Membrane-based separation of potential emerging pollutants

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Abstract

The potential emerging pollutants (PEPs) such as hazardous chemicals, toxic metals, bio-wastes, etc., pose a severe threat to human health, hygiene and ecology by way of polluting the environment and water sources. The PEPs are originated from various industrial effluent discharges including pharmaceutical, food and metal processing industries. These PEPs in contact with water may pollute the water and disturb the aquatic life. Innumerable methods have been used for the treatment of effluents and separating the toxic chemicals/metals. Of these methods, membrane-based separation processes (MBSPs) are effective over the conventional techniques for providing clean water from wastewater streams at an affordable cost with minimum energy requirement. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO) methods as well as hybrid technologies are discussed citing the published results of the past decade.

Keywords

PEPs; Wastewater treatment; MBSPs; Separation; Polymers

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Introduction

Of the World's total availability of water, nearly 71% of Earth's surface is covered by saltwater and people living with the remaining 29% need fresh water to sustain life. The World Health Organization (WHO) estimates that there are more than 1 billion people who cannot get clean water. Health monitoring authorities report that ~4000 children die every day due to waterborne diseases as result of water pollution around the world [1]. Therefore, the world is facing severe drinking water crisis due to environmental hazards. The available water sources are polluted due to human activities and discharge of effluents from industrialization. If proper treatment methodologies are not developed or adopted, then there will be more severe health issues in the near future due to water contamination with waterborne pathogens due to increased discharge of potential emerging pollutants (PEPs) (toxic chemicals, pharmaceuticals, heavy metals, fertilizers, sludge, endocrine disrupters, etc.,) into the water sources [2–4].

There is thus an urgent need via technology innovation to avoid the already strained good water supply for providing human health, and hygiene. Even though distillation-based technologies dominate the industrial scale water treatment approaches, more efforts have been directed to develop economical, energy efficient and straightforward methods such as MBSPs to provide clean water [5,6]. Though several of these MBSPs including some hybrid technologies have been emerged as potential water treatment technologies, yet only a few are successful for a large-scale application.

PEPs are originated from several industrial processes and effluents discharged at the source require clear identification, separation, and disposal as otherwise these wastes can pose serious problems to water quality and ecology at large [7]. The United States Environmental Protection Agency (USEPA) categorized the PEPs as hazardous materials that lack the regulatory standards [8]. The PEP-contaminated wastewaters usually follow many vicious pathways [9,10] as typically displayed in Fig. 1, finally reaching the water sources used for various human consumption. Therefore, handling of PEPs is a severe problem, because the majority of conventional wastewater treatment technologies have repeatedly proven to be inefficient to eliminate even the trace amounts of toxic components [10]. In the case of sewage sludge and soils, PEPs may directly diffuse from the waste streams to reach the groundwater, making the treatment methods even more difficult.

Conventional water treatment methods such as adsorption, bio-oxidation, coagulation, sedimentation, and filtration, in addition to hybrid combinations such as chlorination and UV radiation, have been widely explored in the literature though majority of these approaches are inadequate for an effective treatment of wastewater [11]. On the other hand, water purification via MBSPs even though are somewhat expensive, but they are energy-intensive compared to other conventional treatment technologies. In addition, MBSPs have several distinct advantages, such as producing high water quality with a high rate of precious chemical/metal recovery and having low maintenance costs [12,13].

The objective of the present review is to present an overview of the various membrane-based technologies used for the separation of PEPs, and mainly addressing water pollution issues.

Thus, the MBSPs considered in this review are: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO). Some of the hybrid technologies such as membrane bioreactors (MBRs) and photocatalytic membrane reactors (PMRs) are also covered. A discussion will also be made on the types of membrane materials, their pore characteristics, operating methods to control the filtration processes, and performance test protocols in comparison to other technologies. However, desalination and related technologies, including thermal and solar distillation, will not be covered as these aspects have been reviewed in earlier publications [14–16] (see Fig. 2).

Potential environmental pollutants (PEPs)

The effect of PEPs on human health and ecology even if present in trace quantities is an issue that requires an extensive study in terms of human biology, chemical nature of the PEPs as well as the surrounding atmospheric parameters. Studies in the literature suggest that > 70% of PEPs are environmentally hazardous and toxic to the human health [17]. Though several toxic organic chemicals and metals have potential applications as raw materials in developing industrial products, but their discharge in the atmosphere without proper treatment may pose severe threat to the ecology. Some available data on the production of PEPs (in million tons) are summarized in Table 2 under three categories viz., (i) total production of PEPs, (ii) environmentally harmful PEPs (causing superficial damage), and (iii) PEPs with severe environmental impact. It can be realized that the magnitude of PEPs produced remains constant year-by-year, which may increase in the near future. Among the PEP sources, pharmaceutical wastes including antibiotic drugs, biologics, diagnostic agents, nutraceuticals, fragrances, sunscreen agents, etc., have received the highest attention [18,19] as most of these turn into complex mixtures of PEPs when present in an aquatic environment.

The data compiled in Table 1 are taken from reference [2], where the information was collected from 45 published research articles from various sources. All the WWTPs included primary, secondary and in some cases, even the tertiary treatment. In order to obtain quantitative results for the data mining only the concentrations and removal efficiencies of WWTPs in the dissolved phases such as water sources were included. The median and standard deviations were calculated from three or more concentrations, but only average data are given.

The dioctyl phthalate, also known as DOP, is commonly used as an ingredient in personal care products, food packaging materials, blood containers, and tubings; these are to be treated quite effectively to eliminate their toxicity levels [20]. Polychlorinated biphenyls (PCBs) are another group of PEPs that generally exist in fatty tissues of the humans and are frequently discharged in the environment from various industries and are generally deposited in the sediments due to their limited solubility in water [21]. On the other hand, polyaromatic hydrocarbons (PAHs) are the listed hazardous PEPs on a priority basis by the USEPA. For instance, bisphenol-A is used as a raw material for polycarbonate-based healthcare plastics products. Deblonde et al. [2] carried out a survey on the efficiency of WWTPs to remove the PEPs.

The concentration of PEPs in effluent water ranged from as low as 0.007 to as high as 56.63 g/L, but their removal rate ranged from 0 to 97 %. Phthalates showed > 90% removal, while for antibiotics it varied from 50 to 71%. Analgesics, anti-inflammatory and beta-blockers are the most resistant to degradation with a value of 30–40%. The removal efficiency of pharmaceuticals such as tetracycline, codeine was alarmingly low (> 10%) (see in Table 1). Dyeing of fabrics in textile mills consume enormous amounts of water of which > 98% will end up as wastewater containing PEPs. Majority of textile wastewater will therefore, combine with the urban wastewater, sewage and surface waters to end up contaminating the groundwater, surface water sources as well as the soil [24,22,23]. Organic dyes and metal traces used for dye preparation will further contaminate food that may directly affect the human health (see Table 3).

Various MBSPs for the treatment of PEPs

MBSPs are the well-known separation technologies providing a variety of applications in water desalination, toxic metal separation and recovery of valuables. The membrane processes depend on the nature of membranes that are produced from a variety of materials including polymers, ceramics, zeolites etc., having specific filtering features that depends upon the surface charge, pore size, membrane morphology and hydrophobicity/hydrophilicity characteristics. The MBSPs are available in several modules such as MF, UF, NF, RO, and FO that utilize different types of membranes depending on their pore sizes and morphologies as well as specific separation needs as displayed in Fig. 3. The mode of separation in each of these processes varies from solution-diffusion to molecular diffusion to size exclusive principle [25].

MF membranes have larger pore sizes (0.1 to 5 μm) than the UF membranes, which typically reject materials in size range of 0.1–10 μm. On the other hand, UF membranes with pore sizes of 0.01 to 0.1 μm reject colloidal particles, macromolecules, biopolymers, and viruses whose sizes generally range from 0.01 to 0.2 μm, and the process is based on the size exclusion principle. Commercially, UF has been widely used for wastewater treatment, recovery of surfactants in industrial cleaning, food processing, protein separation, etc. The UF membranes are fabricated from cellulose derivatives, inorganic materials such as TiO_2, Al_2O_3, ZrO, etc in addition to typical polymers such as poly(a__crylonitrile) (PAN), poly(sulfone amide) (PSA), poly(ether sulfone) (PES), poly(vinylidene fluoride) (PVDF), etc. [26].

NF membranes reject molecules in the size range of 0.001–0.01 μm, which includes most of organics, biomacromolecules, and a variety of metallic salts (beyond divalent salts). The performance of NF falls between RO and UF, while the RO membranes are non-porous, prepared from dense polymers with voids, free volume channels or pore sizes ranging from ~0.0001 to 0.001 μm. The RO membranes separate low molecular weight minerals, including metal ions [25]. The most common applications of RO are in the treatment of pulp and paper mill effluents to produce potable water [28,29]. In any of the above membrane processes water flux, high PEP rejection, engineering design, stability under stress, chemical resistance and operating temperature as well as pressures applied govern the choice of polymers [30–34]. In recent years, ceramic or zeolite composite membranes have emerged

as high-performance RO and NF membranes that are successfully commercialized in PEP separations [35–41]. Various configurations based on hollow fiber, tubular, and spiral wound, and flat sheet structures have been employed in domestic and industrial wastewater treatment applications.

The RO technology developed for water desalination studies [42,43] has several issues such as high energy requirement, membrane fouling, and concentration polarization. This has prompted researchers to develop osmotically driven forward osmosis (FO), in which the osmotic gradient across the membrane plays an important role in mass transport and separation [44,45]. Thus, FO is more suitable and energy efficient for treating the feed with a high fouling tendency (e.g., landfill leachate), which may not be economical by RO. However, the standalone FO has some niche applications, such as fertilizer dilution and fruit juice concentration. Initially, FO has been treated as an efficient pre-treatment step for subsequent processes in which purified water can be recovered from the diluted draw solution [44–46]. In the following sections, we will discuss the individual MBSPs for the treatment of PEPs.

Microfiltration (MF)

Research efforts on the utilization of MF have concentrated on the removal of colloidal particles, dyes, organic matter and other high molecular weight soluble PEPs from the waste streams. MF has been generally employed in combination with other techniques for the removal of complex industrial PEPs. For instance, domestic wastewater containing hormones such as estrone (E1), 17β-estradiol (E2), and 17αethynylestradiol (EE2) [47,48] as well as bisphenol A (BPA) that are classified as endocrine disrupters [49]; These compounds even if present in trace quantities can seriously damage the human endocrine system. In efforts to solve this problem, Han et al. [50] employed the bench scale crossflow MF system using a series of membranes prepared from polyether sulfone (PES), cellulose acetate (CA), nitrocellulose, polyester, regenerated cellulose, and polyamide-66 (PA). For the PA membranes having a pore size of 0.2 μm, the wastewater containing 0.2 μM estrogens showed sorption capacity of 81 L m^{-2} (0.44 μg cm^{-2}), while for E1, 150 L m^{-2} (0.82 μg cm^{-2}) for E2, 208 Lm^{-2} (1.23 μg cm^{-2}) for EE2, and 69 L m^{-2} (0.32 μg cm^{-2}) for BPA. The surface adsorption of some of these PEPs at higher concentrations severely affected the membrane performance, causing membrane fouling due to the presence of organic matter in the feed that has significantly affected the flux of PA membrane. In any case, all the PEPs showed a consistent interaction with the polyamide membrane via H-bonding, thereby showing their efficient removal from the feed streams. The above studies indicate the usefulness of PA membranes compared to other cellulose-based membranes used for the treatment of biowastes from polluted water sources.

