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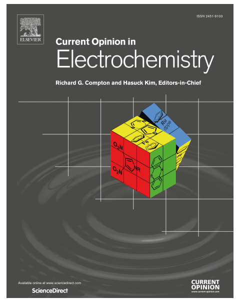

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Electrochemical technologies combined with membrane filtration

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Abstract

The aim of this article is to review the recent progress in the coupling of membrane separation and electrochemical technologies for water treatment. Process integration strategies have been classified in three groups. The first group deals with electrocoagulation and electrooxidation as pretreatment of membrane separation, in most cases aimed at reducing membrane fouling and decay of permeate flux of porous ultrafiltration membranes. The second group is dedicated to electrooxidation as remediation treatment for nanofiltration and reverse osmosis concentrates, which accumulate priority pollutants and emerging contaminants. Finally, the article evaluates the optimal integration of technologies using process systems engineering tools, for producing a single purified water stream, considering not only the minimization of the energy consumption but also of the total costs. Overall, it is concluded that the pre-concentration strategy provides a remarkable enhancement of electrooxidation performance to degrade persistent pollutants.

Keywords

Electrooxidation; electrocoagulation; reverse osmosis; nanofiltration; ultrafiltration; hybrid process; optimization; persistent pollutants; emerging contaminants; priority pollutants; PFAS

Introduction

This article reviews the recent progress about the coupling of membrane separation and electrochemical degradation for the treatment of water impacted by persistent pollutants and emerging contaminants. Both group of compounds behave as recalcitrant substances in conventional water treatment plants (WWTP), and therefore this type of facilities become a significant source of contaminants to the environment. The efficiency of electrochemical oxidation (ELOX) to degrade, mineralize and detoxify persistent pollutants, particularly if boron doped diamond (BDD) electrodes are applied, is well known. However, so far the ELOX practical application is being constrained by several limitations. On the one hand, the low concentration of priority pollutants in most real environmental matrices, typically in the range ng/L to μg/L, makes diffusion the controlling phenomena of the electrochemical process kinetics. Also, the low electrical conductivity of surface water and groundwater electrolytes is a drawback due to the large voltage developed in the electrochemical reactor, which summed up to the low current efficiency observed in the treatment of low concentrated pollutants, increases exponentially the energy consumption.

Nowadays, the implementation of membrane technology at large scale is a reality in water reclamation and drinking water treatment facilities. Ultrafiltration retains suspended solids and bacteria, while nanofiltration (NF) and reverse osmosis (RO) are used for desalination and rejection of toxic compounds. However, the disadvantage of membrane filtration, as it happens in adsorption and ion exchange processes, is the generation of a waste stream that retains the contaminants at a higher concentration than in the original feed water. Dealing with membrane fouling phenomena is also a matter of concern.

At this point, the integration of membrane separation and electrochemical degradation makes sense to solve the limitations of each individual technology [1]. On the one hand, the higher concentration of persistent contaminants in the concentrate of the membrane unit will boost the mass transfer controlled kinetics of electrolysis. Also, the natural content of dissolved salts will achieve higher concentrations, thus increasing the electrolyte conductivity. As a result, the cell voltage of the electrochemical reactor will decrease, making the process less energy consuming.

The first experimental studies on this type of approach were reported in the late 2000s for the mineralization of the organic load retained in reverse osmosis concentrates (ROC) [2, 3]. Shortly afterwards, the literature presents the first attempts to analyze electrochemical oxidation as end-of-pipe treatment in water reclamation facilities, to reduce the impact of pharmaceutical compounds and other emerging contaminants retained in ROCs [4, 5]. These studies showed the outstanding efficiency of the treatment train based on a serial of ultrafiltration (UF), RO and ELOX stages, but also revealed the potential formation of undesirable disinfection by products (DBPs) and oxihalogenated anions [6-8].

