency and stability of the system was proposed.[33] Anaerobic codigestion can offer a solid basis for a new conception of an energetically sustainable join treatment of municipal solids and liquid wastes.

Microalgae-Based Systems. To decrease the aeration requirements associated with AS, the use of systems based on microalgae is an alternative under study. Microalgae are cultivated normally in open raceway ponds and are used for nitrogen removal from WW via assimilation in biomass.[34] They can be applied to WW treatment once most of the organic matter has been removed from the liquid. They can operate in combination with heterotrophic bacteria in such a way that they produce the oxygen required for the activity of the latter, which involves a significant savings in energy consumption. Their main disadvantage is that they require large surface areas for the ponds and a consequent larger power consumption for mixing compared to AS. Furthermore, the difficult separation of produced microalgae, which requires the addition of reagents together with their low biodegradability, generates five times more sludge than AS reduction.[35] However, the produced microalgae biomass can be valorized with them as a source of lipids for biodiesel production with productivities up to around 30% with domestic WW.[36] After lipid extraction, the remaining biomass waste can be used for ethanol production or biogas synthesis and further combustion in the frame of a biorefinery concept, improving in this way the economics of the whole process.[36]

Nutrient Removal: Partial Nitrification-Anammox. When nitrogen removal is required, the only way to guarantee that most of the organic matter contained in the WWTP is used for methane production relies on the use of biological processes different from the conventional nitrification-denitrification ones These processes should consume no or less organic matter than heterotrophic denitrification and requires low energy by a reduction in the oxygen requirements under those of the conventional nitrification process.

The combined partial nitrification-anammox process is fully autotrophic; this means that no organic matter is required. As both processes occur under different environmental conditions (aerobic/anoxic), they can be performed either in separate reactors, the partial nitrification in the aerobic one and the anammox in the anoxic one, or in a single aerobic reactor with granular biomass. Nowadays, both options (two units and one unit) have been applied on the industrial scale by Paques, and the second one is about to be tested by FCC Aqualia in the ELAN process for the treatment of rejection water from an anaerobic sludge digester.[37,38]

This combined process allows a savings of 60% of the energy associated with oxygen supply, a degradation of 100% of the organic matter, and the production of only 15% of sludge compared to the conventional nitrification-denitrification process. In terms of plant operation, the application of this combined process allows a reduction of 40-50% energy consumption by increasing the biogas production by 25% with no reduction in the overall nitrogen removal (70-80%).[39]

Technologies related to the biorefinery concept

Volatile Fatty Acid (VFA) Production. Turning the treatment of residues into the production of chemicals under a biorefinery approach is an attractive alternative that follows the circular economy paradigm. Anaerobic digesters could play in the near future a key role, not only by providing sufficient electrical and thermal energy but also in the development of a platform for production of chemicals. The anaerobic fermentation of organic waste (including sludge from WWTPs) into methane can be considered a mature technology. However, VFAs, which are in the path from organic matter to methane, cannot be produced in an economically feasible way. The simplest way to proceed is to take advantage of the differences in the kinetics of the acetogenic-acidogenic step of AD and the methanogenic one. A very simple strategy of feeding the residue at a shorter hydraulic retention time will allow the washout of the Archaea microorganisms, which are responsible for the transformation of acids [and carbon dioxide (CO_2) + H_2] into methane, from the digester, and as a result, a mixture of VFAs will be obtained. The main challenges to be overcome include product inhibition, pH inhibition, and poor selectivity when the production of a certain VFA is targeted. For that purpose, several reaction/separation schemes have been proposed on the basis of the membranes and electrochemical systems such as ED or ion exchange, although further developments to reach industrial application are required.[40] These long-chain fatty acids can be further used as the basis of a carboxylate platform, which will be able to elongate them to other compounds, such as caproate[41] or bioplastics, with a higher added value.

