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Electro-oxidation of organic pollutants by reactive electrochemical membranes

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HIGHLIGHTS
- Recent advances on reactive electrochemical membranes (REMs) are reviewed.
- Carbon nanotubes and TiO\textsubscript{x} materials have been the most widely studied materials.
- REMs have high electroactive surface area.
- Flow through REMs allow for convection enhanced mass transport of pollutants.
- Scientific challenges and perspectives on the development of REMs are highlighted.

ARTICLE INFO

ABSTRACT

Electro-oxidation processes are promising options for the removal of organic pollutants from water. The major appeal of these technologies is the possibility to avoid the addition of chemical reagents. However, a major limitation is associated with slow mass transfer that reduces the efficiency and hinders the potential for large scale application of these technologies. Therefore, improving the reactor configuration is currently one of the most important areas for research and development. The recent development of a reactive electrochemical membrane (REM) as a flow through electrode has proven to be a breakthrough innovation, leading to both high electrochemically active surface area and convection enhanced mass transport of pollutants. This review summarizes the current state of the art on REMs for the electro-oxidation of organic compounds by anodic oxidation. Specific focuses on the electroactive surface area, mass transport, reactivity, fouling and stability of REMs are included. Recent advances in the development of sub stoichiometric titanium oxide REMs as anodes have been made. These electrodes possess high electrical conductivity, reactivity (generation of *OH), chemical/electrochemical stability, and suitable pore structure that allows for efficient mass transport. Further development of REMs strongly relies on the development of materials with suitable physicochemical characteristics that produce electrodes with efficient mass transport properties, high electroactive surface area, high reactivity and long term stability.

1. Introduction

The management of both quantity and quality of water resources is a major environmental, health and societal concern for both developed and developing countries. For example, the European Union has raised concerns on the increasing concentrations of organic micropollutants in water bodies and imposed regulations on the discharge of organic pollutants. Most recently, the Priority Substances Directive 2013/39/EU amended the Water Framework Directive (2006/60/EC) and Directive 2008/105/EC on Environmental Quality Standards. As another example, the United States Environmental Protection Agency placed several trace contaminants on a “Contaminant Candidate List”, for which information on
occurrence and health effects must be monitored. Efficient water management is also becoming an important economic concern for industrial activities, and as a result water reuse is being implemented by several industrial sectors. To meet the challenges of water quality and quantity, the development of compact, robust and cost effective technologies for the treatment of domestic and industrial effluents containing recalcitrant organic compounds is needed (Joss et al., 2008).

Biological processes are widely used in conventional waste water treatment systems because of their high cost effectiveness for the removal of biodegradable organic matter, nitrogen and phosphorus. However, an additional barrier using advanced water treatment technologies is required for removing non biodegradable organic pollutants from water. Ozone or UV based oxidation processes and activated carbon are the most commonly used methods for upgrading wastewater treatment plants (Joss et al., 2008). However, some organic compounds are still recalcitrant to oxidation by ozone or UV based processes and incomplete mineralization of molecules can lead to the formation of even more toxic by products. Besides, activated carbon is only a separation process, which requires subsequent waste disposal. Membrane processes have also been developed in order to create a physical barrier for the separation of suspended particles (microfiltration); bacteria, viruses, and some dissolved species (ultrafiltration and nanofiltration); or almost all dissolved species (reverse osmosis). Microfiltration and ultrafiltration processes are not able to reach sufficient removal rates of dissolved organic pollutants, and nano filtration and reverse osmosis greatly increase operating costs, due to the high transmembrane pressures required, fouling issues, and management of the membrane concentrate (Luo et al., 2014).

The development of electrochemical processes is currently a major topic of interest in the scientific community because they are showing promise as a next generation technologies for the removal of organic compounds from water (Chaplin, 2014; Sirés et al., 2014; Martínez Huittle et al., 2015; Radjenovic and Sedlak, 2015). They have several technical benefits such as the absence of storage and handling of chemicals, an easily automated operation, as well as a compact and modular reactor design making them attractive for decentralized water and wastewater treatment systems. Anodic oxidation (AO), which is categorized as an electrochemical advanced oxidation process (EAOP), has been shown to be highly effective for the treatment of aqueous organic waste streams. The AO process is based on the removal of contaminants by a combination of direct electron transfer from the contaminant (R) to the anode (Eq. (1)) and the production of large quantities of hydroxyl radicals (OH) from water discharge at the surface of an anode material (M) with high O2 overpotential (Eq. (2)), such as boron doped diamond (Panizza and Cerisola, 2009). The OH is both a very strong oxidant (the thermodynamic potential of OH forma
tion is E° = 2.38 V vs. standard hydrogen electrode (SHE)) and highly reactive species allowing the degradation of a wide range of bio refractory organic compounds (Eq. (3)) (Buxton et al., 1988; Kapatka et al., 2009). Many examples of total mineralization of various organic pollutants and complex effluents have been reported in the scientific literature and comparative studies often indicated that higher mineralization of organic compounds was achieved with AO compared to other advanced oxidation processes (Comminellis and Nerini, 1993; Rodrigo et al., 2001; Canizares et al., 2003; Brillas et al., 2005, 2007; Ozcan et al., 2008; Panizza and Cerisola, 2009; Fernandes et al., 2012; Oturan et al., 2012; Chaplin, 2014; Brillas and Martín Huittle, 2015; Trellu et al., 2016a, 2016b).

\[ R \rightarrow (R)^+ + e^- \]  
\[ M + H_2O \rightarrow M(OH) + H^+ + e^- \]  
\[ R + M(OH) \rightarrow \text{degradation byproducts} \]

However, several scientific challenges still need to be overcome in order to promote the application of AO for water treatment. The OH are produced at an anode surface, and due to their short lifetime they are only present in a thin layer (~1 μm) close to the anode surface (Kapatka et al., 2008, 2009; Donaghue and Chaplin, 2013). Therefore, reactions occur at or near the electrode surface, and at currents at or above the limiting current, electrolysis is limited by mass transport of pollutants from the bulk to the electrode surface. In addition, side reactions such as the oxygen evolution reaction (OER) strongly decrease the current efficiency for target compound oxidation (Panizza et al., 2001; Panizza and Cerisola, 2009; Chaplin, 2014). Currently, most of the electrodes used in AO are conventional plate anodes implemented in parallel plate reactors, for which mass transport is strongly limited by diffusion through a thick (~10–100 μm) stagnant boundary layer (Liu and Vecitis, 2012; Zaky and Chaplin, 2013). The possibility to reach high current efficiency depends mainly on the implementation of a pre concentration step of organic pollutants by adsorption or filtration processes (Ganiyu et al., 2015). It has been shown that the most promising way to avoid diffusion/mass transfer limitations and to increase the electroactive surface area is using porous electrodes in flow through configurations (Vecitis et al., 2011; Liu and Vecitis, 2012; Zaky and Chaplin, 2013; Cuo et al., 2016b). Recent results obtained during the last five years demonstrated that reactive electrochemical membranes (REMs) are a breakthrough technology for electro oxidation of organic pollutants during water treatment. Thus, REMs are becoming a major area of interest in the field of both material science and electrochemical engineering.

Although several review articles thoroughly detailed electro oxidation processes (Brillas et al., 2009; Panizza and Cerisola, 2009; Chaplin, 2014; Sirés et al., 2014; Vasudevan and Oturan, 2014; Brillas and Martín Huittle, 2015; Martín Huittle et al., 2015; Radjenovic and Sedlak, 2015), a summary of recent advancements related to REMs are needed. The objective of this work is to provide a state of the art on the electro oxidation of organic compounds by REMs as well as to highlight the future perspectives of this technology. The emphasis given to electro oxidation mechanisms complements the review by Ronen et al. (2016) on electro conductive and electro responsive membranes. Thus, the main focuses are to review literature related to: (i) the synthesis and characterization of REMs, (ii) the electroactive surface area of REMs (iii), the mass transport of organic pollutants in REM reactors, (iv) the charge transfer and oxidation mechanisms (direct electron transfer, mediated oxidation) using REM materials, and (v) the main issues affecting lifetime of REMs (fouling and corrosion). Finally, main conclusions and perspectives are drawn in order to establish the potential of REMs for the removal of organic pollutants from water.

2. Materials used as REMs

Enhancing the implementation of REMs for water treatment requires the improvement of membrane design, by a fine control of their porous structure and pore size, while maintaining high electical conductivity, mechanical resistance, and efficient mass transport. Indeed, the morphological and physico chemical
properties of membrane materials directly affect their electrochemical activity. In this section, the synthesis and properties of carbon and semi conducting oxide based materials are described. The characteristics of the most utilized REMs have been highlighted in Tables 1 and 2, and their suitability for electro oxidation is discussed in the subsequent sections.

2.1. Carbon based REMs

Many studies utilized conductive carbon materials for the synthesis of REMs, such as graphene (2D base unit), multi wall carbon nanotubes (MWCNTs) (1D structure) and graphite (3D structure). These materials are characterized by a sp² hybridization, allowing the delocalization of π-π electrons in the structures and thus they possess a high theoretical conductivity (Iijima, 1991; Iijima and Ichihashi, 1993; Novoselov et al., 2004; Castro Neto et al., 2009). REMs prepared from graphene and MWCNTs mainly suffer from poor connectivity due to weak van der Waals interactions that limit their electron conductivity (Gao et al., 2014; Liu et al., 2014). However, these materials are effective at coupling adsorption and electro oxidation, due to their high specific surface area (Peigney et al., 2001).

Wang et al. (2009) evaluated MWCNTs packed between two pieces of activated carbon felt that formed a porous cathode anode cell, that was utilized as a seapage MWCNT electrode reactor. Vecitis et al. (2011) proposed another original design of an electrochemical filter using CNTs (Fig. 1 a), which allowed improving electrodechemical and filtration characteristics. In this design, a CNT layer (Fig. 1 b) was deposited by vacuum filtration on a polytetra fluoroethylene (PTFE) filter support (pore diameter of 5 μm) without using a binder (Fig. 1 c and 1 d).