This article is aimed at reviewing the most recent advances on the coupling of membrane separation and ELOX aimed at the treatment of persistent pollutants. Figure 1 presents the process integration schemes that are covered in the present analysis. In the first approach (Fig. 1A), ELOX is applied as pretreatment to reduce fouling on membranes used in tertiary treatments and to reduce the required frequency of membrane cleaning and maintenance. In Fig. 1B the treatment scheme includes membrane pretreatment that results in a purified low salinity water permeate aimed at its further reuse, and a rejection stream that retains contaminants and salts. The membrane pretreatment may include a prior UF stage for retention of suspended solids and bacteria. Typically, the electrochemical treatment of the retentate is thought for decreasing the load of organic pollutants and toxicity before its entrance in the receiving environment. In the third scheme (Fig. 1C) the treatment train produces one single effluent that results from mixing the outputs of the membrane and electrochemical treatment. Next, this article presents a critical review of the recent progress in each of the three schemes, highlighting the relevant advantages and disadvantages in each case, as it is summarized in Table 1.

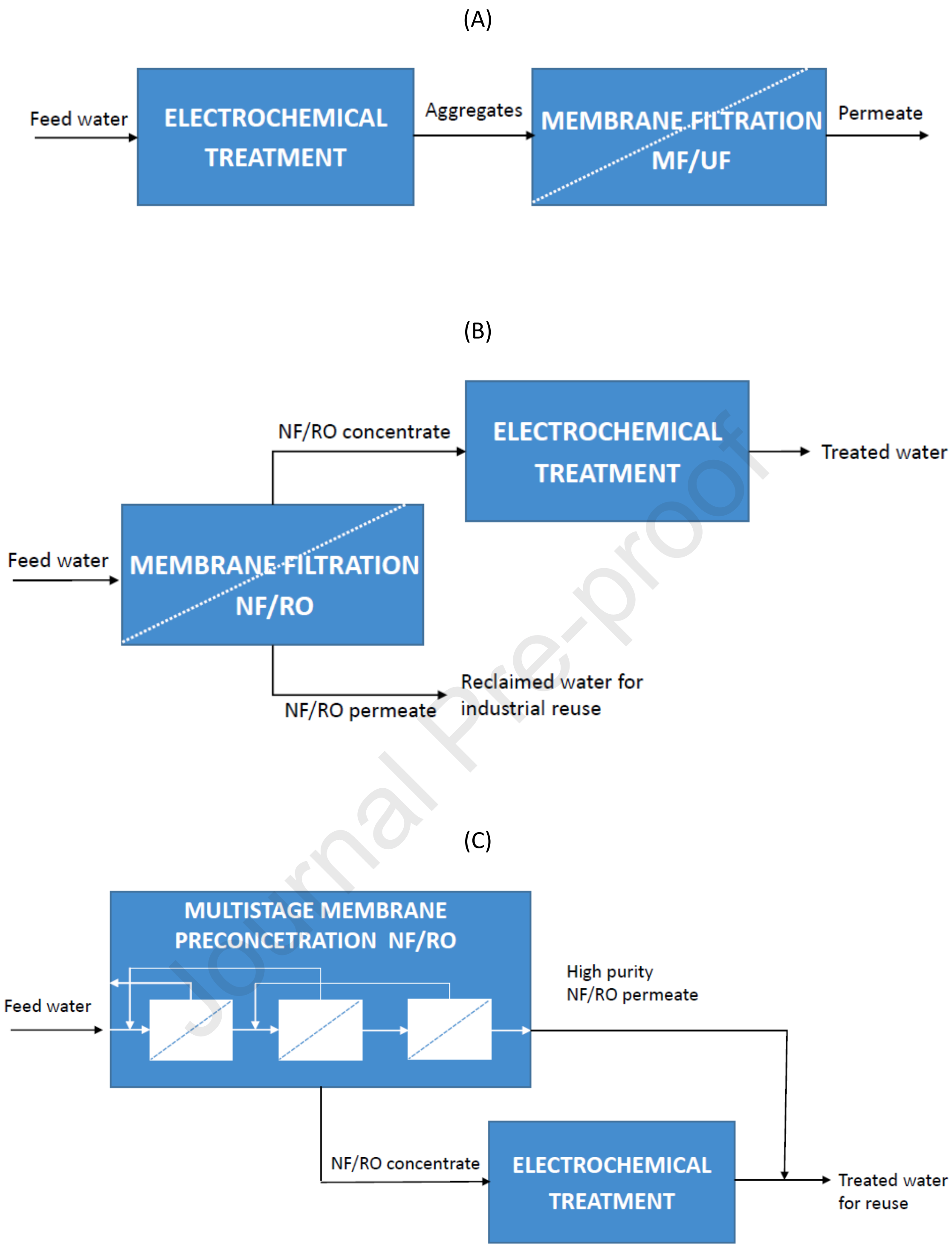

Figure 1. Hybrid water treatment schemes based on membrane separation and electrochemical degradation. (A) Electrochemical pre-treatment is aimed at reducing membrane fouling in porous membrane filtration; (B) Electrolysis as end-of-pipe treatment of highly polluted reverse osmosis /nanofiltration concentrates; (C) Integrated membrane preconcentration and electrolysis for highly purified produced water.