Health and safety regulatory authorities are continually documenting the risks associated with the presence of micro-PEPs involving. progesterone. Apart from MBSPs, Utrilla et al. [51] applied the adsorption method using activated carbon and biopolymers to separate micro-PEPs from wastewater sources, but these methods face shortcomings due to high-pressure drops, clogging, slow mass transfer and lack of appropriate techniques to recover the adsorbed materials. Realizing these drawbacks, Ragab et al. [52] employed the spiral-

wound configuration using zeolite imidazolate metal-organic framework (ZIF-8) nanoparticles incorporated into poly(tetrafluoroethylene) (PTFE) double layer polymer membrane in an MF mode that provided shorter bed height and larger pore s for convective flow. Here, the ZIF-8 nanoparticle-induced MF membrane showed high flux assizes giving a rejection rate of as high as 95% for the PEPs (hormones) even at low operating pressures. The high rejection efficiency data are the result of hormones chemically interacting via H-bonding with the high surface area of ZIF-8 nanoparticles. Therefore, such an approach is good for separating micro PEPs, such as hormones from the waste streams.

The pharmaceutically active compounds (PhACs) such as diclofenac and ibuprofen if present in the concentration ranges of 0.14–1.48 μg/L and 160–169 μg/L [53,54] can be degraded using the UV-based TiO_2 photocatalytic process [55]. However, the photocatalyst used in these processes has to be separated from the contaminated wastewater in order to obtain disinfected potable water. A hybrid MF can be useful in these applications for separating not only the PEPs but also to simultaneously recycle the photocatalyst TiO_2. In continuation of these efforts, Fischer et al. [56] suggested an in-situ TiO_2 synthesis process to develop composite membranes with PVDF polymers using titanium tetra-isopropoxide (TTIP). Furthermore, these photoactive TiO_2-induced composite membranes were used to remove the degraded methylene blue, diclofenac and ibuprofen. Further, the high concentration PEPs, such as carbamazepine, diclofenac, atenolol, azithromycin erythromycin and pesticides (162–240 ng/L) were removed from wastewater in a treatment plant to the extent of ~98% using hybrid MF-RO process [57]. This work demonstrates the performance of a pilot wastewater treatment plant for on-site effluents of a urban wastewater facility. The multi-monitoring approach included selected pharmaceuticals as emerging environmental contaminants, and a group of pesticides to reduce their concentration levels to a minimum of nano-concentration levels.

Liu and Wong [58] in a review article summarized the current contamination status of different PEPs including sewage, surface water, sludge, sediments, soil, and wild animals, by the pharmaceutical and personal care products (PPCPs). The authors further evaluated the adverse effects of these PEPs on human health and hygiene. However, the authors did not mention deeply about the membrane technologies but discussed more about other technologies that are based on chemical treatment methods; they further assessed the potential ecological and health hazard nrisks. In continuation of research efforts on the removal of PPCPs, Wang et al. [59] employed the composite membranes loaded with single-walled and multi-walled carbon nanotubes (SWCNT and MWCNT) onto PVDF membrane surface that significantly enhanced the removal rate of PPCPs, thus demonstrating the potential of MF technology for water treatment polluted with PPCPs. The removal of triclosan (TCS), acetaminophen (AAP), and ibuprofen (IBU) were achieved from 10 to 95%, which increased with increasing number of aromatic rings as well as specific surface area of the fillers. The variation of solution pH from 4 to 10 also influenced the PPCP removal rate up to 70% and higher removal was observed for neutral PPCPs than with the ions due to the reduced electrostatic repulsion. The capability of these membranes to remove PPCPs may be due to the favorable PPCP–CNT interactions.

Ultrafiltration (UF)

Unlike the MF process, UF has a solute rejection regime of above 2 kDa molecular weight for the separation of macro-PEPs. Considering that many of the PEPs fall under the category of macromolecular range, UF has been successful in treating such PEPs from wastewaters [60]. However, for the removal of macro-PEPs in the wastewater containing other organics, UF alone may not produce ultrapure water. In such situations, the UF in combination with the commercial NF membranes can be used to achieve the desired levels of water purity by removing PEP-contaminated secondary effluents [61]. The study included the removal of eleven PEPs present in the municipal secondary effluents that contained various pharmaceuticals and pesticides. The separation was achieved mainly by adsorption of contaminants on the membrane surfaces, since adsorption is the principle mechanism for micropollutants retention by UF membranes, while size exclusion and electrostatic repulsion at high pH values are dominant for NF membranes. The results revealed that both UF and NF are necessary for secondary effluent treatment.

Several studies suggested that hybrid processes in which RO membrane showed severe fouling can be combined with coagulation and disk filtration methods to reduce the fouling. For instance, Chon et al. [62] developed a large-scale water reclamation unit comprising of a combination of coagulation and disk filtration (CC–DF) along with UF/ RO membranes to remove PEPs such as atenolol, carbamazepine, caffeine, and sulfamethoxazole, but the method was not effective to remove PEPs, while RO alone could achieve high removal efficiency. Interestingly, the negatively charged PEPs were retained efficiently by the tight membranes compared to neutral pollutants. In all these studies, membranes were washed by desorbing PEPs from the surface of UF and RO membranes. The removal of micro-PEPs by the hybrid CCDF and UF method was not dependent on the molecular weight of PEPs, but they showed a critical dependence on the RO process.

Micellar-enhanced UF can be a cost-effective alternative to separate the PEPs. In this pursuit, Acero et al. [63] used different micelles, such as sodium dodecyl sulphate (SDS), Triton X-100 (TX-100), Tween 20 (TW-20), cetylpyridinium chloride (CPC) and cetyltrimethylammonium bromide (CTAB) to improve the UF performance for separating PhACs (acetaminophen, metoprolol, caffeine, antipyrine, sulfamethoxazole, flumequine, ketorolac, atrazine, isoproturon, 2-hydroxybiphenyl and diclofenac). It was observed that CPC and CTAB, cationic micelles remove the negatively charged and hydrophilic PhACs. Among all the micelles studied, CPC showed the optimum separation up to 95%.

Several studies included the use of activated carbon as a pre-treatment as well as a post-UF adsorption step for the retention of PEPs. For this purpose, powder-activated carbon-UF or granular-activated carbon-UF was suggested for removing low molecular weight PEPs, which otherwise would be difficult to remove using UF alone [64]. In this study, activated carbon enhanced the rejection rates of PEPs and membrane fouling was minimized. A combined treatment approach based on adsorption and/or coagulation was also employed by Acero et al. [65] using activated carbon in a stepwise UF treatment plant to remove eleven emerging PEPs (acetaminophen, metoprolol, caffeine, antipyrine, sulfamethoxazole, flumequine, ketorolac, atrazine, isoproturon, 2-hydroxyphenyl and diclofenac). In this investigation, low PACs dose of 10–50 mg/L was adequate to remove the PEPs from

wastewater and the importance of combined treatment approach was discussed. Continuing the activities using hybrid approaches.

An UF-NF hybrid system was used by Benitez et al. [66] for separating four PhACs (amoxicillin, naproxen, metoprolol, and phenacetin) from the secondary effluents. In both UF and NF, permeate flow was influenced by the membrane morphology, applied pressure, and operating temperature. The retention coefficients in UF membranes were higher for naproxen than metoprolol with the lowest being phenacetin. In the case of commercial scale membranes, the trend was highest for amoxicillin and lowest for phenacetin, due to tight pore size structures, leading to direct rejection and electrostatic repulsion associated with the membranes. In this study, except phenacetin, NF achieved the highest retention of 80% for PhACs. Further, the flux decline and membrane fouling, were higher for UF, especially while treating the secondary effluent. It may be noted that observations made in this study were almost identical to those by Acero et al. [65]. A comparative assessment of the existing treatment techniques was considered by Boleda et al. [67] using a UF-RO process for removing twenty-nine PhACs to demonstrate that advanced treatment processes can be more efficient over the conventional treatment approaches in eliminating the PhACs up to 94%. This can be attributed to carbon filtration, which is suitable for removing the conventional pollutants, but not the emerging PEPs. This approach was found to be useful especially in drinking water treatment plants for the treatment of an effluent comprising oxy-chlorinated compounds.

Electrochemical oxidation (ECO) processes for waste-water treatment have been widely explored as these methods have proven to be efficient and versatile to handle wastewater. However, to achieve an efficient and cost-effective treatment, these methods require that wastewater should have relatively high conductivity. These methods have the advantage of coupling electricity-driven reactions with the in situ generation of oxidants, which makes this approach an attractive treatment alternative [68,69]. Overall, ECO approach was able to eliminate the PEPs from the RO concentrate streams. Urtiaga et al. [70] applied the ECO method to remove PhACs using a point-of-use hybrid UF-RO system. For major PEPs such as atenolol, bezafibrate, caffeine, and diclofenac, UF was useful up to 20%. The concentrations of PEPs in permeate varied between 4 and 44 ng/L (see Fig. 4 for process details). The ECO of RO reject with diamond electrodes were able to decrease the total PEP contents from 149 μg/L down to 10 μg/L. The authors concluded that at high electro-oxidation intensity, PEPs' concentration reduced drastically.

The impact of surface stress on membrane fouling control was studied by Wray et al. [71] for the removal of organic PEPs using an UF treatment plant for sixteen different PhACs and EDCs. The results of this study showed that retention was dependent on specific water matrix in which increased retention was achieved with higher concentrations of organic matter. Controlled study showed that contaminant scale formation did not act as the secondary selective barrier for retaining the macromolecules and hydrophobic micro-PEPs. Under higher shear stress conditions, a lower fouling retention was improved for water contaminated with higher concentrations of organic matter and biopolymers. The interaction between organic micro-PEPs, mainly hydrophobic, neutral compounds and biopolymers in solution, was responsible for enhanced retention in all the cases.

Often, UF fails to achieve the required standards, and hence, various hybrid technologies have been designed and tested including AOPs [72]. Acero et al. [73] used AOP techniques for the removal of a series of PEPs, such as 1-H-benzotriazole, chlorophene, and nortriptyline, dissolved in different streams. Here, the pre-treated wastewater was fed into UF, and both permeate, as well as retentate were then treated using ozone or chlorine separately. The UF step removed all the PEPs traces except 1-H-benzotriazole. Chlorination and ozonation were also found to be effective in reducing PEPs from the concentrated stream, providing effluent that can be recycled using the activated sludge treatment in WWTPs. These data demonstrate the usefulness of both the treatment methods for the removal of micro-PEPs.

Recently, ultrasound treated AOPs have been used for removing the priority organic PEPs from wastewater and solid wastes [74]. Though ultrasonication works for both biodegradable and non-biodegradable/ refractory organic compounds, but these methods are not widely explored for large-scale applications. Cailean et al. [75] employed the hybrid ultrasonication-UF for the removal of 4-chlorophenol (4-CP), which by the use of homogeneous Sono-Fenton process could degrade 4-CP in less than 1 h up to about 45%. The ultrasound techniques can be effective to control membrane fouling. For instance, Naddeo et al. [76] used the ultrasonic assisted UF process with varying frequencies for cleaning the UF membrane surfaces during PEP removal, which reduced the membrane fouling even at lower frequency of 35 kHz. Especially when PhACs, such as diclofenac, carbamazepine, and amoxicillin are difficult to remove from WWTPs using the ultrasonic method [77], the hybrid UF coupled with ultrasonic irradiation [78] could reject PhACs from wastewater, while UF alone was ineffective as it could only remove up to 10%. Using ultrasonic irradiation, 99.5% PEPs could be removed at 35 kHz frequency.