However, CNT based REMs can be leached into solution during the filtration process (Gao et al., 2014), which is a major issue for water treatment applications because of the cytotoxicity of CNTs (Shvedova et al., 2003). Therefore, researchers also prepared composite CNT materials using polymers binders such as poly vinylidene fluoride (PVDF) (Gao et al., 2014) and polyaniline (PANI) (Wang et al., 1987; Duan et al., 2016), which prevented the CNT release and increased the REM stability and electron conductivity. A similar strategy was utilized with carbon nanofibers (CNFs), which were dispersed in a polyethersulfone (PES) matrix and deposited on an ultrafiltration polymer support (Li et al., 2017).

In summary, CNTs appear to be the most promising carbon materials to fabricate REMs due to their small pores size, high porosity, high specific surface area, and their tunable properties by incorporation of binders (polymer, conductive polymer, and graphene). Subsequent research should focus on nanostructuring of CNT filters, for example with lithographic technics to synthesize uniform and vertically aligned CNTs (Prasek et al., 2011).

2.2. Ceramic membranes

A review of the literature suggests that oxides are very promising materials for the fabrication of REMs. In contrast to CNT and graphene REMs, ceramic processing allows the large scale fabrication of REMs with various shapes, fine control of the pore size and effective grain boundaries during the sintering step. Recent works were focused on developing porous and electrocatalytic ceramic membranes based on carbon or Ti membranes modified with semi conductive materials such as TiO2 or RuO2. Sub stoichiometric Ti oxides (TiOx or Ti6O11-n (4 ≤ n ≤ 10)), also known as Magnéli phases, represent the most promising oxides for REM fabrication. These oxides, which were first synthesized and characterized in the 1950s (Andersson et al., 1957), have an oxygen evolution potential (OEP) and *OH production rate that is comparable to BDD electrodes (Bejan et al., 2009). Common stoichiometric TiO2 phases (rutile, anatase, and brookite) present an n type doping at ambient conditions, due to intrinsic defects related to oxygen vacancies (V0) and interstitial titanium atoms (Tii). In the case of Magnéli phases, the conductivity arises from a restructuring of the crystal lattice to eliminate the oxygen vacancies, which results in the formation of shear planes due to rutile TiO2 and corundum Ti3O2 stacking (Padilha et al., 2016). Among the different Magnéli phases, researchers mainly focused their attention on Ti4O7, due to its high electrical conductivity (≈ 1000 S cm⁻¹) (Smith et al., 1998). More over, Ti4O7 is insoluble in strong acids and bases and more stable than carbon under anodic polarization (Pollock et al., 1984). However, the conductivity of Magnéli materials can also be affected by the porosity of the material, due to contact resistance (Hayfield, 2001; Ye et al., 2015; Guo et al., 2016a). The general route to fabricate porous monolithic Ti4O7 REMs consists of the processing and sintering of a TiO2 porous material (tube, plate, rod, and pellet) followed by a second thermal treatment under a reductive atmosphere (e.g., H2) (Eq. (4)).

\[
4\text{TiO}_2 + H_2 \rightarrow \text{Ti}_4\text{O}_7 + H_2O \tag{4}
\]

In general, the micro structure of the produced materials depends mainly on the choice of thermal treatment temperature and duration, as well as on the mass and density of the TiO2 precursor structure (Table 1) (Hayfield, 2001; Guo et al., 2016b; You et al., 2016). For example, Ti4O7 ultrafiltration membranes were synthetized by reduction of commercial TiO2 ultrafiltration membranes at 1050 °C for 50 h under H2 (Guo et al., 2016b). As another example, a UF layer composed of TiO2 and Ti4O7 was obtained by dip coating of a TiO2 layer on the inner surface of a tubular Al2O3 membrane, followed by a reduction step under 30% H2 in Ar at 1025 °C for 7 h (Geng and Chen, 2016). A REM was also previously fabricated from a commercially available Ebonex® electrode. These macroporous ceramic Magnéli phases were prepared from the reduction of a TiO2 tube under H2 to yield a bimodal porous structure (Table 1), which contains a mixture of Ti4O7, Ti5O9 and Ti6O11 as secondary phases (Hayfield, 2001). The control of the stoichiometry of Magnéli phases according to the choice of precursors and thermal treatment is an interesting challenge for material science. Other chemical reducing agents may be used instead of H2 in order to prepare Magnéli materials, such as Ti (Lu et al., 2012), NH3 (Tang et al., 2012), Zr (Kitada et al., 2012), and carbon (Zhu et al., 2013; Trellu et al., 2018). Recently, the carbothermal reduction of TiO2 proved its efficiency in the synthesis of a macroporous REM composed mainly of conductive Ti5O9 and Ti4O7 phases (Trellu et al., 2018).

Porous Ti4O7 monoliths might overcome many of the carbon materials drawbacks, since Ti4O7 can achieve good interconnection of grains (sintering process), a high stability under anodic polarization, and the generation of hydroxyl radicals by the oxidation of water.