Bioplastics Production. Polyhydroxyalkanoates (PHAs) are biopolymers produced by mixed cultures. They present properties similar to conventional plastics from petroleum origin, and they are called *bioplastics*. They can be produced from relatively highly loaded WW previously acidified to produce an appropriate mixture of VFAs. This condition is fulfilled if the sewage sludge is subjected to this treatment. The complete process includes two units: one for the production of enriched PHA-accumulating bacteria and a second in which PHA accumulation is maximized with part of the previously enriched culture. Both units are fed with the VFA mixture. These biopolymers are stored inside microbial cells exposed to an aerobic dynamic feed, which is composed of a feast-famine regime (presence-absence of substrate in the liquid phase) in sequencing systems such as sequencing batch reactor (SBR) ones.[41]

When this process is implemented, about 0.25 g of VFA/g of volatile sewage sludge (VSS) can be produced from sewage sludge acidification, and 0.43 g of PHA/g VFA can be obtained from VFA accumulation. This amount corresponds to a maximum of 10 wt % of the total sewage sludge produced. According to the company AnoxKaldnes, around 500 tons per year can be produced in a WWTP treating the WW corresponding to a population of 100,000 inhabitants. At the moment in Europe, two companies are developing processes for PHA production from sewage sludge, AnoxKaldnes AB (Sweden) and Paques (The Netherlands). Both are already working on a pilot scale.

Nowadays, some studies are directed to evaluate the possibility of using the organic matter contained directly in the WW to feed a SBR for the production of PHA-accumulating biomass, operated with hydraulic and solid retention times of 3 h and 1-2 days, respectively, and treating loads of 3 g of COD/L·day.[41] The produced PHA-accumulating sludge is used to accumulate the previously obtained VFA-containing effluent produced from a primary sludge fermentation reactor. However, the accumulating capacity of the biomass has to be improved in further research studies because the obtained values reach only around 40% of the maximum capacity.

Impacts and future perspectives of biological treatment

GHG Production. Three gases are produced during biological WW treatment: CO_2, methane (CH_4), and nitrous oxide (N_2O). The last two contribute to the greenhouse effect at 21 and 310 times[42] the effect caused by CO_2.

In the case of methane, a value of average emission of 0.07% of influent removed COD has been found mainly in aeration systems where methane, produced in the sewer or anaerobic zones of the WWTP, is air-stripped.[43] However, the behavior of these emissions is highly dynamic.

With respect to CO_2, this gas is produced during aerobic organic matter oxidation and denitrification processes. The substitution of the former by psychrophilic anaerobic systems and of the latter by autotrophic processes can help to reduce the amount of CO_2 produced in WWTPs. If microalgae systems are implemented, the absorption of this gas is accomplished with a subsequently beneficial effect on the production decrease of the GHGs.

N_2O is formed during the activity of nitrifying and denitrifying organisms. It is an intermediate or byproduct of

Table 2. Innovative Technologies and Potential Upgrading

Improved aspect	Less surface	Reduce/produce energy	Micropollutant removal	Fewer GHGs	Less sludge	Product/nutrient recovery	Water reuse
Secondary treatment							
Partial nitrification-anammox	Yes	Yes		Yes	Yes		
Aerobic granular reactors	Yes	Yes			Yes		
Psicrophilyc AD		Yes		Yes	Yes		
Systems based on microalgae		Yes					
Membrane bioreactors	Yes		Yes		Yes		Yes
Sludge line							
Sludge codigestion		Yes		Yes			
VFA production				Yes		Yes	
Bipolymer production system						Yes	
Partial nitrification-anammox	Yes	Yes			Yes		
Tertiary treatment							
Membranes	Yes		Yes				Yes
AOPs	Yes		Yes				Yes

biological processes.[44] Anammox organisms are able to produce only nitric oxide (NO) but no N_2O.[45]

Future Perspectives. All of the technologies previously discussed and summarized in Table 2 are under development nowadays, and for this reason, future improvements have to be realized with respect to some specific aspects of their operation to reduce energy consumption, maximize methane production, and obtain value-added products.

With regard to AGS research not based on phosphorous removal, it is under development nowadays on the pilot scale,[28–30] and it is expected that in the future new technologies will be available as an alternative to the already existing Nereda process. Some aspects to be considered regarding the operation of these systems are the solid content of the effluent, which has to be reduced previous to its discharge to natural water bodies by means of filtration systems (membrane systems, settlers, sand filters, etc.), which are of special importance during startup operation. Another issue is the reduction of aeration costs, associated with the need of high air flows to retain the required dissolved oxygen concentration and the mixing of WW; this can be accomplished by the use of slow-growing microorganisms, such as nitrifying or phosphorous-removing bacteria.

The spread of the application of microalgae systems requires the improvement of this biomass degradability by means of, for example, a thermal pretreatment of highly concentrated streams of microalgae up to 55%. In this way, more energy can be obtained from the extra methane generated, and this can compensate for the energy consumed in the pretreatment.[46] Furthermore, the beneficial effect of the CO_2 capture by the microalgae should be taken into account to evaluate the process in terms of GHG reduction.