Nanofiltration (NF)

NF has a much tighter pore regime than UF membranes, thus adding several benefits, such as divalent salts and textile wastewater recovery. A case study was performed by Neira-Ruízet et al. [79] on untreated wastewater from agricultural and urban wastes to remove five PEPs viz., carbamazepine, BPA, triclosan, butyl benzyl phthalate, and 4nonylphenol using a commercial NF-270 under a pressure of 800 kPa. The study employed a pre-treatment step for preventing the scaling. The PEPs removal was increased for hydrophobic compounds due to adsorption onto membranes, while water solubility reduced the retention of BPA. Lopen-Muñoz et al. [80] employed NF for the removal of several emerging PEPs viz., sulfamethoxazole, diclofenac sodium, hydrochlorothiazide, 4-acetamidoantipyrine, nicotine and ranitidine hydrochloride using commercial NF-90 and NF-270 membranes. At low pressures, the rejection of PEPs varied almost linearly and steric hindrance and dynamic interaction between the solute PEPs and the membrane interface were responsible to achieve the desired rejection. Solute retention by NF-90 was quite high (> 95%), but for NF-270, it was low, ranging from 75% (for nicotine) to 95% (for ranitinide hydrochloride). The authors concluded that permeate flux and PEPs rejection rate were dependent on the physicochemical properties of pharmaceuticals and membranes in addition to transmembrane pressure.

Polyamide membrane exhibits surface adsorption property leading to poor separation performance [81]. Using surface adsorption as a parameter, Semião et al. [81] studied the adsorption and retention of estrone and estradiol using polysulfone, polyester and polyamide membranes. Among all the membranes tested, polyamide NF membranes showed the highest hormone adsorption. Selective layer morphology and pore size were critical in surface adsorption and retention of PEPs. The size of the pores in association with steric exclusion and pH of the medium were also crucial for surface adsorption of hormones at neutral pH, the high solute and membrane interaction (compared to at pH 11) was attributed to electrostatic repulsive effect of the solute from the membrane surface. In another study, the presence of hormonetype moieties and tert-butyl phenol in secondary wastewater was studied using NF-270 [82]. The authors used a commercial membrane in which PEPs were retained up to 90%. Similar to the work reported by Semiao et al. [81], the present data further demonstrated the importance of steric exclusion for the separation of hormone-mimicking compounds. The influence of pH, ionic strength, and organic matter content was responsible for the separation.

The PhAC elimination using traditional treatment processes have shown limited success [83]. Kim et al. [84] used grafted polyamide membranes with methacrylic acid cross-linked with ethylene diamine (ED) to separate BPA, ibuprofen and salicylic acid to demonstrate 95% rejection for BPA, whereas pristine membrane showed a rejection of 74%. Also, the rejection of ED-modified membrane for ibuprofen and salicylic acid was slightly lower than those of the metallic acid modified membranes. Interestingly, succinic acid membranes recovered their electro-negative surface that helped to retain all the PEPs in the concentrate. In a study by Sun et al. [85] NF hollow fiber membrane having a charged surface was used for the efficient removal of cyclophosphamide. This membrane was fabricated using a hyperbranched polyethyleneimine (PEI) as a cross-linker onto the polyamide-imide backbone. The spongy-like porous membrane support provided a high flux with high structural stability for water permeation even at elevated pressures. Specifically, after crosslinking with PEI, membrane pore size reduced drastically, and surface became more hydrophilic with a positive charge. These synergic effects were responsible for increasing the rejection of ciprofloxacin. Also, high molecular weight of PEI of 60 K has a tremendous effect to exhibit the highest rejection. In continuation of these efforts, Nghiem et al. [86] evaluated the retention of non-ionizable carbamazepine in the presence of ionizable PhACs, sulfamethoxazole and ibuprofen using NF to show that retention of carbamazepine in the concentrate was independent of feed chemistry. The PhAC retention increased when the compound was transformed from neutral to negative charge with an increase in its pKa value. Therefore, retention of the negatively charged sulfamethoxazole and ibuprofen was increased due to increase of ionic strength.

Along with the MBSPs, adsorptive treatment [87] and AOPs [88] have also been attempted for eliminating PEPs from the wastewater. Liu et al. [89] performed a feasibility study of removing antibiotics, namely norfloxacin (NOR), ofloxacin (OFL), roxithromycin (ROX) and azithromycin, from a wastewater treatment plant as per the separation scheme depicted in Fig. 5. High rejections up to 98% could be obtained in all NF experiments. The UV/O_3 process achieved removal efficiencies up to 87%, dissolved organic carbon (DOC) of 40%, increased BOD/ COD ratio of 4.6 times, and a reduction of acute toxicity up to 58%.

Overall, the study demonstrated that NF could efficiently remove all the antibiotics from WWTP effluents, but UV/O$_3$ was able to eliminate antibiotics from the NF concentrate, thus achieving zero discharge of micro-PEPs from the WWTPs.

Developing novel membranes for purification of active pharmaceutical ingredients (APIs) from the classes of genotoxic impurities has been a challenging task [90]. In this pursuit, Martínez et al. [90] used PES-NF membranes to recover 1-(5-bromo-fur-2-il)-2- bromo-2-nitroethane in a crossflow NF configuration with retentions of > 80%. The most prominent results in terms of flux of ethanol were obtained from the membranes prepared with 25% and 75% of PES along with a commercial NF-270 membrane. Organic solvent NF (OSNF) or organophilic NF (ONF), is an emerging technology used for organic-based effluent treatment [91]. Székely et al. [91] used OSNF to remove genotoxic impurities from a total of nine API model feeds having macrolides and amides. The study focused on replacing extractions in traditional purification techniques that helped to API recoveries up to ~80%. In a continuing study on the use of OSNF, Székely et al. [92] evaluated the feasibility of OSNF method for the removal of 1,3-diisopropylurea (IPU) at a dilution ratio of 3 to achieve 90% removal with as low as ~2.5% loss of API. A novel IPU selective molecularly-imprinted polymer (MIP) was also used to remove the trace amounts of IPU, thereby achieving 83% removal for the feed containing 100 ppm concentration in a single step. Here, the combination of OSNF with diafiltration (DF) at a dilution ratio of 3:1 MIP showed a reduction of IPU from 100 mg IPU/g of API to 2 mg IPU/g.

Agricultural fields require the heavy usage of pesticides and hence, their elimination from wastewater sources is necessary to avoid the risk factors. In this regard, Ahmad et al. [93] used four types of commercial NF membranes (NF-90, NF-270, NF-200 and DK) of ~200 MWCO to separate two prominent pesticides viz., dimethoate and atrazine from the contaminated water sources. Among all the membranes tested, commercial NF-90 showed the highest rejection, while NF-90 showed the most significant potential for acetaminophens retention from aqueous media. Perfluro octane sulfonates (PFOS), a new class of PEPs with fluorinated alkane sulfonates, are widely used in surfactants, coating materials, fire retardants, lubricants, metal plating solutions and polymer additives [94]. PFOS are persistent, bio-accumulative, and toxic even at trace concentrations [95]. Among several methods employed for effective removal of trace amounts of PEPs from wastewater, Zhao et al. [96] attempted using NF-270 for removing PFOS from the simulated surface water containing calcium ions. The results showed that increase of calcium chloride concentration enhanced PFOS rejection from 94% to 99% for a feed containing 100 ppb PEP.

Chlorination has been the widely used disinfectant in wastewater treatment. Recent studies have reported that chlorination of organic matter in freshwater results in the formation of disinfection by-products. For instance, trihalomethanes (THM) is a by-product belonging to a new PEP class. NF-200 membrane was used by Uyak et al. [97] to enhance the retention efficiencies of THM. Verliefde et al. [98] summarized the separation data of NF membranes in Table 2 for various PEPs. The data display that NF is effective in removing larger PEPs, smaller hydrophiles as well as charged micro-PEPs. It was suggested that rejection of PEPs by NF can be qualitatively predicted, yet it is a debatable question as to whether RO is preferred over NF as regards the removal efficiencies including the operation and

maintenance costs. According to Yangali-Quintanilla et al. [99], NF appears to be an efficient technique for removing the organic PEPs compared to RO. Neutral PEP such as dioxane can be removed from ~82% to 85% using both NF and RO, but for ionic compounds, removal efficiency can be > 97%.

Composite membranes are the recent trends. For instance, Zeng et al. [100] developed dopamine (DA)- modified halloysite nanotubes (HNT)/PVDF blends by functionalizing HNTs with DA and blending with PVDF. These membranes were tested for removing direct red-28 (DR-28), direct yellow-4 (DY-4) and direct blue-14 (DB-14) dyes. The blend membranes increased the water flux by about 80% compared to nascent counterparts. The modified membranes showed dye rejection of 86% for DR-28, 85% for DY-4 and 94% for DB-14. In efforts to separate micro-PEPs from wastewater and in drinking water sources, Ilyas et al. [101] recently developed weak polyelectrolyte multilayer (PEM)-based hollow fiber NF membranes. Notably, the PEMs consisting of weak polyelectrolytes, such as poly (allylamine hydrochloride) (PAH) and poly (acrylic acid) (PAA) were coated in a layered fashion onto the UF support to obtain PEM-based NF membranes. These membranes were further used to investigate the retention of varying size (200 – 400 g/ mol) micro-PEPs, which were charged and hydrophilic. These micro-PEPs included: atenolol, sulfamethoxazole, naproxen, atrazine, and bezafibrate and membranes prepared at a pH of 6 showed the highest retention up to 80%. Similarly, multi-walled carbon nanotube (MWCNT)-based membranes were prepared [102] and used for the removal of primary effluent PEPs from wastewater. Here, coagulation was used as a pre-treatment to NF operation to overcome the interference of biopolymers and humic acid. But this approach has shown a limited separation ability.

Reverse osmosis (RO)

Recently, there has been a growing interest to utilize hybrid RO/NF membranes for the treatment of PEPs from the sewage and industrial wastewater. Boleda et al. [103] made an effort to study the feasibility using of RO in eliminating certain drugs and metabolites from secondary treated wastes in a pilot plant. Three different commercial membranes (LE, BW30, and XFR) were used for the rejection of a range of PEPs, but no significant data were observed. Realizing the drawback of this study, Ozaki et al. [104] in his study on retention efficiencies of thirteen pharmaceuticals and personal care products (PPCPs) and five EDCs by simultaneous adsorption, size exclusion, and diffusion methods observed that size exclusion was dominant in the tight NF membrane. Separation was improved when solution pH was higher than solute pK_a values, suggesting the importance of electrostatic repulsion.

Drinking water treatment plants equipped with RO and activated carbon filters have been employed for the removal of several micro-PEPs [102]. Here, rejection rates for hydrophilic and small MW sPEPs, such as nitrosodimethyl amine, dioxane, and 2-methylisoborneol were quite low, but solute removal by activated carbon filtration was robust. Also, rejection of antibiotics by both RO and NF processes was > 98% [105,106], where for low MWCO NF membrane, retention for smaller size antibiotics was ineffective, which varied from 0.517% to 0.976% for RO and tight NF, respectively. The N-nitrosodimethylamine

(NDMA), a member of a family of potent carcinogen, N-nitrosoamine, generally found in potable water as a result of disinfection carried out on wastewaters [107]. The critical level of concentration of NDMA in drinking water [108] is estimated to be 10 ng/L. Plumlee et al. [109] observed that solid phase extraction (SPE) method used for NDMA detection showed its presence in the secondary effluent up to 20–59 ng/ L, but by using RO with TFC membranes the NDMA rejection up to ~50–65% was possible.