3. Electroactive surface area of REMs

The reaction of substrates with *OH are often in the diffusion limited range with second order rate constants commonly ranging from 10⁵ to 10¹⁰ M⁻¹ s⁻¹ (Buxton et al., 1988). Experimental and modeling studies have also shown that due to the high reactivity of *OH, they exist in only a narrow reaction zone adjacent to the electrode surface (<10 μm) (Kapila et al., 2009; Mascia et al., 2007; Donaghey and Chaplin, 2013). As a result of these very fast kinetic processes, the use of 2D electrodes, and small reaction zone volumes, the operation of electrochemical water treatment technologies become mass transport limited at relatively low applied current densities (e.g., <5 mA cm⁻²) (Canizares et al., 2006;
<table>
<thead>
<tr>
<th>Anode (working electrode)</th>
<th>Pore size (nm)</th>
<th>Porosity (%)</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>Total specific surface area (m$^2$) (directly from reference or calculated)</th>
<th>Geometric surface area (m$^2$)</th>
<th>Shape</th>
<th>Permeability (L h$^{-1}$ m$^{-2}$ bar$^{-1}$)</th>
<th>Conductivity (S cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous graphite carbon</td>
<td></td>
<td></td>
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<tr>
<td>CNT/activated carbon felt (ACF)</td>
<td>60 - 100 for CNT (&lt;2 for ACF)</td>
<td>85</td>
<td>40 - 70 for CNT</td>
<td>0.0145</td>
<td>Tube</td>
<td></td>
<td>102</td>
<td>0.0028</td>
<td>Korbahti and Tanyolac (2003) Yang et al. (2009)</td>
</tr>
<tr>
<td>CNT/PTFE filter</td>
<td>115 ± 47 (CNT)</td>
<td>85</td>
<td>88.5</td>
<td>1.05</td>
<td>0.0007</td>
<td>Flat</td>
<td>102</td>
<td>102 (CNT)</td>
<td>Vecitis et al. (2011) Gao and Vecitis (2011)</td>
</tr>
<tr>
<td>CNT, Sn$_2$O$_3$-coated CNT, surface-treated CNT</td>
<td>110 ± 10 (CNT)</td>
<td>85</td>
<td>88.5</td>
<td>1.4 for CNT</td>
<td>0.0007</td>
<td>Flat</td>
<td>102, 0.011, 1-200,</td>
<td></td>
<td>Liu et al. (2013)</td>
</tr>
<tr>
<td>CNT, Sn$_2$O$_3$-coated CNT, Bi-doped Sn$_2$O$_3$-coated</td>
<td>110 ± 10 (CNT)</td>
<td>85</td>
<td>88.5</td>
<td>1.4 for CNT</td>
<td>0.0007</td>
<td>Flat</td>
<td>102</td>
<td></td>
<td>Liu et al. (2013)</td>
</tr>
<tr>
<td>CNT/PTFE filters</td>
<td>104 ± 39 (CNT)</td>
<td>85</td>
<td>88.5</td>
<td>1.4</td>
<td>0.0007</td>
<td>Flat</td>
<td>102</td>
<td></td>
<td>Gao and Vecitis (2012b)</td>
</tr>
<tr>
<td>CNT, B-doped CNT, N-doped CNT</td>
<td>104 ± 39 (CNT), 112 ± 46 (B-CNT), 99 ± 42 (N-CNT), 104 ± 39 (CNT)</td>
<td>85</td>
<td>88.5</td>
<td>1.4</td>
<td>0.0007</td>
<td>Flat</td>
<td>102</td>
<td></td>
<td>Liu and Vecitis (2012) Schnoor and Vecitis (2013) Gao and Vecitis (2013)</td>
</tr>
<tr>
<td>CNT/PTFE filter</td>
<td>104 ± 39 (CNT)</td>
<td>85</td>
<td>88.5</td>
<td>1.4</td>
<td>0.0007</td>
<td>Flat</td>
<td>102</td>
<td></td>
<td>Gao and Vecitis (2013)</td>
</tr>
<tr>
<td>Graphene nanoplatelet (GNP): CNT coated GNP/PTFE filter</td>
<td>Inferior to CNT filter (&lt;85)</td>
<td>420 (30%wt CNT) = 67 (30%wt CNT)</td>
<td>0.0007</td>
<td>Flat</td>
<td>2116 (pure GNP) Low conductivity compared to isolated GNP</td>
<td>9.510$^{-2}$ - 3.710$^{-5}$</td>
<td></td>
<td></td>
<td>Liu et al. (2014)</td>
</tr>
<tr>
<td>CNT/PTFE filter combined with CNT-PVDF membrane</td>
<td>86 for pure CNT and 81 for CNT/PVDF</td>
<td>1</td>
<td>0.0007</td>
<td>Flat</td>
<td>510 for CNT and 180 for CNT/PVDF filter</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CNT treated CNT/PTFE filter</td>
<td>104 ± 39 (CNT)</td>
<td>85</td>
<td>120.7 (CNT electro-oxidized), 88.5 (CNT)</td>
<td>1.9 (CNT electro-oxidized)</td>
<td>0.0007</td>
<td>Flat</td>
<td>102</td>
<td></td>
<td>Liu et al. (2015a,b)</td>
</tr>
<tr>
<td>Carbon aerogel (CA), Sn$_2$O$_3$-coated carbon aerogel, Bi-doped Sn$_2$O$_3$-coated carbon aerogel</td>
<td>110 ± 10 (CNT)</td>
<td>85</td>
<td>88.5</td>
<td>1.4</td>
<td>0.0007</td>
<td>Flat</td>
<td>102</td>
<td></td>
<td>Liu et al. (2015)</td>
</tr>
<tr>
<td>CNT, carboxylated CNT/PTFE filters</td>
<td>125 (CNT), 133 (carboxylated CNT)</td>
<td>85</td>
<td>660 (CA)</td>
<td>138</td>
<td>0.0002</td>
<td>Flat</td>
<td>&gt;100 (reported by the manufacturer)</td>
<td></td>
<td>Bakr and Rahaman (2016)</td>
</tr>
<tr>
<td>CNT, B-doped CNT/PTFE filters</td>
<td>116 (CNT) 60 (B-doped CNT)</td>
<td>85</td>
<td>166</td>
<td>0.0007</td>
<td>Flat</td>
<td>102, &gt;100 (reported by the manufacturer)</td>
<td></td>
<td></td>
<td>Bakr and Rahaman (2017)</td>
</tr>
<tr>
<td>Polyaniline (PANI) coated CNT, PVA coated CNT</td>
<td>PANI/CNT: 20 ± 2, PVA/CNT: 46.37 ± 2.37, H$_2$SO$_4$-PANI/CNT (25%), PVA/CNT (28%)</td>
<td>85</td>
<td>3 (PANI/CNT)</td>
<td>2.8 (PVA/CNT)</td>
<td>0.0004</td>
<td>Flat</td>
<td>3 (PANI/CNT): 89.28 ± 3.07 PVA/CNT: 8.83 ± 0.24</td>
<td></td>
<td>Duan et al. (2016)</td>
</tr>
<tr>
<td>Material Description</td>
<td>Pore Size</td>
<td>Membrane Type</td>
<td>Performance Metrics</td>
<td>Source</td>
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<tr>
<td>Sn-doped SnO₂-coated coal-based carbon (CM)</td>
<td>420</td>
<td>Flat</td>
<td>0.0004</td>
<td>Liu et al. (2017)</td>
<td></td>
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<tr>
<td>Fe²⁺ NP catalyst carboxylated-CNT/PTFE filter</td>
<td>24 25</td>
<td>Flat</td>
<td>0.0013</td>
<td>Yanez et al. (2017)</td>
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<tr>
<td>Carbon nanofibers/PES composite forward osmosis membrane</td>
<td>440</td>
<td>Tube</td>
<td>0.0020</td>
<td>Li et al. (2017)</td>
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<tr>
<td>TiO₂-coated carbon membrane</td>
<td>410</td>
<td>Tube</td>
<td>0.0017</td>
<td>Wang et al. (2014)</td>
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<tr>
<td>TiO₂-coated carbon membrane</td>
<td>410</td>
<td>Tube</td>
<td>0.0009</td>
<td>Liu et al. (2016a,b)</td>
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</tr>
<tr>
<td>Ebonex® (TiOₓ) membrane</td>
<td>410</td>
<td>Tube</td>
<td>0.0009</td>
<td>Zaky and Chaplin (2013)</td>
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<tr>
<td>Ebonex® (TiOₓ) membrane</td>
<td>410</td>
<td>Tube</td>
<td>0.0009</td>
<td>Zaky and Chaplin (2014)</td>
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<tr>
<td>Electrospun PSU/ Electrosprayed Ti₄O₇-coated carbon cloth</td>
<td>2990</td>
<td>Tube</td>
<td>0.0016</td>
<td>Santos et al. (2016)</td>
<td></td>
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</tr>
<tr>
<td>Reduced TiO₂ (TiOₓ) UF membrane</td>
<td>2990</td>
<td>Tube</td>
<td>0.0016</td>
<td>Guo et al. (2016a,b)</td>
<td></td>
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<tr>
<td>Ti₄O₇/Al₂O₃ near UF membrane</td>
<td>200-300 (Ti₄O₇)</td>
<td>Tube</td>
<td>0.0063</td>
<td>Geng and Chen (2016)</td>
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<tr>
<td>Ti₄O₇/Al₂O₃ near UF membrane</td>
<td>200-300 (Ti₄O₇)</td>
<td>Tube</td>
<td>0.0063</td>
<td>Geng and Chen (2017)</td>
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<tr>
<td>RuO₂-coated Ti membrane</td>
<td>980</td>
<td>Tube</td>
<td>0.0017</td>
<td>Zhang et al. (2016)</td>
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<tr>
<td>Ti₃O₇/Ti₄O₇ MF membrane</td>
<td>980</td>
<td>Tube</td>
<td>0.0017</td>
<td>Trellu et al. (2018)</td>
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<tr>
<td>Anode (working electrode)</td>
<td>Cathode</td>
<td>Pollutant (Conc., mgC L⁻¹)</td>
<td>Current density (mA cm⁻²)</td>
<td>Cell potential (V)</td>
<td>Anode potential (V)</td>
<td>Permeate flux (L h⁻¹ m⁻²)</td>
<td>Electrolyte (mM)</td>
<td>Reference</td>
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<tr>
<td>CNT/carbon felt</td>
<td>CNT/carbon felt</td>
<td>Red X-3B (18.5)</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td>NaCl (2050)</td>
<td>Yang et al. (2009)</td>
<td></td>
</tr>
<tr>
<td>CNT/PTFE filter</td>
<td>SS</td>
<td>Methylene blue (1.3)</td>
<td>52</td>
<td></td>
<td></td>
<td></td>
<td>NaCl (100)</td>
<td>Vecitis et al. (2011)</td>
<td></td>
</tr>
<tr>
<td>CNT, Sb-doped SnO₂-coated CNT, surface-treated CNT/PTFE filters</td>
<td>SS</td>
<td>Methyl Orange (168)</td>
<td>52</td>
<td>0.1 1.7</td>
<td>1 3</td>
<td>0.4 1.8 (vs. Ag/AgCl)</td>
<td>Na₂SO₄ (100)</td>
<td>Gao and Vecitis (2011)</td>
<td></td>
</tr>
<tr>
<td>CNT, SnO₂-coated CNT, Sb-doped SnO₂-coated CNT, B-doped SnO₂-coated /PTFE filters</td>
<td>SS</td>
<td>Oxalate (100)</td>
<td>52</td>
<td>0.1 3.5</td>
<td>1.8 6</td>
<td>0.7 3.0 (vs. Ag/AgCl)</td>
<td>Na₂SO₄ (10)</td>
<td>Liu et al. (2013)</td>
<td></td>
</tr>
<tr>
<td>CNT/PTFE filter</td>
<td>SS</td>
<td>Phenol (72)</td>
<td>55</td>
<td></td>
<td></td>
<td></td>
<td>Na₂SO₄ (100)</td>
<td>Gao and Vecitis (2012b)</td>
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<tr>
<td>CNT, B-doped CNT, N-doped CNT PTFE filters</td>
<td>SS</td>
<td>Phenol (14 72)</td>
<td>52</td>
<td>0.8 2.1 (vs. Ag/AgCl)</td>
<td>0.1 1.5</td>
<td>1 3</td>
<td>0.4 1.6 (vs. Ag/AgCl)</td>
<td>Na₂SO₄ (100)</td>
<td>Gao and Vecitis (2012a)</td>
</tr>
<tr>
<td>CNT/PTFE filter</td>
<td>SS</td>
<td>Methylene blue (1.3 223)</td>
<td>52</td>
<td>0.1 1.7</td>
<td>1 3</td>
<td>0.4 1.4 (vs. Ag/AgCl)</td>
<td>NaCl (10)</td>
<td>Liu and Vecitis (2012)</td>
<td></td>
</tr>
<tr>
<td>CNT/PTFE filter</td>
<td>Ti or CNT</td>
<td>Fe(CN)₆⁴⁻ (12 180)</td>
<td>7 140</td>
<td></td>
<td>0.8 0.7 (vs. Ag/AgCl)</td>
<td>2 3.5</td>
<td>0.8 2.1 (vs. Ag/AgCl)</td>
<td>Na₂SO₄ (100)</td>
<td>Schnoor and Vecitis (2013)</td>
</tr>
<tr>
<td>CNT/PTFE filter</td>
<td>SS</td>
<td>Phenol (72)</td>
<td>55</td>
<td></td>
<td>0.0 0.7 (vs. Ag/AgCl)</td>
<td>2 3.5</td>
<td>0.8 2.1 (vs. Ag/AgCl)</td>
<td>Na₂SO₄ (100)</td>
<td>Gao and Vecitis (2013)</td>
</tr>
<tr>
<td>Graphene nanoplatelets: CNT/PTFE filter</td>
<td>SS</td>
<td>Fe(CN)₆³⁻ (6 120)</td>
<td>52</td>
<td></td>
<td>0.0 0.7 (vs. Ag/AgCl)</td>
<td>2 3.5</td>
<td>0.8 2.1 (vs. Ag/AgCl)</td>
<td>Na₂SO₄ (10)</td>
<td>Liu et al. (2014)</td>
</tr>
<tr>
<td>CNT/PTFE filter combined with CNT-PVDF membrane</td>
<td>CNT/PTFE filter combined with CNT-PVDF membrane</td>
<td>Nitrobenzene (7.2)</td>
<td>55</td>
<td></td>
<td>0 4</td>
<td>0 4</td>
<td>0 4 (vs. Ag/AgCl)</td>
<td>Na₂SO₄ (10)</td>
<td>Gao et al. (2014)</td>
</tr>
<tr>
<td>CNT surface-treated CNT/PTFE filter</td>
<td>SS</td>
<td>Phenol (72)</td>
<td>55</td>
<td></td>
<td>0 4 0.7 (vs. Ag/AgCl)</td>
<td>2 3.5</td>
<td>0 4 (vs. Ag/AgCl)</td>
<td>Na₂SO₄ (100)</td>
<td>Gao et al. (2015a,b)</td>
</tr>
<tr>
<td>CNT/PTFE filter</td>
<td>Ti or CNT</td>
<td>Tetracycline (53)</td>
<td>52</td>
<td></td>
<td>0 3</td>
<td>0 1 1.8 (vs. Ag/AgCl)</td>
<td>Na₂SO₄ (10)</td>
<td>Liu et al. (2015)</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td></td>
<td>Synthetic and real spiked effluent</td>
<td>300</td>
<td></td>
<td></td>
<td>2.5 12.5</td>
<td>Na₂SO₄ (10)</td>
<td>Liu et al. (2016a,b)</td>
<td></td>
</tr>
<tr>
<td>Anode (working electrode)</td>
<td>Cathode</td>
<td>Pollutant (Conc., mgC L(^{-1}))</td>
<td>Current density (mA cm(^{-2}))</td>
<td>Cell potential (V)</td>
<td>Anode potential (V)</td>
<td>Permeate flux (L h(^{-1}) m(^{-2}))</td>
<td>Electrolyte (mM)</td>
<td>Reference</td>
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<tr>
<td>Carbon aerogel, SnO(_2)-coated carbon aerogel, Sb-doped SnO(_2)-coated carbon aerogel</td>
<td>SS</td>
<td>Tetracycline (30)</td>
<td>0.1</td>
<td>0.4</td>
<td>12.8</td>
<td>Na(_2)SO(_4) (69)</td>
<td>Bakr and Rahaman (2016)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT, carboxylated CNT /PTFE filters</td>
<td>Ti</td>
<td>Methylene blue (3)</td>
<td>0.17</td>
<td>3</td>
<td>20</td>
<td>Nothing or Na(_2)SO(_4) (10)</td>
<td>Duan et al. (2016)</td>
<td></td>
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<tr>
<td>Sb-doped SnO(_2)-coated coal-based carbon</td>
<td>SS</td>
<td>Tetracycline (30)</td>
<td>0</td>
<td>4</td>
<td>150</td>
<td>Na(_2)SO(_4) (100)</td>
<td>Liu et al. (2017)</td>
<td></td>
<td></td>
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<tr>
<td>Fe(^{0}) NP doped CNT/PTFE Pt filter</td>
<td>SS</td>
<td>Ibuprofen (0.7 15)</td>
<td>0.5</td>
<td>1 (vs. Ag/AgCl)</td>
<td>32</td>
<td>NaCl (10)</td>
<td>Bakr and Rahaman (2017)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT, B-doped CNT /PTFE filters</td>
<td>Ti</td>
<td>Bisphenol A (0.8 80)</td>
<td>0.1</td>
<td>0.3</td>
<td>128</td>
<td>NaCl (0 100)</td>
<td>Bakr and Rahaman (2017)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT/PEI forward osmosis membrane</td>
<td>Ti</td>
<td>Phenol (360)</td>
<td>0</td>
<td>3</td>
<td>5</td>
<td>Na(_2)SO(_4) (10000)</td>
<td>Li et al. (2017)</td>
<td></td>
<td></td>
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<tr>
<td>TiO(_2)-coated carbon membrane</td>
<td>SS</td>
<td>Diesel fuel/Tween 80 (200 mg L(^{-1}))</td>
<td>0.67</td>
<td>2</td>
<td>80</td>
<td>Na(_2)SO(_4) (104)</td>
<td>Yang et al. (2011)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO(_2)-coated carbon membrane</td>
<td>SS</td>
<td>Diesel fuel/Tween 80 (200 1000 mg L(^{-1}))</td>
<td>0.67</td>
<td>2</td>
<td>80</td>
<td>Na(_2)SO(_4) (104)</td>
<td>Yang et al. (2012)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO(_2)-coated carbon membrane</td>
<td>SS</td>
<td>Phenol (144 720)</td>
<td>0.3</td>
<td></td>
<td>112 971</td>
<td>Na(_2)SO(_4) (104)</td>
<td>Wang et al. (2014)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO(_2)-coated carbon membrane</td>
<td>SS</td>
<td>Tetracycline (30 150)</td>
<td>0.5</td>
<td>2.5</td>
<td>50 150</td>
<td>Na(_2)SO(_4) (104)</td>
<td>Liu et al. (2016a,b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ebonex(^{®}) (TiO(_x)) membrane</td>
<td>SS</td>
<td>Fe(CN)(_6)^{3-} (60)</td>
<td>0</td>
<td>3.5</td>
<td>15 80</td>
<td>NaClO(_4) (10)</td>
<td>Zaky and Chaplin (2013)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ebonex(^{®}) (TiO(_x)) membrane</td>
<td>SS</td>
<td>p-methoxyphenol (84)</td>
<td>0</td>
<td>3 (vs. SHE)</td>
<td>35 55</td>
<td>NaClO(_4) (10)</td>
<td>Zaky and Chaplin (2014)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrospun PSU/Electrosprayed TiO(_2)-coated carbon cloth</td>
<td>BDD</td>
<td>Phenol (72)</td>
<td>1</td>
<td></td>
<td>6100</td>
<td>K(_2)HPO(_4) (100)</td>
<td>Santos et al. (2016)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reduced TiO(_2) (TiO(_x)) UF SS membranes</td>
<td>SS</td>
<td>Fe(CN)(_6)^{3-} (60)</td>
<td>0</td>
<td>3.14 (vs. SHE)</td>
<td>50 1500</td>
<td>K(_2)HPO(_4) (100) NaClO(_4) (100)</td>
<td>Guo et al. (2016b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuO(_2)-coated Ti membrane</td>
<td>SS</td>
<td>Tricyclazole (11 57)</td>
<td>3</td>
<td>20</td>
<td>417</td>
<td>Na(_2)SO(_4) (35)</td>
<td>Zhang et al. (2016)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO(_2)/TiO(_2) MF membrane</td>
<td>SS</td>
<td>Oxalic acid (18 870)</td>
<td>6</td>
<td>30</td>
<td>100 3000</td>
<td>Na(_2)SO(_4) (50)</td>
<td>Trellu et al. (2018)</td>
<td></td>
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</table>
Donaghue and Chaplin, 2013). Most treatment systems are there for operated under mass transport limited conditions, where reaction rates are governed by the diffusion of contaminants to the electrode surface. Therefore, current research is focused on the development of high electroactive surface area electrodes that utilize strategies to maximize mass transport rates (Guo et al., 2016b; Nayak and Chaplin, 2018).