The only way to maximize the organic matter content of the WW to be used for methane production is to substitute the conventional nitrification-denitrification system with a partial nitrification-anammox one. However, at the moment, more research work is required to establish the appropriated operational conditions to operate this process in the water line of WWTPs characterized by low nitrogen concentrations and low-temperature conditions.[38]

In the recovery of value-added products from WW, such as the PHA production process, two main aspects need to be researched: (1) maximization of the accumulation inside the biomass to produce significant amounts of PHA and (2) optimization of the downstream process for the separation of the product. For PHA to be competitive in the market, the production costs should be reduced to 3 Euro/kg of PHA.

From the environmental point of view, the generation of GHGs is one important drawback in WWTPs that can be faced through the application of different measures:

1. To maximize energy production, it is advisable to recover 100% of the methane through the prevention of AD by the anaerobic digesters.
2. With respect to CO_2 production, in processes where the organic matter, is oxidized, oxidation or heterotrophic denitrification should be avoided.
3. Finally, the establishment of the adequate operational conditions in the nitrogen removal process; this prevents or significantly reduces the N_2O production, such as in the case of the nitrite accumulation.

Figure 5 presents an overview of the transition from conventional to more efficient WWTPs.

Emerging Pollutants and the Role of AOPs in Their Abatement

The presence of OMPs, including pharmaceuticals, personal care products, hormones, and industrial compounds such us phenols, has appeared in the last decade as an issue of public concern because of evidence of their impact on surface waters. Recently, the European Union has included three of these compounds in the watch list before their regulation in the water directive. Because of the origin of OMPs, which is directly associated with human activity, WWTPs appear as the main way that they enter into the environment, and a number of studies have been performed to determine the fate of OMPs in WWTPs.[47] Two main conclusions were derived from important research efforts: (1) their removal is largely dependent on the technology applied and on the operating conditions,[47] and (2) some types of OMPs are not sufficiently removed no matter what technology is applied in primary and secondary treatments, and a further tertiary treatment is required for a substantial reduction of their concentration. After analyzing environmental impacts, economic costs, and social perception, the Swiss government decided to force many WWTPs to install efficient posttreatment units over the next 15 years. Most likely, many other countries will make