Scheme A. Electrooxidation for reducing membrane fouling.

Scheme (A) in Figure 1 refers to pre-electrooxidation of feed water before its membrane filtration, aimed to alter the quantity and quality of water constituents and subsequently modify their interactions with the membrane [9, 10].

Among the works that studied electrochemical technology as pretreatment of membrane separation, most of the investigations were aimed at reducing membrane fouling phenomena. Gonzalez-Olmos et al. [11] reported the pretreatment of the secondary effluents of a municipal wastewater treatment plant (WWTP) using BDD anodes. The results showed that the electrochemical pretreatment decreased by 36–67% the transmembrane pressure (TMP) in the next UF step, and consequently the membrane fouling. The integrated ELOX/UF scheme also enhanced the removal of dissolved organic carbon (DOC) by 40%. The reduction of the TMP observed in the UF unit was satisfactorily correlated to the applied current density in the ELOX unit, showing the relation between the degradation of the main organic constituents of water (humic acids (HA), fulvic acids, natural organic matter) and the reduction of the membrane fouling.

Several studies reported an electrochemical stage that combined electrocoagulation (EC) and anodic oxidation. Du et al. [12] combined the electrolysis of sulfamethazine (SMZ) antibiotic with EC to prevent fouling in a subsequent UF, which employed a ceramic membrane. Raw surface water spiked with SMZ was used to validate the effectiveness of the combined process. In the first electrochemical stage, peroxymonosulfate was electrochemically activated to generate strong oxidants that degraded SMZ and HAs, and at the same time the iron sacrificial anode was promoting EC of natural organic matter and suspended solids. The UF membrane retained the aggregates, showing that larger aggregates minimized membrane fouling and improved the filtration performance. Overall, the electrochemical reactor was responsible for most of SMZ removal. In the same vein, Chen et al. [13] and Du et al. [14] studied the removal of HAs, phosphorous, manganese and atrazine.

The lower cost and easier availability of polymeric membranes makes them the preferred option for water treatment, although polymers are less resistant to oxidative conditions than inorganic ceramic membranes. Nevertheless, the recent progress in photocatalytic membranes points to PVDF polymeric membranes as stable materials for coupled membrane separation / advanced oxidation [15]. The EC/ELOX membrane reactor (ECOMR) designed by Sun et al. [16] incorporated an aluminum cathode, a Ti-Ru anode and PVDF hollow fiber UF membranes, that was able to alleviate membrane fouling due to the synergies of oxidation and coagulation under the electric field. The ELOX process broke up the carboxylic functional groups and aromatic structures of HAs, which had a significant influence on modulating the porosity of the cake layer, resulting in the formation of more porous cake layers that were easy to clean off in the backwash step. Similar results were reported in absence of ELOX conditions in parallel studies dedicated to the effect of the applied electrical field [17, 18]. Recently Xu et al. [19] reported the mitigation of the UF membrane fouling by means of spontaneous galvanic microcoagulation phenomena. In this device, the slow release of ferrous ion contributed to the reduction of biopolymers in the UF unit, resulting into low TMP increasing rate. A recent study reports the potentiality of EC/ELOX/UF/RO trains for treatment of heavily polluted industrial wastewater [20]. The incorporation of the ELOX stage to degrade certain chemicals contributed to reducing the irreversible damage of the thin-film RO membrane due to chemical attack that had been previously observed. EC pretreatment has also been demonstrated for mitigation of fouling and wetting in direct contact membrane distillation working in continuous mode for > 400 h with stable water flux working in the production of highly concentrated brines [21].