BPA is another possible toxic PEP that has been widely explored by membrane technologies. In one particular study, Khazaali et al. [110] used the low-pressure RO at the critical range of pressure (408–476 kPa) for the effective separation of BPA. It was found that by changing the pH from 8 to 10, BPA rejection decreased, but when BPA was ionized, the interaction between the ions caused higher rejection rate. At more elevated feed concentrations, the effect of concentration polarization was more significant, and BPA concentration in the permeate was elevated. In any case, a maximum of 87% BPA rejection was possible at 50 mg/L feed concentration.

Cyclophosphamide (CP) is one of the commonly used drugs in chemotherapy, which adversely affects the living organisms if present in water. The rejection of CP in feed water using NF, RO and MBR was investigated by Wang et al. [111]. It was found that RO was effective in CP retention up to 90%, but the rejection of CP was 20–40% in NF. For MBR effluent treatment, CP rejection rate by NF was enhanced, suggesting that both MBR-RO and MBR-NF hybrid systems are promising for the treatment of real wastewater containing CP.

In continuation of the research efforts to address the removal efficiencies of micro-PEPs, Al-Rifai et al. [112] evaluated a range of micro-PEPs at different processing conditions in a wastewater recycling plant. The removal efficiencies of eleven PhACs and two EDCs were examined using MF and RO processes to find that salicylic acid was abundant in WWTP effluent (11–38 μg/L), followed by BPA (6 to 23 μg/L). Further, the concentration of all PEPs decreased drastically from primary to secondary treatment. Significant retention efficiencies in recycled water was > 97%, resulting in product water concentrations of < 0.1 μg/L for most PEPs (apart from BPA (0.5 μg/L)). Even though > 0.5 μg/L was measured in product water for BPA, but its presence is a serious concern. In a parallel study, AOP was combined with RO as an alternative approach to remove PhACs from the organic matter effluent and other inorganic constituents. In efforts to address this problem, Abdelmelek et al. [113] examined the removal of PhACs using RO and the retentates were further treated by AOP. Here, degradation was monitored by excitation-emission matrix spectroscopy, where the *OH radical associated with proteins in RO retentate suggested efficient removal of PhACs. The results from AOP treatment also revealed that MBSP could efficiently remove the PPCPs from the effluent even in the presence of both organic and inorganic constituents.

A new class of PEPs known as β-blockers was identified that can cause severe risks to human health. Among these, some are the commonly used drugs, such as metoprolol and propranolol, classified as potentially toxic to aquatic organisms. Benner et al. [114] studied the effect of ozonation for the mitigation of β-blockers. The ozonation of RO brine effluents

was sufficient to eliminate the β-blockers. However, tests on chlorinated and non-chlorinated WWTP effluent showed increased ozone stability, giving a decrease in *OH radical exposure, proving the effectiveness of RO for the removal of β-blockers.

The treatment of sewage wastewater has been a challenging task using the conventional methods. However, realizing that oxidation processes can reject the organics from the contaminated streams, James et al. [115] developed a hybrid advanced oxidation reverse osmosis (AOP-RO) method to treat PEPs from the secondary municipal wastewaters. Using this method, > 99% of PEPs and endocrine disrupting chemicals (EDCs) were removed successfully in a pilot-scale experiment. Interestingly, for the EDC removal such as N-nitrosodimethylamine (NDMA), the H_2O_2 dose was crucial. Further, Alonso et al. [116] used a pilot scale commercial spiral wound membrane to remove the antibiotic (ciprofloxacin) from wastewater with a high ionic strength using RO, which could remove ciprofloxacin up to > 90%. From the forgoing, it is realized that RO method can not only be useful as an effective technique for water desalination, but also quite useful for the treatment of various effluents.

Forward osmosis (FO)

In recent years, forward osmosis (FO) is becoming more popular among other MBSPs used for wastewater treatment as well as desalination. The method utilizes osmotic gradients artificially created by the high concentration draw solution across the membrane. In contrast to other MBSPs, FO is less vulnerable to fouling and hence, the method finds wider applications in wastewater treatment, food industry, to concentrate biomacromolecules, recover valuable metals, remove toxic metals, etc. [117]. FO operates at zero hydrostatic pressure, providing a sustainable water treatment, but the method has not yet reached the commercial success except for seawater desalination, probably because of lack of suitable FO membranes. The essential components required for efficient FO process include: (i) membranes that are less prone to susceptibility to internal concentration, (ii) efficient draw solutions and (iii) effective draw solution recovery process.

Quite interestingly, aquaporins that are the naturally occurring water channels in proteins are used as semi-permeable water pathways in FO [118]. Aquaporins embedding vesicles in TFC (< 200 nm) membranes can be deposited onto a porous polysulfone flat sheet support [119] to act as FO channels. These membranes made of aquaporin have shown > 90% rejection of urea with a pure water permeation rate of 10 L/m^2 h against 2 M NaCl as the dissolved salt. Innumerable studies have been performed utilizing FO for the separation of PEPs from wastewater sources. Here, we will discuss only the representative data collected from various sources and more details can be found from the literature. For instance, a study by Hancock et al. [120] investigated the rejection of PEPs using FO and compared its efficiency with a hybrid FO-RO system both at the laboratory and pilot scales as shown in Fig. 6. Using both the systems, more than thirty PEPs of different kinds, including non-ionic, hydrophobic, negatively and positively charged species have been analysed and found that rejection of non-ionic compounds increased with increasing molecular weight of PEPs. The RO showed better rejection rate than the FO for BPA, but FO has shown better rejection

rate up to > 99% for methylparaben, oxybenzone, amitriptyline, and triclosan pesticides compared to RO.

The above findings prompted several researchers to focus on the separation of PEPs of different kinds. In one such a study, Linares et al. [122] investigated the differences in the rejection of thirteen different PEPs found in wastewater sources containing five hydrophilic nonionic, three hydrophobic nonionic and four hydrophilic ionic micro-compounds. The secondary wastewater effluent (SWWE) was used as the feed and the resulting effluent was desalinated at a low pressure with the RO membrane. In standalone FO mode, the rejection of hydrophilic neutral compounds varied between 49% and 85%, while for hydrophobic neutrals, the rejections ranged from 40% to 88%. For ionic PEPs, rejections ranged between 93% and 97%. This type of tendency suggests different types of interacting modes of PEPs with the membrane material.

In a continuing study to utilize hybrid technologies, Alturki et al. [123] tested different commercial cellulose acetate (CA)-based membranes for FO, pressure retarded osmosis (PRO) and RO processes. Compared to other NF membranes of similar MWCO, such as the commercial cellulose triacetate (CTA) membrane, CA membranes showed a higher water flux with better PEPs retention. In the RO mode, electrostatic interactions played a significant role in the retention of electro-active PEPs. In FO and PRO modes, the retention of active PEPs was governed by the electrostatic interactions between the membrane matrix and the solute, while the rejection of neutral compounds was dominated by the size exclusion in which retention was higher for PEPs with high MW. In all the cases, retention of neutral PEPs was higher in FO compared to RO.

Haloacetic acids (HAAs) are the well-known disinfection by-products (DBPs) present with highest concentrations in chlorinated or chloraminated sewage treatment plant effluents. Trichloroacetic acid (TCAA) concentration can be as high as 471 μg/L in chlorinated wastewater effluent as analysed by ultra-performance liquid chromatography-electrospray ionization tandem mass spectrometry (UPLC-MS/ MS) [124]. FO was employed by Kong et al. [125] to study the rejection of HAAs by performing reverse draw solute permeation experiments. The retention ratio for each HAA increased with an increased draw solute (DS) concentration for the active layer facing the feed water (ALFW) orientation. The rejection rates for all the HAAs were more than 95% for AL-FW orientation, but ranged from 74% to 89% for the active layer facing the draw solution (AL-DS) orientation in 1 M NaCl draw solution, while reverse draw solute flux of AL-FW orientation was lower compared to AL-DS orientation.

The processing of industrial effluents containing organic PEPs such as phenols, aniline, and nitrobenzene [126] is somewhat difficult because these may penetrate into the barriers of the existing treatment techniques, making them ineffective [127]. The eight commercially available activated carbons were studied for removing organic micro-PEPs to test their removal efficiencies. Among other MBSPs, RO was preferred for the removal of organic micro-PEPs, but high operating pressure in RO was expensive and membranes usually had fouling problems [128]. In efforts to address this issue, Cui et al. [129] compared the efficiency of FO in (i) lab-scale FO membranes under both FO and RO modes and (ii)

commercially available RO membranes to remove the organic PEPs. The lab-scale fabricated FO membranes having a thin-film polyamide layer onto the ultra-porous support provided rejections in the range of 72–90%. In FO and pressure retarded osmosis (PRO), effects of pH and membrane orientation on the permeate flux and PEP retention for carbamazepine and sulfamethoxazole were investigated [130] to find that permeate flux was lower in FO than in PRO mode. The retention of neutral carbamazepine was pH independent of both the operation modes, but its retention was lower in PRO mode than in FO. Authors suggested a steric barrier as the probable cause for such separation patterns for neutral carbamazepine in FO.

Direct contact membrane distillation (DCMD) and FO were studied [131] for the removal of estrone and 17β-estradiol. The DCMD showed > 99% for the hormone, > 99.9% for urea, and > 99% for ammonia rejections at a constant flux. On the other hand, FO removed estrone and estradiol equally, but hormone rejection was affected by the initial feed concentrations. The quantity of olive mill wastewater generated from olive oil industries is typically ~5 m^3/ton, leaving a high COD (220 g/L) in wastewater, but the presence of antibacterial phenolic compounds made it quite difficult to treat [132]. In this case, FO was also a useful technique to remove olive mill wastewater discharged from oil extraction industries. Another study by Gebreyohannes et al. [133] used a single step FO plant to purify olive mill wastewater against 3.7 M $MgCl_2$ draw solution up to the extent of > 98% rejection that included biophenols. On the other hand, MBR-based pre-treatment before FO could reduce up to 92%, resulting in 30% flux enhancement and the recovery rate was 95% pure water permeability with cellulose triacetate (CTA) membranes.

Han et al. [134] developed a hybrid process of FO–coagulation/flocculation (CF) for treating textile dye wastewater. FO was used for the spontaneous recovery of water from wastewater via FO-CF, which exhibited unique advantages of high-water flux and recovery rate with an initial water flux of 36.0 L/m^2 h and a dye rejection of 99.9% against 2 M NaCl as the draw solution. At high flux rates of around 12.0 L/m^2 h, 90% water recovery was achieved from the wastewater. The formidable issue regarding the trace containing PhACs from the wastewater using FO concentrate remained an unsolved issue. To address this problem, Liu et al. [135] designed an integrated FO system with an electrochemical oxidation (ECO) referred to as FO with ECO method. A synergistic effect was observed in this hybrid method wherein, antibiotic rejections by the FO were increased due to the degradation of antibiotics, while ECO was improved by this method (see Fig. 7). Results demonstrate that hybrid method has excellent rejection of antibiotics up to 98% by degrading > 99% of PhACs after 3 h of operation.

Both bench scale and pilot scale applications for landfill leachate treatment containing a range of PEPs has been investigated [136] by the FO process by a novel method combining activated sludge in hybrid combination with the FO for wastewater treatment and this approach has many advantages over other methods. A high rejection rate was achieved from FO method by retaining a small amount of PEPs in a biological reactor, thus significantly enhancing their retention time in the reactor. However, the recent report on short-term bench scale studies [137] indicated that OMBR may be a better alternative for the well-designed treatment solution to produce high-quality water.

Hybrid technologies

Membrane bioreactors (MBRs)

Except for membrane modules and aeration steps, MBR treatment is quite similar to the conventional activated sludge (CAS) treatment techniques in which biodegradation and separation takes place simultaneously. Radmanovic et al. [138] used both MBR and CAS methods to assess the removal efficiency of PhACs at different operating conditions. Among them, MBR showed higher PhAC-PEPs removal (~80%) than the CAS technique. The membrane part of MBR typically comprises MF regime (0.4 μm) pores, since the size of organic flocs to be separated from wastewater are around 10–100 μm. Even in some cases, low MWCO membranes have been used to improve the efficiency of MBRs [139], but the use of low, tight membranes increased the energy consumption since their permeability was lower than the loose MF membranes that requires high operating pressures. Petrovic et al. [140] studied the removal of PhACs using flat sheet (0.4 μm pore size) as well as hollow fiber (0.05 μm pore size) membrane modules. The PEPs removal in flat sheet was better than hollow fiber membrane module due to higher surface area and lower MWCO of UF offered by the hollow fiber module.

MBR units in paper mills have shown exceptional PEPs removal efficiencies when combined with MF. Also, dimensions of tubular membranes had an influence on the quality of permeate in which 8-mm tubular PVDF membrane installed outside the bioreactor drastically reduced the COD [141]. The MBR-treated effluent was re-circulated with no detrimental effect on product quality, which saved fresh intake of water from a paper mill for bleaching process by 80% and discharge by 50% [141]. In a pilot scale hybrid combination of MBR with NF, Li et al. [142] treated textile wastewater containing COD, organic PEPs, color, and turbidity to achieve > 90% removal efficiency with a simultaneous water recovery. The NF membrane showed considerable fouling due to the presence of protein-like substances and a small amount of humic acid (650–6,000 Da). In another study, performance of a commercial side stream membrane bioreactor (SSMBR) and submerged membrane bioreactor (SMBR) was studied for the treatment of textile wastewater [143]. The SSMBR showed COD removal up to > 90%, with a color rejection of 20–90%.

A two-stage MBR system was used [144] under extended sludge age condition to enrich the nitrifying bacteria. During the MBR operation, organic removal efficiencies exceeded 90%, while the phenolic PEPs such as BPA and 4-methyl-2,6-di-tert-butyl phenol (BHT) were removed to the extent of 65% and 75%, respectively. Furthermore, BPA and BHT were biodegraded to the extent of 88% and 75%, respectively by the enriched nitrifying sludge. A recent review by Besha et al. [145] addressed the PEP separation by a activated sludge and MBR processes. The author discussed RO, FO and MBRs methods along with their advantages for wastewater treatment. The review also provided an overview of PEPs on the microbial activities.

The sludge retention time (SRT) and liquid flux rate control the MBR process. Komesli et al. [146] investigated the removal efficiencies of five EDCs (diltiazem, acetaminophen, progesterone, estrogen, and carbamazepine) using one full scale and one pilot scale MBR plant considering the effect of SRT. Diltiazem was completely removed to the extent of >

85%. The carbamazepine was not removed in both the plants, while the removal of progesterone and estrogen remained identical in both the plants. The difference in performance of full scale MBR and pilot MBR is attributed to the occurrence of vibrations on membrane surfaces in full scale applications, which helped to remove the surface foulants.

Raghavan et al. [147] studied the removal of 12 antibiotics belonging to 5 different classes in an osmotic membrane bioreactor (OMBR). The FO showed > 75% rejection for all the antibiotics, but some antibiotics like ciprofloxacin and roxithromycin showed biodegradation as a significant removal pathway, while ofloxacin and roxithromycin showed the highest biosorption onto activated sludge. Over all, OMBR was effective for treating antibiotics from the wastewater. Park et al. [148] studied the effect of addition of two coagulants viz., polyaluminium chloride (PACl) and chitosan into MBR system for the removal of pharmaceuticals and PPCPs. By adding coagulants, membrane permeability increased remarkably 2.3 and 2.8 times for PACl and chitosan, respectively. Chitosan showed little effect as a coagulant in PPCPs removal, but PACl showed increased membrane efficiency up to 17–23%. Overall, the combination of MBR with coagulation could reduce membrane fouling and increase operation time.

On the whole, it appears that MBRs in conjunction with MBSPs are the efficient combination for removing PEPs. Among the different membrane processes, FO would be an ideal choice as it consumes lesser energy than other MBSPs such as RO and NF. It may be concluded that the main processes for biodegradation of emerging PEPs in the MBR system is the biodegradation catalyzed by enzymes. In terms of operation conditions, high solid retention time, low pH, higher nitrogen loadings and anaerobic conditions seem to favor biodegradation. However, longer retention time and unavailability of proper mechanism for degradation are some of the shortcomings of this process.

Photocatalytic membranes/reactors (PMs/PMRs)

Photocatalytic membranes (PMs) and photocatalytic membrane reactors (PMRs) have been of recent trends to provide greater synergistic advantages for PEPs removal, but these methods can be more effective when combined with MBSPs. In such a configuration, suspended photocatalysts can mineralize the organics to minimize fouling and enhance the membrane efficiency [149]. PMRs comprise of (i) TiO_2 powder suspended in the reactors and (ii) reactors with the immobilized TiO_2 onto the substrate material (e.g., glass, quartz, mesoporous materials, stainless steel or polymers) [150]. In the latter, location of where the photocatalyst is impregnated onto the support has some drawbacks. These drawbacks restrict the mass transfer and block the active surface, resulting in lesser access to irradiation and reaction mixture as well as the possibility of catalyst deactivation.

Among the various types of membrane reactors described in this review, PMRs are particularly interesting because it combines the advantages of classical photoreactors and membrane processes. Some of the main advantages of PMRs include simplification of cleaning/purification, no sludge production, and saving of chemicals as well as energy that make their utilization in the treatment of PEPs more attractive. Investigations have been made on both the configurations of PMRs, depending on the type of membrane modules.

Among these, the submerged membrane photoreactors have been successfully used for obtaining high-quality water, as depicted in Fig. 8 [151].

The design of self-cleaning membranes for eco-friendly separation have met with a limited success. The PMRs that simultaneously separate and mineralize the organic PEPs in the feed stream have the better potential as self-cleaning membranes. Thus, TiO_2-based PMs have shown advantages such as anti-fouling ability due to photocatalytic degradation of foulants and confining PEPs within the photocatalytic chamber. Photocatalysts also could offer high flexibility to suit to various membrane modules for industrial applications. Moosemiller et al. [152] performed concurrent membrane separation and TiO_2-based photocatalytic oxidation processes simultaneously using γ-Al_2O_3 and TiO_2 supported ceramic membranes and found them to be more stable [153].

Compared to other semiconducting metal oxides, TiO_2 received the greater attention due to its excellent characteristics to photodegrade organic PEPs present in contaminated water in the presence of UV light irradiation. The TiO_2/polymer composite photocatalytic membranes have multi-functional properties such as ability to photocatalytically remove the fouling of PEPs on membrane surface, the ability of high disinfection to produce clean water from wastewater at a high membrane-flux with a low fouling potential. Such composite membranes have excellent aqueous stability for efficient and large-scale water-treatment applications. For instance, TiO_2 nanostructures (0D to 3D) functionalized with various polymeric membranes via different strategies were investigated to understand the removal efficiency of various PEPs under different light sources (see Table 4). The higher removal efficiency of photocatalytic composite membrane was attributed to a synergistic effect between the polymeric membrane and nano-TiO_2, well-designed morphological structures, excellent stability of composite membrane, high catalytic activity and recyclability.

Ceramics are a special class of membrane materials that are prepared by electrospinning, coating, hot-pressing, sol–gel, hydrothermal synthesis-filtration, grafting, electrochemical deposition, as well as by various other methods followed by etching and anodizing TiO_2 film onto suitable supports [154]. The photocatalytic efficiency of TiO_2-PMs can be improved via doping with WO_3 such as silicon (Si). Doping TiO_2 with Si is an efficient way to enhance photocatalytic capability, thermal and mechanical stability, quantum-size effect and surface wettability of the photocatalyst [155]. Further, Ag-doped TiO_2 has been able to exhibit improved photocatalytic efficiency and bactericidal capability [156]. On the other hand, TiO_2 doped with tungsten showed enhanced visible light absorption by narrowing the energy band gap, thereby increasing the possibility for solar photocatalysis [157]. Thus, doping with tungsten or combining with WO_3 could impart better band gap reduction, leading to better photochemical degradation. Several PhACs and their active metabolites have been treated efficiently by both PMRs and PMs. Molinari et al. [158] utilized the combined polycrystalline TiO_2 and NF processes with different membranes for photocatalytic degradation of PhACs like furosemide, ranitidine (hydrochloride), ofloxacine, phenazone, naproxen, carbamazepine and clofibric acid in a PMR process. However, the rejection values of any of these PEPs did not exceed 30%, suggesting that the method used is not effective for the separation.

In the past, PMs have been studied for removing humic acids [154], textile dyes [159], and bacterial disinfection [160], but some limited studies are available on the remediation of PhACs. One of the most relevant studies on the removal of PhACs by PMs was reported [161], wherein TiO_2 nanofibers integrated with stainless-steel filters were used for the complete removal of PEPs such as antihistamine and cimetidine drugs through a photocatalytic process. Electrospun TiO_2 nanofibers were integrated into the stainless-steel filter through hot pressing with a PVDF nanofiber as an interlayer or a binder with > 99% removal of PEPs. Here, the presence of suitable binding layer has reduced the contact between PhACs and TiO_2 layer, thereby giving increased flux. Such composite membranes are highly suitable for photocatalytic degradation of organic PEPs [162,163] due to the rapid charge separation in electron-transfer processes. Different metal oxides and carbon materials have been coupled with polymer membrane supports by numerous researchers and they studied the photocatalytic composite membranes for the removal of various environmental pollutants and the results are presented in Table 4.

Concluding remarks and future trends

Innumerable studies in recent years have witnessed the presence of aggressive PEPs in water sources and this has created adverse effects on human health, hygiene and ecology. This situation has created continued pressure on researchers to develop newer water treatment technologies since natural attenuation and conventional treatment processes are not suitable to remove all the emerging PEPs. An overview of the state-of-the-art technologies based on MBSPs that are available to remove the toxic PEPs from wastewater sources at an affordable price is need of the present scenario. The PEPs are originated in many different groups such as synthetic chemicals, pharmaceutically active compounds, naturally occurring constituents and biological species such as microorganisms, etc. Therefore, their treatment technologies vary widely depending on the nature of the effluent.

Among the many conventional methods, MBSPs, predominantly NF and RO techniques, have proven to be suitable for removing many PEPs. In some situations, a hybrid technology may be more relevant. The recently developed hybrid MBR and FO techniques in combination with methods such as AOPs and PMs/PMRs have become quite popular in the present scenario. It is realized that despite several inherent limitations, the MBSPs are quite effective to achieve the removal efficiencies compared to other conventional water treatment technologies. The main trends in this field are highlighted along with the recommendations for further improvements/developments in the current status along with knowledge gaps and future directions.

Thousands of pharmaceuticals are produced every year of which only < 5% are detected for treatment. These include preservatives, antioxidants and flavorants used in cosmetics are the lesser studied PEPs in WWTPs. Therefore, more efforts are needed on treatment approaches including their toxicities, detection, separation and degradation. FO is another promising technology that has not yet been widely explored. The energy consumption in FO is much lesser than RO and NF being used for this purpose. Hence, future work should focus on improving the efficiency by developing newer membranes and integrating along with it some novel hybrid technologies such as AOP and other techniques.

Conducting a comparative study on the treatment of emerging wastes from the wastewater sources, though is a formidable task, yet more efforts are needed to develop different filtration technologies that can provide reliable data at a lesser cost. Another issue is that majority of the reported studies have been conducted in the laboratories, and mostly these are limited to a single component pollution approach in aqueous media. Therefore, problem still exists to direct use such data on a commercial scale. Majority of studies have performed experiments using synthetic wastes, but more research efforts are needed using the real wastewater or other complex real case scenarios to address the problem for their better commercial exploitation. We also realize that no single MBSPs is efficient in the removal of complex PEPs, but MBSPs coupled with AOPs, carbon adsorption, MBRs, etc., could complement each other to achieve maximum separation. In any case, it is important to involve multi-disciplinary scientists, technical cooperation, policymakers and stakeholders to strengthen the emerging PEPs detection, separation and degradation at the global level.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgment

Abbreviations:

PEO	poly(ethylene oxide)
MB	methylene blue
PVDF	polyvinylidene difluoride (PVDF)
PSF	polysulfone
PVDF-TrFE	poly[(vinylidenefluoride-cotrifluoroethylene]
PVC	polyvinyl chloride
AT-POME	aerobically treated palm oil mill effluent
PAN-PDA	polyacrylonitrile-polydopamine
PI	polyimide
PVDFTrFE	poly(vinylidenefluoride-trifluoroethylene)
BPA	bisphenol A
PEI	poly(ether imide)
PES	poly(ether sulfone)
PVA	polyvinylalcohol

PM	photocatalytic membranes
PMRs	photocatalytic membrane reactors
AO 7	acid orange 74
O-CP	orthochlorophenol
M-NP	M-Nitrophenol
MO	methyl orange
CA-PU	cellulose acetate-polyurethane
RR 11	reactive red
RO 84	reactive orange
DR 28	direct red
DY 4	direct yellow
DB 4	direct blue
GO	graphene oxide
BSA	bovine serum albumin
s-PBC	sulfonated pentablock copolymer
PDA	polydopamine
GQDs	graphene quantum dots
g-C$_3$N$_4$	graphitic carbon nitride
NO$_x$	nitrogen oxides
WWTP	waste water treatment plants
PCBs	polychlorinated biphenyls
PAHs	polyaromatic hydrocarbons
PAN	poly(acrylonitrile)
PSA	poly(sulfone amide)
PES	poly(ether sulfone)
PVDF	poly(vinylidene fluoride)
BPA	bisphenol A
CA	cellulose acetate
PTFE	poly(tetrafluoroethylene)

TTIP	titanium tetra-isopropoxide
SDS	sodium dodecyl sulphate
CTAB	cetyltrimethylammonium bromide
ECO	electrochemical oxidation
NOR	norfloxacin
OFL	ofloxacin
ROX	roxithromycin
APIs	active pharmaceutical ingredients
IPU	diisopropylurea
PFOS	perfluro octane sulfonates
THM	trihalomethanes
MTBE	methyl tertiary butyl ether
PFOS	perfluro octane sulfonates
DA	dopamine
PEM	polyelectrolyte multilayer
PAH	poly(allylamine hydrochloride)
PAA	poly(acrylic acid)
NDMA	N-nitrosodimethylamine
SPE	solid phase extraction
CP	cyclophosphamide
AOP-RO	advanced oxidation reverse osmosis
EDCs	endocrine disrupting chemicals
NDMA	N-nitrosodimethylamine
HAAs	haloacetic acids
CAS	conventional activated sludge
MBR	membrane bioreactors
SSMBR	side stream membrane bioreactor
SMBR	submerged membrane bioreactor
OMBR	osmotic membrane bioreactor

| **PACl** | polyaluminium chloride |

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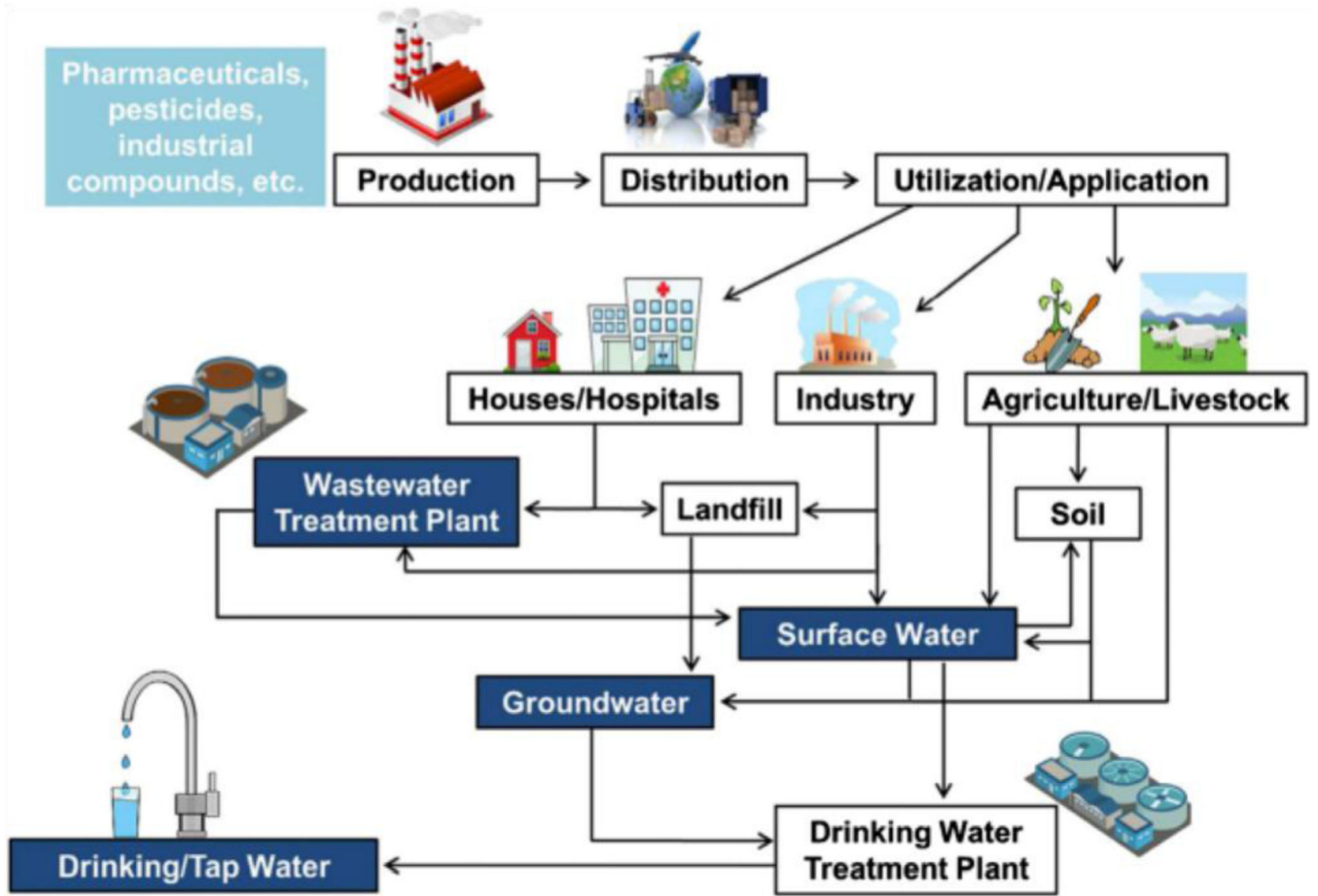
Fig. 1.
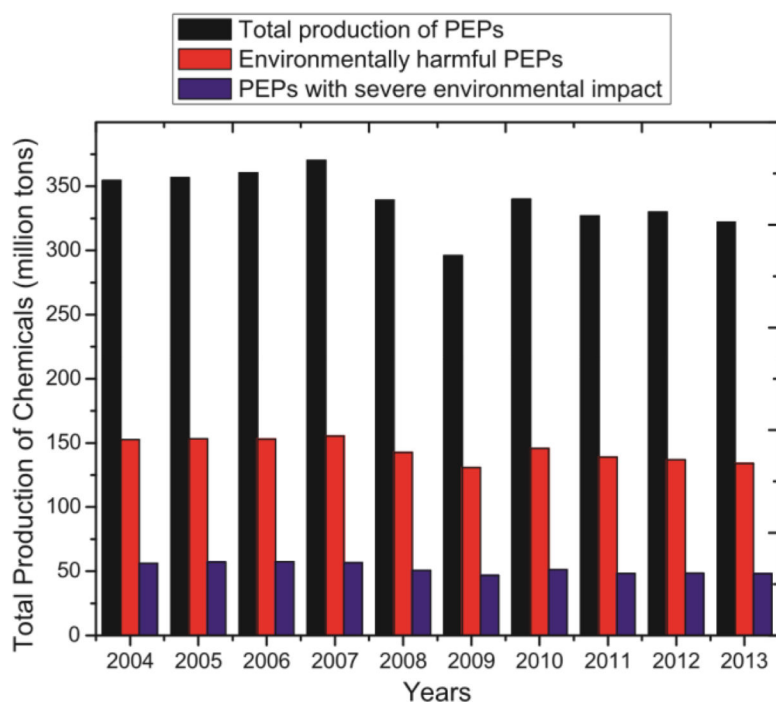Typical sources of PEPs. Reprinted with permission from Ref. [8], copyright (2016) Elsevier.

Fig. 2.
The yearly production indicators of PEPs with environmental impact (million tons)
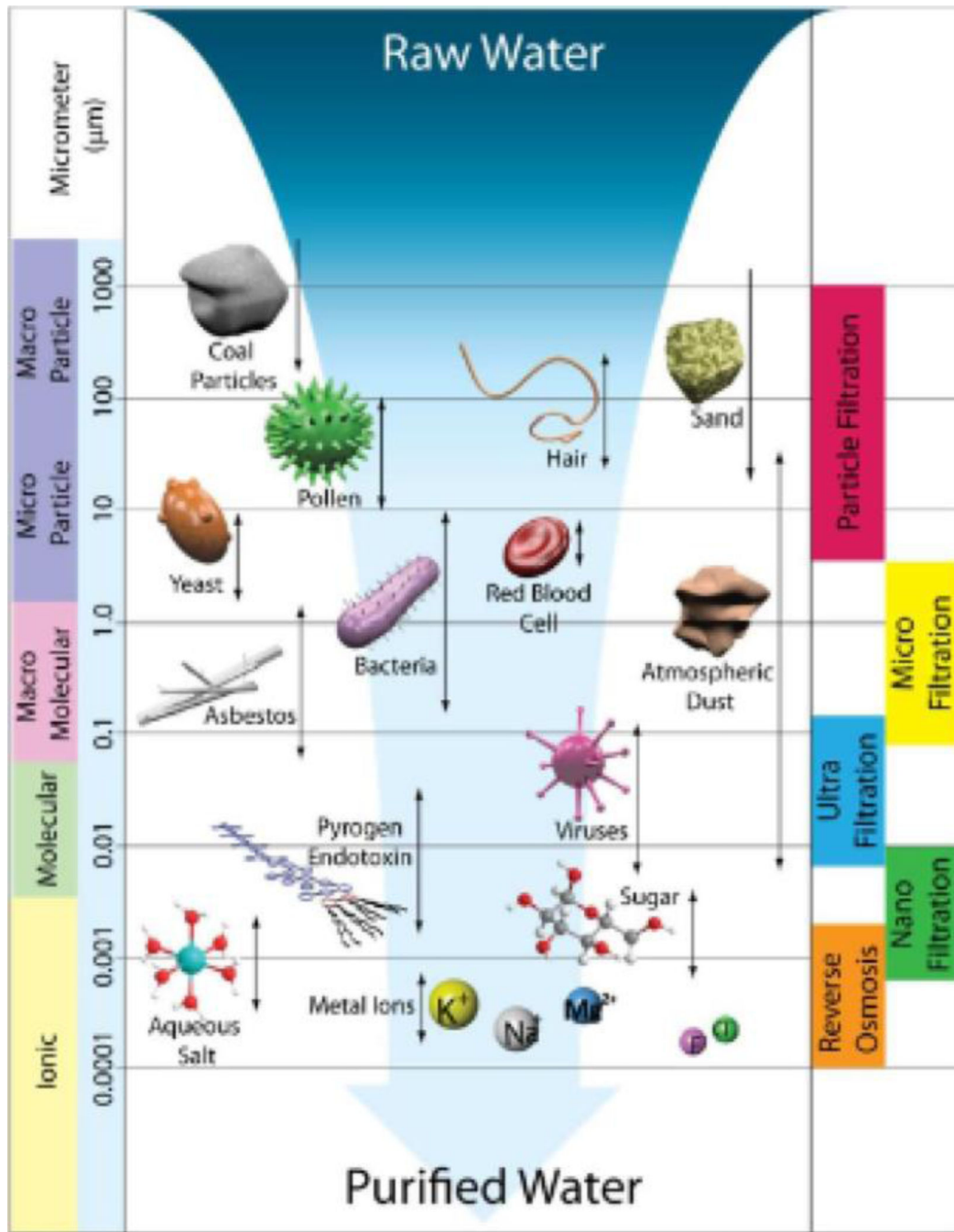assessment [re-drawn from http://ec.europa.eu.

Fig. 3.
MBSP spectrum including process name, size range and potential solute rejected over the prescribed range of pores. Reprinted with permission from Ref. [27], copyright (2016) Royal Society of Chemistry
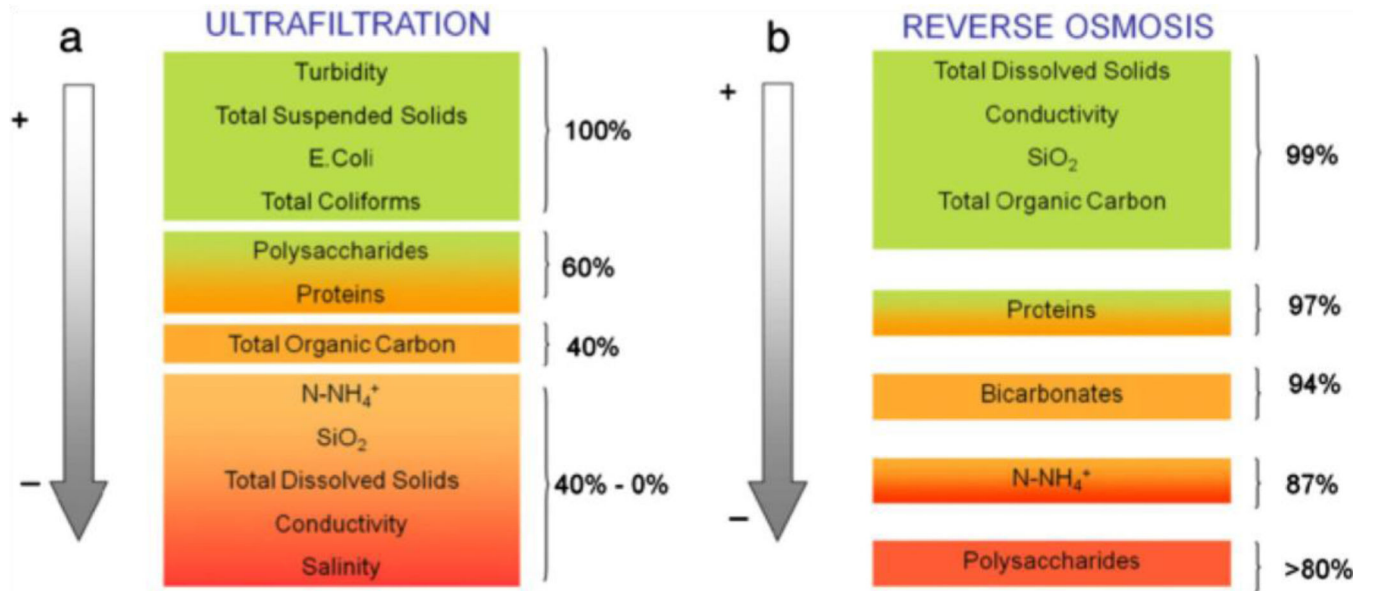
Fig. 4.
Summary of micro-PEPs removal during (a) UF and (b) RO treatment. Reprinted with permission from Ref. [70], copyright (2013) Elsevier.
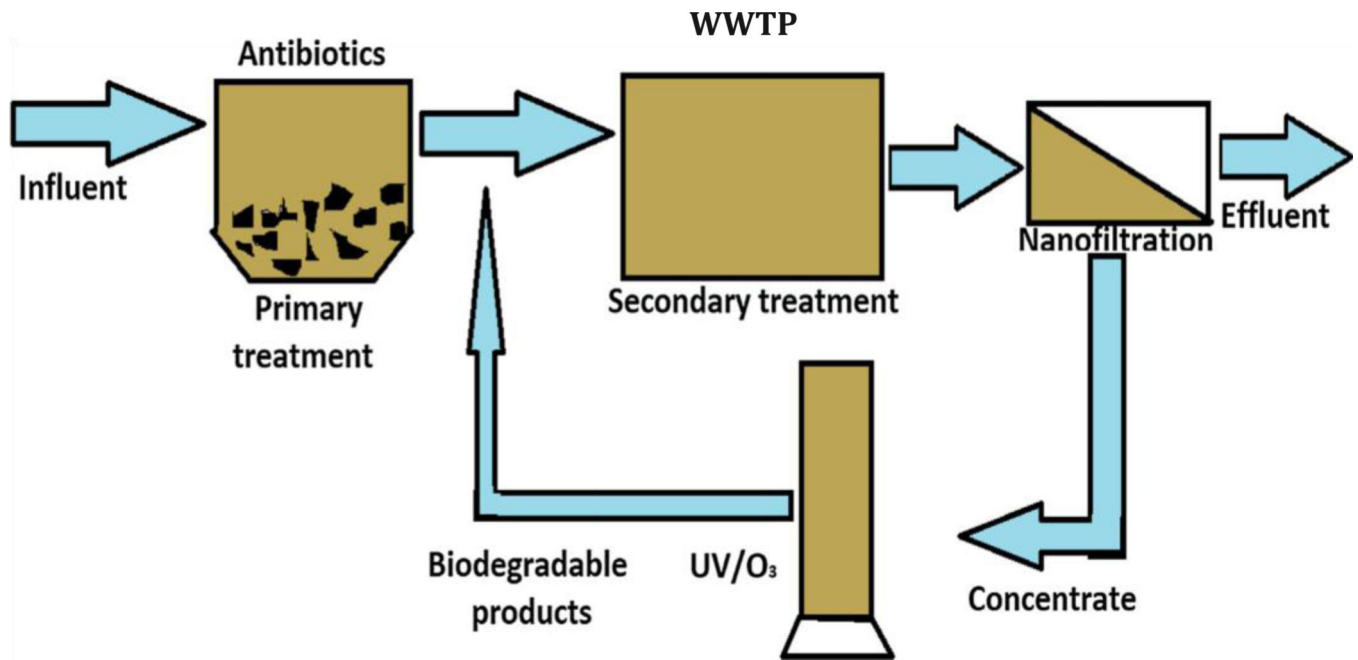
Fig. 5.
Hybrid NF combined with adsorption/AOP used for wastewater treatment. Redrawn with permission from Ref. [89], copyright (2014) Elsevier.

Fig. 6.
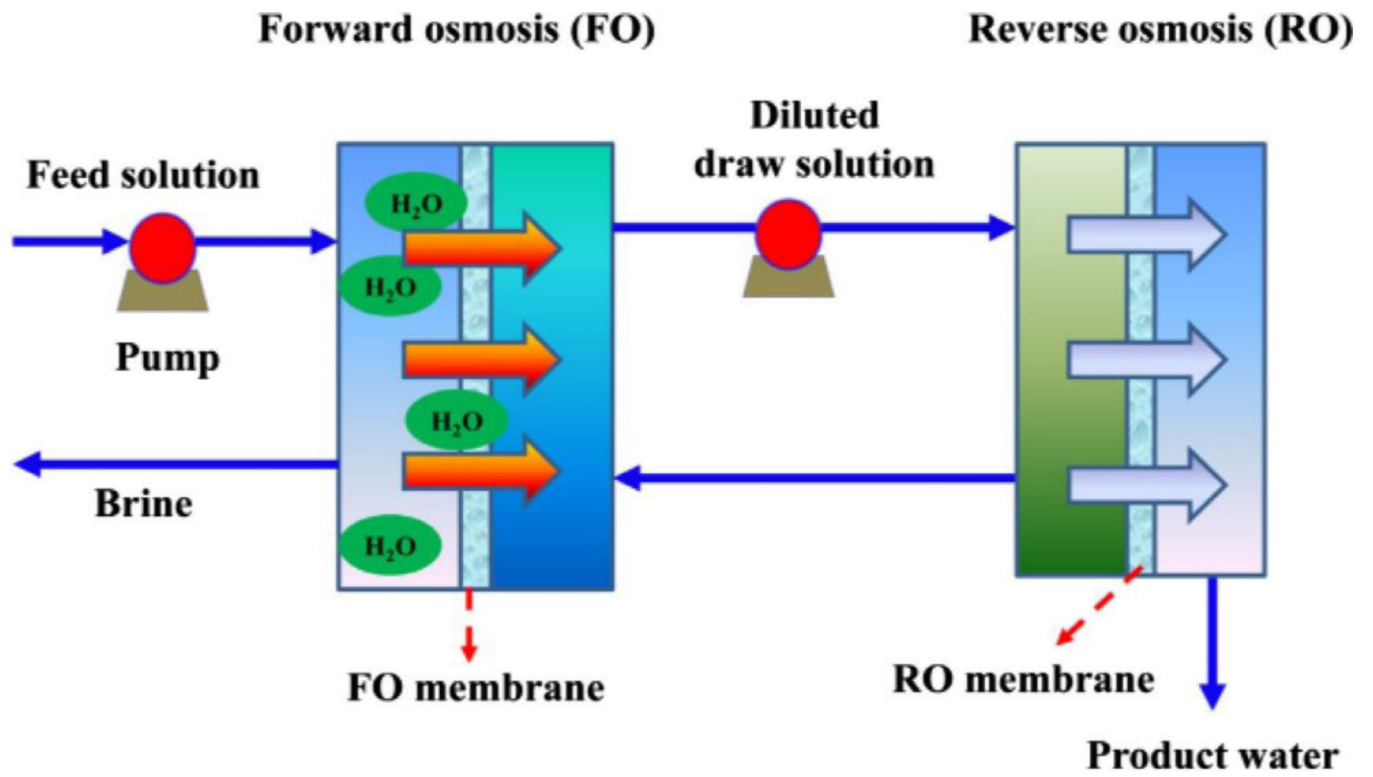Schematics of FO-RO hybrid system. Reprinted with permission from Ref. [121], copyright (2014) Elsevier.
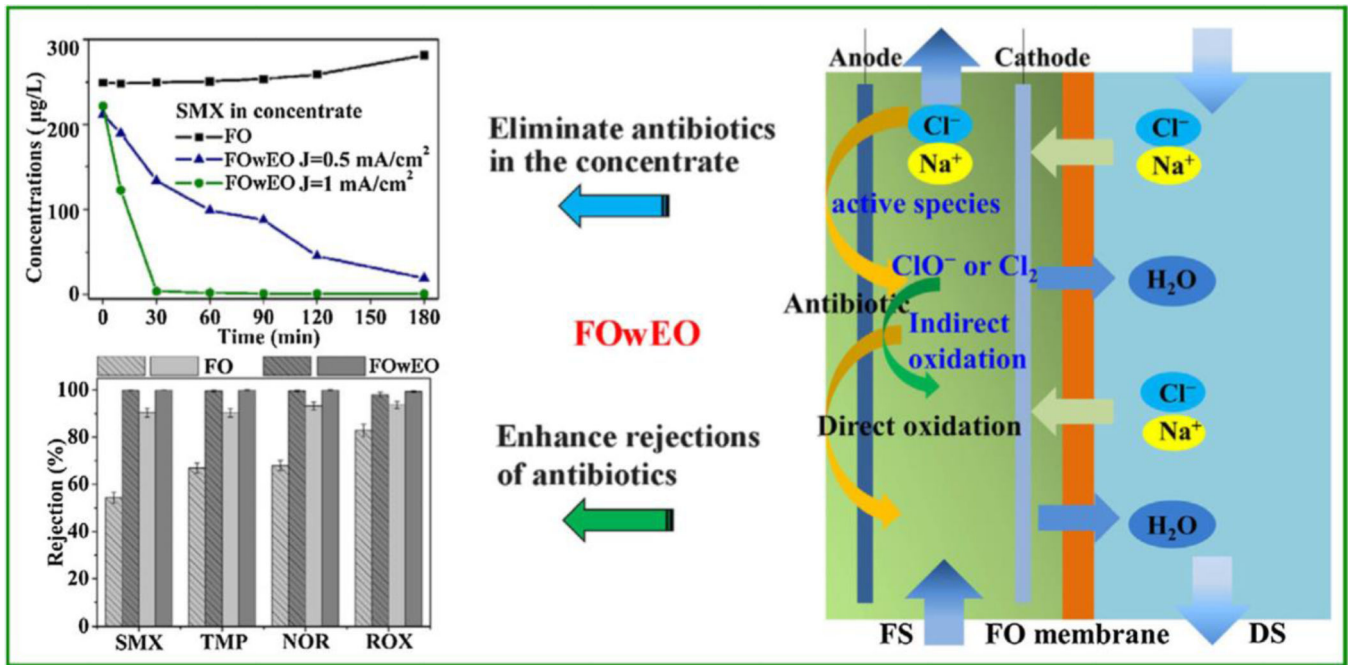
Fig. 7.
Schematics of FOwEO process showing enhanced rejection and elimination of antibiotics simultaneously. Reprinted with permission from Ref. [135], copyright (2015) Elsevier.
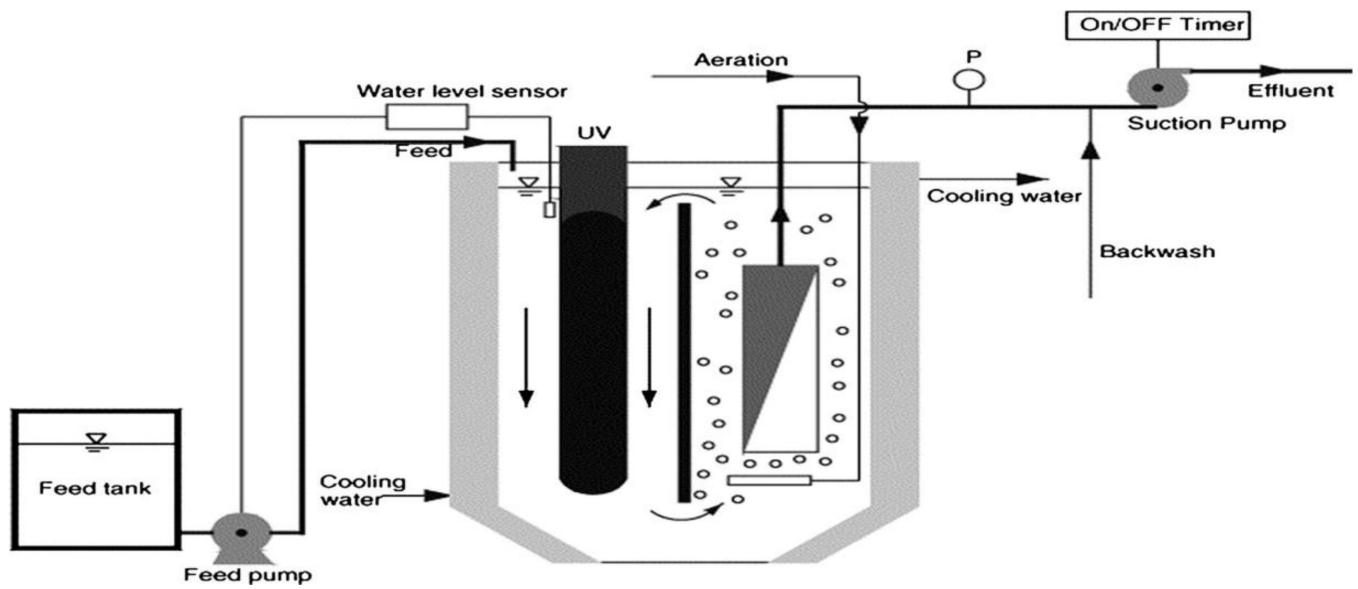
Fig. 8.
Submerged membrane photocatalytic reactor. Reprinted with permission from Ref. [151], copyright (2006) Elsevier.

Table 1

Concentration of various PEPs in effluents and their removal by wastewater treatment plants (WWTP). (data compiled from Ref. [2])

Types of PEPs	Chemical name	Concentration (μg/L) in effluent	% Removal rate by WWTP[*]
Phthalates	Diethyl phthalate	19.64	96.5
	Dibutyl phthalate	12.44	95.8
	Benzyl butyl phthalate	9.17	92.4
	Di-(-2-ethyl hexyl) phthalate	39.68	90.2
	Di methyl phthalate	2.07	71
Psyco-stimulants	Caffeine	56.63	96.9
	Paraxanthin	2.07	71
Desinfectants	Triclosan	0.85	76.8
Cosmetics	Galaxolide	4.28	76.2
	Tonalide	0.87	76.2
Diuretics	Furosemide	0.41	59.8
	Hydrochloro thiazide	2.51	53.2
	Diatrioate	3.3	0.2
β-Blockers	Metoprolol	1.53	55.8
	Propanolol	0.19	48.5
	Sotalol	1.66	52.6
Analgesics and anti-inflammateries	Ibuprofen Ketoprofen	13.4 0.48	74.2 31.1
	Ketorolac	0.41	44
	Clofibric acid	0.21	39.1
Antiepileptics	Antipyrin	0.04	32.5
	Codein	2.86	32.5
	Diclofenac	1.04	34.6
Antibiotics	Doxycyclin	0.65	35.4
	Norfloxacin	0.11	54.3
	Sulfamethoxazole	0.32	17.5
	Trimethoprim	0.43	1.4

[*] WWTP/STP =Waste Water Treatment Plants.

Table 2

Qualitative rejection values for various PEPs. Reprinted with permission from Ref. [98], copyright (2007) Elsevier.

PEPs	Molar mass (g/mol)	Rejection (%)
Hormones 17 β-Estradiol	272	85–100
17 α-Ethinylestradiol	296	n.a.
Estrone	270	60–90
Progesterone	314	90–100
Testosterone	288	80
Industrial chemicals Bisphenol A	228	70
p-Dimethyl phthalate	194	65–80
p-Diethyl phthalate	222	65–80
Nonyl phenol	220	70–90
MTBE	88	89.6
PFOS	152	97
Pesticides Atrazine	216	68–98
Simazine	202	75–93
Chloropyrifos	350	> 99
Pharmaceuticals Primidone	218	72–87
Carbamazepin	236	93
Ibuprofen	206	30–95

Table 3

TiO2-based hybrid photocatalytic membranes used for the removal of various PEPs.

Target pollutant	Membrane type	Light source	% Removal	Ref.
Alkaline MB	PEO	Xe-mercury	-	[164]
MB	PAN-PDA	150 W Vis. Light	90.00	[169]
MB	PVDF/ZnO	(300 W Xenon) Vis. Light	80.00	[171]
MB	PVDF-TrFE	UV light	100.00	[183]
MB	PVA/bentonite	No light	94.00	[179]
Tetrazine	PVDF-TrFE	Sun light	77.77	[165]
Acidic Acid orange 7	Quartz fiber	UV light		[173]
Acid orange 7	PEI	UV light	90.40	[174]
Acid orange 7	PVA/bentonite	No light	85.00	[179]
Phenolic Phenol	PSF	50 W	74.00	[180]
BPA	PVDF	Halogen UV light	85.00	[172]
BPA	PSF	Vis. Light	92.30	[176]
2,4-dichlorophenol	PES	Vis. Light	63.74	[175]
Azo compound Congo-red	PVC	UV light	95.00	[166]
Fluorescent Eosin yellow	PSF	Vis. Light	92.00	[167]
Miscellaneous AT-POME	PVDF	UV light	67.30	[168]
Toluene	PI	UV light	74.96	[170]
Oil-water separation	PVA	UV light	99.00 oil rejection	[177]
Cr (VI)	Chitosan	Vis. Light	54.00 at pH 4	[178]
CO_2 reduction	PVDF	UV light	19.80 μmol/	[181]
Bromate	Bromate	UV light	$G_{catalyst}$/hour > 90.00	[182]

Table 4

Metal oxides and nanocarbons-based composite photocatalytic membranes used for the removal of PEPs.

Membrane type	Target PEPs	Light source	Removal (%)	Ref.
ZnO/PAN	MO	UV light	99	[184]
ZnO/CA-PU	RR 11	UV light	98	[185]
	RO 84		90	
ZnO/PES	MB	UV light	70	[186]
Halloysite/PVDF	DR 28	Vis. Light	86.5 85	[187]
	DY 4		93.7	
	DB 4			
WO$_3$/membrane-coated stainless meshes	MB	UV light	99.9	[188]
H4SiW12O40/CA	Tetracycline	300 W	63.8	[189]
	MB	mercury lamp	94.6	
Ag$_3$PO$_4$/PAN	MB	200 W	98	[190]
		mercury light		
CuMn$_2$O$_4$/ceramic membrane	Benzophenone-3	UV light	81.1	[191]
SiO$_2$on SiC substrate	MB	UV light	72	[192]
GO-TiO$_2$/PVDF	BSA	UV light	92.5	[193]
GO/s-PBC	MB MO	UV light	88 70	[194]
rGO-g-C$_3$N$_4$/CA-PDA	MB	Vis. Light	99.8	[195]
GO/Triethanolamine- TiO$_2$	Congo Red	UV light	68	[196]
g-C$_3$N$_4$/Carbon fabric	NO$_x$	Vis. Light	64	[197]
Bi$_2$O$_2$CO$_3$-MoS$_2$/Carbon fabric	NO	Vis. Light	68	[198]
g-C$_3$N$_4$-CNTs/Al$_2$O$_3$ membrane	Phenol	Vis. Light	94	[199]