The use of high surface area 3D electrodes in parallel plate configurations only result in a small increase in reaction rates, as features of electrode roughness are smaller than the diffusion length and therefore become averaged into the diffusion field (Bard and Faulkner, 2000). However, REMs have the advantage of having a high specific surface area available for electrochemical reactions (Zaky and Chaplin, 2013; Guo et al., 2016b), due to the convection enhanced transport of dissolved species and the very small pore diameters that allow for fast radial mass transport inside the pores (Liu and Vecitis, 2012; Zaky and Chaplin, 2013; Guo et al., 2016b). The electrode’s porous structure, electrical conductivity, and whether the reaction is limited by charge or mass transfer will all affect the electroactive surface area available for reaction (Alkire and Gracon, 1975; Trainham and Newman, 1977a,b, 1978; Lasia, 1997).

The total electroactive surface area available for reaction using REMs was estimated by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) methods under flow through conditions (Zaky and Chaplin, 2013; Guo et al., 2016a, 2016b; Jing and Chaplin, 2016). These methods rely on measuring the charging current and calculating the double layer capacitance ($C_d$), which can be converted to an electroactive surface area estimate by assuming a value for the specific capacitance (i.e., $\mu F/cm^2$). For metal oxide electrodes values of 10–100 $\mu F/cm^2$ were proposed (Antropov, 1972). Calculation of the electroactive surface area by these methods provides an upper bound estimate, which is indicative of the surface area assessable to the supporting electrolyte and available for electrode charging. Comparing these estimates to the total surface area of REMs measured by Hg porosimetry, indicated that only a fraction of the total surface area of the REMs were electroactive (i.e., 1.5–11.4%) (Zaky and Chaplin, 2013). In either case, these scenarios show the importance of synthesizing electrodes with a high conductivity and interconnectivity of the fluid transport pores. Engineering of the porous REM structure has received little attention and is an important area for future research.

The total electroactive surface area measured by EIS and CV methods is the maximum possible area available for reaction, and the actual surface area that participates in reaction depends on whether the reaction of interest is limited by charge or mass transfer (Trainham and Newman, 1977a,b, 1978; Lasia, 1997). Under the condition of charge transfer control, the potential drops drastically with distance from the counter electrode (or depth into the REM). This condition was investigated rigorously in porous electrodes assuming Butler Volmer kinetics, and numerical simulations indicated that the potential drop is a function of the electrolyte and electrode conductivity, specific surface area, counter electrode placement, and kinetic parameters (i.e., exchange current density, electron transfer coefficient) (Trainham and Newman, 1977a,b, 1978; Lasia, 2008). For facile reaction kinetics the potential may drop significantly and since the current is exponentially related to the potential (according to Butler Volmer kinetics) reactions are restricted primarily to the surface closest to the counter electrode (Trainham and Newman, 1977a,b, 1978; Lasia, 2008). Under this situation the reactive surface area is significantly less than the total electroactive surface area.

Under conditions of mass transport control and negligible potential drop in the electrode phase, the concentration and potential profiles with depth into the REM can be calculated analytically (Fedkiw, 1981). The concentration profile ($C(y)$) follows an exponential decrease with distance into the REM, according to Eq. (5).

$$\frac{C(y)}{C_F} \exp \left( -\frac{a \frac{k_m}{L} y}{J} \right)$$

where $k_m$ is the mass transfer coefficient (m/s), $a$ is the specific surface area (m$^-2$), $J$ is the REM flux (m/s), $L$ is the REM thickness, $C_F$ is the feed concentration (mol m$^-3$), and $y$ is the distance into the REM.