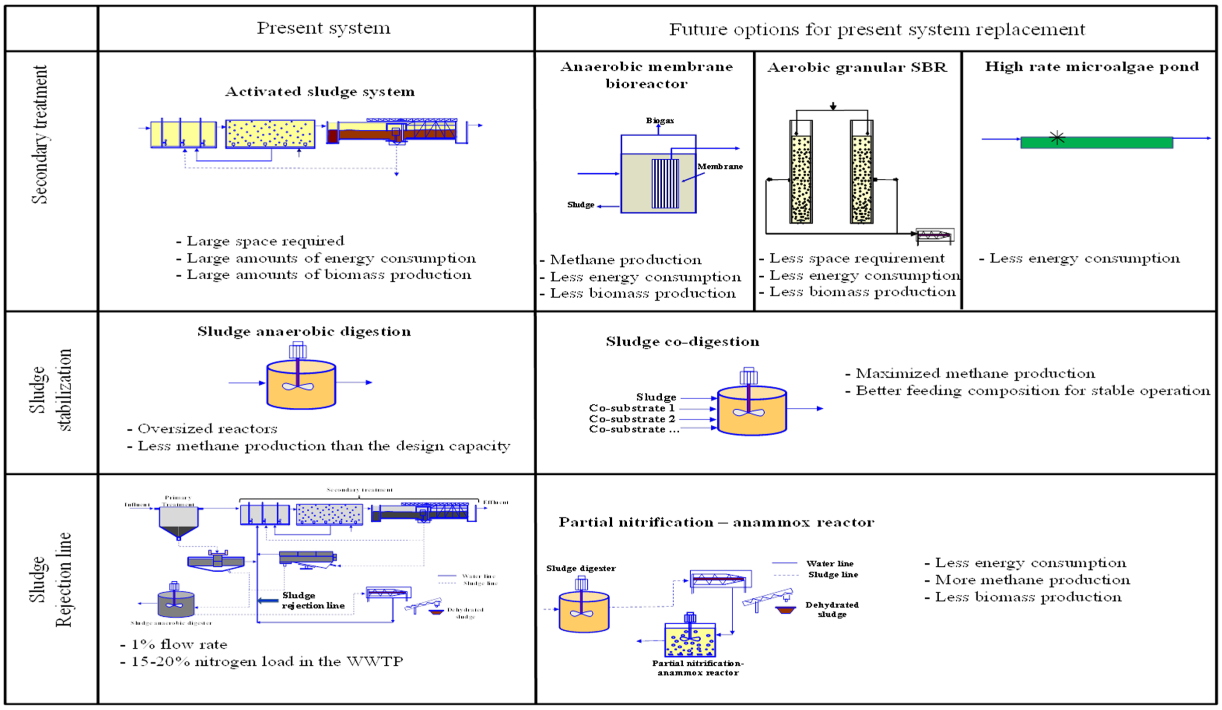

Figure 5. Transition from conventional WWTP units to improved future alternatives.

similar decisions in the near future; this opens new opportunities for innovative posttreatment units, where a prominent role of advanced oxidation units is expected.

AOPs are defined as processes at room temperature that are based on the generation of highly reactive radicals, especially hydroxyl radicals.[48,49] Nowadays, this definition is extended to other oxidation processes operating at conditions other than the mild conditions previously defined. AOPs are responsible for decreasing the toxicity and at the same time increasing the biodegradability of the effluents treated; they are able, in some cases, to reach almost the complete mineralization of contaminants.[21] Table 3 shows a nonexhaustive list of AOPs.

Hydroxyl radicals (•OH) have a high standard reduction potential ($E_o = 2.80$ V) compared with other conventional oxidants [E_o (O_3) = 2.08 V, E_o (H_2O_2) = 1.78 V, E_o ($KMnO_4$) = 1.70 V, E_o (Cl_2) = 1.36 V]. Only fluorine ($E_o = 3.06$ V) has a higher value of E_o. The high reactivity of hydroxyl radicals makes this species extremely unstable and reactive. Additional advantages of hydroxyl radicals are (1) the fact that it does not introduce any strange atoms into the water matrix, (2) it is not a selective oxidant, and (3) it can degrade practically all organic substances.[50,51]

According to the scientific literature, AOPs are adequate when the organic load, measured as COD, is less than 2 g/L, but they can be used at levels up to 10 g/L.[52] Figure 6 shows the range of total organic carbon (TOC) flow rate of the water effluent to be treated for the optimal operation of various AOPs.[53]

Photo processes use UV and visible radiation; the modeling of photoreactors to be used for water treatment is a current

Table 3. Nonexhaustive List of AOPs

Classics	Dark processes	Ozone Ozone/H_2O_2 Fenton (Fe^{2+}/H_2O_2) Electrochemical
	Photoprocesses	Water photolysis Ozone/UV UV/H_2O_2 Photo-Fenton (UV-visible/Fe^{3+}/H_2O_2) Photocatalysis
Hot	Electron beam Hydraulic cavitation and sonolysis Nonthermal plasma Supercritical wet oxidation Wet oxidation	

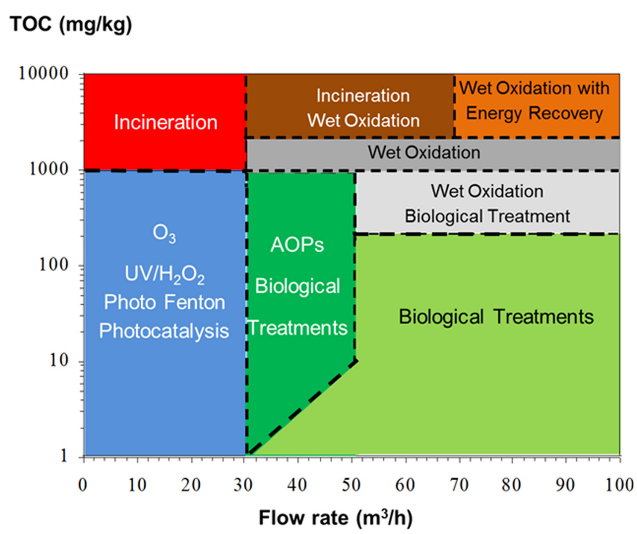

Figure 6. Suitability of water treatment according to TOC.