Scheme B. Electrooxidation as end-of-pipe treatment of reverse osmosis concentrate

The treatment of ROCs generated in water reclamation facilities is one of the main topics of research when dealing with integration of electrochemical technology in water treatment schemes. ROCs typically retain highly recalcitrant organic load, after the removal of biodegradable organics in the secondary treatment applied in the WWTP. BDD anodes were employed to treat low salinity ROCs from a water reclamation facility spiked with tramadol, an analgesic that shows persistency in WWTPs [22]. Tramadol degradation was very effective, although COD removal was poor, likely a result of the low current intensity applied (0.4 – 1.2 mA cm^{-2}). That study also reported the formation of absorbable organic halogens (AOX), which could be potentially eliminated by increasing the treatment time, as suggested by the authors. However, this approach could conduct to the electrogeneration of undesirable inorganic chlorine derivatives, such as chlorate and perchlorate [7, 23]. In the same vein the use of solar-assisted ELOX to treat the NF concentrate of an urban WWTP effluent, demonstrated 80% removal of a group of fourteen microcontaminants with 2.7 kWh m^{-3} power consumption [24], although at the expense of chlorate generation, that would require a risk assessment prior to the use of treated water for irrigation.

Chen et al. [25, 26] studied the ROC treatment using an innovative flow-through anode structure, that consisted of a three-dimensional macroporous TiO_2 nanotube array built on a SnO_2-Sb /PbO_2 base layer. Using the electrode prepared, the results showed a notable reduction of the energy consumption that was needed to eliminate the recalcitrant organic load. The improvement was attributed to the higher porosity of the anode, compared to traditional flow-by reactors. The flow-through electrochemical cell eliminated 76 gCOD kWh^{-1}, a magnitude that is still under the performance of BDD anodes for similar ROC [4]. The search of more affordable anode materials to treat ROC includes Co doped- PbO_2 [27]. In the latter reference, quinoline was selected as model pharmaceutical compound used to spike simulated ROC. Overall, the removal of quinolone was much faster than the decay of COD.

The ELOX treatment is extended to ROCs from heavily polluted industrial effluents and landfill leachates. Wang et al. [28] selected a PbO_2/Ti electrode for treating ROCs of printing and dying wastewater, because of its low price, high oxidative performance and good stability compared to BDD, SnO_2-SbO_2/Ti, IrO_2/Ti and RuO_2/Ti, according to the authors' own analysis. Overall the high salinity of the industrial effluent benefited color removal, which reached 99% reduction after passing only 3 A h^{-1} L^{-1}, although the mineralization of more persistent intermediates was barely moderate. Although chloride reduction was observed, the authors did not report on the likely formation of perchlorate anions.

Using NF in the preconcentration stage may introduce a few distinctive features. NF retains sulfate, but permits the partial passage of chloride. By using NF preconcentration for the landfill leachates ELOX treatment, the concentrate with lower chloride content was less prone to form organohalogenates and perchlorate by-products, even in the high oxidative conditions produced by the Ti_4O_7 anode combined with electro-Fenton [29]. That study also found a great biodegradability enhancement of the electrolysis effluent, thus making possible the recirculation of the residual DOC towards the biological treatment of the landfill leachate in order to achieve higher COD removal without longer electrochemical treatment time. Several authors report recent studies dealing with the coupling of electrochemical pretreatment as a means to increase the biodegradability of bisphenol A, p-cresol and ibuprofen [30]. The progress towards industrial application of hybrid membrane-electrochemical process in the petrochemical industry was investigated by da Silva et al. [31], using BDD/Nb anodes to treat the ROC produced from a petrochemical wastewater. The ELOX treatment was efficient in the removal of monomers and solvents used in the fabrication of polymers and adhesives. The energy consumption was reduced to 66.5 kWh kg^{-1} of COD. Ren et al. determined the optimal condition of the EC/ELOX treatment of the ROC produced in a municipal solid waste incineration power plant [32].

Poly- and perfluoroalkyl substances (PFAS) are considered substances of very high concern (SVHC) due to their persistence, mobility and bioaccumulation properties. PFAS, also known as forever chemicals, are extremely resistance to bioremediation. The solution to PFAS degradation might be in BDD electrooxidation, as it has been shown for legacy PFOA and PFOS, as for complex PFAS mixtures in the sub-microgram L^{-1} concentration range [33, 34]. Membrane pre-concentration has been studied to increase PFAS concentration and electrolyte conductivity in the ELOX treatment. Soriano et al. [35] published a pioneering study considering NF preconcentration for treatment of perfluorohexanoic acid (PFHxA) in industrial effluents, showing PFHxA removals > 97%, accompanied with excellent mineralization (TOC removal > 95 %). Pica et al. [36] have extended this approach to the removal of hexafluoropropylene oxide dimer acid (GenX) in model solutions. Both studies presented a comprehensive analysis of the energy savings assigned to the preconcentration approach. Overall, the energy consumption of the electrolysis stage was reduced by a factor of 6, considering 1-log reduction of the PFAS concentration.