Under mass transport control the reactive surface area can reach that of the electroactive surface area and is dependent on mass transport parameters (i.e., $k_m$, $J$). The potential drop with depth into the REM is typically approximately linear and since under mass transport control the current is no longer an exponential function of potential the entire REM thickness can be utilized for reaction. However, the above analysis only applies for thin REMs, as the potential drop in solution can be significant for thick REMs and eventually lead to charge transfer limitations. Therefore, further studies are required for developing counter measures such as additional current feeders or improvement of the reactor design. One such approach would be a design that utilizes a stack of thin REMs, each separated by a thin gasket. A stack of thin, alternating anodes and cathodes would allow for sequential oxidative/reductive electrochemistry, a high utilization of the surface area, and minimal potential losses due to solution resistance.

In general there has been little attention dedicated to understanding reactive transport in REMs. However, there is a large body of literature available for packed bed flow through electrodes that are applicable to REMs (Trainham and Newman, 1977a,b, 1978; Fedkiw, 1981; Risch and Newman, 1984). This type of analysis can greatly enhance REM development and optimization and is a critical area for future study.

4. Convection-enhanced mass transport of organic pollutants

For the analysis of AO of organic pollutants using conventional
2D electrodes, the most widely used approach is to consider that the electro oxidation takes place either under mass transfer limitations or under charge transfer limitations (Comminellis et al., 2008; Panizza and Cerisola, 2009). The mass transfer limit can be estimated from the limiting current density \(i_{lim}\) (Eq. (6)), which is related to the mass transfer rate constant and concentration of organic compounds (Panizza et al., 2001; Rodrigo et al., 2001; Comminellis et al., 2008).

\[
i_{lim}(t) = 4Fk_mC_{OD}(t)
\]  

(6)

In Eq. (6), \(i_{lim}\) is the limiting current density \((\text{A} \text{m}^{-2})\) at time \(t\), 4 is the number of electrons exchanged from \(O_2\), \(F\) is the Faraday constant, \(k_m\) is the mass transfer rate constant \((\text{m} \text{s}^{-1})\) and \(C_{OD}\) is the chemical oxygen demand \((\text{mol} \text{m}^{-3})\) at time \(t\). A mixed kinetic regime can also exist, particularly when strong, stable oxidant species are generated that are transported to the bulk solution (e.g. chlorine, ozone, persulfate) (Martínez Huitle and Ferro, 2006; Panizza and Cerisola, 2009; Martínez Huitle et al., 2015).

At currents above \(i_{lim}\), electro oxidation occurs under mass transfer control and the current efficiency strongly decreases with increases in current (Panizza and Cerisola, 2009). This often compromises the energetic sustainability of the AO process for the treatment of low concentration pollutants. Mass transfer limitations can be reduced by (i) coupling electro oxidation with a pre concentration step (Ganiyu et al., 2015), (ii) continuously adjusting the current density to the limiting current density during treatment (Panizza et al., 2008), and (iii) improving the fluid dynamics in the electrochemical cell in order to increase the mass transfer rate (Vectis et al., 2011; Zaky and Chaplin, 2013; Martínez Huitle et al., 2015).

Using conventional plate electrodes in a batch cell, stirring conditions are one of the most crucial parameters for AO efficiency (de Oliveira et al., 2011). Continuous systems such as flow by reactor configuration are more suitable for improving hydrodynamic conditions and for implementation of large scale electrochemical cells (Panizza et al., 2007; dos Santos et al., 2014; Martínez Huitle et al., 2015). Mass transfer processes over a flat plate or in a pipe are often analyzed by nondimensional groups, including the Sherwood number \((Sh\), Eq. (7), ratio between convective and diffusive mass transport\) and the Reynolds number \((Re\), Eq. (8), ratio of inertia to viscous forces\), as well as the Schmidt number \((Sc\), Eq. (9), ratio of viscosity to diffusivity\), as well as a nondimensional shape factor \((Le\), which depends on the geometry of the electrochemical cell\). Values for \(k_m\) can be estimated by using correlations, typically under the form of Eq. (10) (Canizares et al., 2006).

\[
Sh = \frac{k_md}{D}
\]  

(7)

\[
Re = \frac{ud}{\nu}
\]  

(8)

\[
Sc = \frac{\nu}{D}
\]  

(9)

\[
Sh = \frac{k_md}{D} \cdot aRebSc^cLe^d
\]  

(10)

In the equations above, \(d\) is the characteristic length of the system, \(D\) the diffusion coefficient of the organic compound in water, \(u\) the fluid velocity, \(\nu\) the kinematic viscosity of the fluid and \(a, b, c, d\) are constants that are determined empirically. Maximum \(k_m\) values that can be achieved are often on the order of \(10^{-6} - 10^{-5} \text{ m} \text{s}^{-1}\) (Canizares et al., 2006). For example, Zaky and Chaplin (2013) determined a diffusion limited mass transfer rate at the surface of an anode under the form of a pipe as \(4.32 \times 10^{-6} \text{ m} \text{s}^{-1}\) (Re = 1270; inner diameter and length of the electrode was 1.7 cm and 20 cm, respectively).

One of the main issues of using conventional plate electrodes is the limitation of mass transport through the external diffusion boundary layer \((\delta_b)\). The steady state \(\delta_b\) in flow by electrolysis cells can be as high as 100 \(\mu\)m, according to the cross flow velocity and the channel spacing. Thus, the efficiency of the process relies on the diffusion of contaminants through this layer. In this configuration, the use of high surface area electrodes only slightly increases \(k_m\) values because the features of electrode roughness are smaller than the diffusion length. Therefore, implementation of porous electrodes in a flow through configuration is the most promising way to overcome diffusion limitations. Using REMs in flow through mode lead to a convective increase of \(k_m\), according to the steady state balance between forward convection and diffusion (Liu and Vecitis, 2012). At high flow rates, \(\delta_b\) can reach a theoretical length of less than the electrode pore radius. This type of analysis assumes straight, cylindrical pores, where the time scale of diffusion \((t_D)\) (Eq. (11)) and convection \((t_C)\) (Eq. (12)) can be estimated.

\[
t_D = \frac{r_p^2}{D}
\]  

(11)

\[
t_C = \frac{l}{\nu}
\]  

(12)

In the equations above, \(r_p\) is the average pore radius \((\text{m})\), \(D\) is the diffusion coefficient of the organic compound \((\text{m} \text{s}^{-1})\), \(l\) is the electroactive thickness, and \(\nu\) is the average pore velocity \((\text{m} \text{s}^{-1})\). Using TiOx REM \((r_p = 0.85 \mu\text{m}, l = 880 \mu\text{m})\) for electro oxidation of Fe(CN)\(_6^3\)-, it was reported that diffusion limitation \((t_D > t_C)\) would only occur at \(J > 1.3 \times 10^5 \text{ L}^{-1} \text{m}^{-2} \text{h}^{-1}\) (Zaky and Chaplin, 2013), which is much higher than normal operating conditions of microfiltration membranes. The smaller the electrode pore size, the lower \(t_D\) and the lower the diffusion limitations. However, small pore size also strongly increases pressure drops across the REM and the permeability (in terms of \(L \text{h}^{-1} \text{m}^{-2} \text{bar}^{-1}\)) of REM decreases. This means that higher transmembrane pressure has to be invoked as a driving force for increasing the permeate flux (i.e. the convection rate). This is the reason why the performances of an ultrasound TRREM \((3200 \text{ Lh}^{-1} \text{m}^{-2} \text{bar}^{-1})\) surpassed those of Ebonex\(^®\) electrodes \((50–70 \text{ Lh}^{-1} \text{m}^{-2} \text{bar}^{-1})\), which was not tailored for water treatment (Zaky and Chaplin, 2013; Guo et al., 2016b). Besides, one of the main advantages of using CNT REMs is the possibility to generate a thin filtration layer \((41 \mu\text{m})\) with low pore size \((115 \text{ nm})\) and high porosity (85%), leading to a permeability in the range 500–2000 \(\text{Lh}^{-1} \text{m}^{-2} \text{bar}^{-1}\) (Liu and Vecitis, 2012).

Fig. 2. Mass transport rate \((k_m)\) reported in the literature according to the electrochemical cell configuration. In the bottom left, evolution of the diffusion boundary layer \((\delta_b)\) in batch and flow-through configurations. (a) dos Santos et al. (2014); (b) Schnoor and Vecitis (2013); (c) Guo et al. (2016b).
Thus, Vecitis et al. (2011) reported a diffusion and convection characteristic time of 3.3 μs and 1.2 s, respectively, for the electro oxidation of a dye molecule in a CNT/PTFE REM.

However, since actual electrode pores are not completely straight and cylindrical, δ_0 will be larger in experimental setups. A good approximation of k_m as a function of the pore fluid velocity is given by Eq. (13).

\[ \frac{\epsilon k_m}{\partial t} = m_1 \left( \frac{\nu}{\partial t} \right)^{1/3} \]  

(13)

where \( \epsilon \) is the REM porosity, \( a \) is the specific surface area (m\(^{-1}\)), and \( m_1 \) is an experimentally determined constant. This correlation was applied to numerous packed bed electrodes and should also be applicable to REMs (Wilson and Geankoplis, 1966).