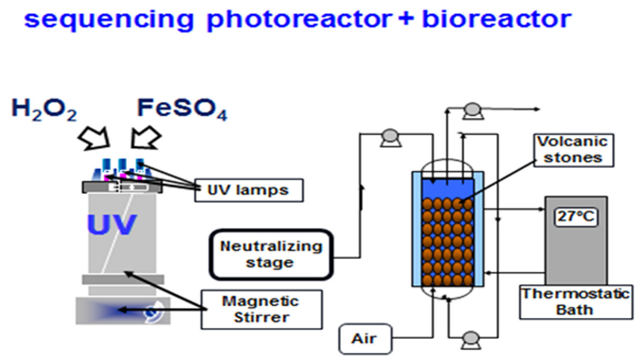

Figure 7. Flow diagram of a hybrid process combining photooxidation and biological treatment.

topic in AOPs with important contributions from chemical engineering fundamentals.[54,55] Ozone and electrochemical oxidation belong to a group of AOPs where the primary oxidant can react directly with pollutants (direct oxidation) and also through hydroxyl radical formation (indirect oxidation). Nowadays, the use of ozone oxidation in water and WW treatment is increasing in developed countries. Electrochemical oxidation has been widely studied in recent years because of the development of more efficient anodic materials, which has expanded their potential applications from WW tertiary treatment,[21] the mineralization of high-organic-load WW,[56–58] and the remediation of aquaculture water.[59]

Future perspectives

Nowadays, the main challenges that face the development of AOPs focus on the design of hybrid processes, the development of solar photooxidation processes, and the Fenton oxidation at circumneutral pH.

Hybrid Processes. One of the main drawbacks of AOPs is associated with the costs of the chemicals and energy needed for their application. To improve the treatment efficacy and to reduce costs, hybrid processes have been considered. Among them, it is worth mentioning their integration with membrane stages that allow TOC concentrations to be reached that are high enough for the optimum performance of AOPs;[60–62] the development of TiO_2-based photocatalytic membranes belongs to this process category.[18,19]

Additionally, as biological treatment is much more cost effective than AOPs, the sequencing and combination of biological treatment and AOPs has been considered a good option for treatment.[63,64] AOPs increase the biodegradability of WW effluents and also reduce the toxicity when the correct oxidant dose is applied. This combined process shown in Figure 7 and has been reported to treat WWs containing pesticides, herbicides, pharmaceuticals, and/or emerging contaminants and WWs coming from the textile industry, oil industry, pulp mills, olives mills, wineries, distilleries, and landfill leachates.[65]

Combinations of AOPs with other physical treatments, such as coagulation, activated carbon adsorption,[66] and biological activated carbon adsorption,[67] have been reported as interesting treatment alternatives.

Solar Photooxidation Processes. A number of different AOPs have used UV light, either from artificial radiation sources such as lamps or from natural sources such as the sun.[68] It is interesting to note that approximately 4% of the solar spectra at sea level corresponds to UV radiation (<400 nm). The photochemical treatment, although partially solving the problem of the refractory compounds, has some negative aspects in its practical application, such as the high cost associated with the generation of the UV radiation. Furthermore, not all of the emitted radiation is used; only the absorbed radiation and only a fraction of this radiation promotes chemical changes. This fact causes some photodegradation reactions to have very slow kinetics. The main limitations to the photochemical process are the cost of the chemicals used, the cost of UV-visible radiation, the gas-liquid mass transfer rate (in the case of O_3), and the requirement that the effluent must have suitable UV-light transmission. Nevertheless, the high oxidizing power and the absence of residues (except for the homogeneous photo-Fenton) are among the advantages of photochemical oxidation processes. In addition, because the wavelength spectra of the sun is 300-3000 nm, solar photo-Fenton appears to be one of the best potential alternatives for use in oxidation treatment.

The TiO_2 photocatalytic process, which may generate hydroxyl radicals without the need to add chemicals such as ozone or hydrogen peroxide, is one of the most promising methods for abating pollutants from water.[69] There is a large number of publications in the scientific and technical literature but very few applications at industrial scale. Nowadays, new materials, some of them using TiO_2, nanotubes, or zeolites as basic compounds, are being built to extend the absorption spectra to the visible region.[70]

Fenton Processes at Circumneutral pH. The highly acidic pH required by Fenton and photo-Fenton processes is one of the major drawbacks as acidification is required for most effluents; this is followed by a neutralization step before the treated water can be discarded. There is a very narrow pH range of operating conditions (pH 2-3) in Fenton and photo-Fenton treatments. In the Fenton reaction, iron ions act as a catalyst, and to prevent their precipitation as inactive oxyhydroxide iron species, it is essential to keep the pH at an accurate value. To overcome many of the disadvantages associated with conventional Fenton and photo-Fenton operational conditions and to take advantage of their good performance, the processes should be modified. For the real application of Fenton and photo-Fenton processes, operation under a wider pH range is essential; this results in a modified or Fenton-like process. Fenton- and photo-Fenton-like processes at neutral pH can be performed in two different modes, homogeneous and heterogeneous. A homogeneous Fenton-like process at neutral pH can be carried out with substances that are able to solubilize iron in a wider range of pH than conventional photo-Fenton processes. These substances are called *chelating agents* and are able to form photoactive species ($Fe^{3+}L$) that can be used to keep the iron solubilized. Chelating agents are substances that are normally absent in WWTP effluents. Thus, if they have to be used as reactants, they have to be added during the treatment. Then, it is easy to understand that properties such as biodegradability and toxicity have to be evaluated to select the correct chelating agent to form iron complexes. The strength of the ligand to form complex species (chelating ability), which substantially depends on the chemical structure, is also an important parameter in establishing and limiting the quantity of chelating agent that needs to be added to the solution to keep at a minimum its contribution to the TOC concentration. Furthermore, the use of some not very expensive chelating agents[71–74] also prevents iron sludge formation once the pH has been adjusted to neutral conditions.

Conclusions

New approaches incorporating the principles of sustainability have motivated the search for technological solutions to provide society with ample sources of water and to protect the existing ones at the same time.

The well-known advantages of membrane technology, including its small process footprint, superior separation efficiency, and easy maintenance, make these technologies essential parts in the design of sustainable processes for drinking water, brackish and seawater desalination, and WW treatment and reuse. Filtration technologies, LPMs and HPMs, operating alone or as part of hybrid processes, will play a key role in providing high-quality water. RO, the most prominent membrane technology in seawater desalination, has emerged as the leader in future desalination plants. The particular application of ED to desalinate brackish water or the advantages of MD when combined with renewable energy sources will offer additional alternatives that will complement the portfolio of membrane technologies in the water-treatment sector. Finally, FO, an LPM emerging technology, shows promising prospects in the design of hybrid processes for water remediation and desalination. Despite the healthy situation of membrane technologies, there is still the need for research to develop new membrane materials with higher fouling resistances, higher water permeabilities, and higher rejection of undesirable constituents; a decrease in the energy consumption and the coupling of the technologies to renewable energy sources are also challenging aspects to be overcome in the near future.

The re-engineering of existing WWTPs is an essential part of the sustainability of water treatment by protecting natural water bodies at the same time from the discharge of polluted WW. From the original plants, consisting of a primary, secondary, and sometimes a tertiary stage, with different biological and physicochemical processes available for each stage of the treatment aimed at removing or decreasing the presence of major constituents, the use of innovative technologies and processes promotes the shift from conventional to self-sufficient WWTPs with the possibility of the recovery of value-added products and obtaining water with high quality for further reuse.

Innovative biological technologies and new process concepts will play a key role in reducing energy consumption, maximizing methane production, and obtaining value-added products. AGS technology has proven to offer similar performances as AS systems with important savings in the required surface for their implantation (25%) and energy consumed (65-75%); the technology operates at full scale, but further improvements in reducing the solid content of the effluent previous to its discharge to natural water bodies and in reducing the aeration costs are still needed. Microalgae-based systems offer the beneficial effect of CO_2 capture, but they require large surface areas for their implantation and higher power consumption when compared to conventional AS systems, and they need a pretreatment stage to improve the biomass degradability. Hybrid processes that combine the nitrification stage with anammox maximize the organic matter content of the WW to be used for methane production, but more research is needed to optimize the operational conditions and overcome the low nitrogen concentration and temperature characteristics in the water line of WWTPs. Biorefinery processes aiming to produce PHA need maximization of the accumulated biomass and downstream separation of the product.

AOPs, which most of them have the potential to generate powerful oxidizing agents such as hydroxyl radicals, have stimulated a large number of studies focused on degrading recalcitrant constituents at even very low concentrations. These technologies are unique in the complete mineralization of a large variety of water constituents. The design of hybrid processes that integrate membrane units (for concentration objectives), together with different AOPs (oxidation and mineralization objectives), offers the most valuable option for destroying harmful micropollutants and preventing their accumulation in the environment. Combinations of AOPs with biological treatment is an interesting alternative for meeting water discharge standards in a cost-effective way. In addition, the design of hybrid processes, the development of solar photooxidation processes, and the Fenton oxidation at circumneutral pH are among the most interesting alternatives in the near future.

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