Scheme C. Integrated membrane preconcentration and electrolysis for highly purified produced water.

In scheme C of Figure 1, the integration of membrane and electrolysis is aimed at producing a unique purified effluent, instead of two separated effluents. Madsen et al. [37] published one of the first attempts to evaluate the benefits of integration by taking into consideration the energy consumption of both membrane filtration and ELOX stages for treatment of pesticide 2,6-dichlorobenzamide (BAM) in groundwater used for drinking water supply. The analysis concluded that the process would be benefitted of using low pressure RO membranes, that retain most of the salinity in the concentrate, compared to NF membranes that permit the passage of chloride with the permeate. The higher chloride retention also enhanced indirect oxidation reactions by the electro-generated active chlorine. Overall, the energy savings of the integration strategy were estimated to be higher than 94% compared to the ELOX-only BAM treatment, for 1-log BAM removal. This tool has been recently applied to the treatment of effluents of fluoropolymer manufacturing, by combining nanofiltration and BDD anodic oxidation [38]. Interestingly, the benefits of integration were found to be closely tighten to the membrane separation performance and the electrochemical degradation rate of persistent PFHxA. The use of a highly productive but less selective NF270 membrane provided 50.7%

energy savings for 1-log removal ratio, but the hybrid strategy did not bring any benefit for more severe 2-log target removal. Remarkably, the tighter NF90 membrane achieved 76.7% and 59.2% energy savings for 1-log and 2-log PFHxA removal ratios, compared to the direct BDD electrolysis. The lower energy savings reported in [38] compared to [37] are likely due to the more recalcitrant nature of perfluorocarboxylic acids.

Integration of membrane filtration and electrochemical oxidation goes a step ahead by applying process systems engineering tools, to minimize the total costs, that include investment, energy consumption and operation and maintenance costs [39]. Reported results highlighted the benefit of this approach exemplified for 3-log PFHxA removal, when the solution of the cost minimization problem resulted in a two-stage membrane pre-concentration layout using the NF90 membrane followed by ELOX treatment of the NF concentrate, with 78.4 % total costs savings compared to ELOX only treatment. It is worth mentioning that the highest cost was assigned to the purchase and substitution of BDD electrodes, which was markedly higher than the cost of electricity supply to high pressure pumps and power rectifiers. More recently, a similar approach has been applied to the treatment of PFAS in groundwater impacted by contaminated soil due to the use of aqueous film forming foam (AFFF) in low concentration range (~70 µg L^{-1} , as sum of PFOA, PFOS, PFHxA, PFPeA, PFBA, and 6:2 FTSA) [40]. Due to the extremely low target concentration imposed at the end of the treatment train after mixing the permeate of membrane filtration and the ELOX effluent (70 ng L^{-1}, as from EPA health advisory levels in drinking water), the optimized solution imposed 4 membrane stages, for consecutive filtration of the permeate water, with intermediate water pressurization. Nevertheless, the optimized solution saved 76.6% of the total costs, compared to the ELOX-only treatment.

There is one novel configuration that combines membrane electrodialysis (ED) as a means for concentrating chlorinated pollutants, and ELOX of the ED concentrate at the anodic chamber [41]. This scheme has been applied in a single device, although the separation and degradation functions are provided by separate surfaces, therefore, the effect of varying the anion exchange membrane, the electrolyte composition and the anode material can be studied separately. Authors concluded that the combined electrodialysis/electrooxidation configuration overcomes electrooxidation alone for systems in which the transport rate surpassed the degradation rate [42].