Fig. 2 shows different values of k_m reported in the literature according to the electrochemical cell configuration (batch, flow by, and flow through). Operation of AO under convective limited conditions is a great advantage; since k_m can be simply increased by performing electro oxidation at a higher permeate flux. While Yang et al. (2009) reported a 1.6 fold improvement of k_m using a flow through configuration, Liu and Vecitis (2012) showed an increase in the mass transfer limited current density from 0.97 (in batch) to 6.1 mA cm\(^{-2}\). Even better, the study of Guo et al. (2016b) reported a convection enhanced k_m for Fe(CN)\(_6\)\(^{3-}\) of 1.6 \( \times 10^{-4} \) m \( \text{s}^{-1} \), close to the estimated charge transfer limit. Thus, for the treatment of low concentrations of organic compounds, the current efficiency can be improved simply by increasing the permeate flux (i.e. the convection rate). For example, the current efficiency for the removal of oxalic acid (TOC = 24 mg L\(^{-1}\)) by TiO\(_x\) REM increased from 25% to 84% at 90 and 561 L h\(^{-1}\) m\(^{-2}\) respectively (Fig. 3). Guo et al. (2016b) proposed a semi empirical analysis of reaction kinetics in REMs for the determination of the observed rate constant (\( k_{\text{obs}} \)). It takes into account reaction (\( k_r \)), diffusion (\( k_d \)) and convection (\( k_c \)) rate constants (Eq. (14), (15)). This approach highlights that the decrease of the diffusion limitations can create a new challenge: increasing the reactivity of REMs (\( k_c \)) in order to take advantage of the convection enhanced mass transfer in flow through electrochemical cells.

\[ k_{\text{obs}} = \left( \frac{C_{\text{in}}}{C_{\text{in}}} \right) \frac{C_{\text{out}}}{C_{\text{in}}} k_c \frac{k_c}{1 + \frac{k_d}{k_c}} \]  

(14)

where, \( C_{\text{in}} \) and \( C_{\text{out}} \) are the concentration of organic compounds in the influent and effluent of the REM, respectively, Q is the permeate flux (m\(^2\) s\(^{-1}\)), A is the geometric surface area of the REM (m\(^2\)), \( k_d \) is the convection rate constant (m s\(^{-1}\)) and \( k_c \) (kinetic rate constant) according to the limiting process.

Organic compound adsorption is another important parameter to consider during REM operation, particularly when using CNTs (Vecitis et al., 2011; Liu and Vecitis, 2012; Liu et al., 2015). Adsorption can increase the effective residence time of target pollutants within the electroactive pore structure. For example, the differences in electro oxidation efficiency of oxalate, formate, formaldehyde and alcohols were reported to be attributed to different sorption kinetics (Liu et al., 2013). Thus, a strategy for enhanced performance is to tailor the electrode surface chemistry for strong adsorption of organic pollutants (Gao and Vecitis, 2011; Liu et al., 2013; Gao et al., 2015a). However, adverse effects can also arise from adsorption. For example, reactive site saturation by adsorbed tetracycline was observed to limit the overall electro oxidation kinetics (Liu et al., 2015).

5. Charge transfer and oxidation mechanisms

Apart from the high electroactive surface area and convection enhanced mass transport, the efficiency of AO depends on the reactivity of the REM. The choice of both the electrode material and operating conditions strongly influences charge transfer mechanisms. Table 2 summarizes operating conditions reported in studies investigating the AO of organic pollutants using REMs. The studies on TiO\(_x\) coated carbon membranes were also included in Table 2, as these materials can also form \( \cdot \text{OH} \) under anodic polarizations (Wang et al., 2014). The process is similar to the well known photocatalytic process, but the nature of the energy input is different.

5.1. Oxygen evolution potential

Anode materials used for AO are often divided into two main classes according to their OEP (Fig. 4): (i) “active” electrodes with low overpotential for OER (<0.3/0.4) and (ii) “non active” electrodes with high overpotential for OER (>0.4) (Panizza and Cerisola, 2009; Martínez Huitle et al., 2015). Only non active electrodes are able to generate large quantities of \( \cdot \text{OH} \) from water oxidation (\( E^\circ = 2.38 \) V vs. SHE) that are physisorbed at the electrode surface and are readily available for oxidation of organic compounds. The production of other oxidant species such as ozone (\( E^\circ = 1.51 \) V vs. SHE) or sulfate radicals (\( E^\circ = 2.4 \) V vs. SHE) is also possible (Martínez Huitle et al., 2015). Anode materials can also be classified according to their selectivity for \( \cdot \text{OH}, \text{H}_2\text{O}_2, \) or \( \text{O}_2 \) evolution, as analyzed by Siahrostami et al. (2017). Thermodynamically, the
selectivity of an anode material for the formation of *OH from water oxidation depends on the free energy of the adsorbed *OH. If the free energy of the adsorbed *OH is comparable to that of the aqueous phase *OH, then it will desorb from the anode surface and be available for reaction. Conversely, if the free energy of the adsorbed *OH is significantly lower than the aqueous phase *OH, it will not desorb and will react to form O₂ or H₂O₂ (Siahrostami et al., 2017). In addition, the OER can also affect the electrocatalytic activity of the material due to oxygen bubbles blocking reactive sites (Liu et al., 2013). These oxygen bubbles, as well as H₂ production at the cathode, were reported to increase pressure drop across the REM due to the decrease of the active filtration area (Trellu et al., 2018).

5.1.1. CNT based REMs

One of the most widely used material as REM is carbon, which is considered as an “active” electrode. For example, an OEP of 1.7 V vs. SHE was reported for activated carbon fibers (Fan et al., 2008). At low potential, electro oxidation of organic compounds is possible by direct electron transfer reactions that are dictated by the electrocatalytic activity of the material (Panizza and Cerisola, 2009). However, some organic compounds are recalcitrant to direct electron transfer (e.g., p-benzoquinone), thus leading to incomplete oxidation. Moreover, electropolymerization can also occur (Belhadj Tahar and Savall, 2009a, 2009b) and adsorption of polymers at the anode surface leads to a strong decrease of the electrocatalytic activity of the material (Panizza and Cerisola, 2009). This issue is of paramount importance when using REMs in filtration mode, since it can also lead to membrane fouling and increased pressure drop across the membrane (Gao and Vecitis, 2012a, 2013; Zaky and Chaplin, 2013, 2014; Trellu et al., 2018). This phenomenon was clearly highlighted by Gao and Vecitis (2012b), who observed CNTs coated by polyphenols and polyphenylene oxides, which were generated from phenol electropolymerization along the entire depth of the CNT layer (~40 μm). A greater amount of phenol removal was observed at anode potential of 0.82 and 1.6 V vs. Ag/AgCl, compared to 2.1 V vs. Ag/AgCl. Low anode potentials favored electropolymerization of phenols and allowed a physical separation (by adsorption on the electrode surface) of electro generated polymers (Trellu et al., 2018). However, this process is not a long term sustainable method for the removal of organic compounds such as phenol, because of the difficulty in removing polymers from membrane pores (Gao and Vecitis, 2013). Thus, it is necessary to operate REMs at higher anode potential, in the potential region of water oxidation, in order to be able to achieve aromatic ring opening. However, when high anode potentials are required for the complete oxidation of complex molecules, carbon materials suffer from a decrease in current efficiency (due to the OER) and significant electrode corrosion (Liu et al., 2013). For this reason, CNT doping was the focus of several studies, with the aim of increasing both the overpotential for OER and the stability of the electrode. For example, Gao and Vecitis (2012a) demonstrated that boron doped CNTs were able to reduce the extent of electropolymerization, because of the higher work function (i.e. the energy difference between the material Fermi level and the vacuum level) that enhanced the number of electrons transferred for phenol oxidation. Opposite results were obtained by using nitrogen doped CNTs, i.e. lower work function and electropolymerization enhancement. Another strategy that was utilized involved the coating of CNTs with a material possessing a high conductivity and overpotential for the OER. Liu et al. (2013) fabricated Bi doped SnO₂–coated CNTs, and similar materials were also synthesized by replacing Bi with Sb. However, using Sb is of less interest for water treatment applications because of the toxicity of Sb. The OEP was increased from 1.27 V vs. Ag/AgCl for the uncoated CNT anode to 1.71 V vs. Ag/AgCl for the Bi doped SnO₂–coated CNT (Liu et al., 2013). Moreover, the Tafel slope of this material was 1.05 V dec⁻¹, which is higher than those measured on BDD (0.29 V dec⁻¹) (Zhao et al., 2010), indicating relatively slow OER kinetics. Thus, a 2–8 fold increase of the mineralization kinetics for oxalate and other organic compounds, such as ethanol, methanol, formaldehyde and formate were observed.

5.1.2. Magnéli phase based REMs

Studies on the use of TiO₃ materials showed the most promising results on the possibility of using a REM for high yields of *OH formation. The OEP reported in the literature for TiO₃ materials (mainly Ti₄O₇) ranged between 2.2 and 2.7 V vs. SHE (Graves et al., 1991; Grimm et al., 1998; Kobrecka and Przyłuski, 1994; Miller Folk et al., 1989), similarly to the widely used (but expensive) BDD anode (2.3 V vs. SHE). Guo et al. (2016b) demonstrated the formation of *OH by studying the degradation of organic compounds used as *OH probes. A strong enhancement of the conversion of these *OH probes were observed when increasing the anode potential from 2.14 to 2.64 V vs. SHE. Such degradation mechanisms indicated the production of *OH and the anode potential required is consistent with the thermodynamic potential for *OH formation. Thus, high anode potential can be used in order to avoid electropolymerization and to degrade refractory organic compounds by *OH mediated oxidation.

5.2. Permeate flux, hydraulic residence time and charge transfer limitation

Different operating conditions can also affect the electro oxidation efficiency. First, the permeate flux and the hydraulic residence time are crucial parameters because of mass transport considerations and reaction time, as discussed in section 3. Increasing the permeate flux too much may also favor the OER by sweeping gas bubbles from the REM surface and enhancing the OER (Guo et al., 2016b; Trellu et al., 2018). This mechanism was attributed to lower removal rates and current efficiencies at high flow rates (Fig. 3) (Guo et al., 2016b; Trellu et al., 2018). In the study of Guo et al. (2016b), the maximum current efficiency for oxalic acid oxidation was 84% at a flux of 561 L·m⁻²·h⁻¹ using a Ti₄O₇ REM and 49% at a flux of 194 L·m⁻²·h⁻¹ using a Ti₅O₁₁Ti₆O₁₁ REM. The differences arose from the lower reactivity of the Ti₅O₁₁ phase. Different optimal values of TOC flux and maximum current efficiency were also achieved according to the current density (Trellu et al., 2018). Thus, the kinetic rate constant (k₅) of a REM is an important parameter to consider. This charge transfer limit is governed by the electron transfer rate and by chemical reaction kinetics between organic compounds and electrochemically produced oxidants. Using Fe(CN)₆³⁻ as a model compound, this kinetic limit was calculated to be 1.64 × 10⁻⁴ m·s⁻¹ by using an ultratrace TiO₃ electrode (Guo et al., 2016b), while Schnoor and Vecitis (2013) reported k₅, 1.0 × 10⁻⁴ m·s⁻¹ using a CNT REM.

5.3. Influence of anodic potential distribution within the REM

The potential drop according to the electrode depth in the REM can also influence oxidation mechanisms. The anode potential is sufficiently high for the formation of *OH only in the top portion of the REM closest to the counter electrode (jing et al., 2016), as explained in section 2. Therefore, when the TOC flux ([TOC]_{influence} ) is higher than the convective mass transport limit, organic compounds reach a depth into the REM where the potential is too low for significant *OH production and therefore only direct electron transfer reactions occur. This mode of operation can decrease the efficiency of the process because of the electropolymerization
phenomena and presence of organic compounds refractory to direct electron transfer reactions (Zaky and Chaplin, 2014; Trellu et al., 2018). In order to avoid such adverse effects, it is necessary to adjust the operating conditions (TOC flux and current density), so that reactions are limited by convective mass transport and organic compounds are degraded close to the REM surface where *OH are generated (Trellu et al., 2018). These mechanisms have to be taken into consideration for optimization of the process. For example, Trellu et al. (2018) reported that a much higher mineralization current efficiency was achieved at 6 mA cm\(^{-2}\) compared to 30 mA cm\(^{-2}\) for the treatment of a TOC flux of paracetamol of 5 g m\(^{-2}\) h\(^{-1}\), but the contrary was observed for the treatment of a TOC flux of 15 g m\(^{-2}\) h\(^{-1}\) (Fig. 5). Increasing the current density was also observed to prevent REM fouling by electropolymerization of phenol (Trellu et al., 2018).

5.4. Conductivity and electrolyte concentration/composition

The conductivity and electrolyte concentration/composition of the influent can also strongly influence electro oxidation efficiency and reaction mechanisms. First, the presence of ions such as Cl\(^{-}\) and SO\(_4\)\(^{2-}\) can lead to the formation of additional strong oxidant species (active chlorine, SO\(_4\)\(^{2-}\)). The formation of these species favors electro oxidation in the bulk solution and was therefore observed to improve the oxidation efficiency in mass transport limited configurations (Martínez Huitte et al., 2015). In contrast to batch re actors, it was observed that a decrease of the ionic strength (from 100 to 1 mM of Na\(_2\)SO\(_4\)) did not significantly increase the charge transfer resistance (Schnoor and Vecitis, 2013). This result was attributed to the flow through configuration and continuous convective renewal of fresh electrolyte to the REM surface, which resulted in a hydrodynamic reduction of the charge transfer resistance (Schnoor and Vecitis, 2013).

5.5. Cathode material

The nature of the cathode material was also shown to be an important consideration. For example, the use of a CNT cathode significantly improved charge transfer efficiency by comparison to perforated Ti as cathode materials (Liu et al., 2015; Schnoor and Vecitis, 2013). The total cell potential required for total conversion of 1 mM Fe(CN)\(_6\)\(^{3-}\) by using CNT as both anode and cathode was 1 V lower than for the electrochemical cell using a Ti cathode. In this two electrode cell, lower cathode potential was required for water electro reduction by using CNT, thus leading to a shift in the potential distribution towards the anode and strongly reducing the energy required for the overall electrochemical process. Besides, the electrochemical cell configuration and cathode material can also be optimized in order to achieve single pass, sequential reduction oxidation of pollutants, as reported for nitrobenzene by Gao et al. (2014).

CNTs were also used in a sandwich membrane stack in order to perform sequentially EF and AO processes (Gao et al., 2015b). The membrane stack consisted of a CNT filter cathode for H\(_2\)O\(_2\) generation, which contained COO\(^{-}\) functional groups with chelated Fe\(^{2+}\) ions that were capable of participating in the Fenton's reaction at neutral pH and that could be electro regenerated, an insulating separator and a CNT filter anode. This study emphasized synergetic effects from the sequential combination of EF and AO in filtration mode, thus constituting an interesting proof of concept of this innovative reactor design. Performing the EF process at neutral pH is a significant advantage, which has been the goal of several heterogeneous catalyst synthesis studies (Banuelos et al., 2013; Ammar et al., 2015; Ganiyu et al., 2017).

6. REM lifetime

6.1. Fouling

Despite continuous improvements aimed at mitigating fouling in membrane processes, the fouling issue in membrane filtration for water treatment remains the most significant challenge. Fouling is problematic for both ceramic and polymeric membranes, where colloids, macromolecules, and microorganisms are responsible for the formation of fouling layers (Guo et al., 2012). The main fouling mechanisms for microfiltration and ultrafiltration membranes are (i) deposition (cake formation) (Yuan et al., 2002), (ii) pore blockage (Yuan et al., 2002; Costa et al., 2006; Wang and Tarabara, 2008; Guo et al., 2012; Lee et al., 2013; Dilaver et al., 2018) and (iii) adsorption (hydrophobic and electrostatic interactions) (Fan et al., 2001; Lee et al., 2004; Costa et al., 2006; Jung et al., 2006; Yamamura et al., 2007; Xiao et al., 2011; De Angelis and de Cortezzi, 2013). Particularly, the hydrophobicity of the membrane material is a crucial parameter that often governs fouling (Howe and Clark, 2002; Xiao et al., 2011; Lee et al., 2013; Geng and Chen, 2016). Using several model foulants (i.e., polyethylene glycol, natural humic acid and a mixture of organic and inorganic solutes), comparative studies highlighted that ceramic materials such as TiO\(_2\) with higher hydrophilic character (15.6 ± 3.4° water contact angle) than PVDF (69.3 ± 2.9°) were less susceptible to fouling by hydrophobic organic molecules or colloids (Lee et al., 2013). On the contrary, hydrophobicity and \(\pi\) interactions of CNT filters (contact angle 66.2 ± 2.7°) favor strong adsorption of water contaminants, such as aromatic compounds or natural organic matter (Liu and Vecitis, 2012). Because of the lower hydrophobic interactions between organic foulants and ceramic materials, the main fouling mechanism of ceramic membranes is related to initial pore blocking and a fast transition to cake formation, which is primarily removed by a physical cleaning (Guo et al., 2012; Lee et al., 2013; Dilaver et al., 2018). Besides, electrostatic interactions between the membrane and charged compounds have also be taken into consideration in order to limit membrane fouling and improve the efficiency of physical cleaning of membranes (Lee and Kim, 2014; Zhang and Vecitis, 2014).
Further mechanisms have to be considered when studying REMs (Jing et al., 2016; Ronen et al., 2016; Formoso et al., 2017). The combination of filtration processes with other processes is an important current area of research in order to avoid fouling issues. In particular, oxidation at the interface combined with enhanced electrostatic repulsive forces of foulants was reported to lead to a non negligible delay in membrane fouling of membrane electro oxidizers (e.g. Alumina Ceraflo membrane) (Ronen et al., 2016; Formoso et al., 2017; Mameda et al., 2017). Coupling membrane and electro oxidation processes provides a promising tool to ensure both the removal of targeted molecules and high throughput via the prevention of fouling (Geng and Chen, 2017). Thus, self cleaning electrochemical membrane reactors are expected to emerge in the next few years (Yang et al., 2011; Ahmed et al., 2016; Ronen et al., 2016; Formoso et al., 2017).

In electrically enhanced filtration processes, the applied electric field can also increase electrostatic repulsions. For example, Geng and Chen (2016) observed the repulsion of negatively charged molecules (e.g. humic acids) by a TiO2/Al2O3 composite under cathode polarization (Huotari et al., 1999; Geng and Chen, 2016, 2017). This phenomenon can be described by the extended Nernst Planck equation (Eq. (16)), which takes into consideration diffusive, migrative, and convective fluxes.

\[
J_i = D_i \frac{\partial C_i}{\partial x} + D_i \frac{R T}{F} \frac{\partial \phi}{\partial x} + C_i \nu(x)
\]  

(16)

where \( J_i \) is the averaged flux of the charged species \( i \) (mol m\(^{-2}\)s\(^{-1}\)), \( C_i \) is the concentration in the solution (mol m\(^{-3}\)), \( D_i \) is the diffusion coefficient (m\(^2\)s\(^{-1}\)), \( z_i \) is the valence number of the charged species \( i \), \( F \) is the Faraday constant (9.648 \times 10^4 C \cdot mol^{-1}), \( R \) is the ideal gas constant (8.314 J \cdot mol^{-1} \cdot K^{-1}), \( T \) is the absolute temperature (K), \( \frac{\partial \phi}{\partial x} \) is the electrical field (V m\(^{-1}\)) and \( \nu(x) \) is the velocity of the fluid through the porous media (m s\(^{-1}\)).

If the applied electric field reaches a critical value, the combined diffusive and convective fluxes towards the REM (Geng and Chen, 2017) will be balanced by the migrational flux away from the REM. Under conditions where the diffusive flux is negligible compared to convection, the theoretical value for the critical electric field strength \( \Phi_{critical} \) at which the net ion migration velocity towards the REM is zero can be estimated by Eq. (17) (Huotari et al., 1999).

\[
\Phi_{critical} = \frac{\nu(x)}{u_i}
\]

(17)

where \( u_i \) is the mobility of the charged species.

Electrostatic interactions can also be enhanced between negatively charged species and the anode, which enhances organic compound adsorption (Liu and Vecitis, 2012; Zhou et al., 2017). Degradation of the adsorbed molecules at the REM surface can prevent the formation of the fouling layer (Ahmed et al., 2016). However, if electro oxidation kinetics is not sufficient to degrade adsorbed molecules, REM fouling can occur by one of the prevailing mechanisms, which is dependent on the solute size and hydrophobicity. For example, the electrochemical filtration of polystyrene (PS) microspheres (1.58 \( \mu \)m) through a TiO\(_2\) REM (active layer pore size \( < 10\) nm), resulted in intermediate pore blocking followed by cake layer formation and reduced the access of solutes to the electroactive surface. However, the fouling layer was easily removed using a backwash with either anodic or cathodic potential on the REM (Jing et al., 2016).

Electrochemical processes can also have adverse effects on membrane fouling when electropolymerization of organic compounds occurs at the surface of anode materials, especially with phenolic compounds, (Belhadj Tahar and Savall, 2009a; Comninellis and Nerini, 1995; Gao and Vecitis, 2013; Yang et al., 2013; Ahmed et al., 2016; Trellu et al., 2018). Phenol polymerization is due to the production of intermediate phenolic free radicals that adsorb on the electrode surface and polymerize by radical chain reaction mechanisms (Comninellis and Pulgarin, 1991; Ferreira et al., 2006; Gao et al., 2015a). The formation of adsorbable recalcitrant polymers inside REM pores can be avoided by using high O\(_2\) overpotential anodes such as TiO\(_2\) and appropriate operating conditions to achieve the total mineralization of phenolic compounds (Trellu et al., 2018). Another side effect to take into consideration is the precipitation of salts that are present in the electrolyte (Gao and Vecitis, 2012a). In the EF system, ferric ions can also precipitate into Fe(OH)\(_3\) at pH values higher than 6. Thus, an optimal pH of 3 has to be maintained in order to avoid the precipitation of iron (III) hydroxide at the membrane surface that could greatly affect the flux through the porous electrode (Xu et al., 2016). Such precipitation phenomena can reduce the degradation rate by decreasing the number of active sites for adsorption or reaction and by reducing mass transfer because of lower flux (Li et al., 2016; Zhou et al., 2017). For the treatment of real effluents containing metallic ions, electro deposition on cathodic polarized REMs might also contribute to flux decline.

Bubble flow resistance is also responsible for flux decrease in REMs without any relation to common fouling mechanisms (Geng and Chen, 2017; Trellu et al., 2018). Gas bubbles are generated at the anode surface during water electrolysis when the anode potential exceeds the OEP (Saleh, 2007; Kapakta et al., 2010). They act as a shield and prevent molecules from reaching the reactive surface (Liu et al., 2013; Sun et al., 2013). Electro generated gas bubbles are then swept from the membrane surface by the convective flux (Guo et al., 2016b; Trellu et al., 2018). From another point of view, several studies mentioned that these gas bubbles could be used as a physical barrier to prevent fouling (Ahmed et al., 2016) or increase the electrochemical backwash efficiency by lifting the fouling layer (Wu et al., 2008; Jing et al., 2016; Jing and Chaplin, 2016).

As regards to the fouling issue, it is also important to mention that ceramic membranes used as REMs are robust from a mechanical, thermal and chemical standpoint. These characteristics allow them to withstand harsh cleaning conditions to remove foulants by backwash, solvent or acid base chemical treatment and even polarity reversal (Hayfield, 2001; Gao and Vecitis, 2013; Lee et al., 2013; Dashtban Kenari and Barbeau, 2016; Guo et al., 2016b).

These studies highlighted the potential positive and negative effects occurring during REM operation regarding fouling. However, only few studies have been conducted and more work is needed to investigate the ability of REMs to reduce fouling and enhance regeneration in complex real water matrices.

### 6.2. Corrosion

The cathode material is usually less susceptible to corrosion as confirmed by several studies with various electrode materials such as graphite (Ayadi et al., 2013), CNT (Gao et al., 2015a,b), graphene composite (Zhao et al., 2013) and graphite felt on PTFE (Ren et al., 2016). However, using a REM as an anode can cause both passivation and corrosion of the material. Therefore, the development of anode materials with high anodic stability is of great importance, in particular for organic compound oxidation processes that require application of relatively high potentials.

Because the standard potential of carbon oxidation reactions is 0.207 V vs. SHE (Kinosita, 1988), corrosion of carbon based REMs is often inevitable at high anode potentials. The oxidation of carbon to CO\(_2\) and/or CO leads to the destruction of the carbon electrode. For example, Yi et al. (2015) investigated the mechanisms of
electrochemical degradation of MWCNTs in acidic media. At high anode potential for OER, MWCNTs undergo an electrochemical activation by the formation of oxygenated functional groups, followed by a passivation due to a fully covered oxide layer (Ohmori and Saito, 2012; Tominaga et al., 2014; Yi et al., 2015). Therefore, it is necessary to modify carbon based anodes in order to extend their lifetime. Attempts to increase the resistance to AO of CNTs were centered on anchoring or coating metal nanoparticles (Co3O4, Bi doped SnO2) at their surface (Liu et al., 2013; Lu and Zhao, 2013). Results demonstrated an increase of the stability for potentials up to 2.2 V vs Ag/AgCl by using nanocrystalline Co3O4 (Lu and Zhao, 2013). Some studies also showed that the synthesis of a composite CNT material (PVDF/CNT on PTFE filter (Gao et al., 2014) or PANI as conductive polymer mixed with CNTs (Duan et al., 2016)) increased the lifetime of CNTs used as REMs.

In addition, REMs based on TiO2 seem to be the most promising materials in water treatment applications. In fact, TiO2 has high nificant resistance to corrosion in alkaline or acidic media, and can be used as either an anode or cathode (Pollock et al., 1984). However, TiO2 is not totally immune to passivation phenomena. Based on stoichiometry, the proportion of Ti3+ to Ti4+ is equivalent in TiO2, but for example, in the study of Pouilleau et al. (1997), XPS analysis indicated a larger proportion of Ti4+ at the surface (the survey thickness is a few nm with this technique). Thus, these results suggested that a natural passivation layer of a few nm of TiO2 is spontaneously formed on the TiO2 surface when exposed to ambient air at room temperature (Pouilleau et al., 1997). However, the related mechanisms are neither well understood nor described in the literature. Moreover, data obtained from XPS must be considered with caution, due to the electron beam, which can oxidize the titanium oxide surface. In the literature, the distinction between passivation and corrosion layers (>10 nm) is not well established, and authors commonly use the term of passivation. These passivation or corrosion layers were characterized by in situ energy dispersive X ray diffraction (Rowles et al., 2012) or EIS (Waraka et al., 2003) from 1.6 V vs. SHE. Electrochemical analysis appears to be the most relevant method to characterize the duraibility of REMs under anodic polarization. Some studies reported that the passivation was reversible upon cathodic polarization (El Sherif et al., 2010), while other studies reported the contrary (Waraka et al., 2003). More detailed studies on the passivation and reduction of Magnéli phases are needed in order to understand how to efficiently manage these anodes during water treatment applications.

7. Conclusions

The development of REMs is a breakthrough innovation for electro oxidation processes. The possibility to implement REMs in flow through configurations allows for the advantage of convection enhanced mass transport and high electroactive surface area. Diffusion limitations usually limit the efficiency of electro oxidation processes can be minimized. Current efficiencies reported with REMs can reach much higher values than those reported for conventional 2D electrodes. From the current status of knowledge, it is possible to analyze reaction kinetics in these 3D systems according to a semi empirical approach, which takes into consideration reaction, diffusion and convection rate constants. The development of effective REMs depends on these three parameters. Thus, an ideal REM must present the following characteristics:

- High conductivity and interconnectivity of the fluid transport pores;
- Suitable porous structure in order to avoid diffusion limitations (e.g. small pore size) and maintaining a high permeability (e.g. thin active filtration layer, high porosity);
- High reactivity, which can be evaluated by determining the electron transfer rate and/or by using probe molecules in order to assess electro oxidation mechanisms (direct electron transfer, *OH mediated oxidation);
- Long lifetime, including fouling and corrosion issues;
- Cost effective and environmentally friendly synthesis methods;
- Absence of toxicity.

Thus, development of REMs strongly relies on innovations in material science. The use of CNTs has been widely studied mainly because of their high conductivity, and suitable pore structure (high permeability, low pore size). However, corrosion issues occur at high anode potentials and the cytotoxicity of CNTs might prevent their widespread use. Recently, TiOx materials, known as Magnéli phases, appeared as very promising materials. By comparison to CNTs, corrosion is strongly reduced and their monolithic structure is more compatible to water treatment applications than nano materials. Moreover, the high oxygen overpotential of TiOx materials allows the electro generation of large quantities of *OH. Improving the reactivity of REMs is currently a critical parameter in order to take full advantage of the increase mass transfer rates. In addition, once the removal of organic compounds is kinetically limited, adverse effects have been reported from (i) the increase of the competition from O2 evolution at high permeate flux and (ii) electropolymerization phenomena and presence of organic compounds refractory to direct electron transfer in the REM layer where *OH cannot be generated because of potential drop in the REM depth.

Recent advances in REMs open the way towards broader applications of electro oxidation processes for the removal of organic pollutants. Therefore, scientists and engineers must face several challenges in the near future. Particularly, here are some critical points that must be addressed:

- Development of REM materials with suitable characteristics, as described above;
- Improving the understanding of reactive transport in REMs including a rigorous analysis of reaction kinetics and mass transport in flow through REMs, which is complicated by the variation of the electrode potential according to the electrode depth;
- Investigation of the efficiency of the process for the treatment of different real effluents;
- Evaluation of the formation of toxic by products, such as per chlorates or halogenated organic compounds, because one of the main drawbacks of electro oxidation processes is the potential formation of toxic byproducts;
- Investigation of the long term lifetime of REMs and implementation of procedures for preventing fouling and corrosion issues, if necessary;
- Complete life cycle analysis of the process in order to assess the competitiveness of the process, by comparison to other technologies.

These studies are required for the identification of an optimal process configuration. Then, it will be possible to determine the potential of REMs for application in full scale water treatment.

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