Conclusions

The development of hybrid processes that combine electrochemical and membrane technologies is gaining importance in the area of environmental applications of electrochemistry. Membrane separation by means of nanofiltration and reverse osmosis increases the concentration of persistent pollutants, that results in faster electrochemical degradation kinetics. At the same time the higher electrolyte conductivity enables reducing the power demand of the electrochemical stage. Most studies select boron doped diamond anodes, because of their efficient role for degrading persistent pollutants, included the group of poly- and perfluoroalkyl substances (PFAS) of very high concern, although metal oxides and titanium sub-stoichiometric oxides are also gaining importance. Reverse osmosis is the preferred option, although some nanofiltration membranes offer one singular advantage, that is their high permeability to chloride. Process integration methodologies revealed that the size of the electrochemical reactor can be drastically reduced by the membrane pre-concentration, making the integrated process much less energy demanding that the ELOX-only approach, thus providing the desirable process intensification.

Based on this literature review, there are important aspects that should be considered and/or studied more in depth to progress in the integration of membrane separation and electrochemical technologies:

- About EC as pre-treatment for ultrafiltration, studies reported so far are laboratory scale dead-end filtration systems working in single batch mode. Therefore, more knowledge is needed about the analysis of the continuous operation of the UF unit in consecutive production/backwash cycles and the way to connect EC to UF. Insights into the mechanism that provides EC aggregates with better properties than chemical coagulation for reducing membrane fouling is also a matter of interest.
- About ELOX as post-treatment of RO/NF concentration, very few studies focus on the formation of organic and inorganic halogenated by-products. More information is needed about this matter of concern, particularly when high chloride concentration is achieved during the membrane pre-concentration stage.
- For degradation of very persistent pollutants, the cost of purchase and replacement of BDD anodes governs the total costs of the treatment process. There is a need to fabricate stable, long-lasting anodes materials with similar degradation properties as BDD, but at significantly lower cost.

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** This article presents for the first time the optimization of hybrid RO/ELOX for minimization of total costs. Important to note that the membrane filtration considers a cascade of membrane units for consecutive filtration of the permeate. The integrated process reduced drastically the BDD anode area requirement to achieve 4-log reduction of PFAS concetration in the treated effluent.

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Table 1. Summary of the main characteristics of the integration of membrane separation with electrochemical water treatment. A selection of applications is highlighted.

Configuration	Objectives	Mechanisms	Electrochemical process	Membrane separation	Application	References
Electrochemical pre-treatment before membrane filtration	- To reduce membrane fouling phenomena - To reduce transmembrane pressure - To reduce the energy consumption of membrane filtration	- ELOX alters the quantity and quality of organic compounds in water, which modify their interactions with the membrane - EC forms larger aggregates of NOM, facilitating membrane filtration	BDD, MMO anodes Al and Fe cathodes	Ceramic UF membranes withstand oxidative conditions created in ELOX pretreatment PVDF/PTFE UF polymer membranes are less costly and still resistant in oxidative conditions	- Analysis of mechanisms - Effluent of municipal WWTP - Removal of pharmaceuticals - Removal of NOM, metals, P - Surface water - Industrial wastewater - Hydraulic fractioning produced water	9, 10, 16, 17 11, 18 12, 13 14 19 20 21
Electrooxidation as end-of-pipe treatment of RO concentrate	- To mitigate the environmental impact of the discharge of RO retentate. - To reduce the energy consumption of ELOX.	RO increase the concentration of salts and organic pollutants in the retentate, - The higher electrolyte conductivity reduces the electrochemical cell voltage - The higher concentration of organics promotes diffusion controlled ELOX degradation kinetics	BDD SnO_2 and PbO_2 Co doped PbO_2 TiO_2 nanotube arrays Substoichiometric titanium oxides	UF NF RO	- Water reclamation of municipal WWTP secondary effluents. - Degradation of pharmaceutical compounds - Landfill leachates - Industrial wastewater - PFAS in industrial streams	2,4,5 4,5,22,24,27 23,29 28, 31, 32 35,36
Integrated membrane preconcentration and electrolysis for highly purified produced water	- To reduce the total costs of water treatment - To achieve very high removal ratios of POPs and priority contaminants	- Selective RO is applied to produce high quality permeates (1) - ELOX treatment of the retentate degrades POPs (2) - Process systems engineering is applied for integration of stages (1) and (2) considering minimization of total costs to accomplish with ambitious removal objectives	BDD MMO	NF RO ED	- Pesticides treatment in drinking water supply - PFAS in industrial wastewater and groundwater - Herbicides	37 38, 39, 40 41, 42

Note: The meaning of abbreviations is detailed along the main text.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: