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Electrically and Electrochemically Assisted Nanofiltration: A Promising Approach for Fouling Mitigation

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<http://dx.doi.org/10.5772/intechopen.75819>

Abstract

Membrane fouling is regarded as the most critical bottleneck for the widespread application of membrane separation technology. The application of electricity to the surface of membrane provides a promising alternative for fouling mitigation, which may involve the following effects such as electrophoresis, electroosmosis, and electrooxidation. Electrophoresis and electroosmosis influence the movement of charged species (ions or molecules) or movement of fluid adjacent to charged surface under the applied electric field, while electrooxidation functions by degrading species accumulated in the concentration polarization layer and fouling layer to resume permeate flux. Different membrane modules have been developed to satisfy the requirement of electrode assembly. Meanwhile, this coupled process also promotes the development of stable and conductive electrodes including membrane electrodes. Successful applications have been found in the areas of ion separation and treatment of dye wastewater, arsenic contaminated wastewater, antibiotic contaminated wastewater, etc. Compared with microfiltration (MF) and ultrafiltration (UF), existing research in the nanofiltration (NF) is still limited. The increasing applications of NF in practice because of its unique separation capability will definitely trigger more investigations on this electrically or electrochemically combined antifouling technique.

Keywords: membrane antifouling, electrophoresis, electrooxidation, nanofiltration, membrane module

1. Introduction

Nanofiltration (NF) can distinguish species based on their size and/or valence [1]. The major drawback of NF lies in inherent membrane fouling caused by concentration polarization and

pore blockage, similar to other typical membrane separation processes. Membrane fouling significantly decreases permeate flux with time and shortens membrane service life, requiring mechanical or chemical cleaning or even complete replacement of the membrane elements after certain operation time [2]. Therefore, effective antifouling technique is in high demand to make the membrane separation processes economically more competitive.

The electrically or electrochemically combined separation process has been presented as an effective fouling control strategy through in situ membrane cleaning. The utilization of an external adjustable electric field in membrane filtration was first investigated and denoted as electrofiltration, which has been thoroughly studied for decades [3]. It is the combination of two driving forces: pressure and electric field, which are mainly used for the separation of charged molecules or particles. Most studies published previously in the literature refer to electro-microfiltration (EMF) or electro-ultrafiltration (EUF) with the feed solutions of minerals [4], emulsions [5], macromolecules [6], etc. It functions by dragging the charged foulants away from the membrane surface within the electric field. The electroosmosis flow generated by the superimposed electric field may also contribute to the enhanced permeate flux.

Compared with electrofiltration, there are relatively fewer studies about the combination of electrooxidation with membrane separation. However, the effectiveness of such electrochemically assisted separation process in membrane fouling control has drawn increasing attention with more research focus shifted to this area. With the contribution of electrochemical degradation of organic foulants concentrated at the membrane surface, the permeate flux could be resumed, and the permeate quality could be improved at the same time. The organic foulants treated by this coupled technique include oily emulsion [7], dyes [8, 9], phenols [10], natural organic matters [10], etc.

There are relatively fewer reports about electrically and electrochemically assisted NF than MF and UF. Moreover, corresponding module designs for such coupled NF process are limited as well, mainly presented as the “sandwich” configuration of membrane between two electrodes, whereas more compact module design with membrane performing dual functions of filter and electrode has already been well developed in MF and UF. This chapter aims to present the electrically and electrochemically assisted filtration process from the working principles first and then the existing developed membrane modules with different designs for embedded electrodes, followed by typical applications of coupled NF process. Toward the end, some possible aspects for future research are discussed in order to make the electrically and electrochemically assisted NF more practical and economically competitive.

2. Working principle

2.1. Electrophoresis and electroosmosis

Most particles acquire a surface charge when in contact with a polar (e.g., aqueous) medium because of ion adsorption or ion dissolution. This surface charge influences the distribution of nearby ions of opposite charge and leads to the formation of an electrical double layer at

the interface between the particle and the dispersion medium. The double layer contains two parts, the stern layer and the diffuse layer, with boundary named slipping plane. The zeta potential ζ is the electric potential at the slipping plane relative to a point in the bulk fluid. If electric voltage is applied, the charged particle (plus ions within the slipping plane) will likely be repelled toward the electrode of opposite charge, which is termed as electrophoresis. The velocity of charged particles (plus ions within the slipping plane) closely depends on the zeta potential ζ and the strength of the electric field [11]. The electrophoretic mobility, which is defined as the electrophoretic velocity per electric field, has a positive correlation with the zeta potential according to the Smoluchowski equation Eq. (1). This equation is valid in most cases for particles or colloids in aqueous media [12],

$$u_e = \frac{\zeta \varepsilon_0 \varepsilon_r}{\mu} = \frac{v_e}{E} \quad (1)$$

where u_e is the electrophoretic mobility of charged particles ($\text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$), ζ the zeta potential (V), ε_0 the permittivity of free space ($\text{F} \cdot \text{m}^{-1}$), ε_r the dielectric constant (dimensionless), μ the viscosity of the fluid ($\text{Pa} \cdot \text{s}$), v_e the electrophoretic velocity ($\text{m} \cdot \text{s}^{-1}$), and E the magnitude of electric field ($\text{V} \cdot \text{m}^{-1}$).

Electroosmosis is the motion of liquid under an applied potential across a porous material such as membranes. Similar to the electric double layer in a charged particle, the electric double layer also exists on the surface of porous material, which could be ionized when in contact with a polar medium. Ions in the diffuse layer migrate toward the electrode with opposite charge. Since ions are solvated, the solution is also dragged along, producing the electroosmotic flow [13].

When electrophoresis is combined with membrane separation, the combined system is usually termed as electrofiltration in short. Electrophoresis-assisted membrane was first mentioned by Bier as the so-called forced-flow electrophoresis for the reduction of membrane pore blockage, followed by similar research for the treatment of different feed solutions [5, 14–16]. The electrofiltration method is the consequence of the fact that charged droplets or particles in the feed solution could migrate away from the membrane surface in the electric field, which helps to reduce concentration polarization and mitigate membrane fouling. A typical schematic representation of electrophoresis-assisted filtration (electrofiltration) configuration is shown in **Figure 1** for the removal of negatively charged particulates using polysulfone membrane [17]. Besides flux enhancement by applied electric field, an electroosmotic flux is expected toward the cathode because of the negative charges carried by the membrane under neutral condition. However, if the membrane elements are utilized as both the electrode and the filtration media, the electroosmosis flow could be regarded as zero because there is no electric potential difference across the membrane [5]. Electrofiltration requires low conductivity of feed solution as well as high applied electric field to achieve high mobility of charged particulates and hence high productivity of the filtration process. The antifouling effects of electrofiltration membranes depend on many factors, such as magnitude of the electric field, concentration of the feed solution, electrode material and arrangement, size and zeta potential of the feed particles, etc.

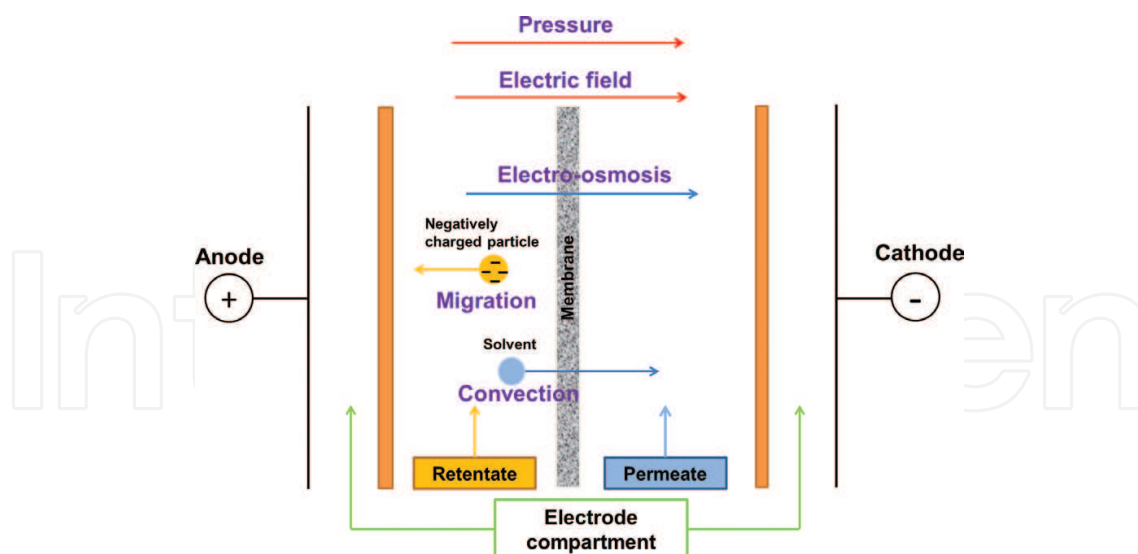
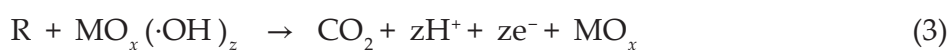


Figure 1. Schematic diagram of the electrofiltration process [18] (reproduced with permission).

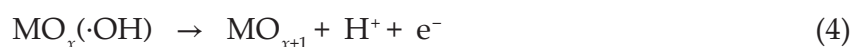
2.2. Electrooxidation

Electrooxidation could be divided into indirect and direct electrooxidation processes. Indirect electrooxidation could be achieved by electrochemically generated chlorine, hypochlorite, hydrogen peroxide, or ozone [19]. It is also possible to use mediators, which are metal ions oxidized on an anode from a stable and low valence state to a reactive and high valence state, to treat mixed and hazardous wastes [20]. For direct electrooxidation process, the anode surface could generate either physisorbed active oxygen ($\text{MO}_n\cdot\text{OH}\cdot$) or chemisorbed active oxygen (MO_{n+1}). Physisorbed oxygen reacts directly with oxidizable organic compounds acting as a source of hydroxyl radicals. $\beta\text{-PbO}_2$, Sb-doped SnO_2 , and Boron-doped diamond (BDD) exemplify this type of anode. Chemisorbed active oxygen is generated if the anode material MO_n is oxidizable and $\text{MO}_n\cdot\text{OH}\cdot$ is further oxidized to MO_{n+1} , which initiates oxidation process by a two-electron transfer mechanism. Examples of this kind of anode are IrO_2/Ti , RuO_2/Ti , etc. In general, $\cdot\text{OH}$ is more effective for pollutant oxidation than O in MO_{x+1} . The two mechanisms are illustrated as below Reactions (2)–(5) [21].

Oxidation by physisorbed active oxygen:



Oxidation by chemisorbed active oxygen:





The essential part of an anodic oxidation process is the selection of anodic material. An ideal anode should possess high electro-catalytic activity, high electrochemical stability, and affordable material cost. Meanwhile, it should also have a high overpotential for O₂ evolution so that Reactions (2) and (4) can proceed with high current efficiency. Otherwise, most of the electric current supplied will be consumed in splitting water.

Graphite and Pt electrodes can be effective only at very low current densities or in the presence of high concentrations of chlorides or metallic mediators [22]. PbO₂ is the most widely investigated anode material because of its relatively low cost and high current efficiency [23]. However, it suffers from severe electrochemical corrosion and causes secondary Pb²⁺ pollution. SnO₂ has been reported to have a high overpotential of oxygen evolution. Its stability is very poor [24]. Sb-doped SnO₂ electrodes have been developed including Ti/SnO₂-Sb, Ti/SnO₂-Sb-CNT [9] and Ti/SnO₂-Sb₂O₃-Y [25]. However, the performance still needs further improvement. Although IrO₂-based anodes (including dimensionally stable anodes (DSA)) have also been used for anodic oxidation of organic pollutants [26–28], such type of electrodes would have low current efficiency because of low overpotential of oxygen evolution. Meanwhile, because chemisorbed active oxygen is mainly generated at the IrO₂-based anodes, partial degradation of certain pollutants in wastewater has been mostly achieved, instead of complete mineralization [21, 26]. Boron-doped diamond (BDD) electrodes are attractive candidates for electrooxidation because of their high electrochemical stability, large electrochemical window, and high electrochemical activities for the degradation of pollutants. However, the fabrication process usually involves complex preparation procedures, severe operation conditions, and high equipment cost. It is also a challenge to deposit the diamond layer on common electrode substrate such as titanium [24, 29–31]. Another material worth mentioning is Magnéli titanium suboxides. They have high corrosion resistance and are capable of conducting mineralization reactions of organic pollutants such as trichloroethylene [32], *p*-nitrosodimethylaniline [33], *p*-benzoquinone (BQ) [33], coumarin [34], phenol [35], etc. The most conductive phase of Magnéli titanium suboxides, Ti₄O₇, has similarly large O₂ evolution potential to BDD electrode. With nanotube array morphology, it even possesses comparable electrochemical activity to BDD as well [35]. The preparation temperature of Ti₄O₇ is over 800°C requiring H₂ atmosphere. Partial oxidation may occur if the electrodes have been utilized multiple times. Therefore, it is still highly needed to develop new electrodes with high electrooxidation efficiency, high electrochemical stability, as well as acceptable material and fabrication cost.

The combination of electrooxidation with membrane filtration has been studied for a couple of years. With the contribution of electrochemical degradation of organic foulants concentrated at the membrane surface, the permeate flux of the hybrid membrane filtration process could be significantly enhanced. One schematic diagram of the membrane separation with electrooxidation assistance is shown in **Figure 2**. In order for electrooxidation effect to occur, many

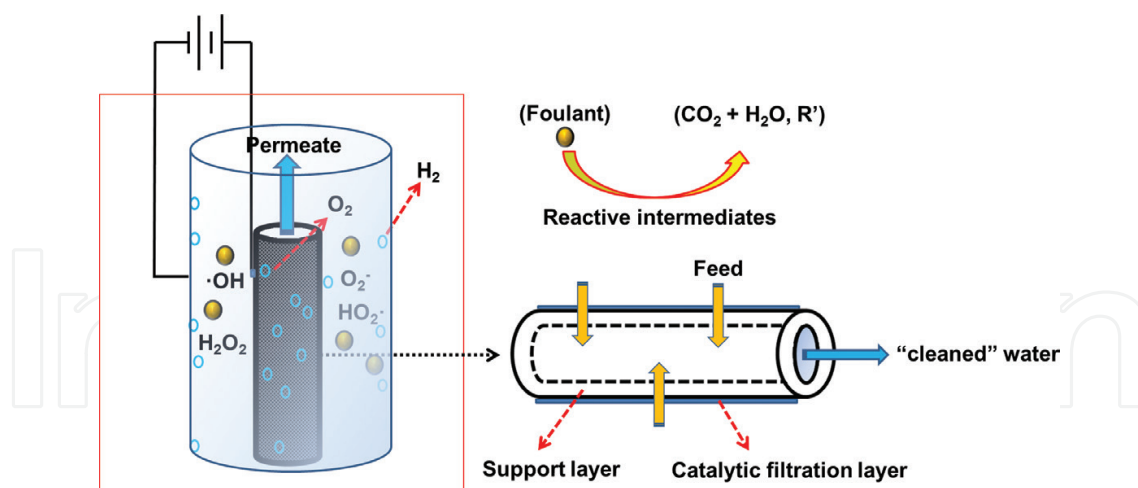


Figure 2. Schematic diagram of electrooxidation-assisted filtration [18] (reproduced with permission).

researchers developed conductive membrane electrodes to serve as the anode. However, O_2 gas may be induced if the applied potential is above the overpotential window, resulting in bubbling resistance to adversely affect the permeate flux [36, 37]. One possible solution is to locate the anode in close vicinity with the membrane surface to minimize the bubble resistance. With such kind of configuration, the induced O_2 gas may make the fluid near the membrane surface turbulent and further reduce concentration polarization and/or gel layer resistance [7, 38]. The detailed mechanism for the coupled process is still not well understood, requiring further fundamental investigation.

3. Electrically/electrochemically assisted membrane module design

3.1. Membrane material

Different from the porous membranes for UF and MF, the membranes in NF are mostly dense with pore sizes from 1 to 10 nm. Generally speaking, organic polymers present a fixed electric charge, which is mostly negative. Inorganic ceramics can be positively or negatively charged depending on the pH of bulk solution and isoelectric point of the membrane material [1].

3.2. Electrode material

For electrically assisted membrane filtration (electrofiltration), the anode and the cathode are normally separated from the membrane element. To date, the most commonly applied anodic material has been reported to be noble metal/metal oxides (e.g., platinum, iridium oxide)-coated titanium [39–41]. Graphite or stainless steel may also be used [1, 42, 43], but electrode corrosion is likely to occur after long-time operation. There is usually a wide range of selection for the cathodic material.

When the membrane itself serves as the electrode (i.e., membrane electrode) during electrofiltration, the membrane support layer or the modified layer could serve as the electrode. Conductive polymers are possible candidates which may provide membranes with electrical conductivity. Typical conductive polymers include polyaniline (PANI), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT), polyphenylene vinylene (PPV), etc. Their good conductivity is owing to the high electron mobility in the conjugated p-orbitals upon doping. Long-term stability should be considered when using conductive polymers as membrane electrodes. Meanwhile, the high hydrophobicity of these polymers may have a negative impact on filtrations of organic feed solutions. With much higher thermal and chemical stabilities, conductive inorganic materials, such as carbon- (used as membrane support), noble metal-, or metal oxides-based composites (used as modified layer), are possible alternatives of membrane electrodes for electrofiltration [44]. Electrochemical corrosion in alkaline condition is the common problem for carbon membranes [45]. The cost issue should be considered for noble metal- or metal oxides-based composites as conductive modified layers [36]. Magnéli Ti_4O_7 has also been utilized as membrane electrodes for electrofiltration [35, 46, 47]. The issue that should be considered for Magnéli Ti_4O_7 membrane electrode is partial oxidation to other Magnéli titanium suboxides with higher oxidation states if the electrolyte conductivity used for electrofiltration is high.

For electrooxidation-assisted membrane filtrations, polymers are seldom utilized, and the anodic materials are mostly composed of carbon, noble metal/metal oxides, doped SnO_2 , or BDD. Typical fabricated membrane electrodes for electrochemically assisted MF and UF include the TiO_2 /carbon composite membrane developed for oily water filtration [7]; the Boron-doped diamond (BDD)/Ti membrane developed for the treatment of Disperse Blue 2BLN powder [8]; the carbon nanotube (CNT)/ Al_2O_3 flat sheet composite membrane developed for the filtrations of silica spheres, latex particles, phenol, and natural organic matter (NOM) [10]; and the Ebonex membrane (mixture of the Magnéli phases of Ti_4O_7 and Ti_5O_9) for the removal of organic pollutant such as *p*-methoxyphenol [48]. Issues to consider when using these developed membranes include electrochemical instability of carbon membranes (usually graphite) [45, 49], sophisticated fabrication of BDD in membrane modification [10], and also possibly oxidation of Ebonex to higher oxidation states after repeated use. Up to now, the research on NF with electrooxidation assistance is limited. One typical research is conducted by Xu and coworkers using doped SnO_2 as anode in vicinity of membrane surface to degrade membrane foulants simultaneously with the separation process [25, 38]. Better performance may be achieved if replacing the electrode in their research with the materials developed for electrooxidation-assisted MF and UF or other typical materials for electrooxidation as mentioned in Section 2.2.

3.3. Membrane module configuration

Membrane module design is essential for the realization of electrically or electrochemically assisted membrane filtration. The styles of electrode assembly into the module should consider several parameters, including the types of membrane elements, the major working effect for membrane antifouling, and possible side effects brought to the feed or permeate solution. Generally speaking, most membrane modules with electrophoresis as the main antifouling

mechanism are constructed with flat sheet membrane elements with exerted electric field provided between two separate electrodes on either side of the membrane [4, 15, 16, 40, 41, 50]. Some electrooxidation-assisted membrane module also follows this style of electrode assembly with the anode in close vicinity of the membrane element [25, 38]. To make the system more compact and energy efficient, the membrane element itself could serve as both the electrode and the filtration media via the utilization of a conductive membrane support [5] or the modification of a conductive layer on a non-conductive membrane support [36]. The compact module design also promotes the development of electro-catalytic membranes (usually as membrane anode) as well, which could degrade foulants accumulated on the membrane surface simultaneously with the separation process through electrooxidation [7, 8, 51, 52], leading to higher permeate flux and better permeate quality.

The membrane modules presented below are some typical examples. Actually, these electrically or electrochemically assisted module designs should be applicable to all kinds of pressure-driven separation processes including MF, UF, NF, and RO, but the membrane elements and operation conditions should change accordingly.

3.3.1. Flat sheet membrane module

Figure 3 presents a flat sheet module design for electrophoresis-assisted arsenic wastewater treatment. The design utilized solid graphite plate as the anode and perforated graphite as the cathode. The electric contacts to external power supply were also made of graphite. With cathode located in the permeate side, it was possible to repel negatively charged H_2AsO_4^- and H_2AsO_3^- away from the membrane surface and retain relatively higher flux for longer operation time with applied electric field [43].

3.3.2. Tubular membrane module

According to the study of Wakeman and coworkers, tubular geometry modules would have the most effective use of electrical power when used as an aid to prevent membrane fouling [14]. Because of the annular structure of tubular membrane elements, the module design for the hybrid process is more complex compared with flat sheet membrane module. In general, a rod or wire needs to be inserted into the inside of membrane and fixed at two terminals.

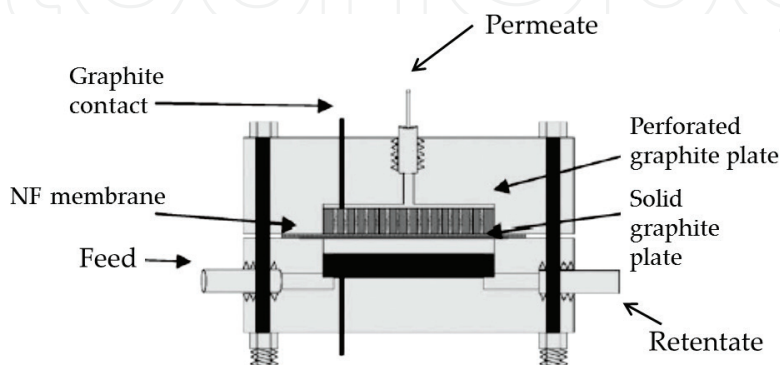


Figure 3. Flat sheet membrane module designs with electrophoresis assistance [43] (reproduced with permission).

Cylindrical netting is then required to surround the outer surface of membrane as the other electrode. Part of a typical tubular module design is shown in **Figure 4**, with rod electrode and cylindrical netting electrode composed of the same or different materials. The electric field distribution is more complex compared with flat sheet membrane module where the electric field distribution resembles that of a typical parallel-plate capacitor.

3.3.3. Module with functional membrane element

Just as mentioned before, in order to make the module more compact, the membrane element can also be utilized as one electrode if the inner or outer surface is conductive. Corresponding electric contact needs to be designed to connect with external power supply. The authors have developed one kind of membrane module that could act as membrane elements with either inner or outer surface conductive [18]. As shown in **Figure 5**, the electric contacts of (2) and (3) could connect the inner and outer surfaces of membranes, respectively, to the power supply. Both electric contacts were provided through stainless steel rods combined with graphite rods. The other non-membrane wire electrode could be inserted through the module terminals which were sealed with silicone rubbers.

3.3.4. Separate compartment of electrodes

For electrophoresis-assisted membrane filtration, low conductivity of feed solution is usually required. However, electrolysis is generally unavoidable at the high potential applied for electrophoresis. Similarly, electrolysis will occur if the voltage supplied exceeded the electrochemical window for electrooxidation-assisted filtration. Due to gas formation and other electrochemical reactions that occurred at the electrodes, alteration of pH may occur, which may damage the components within the feed or permeate solutions (e.g., biomolecules). Besides using buffer solution, external compartments can be placed on either side of the electrodes to avoid changes in the process streams. These compartments are separated from the retentate and permeate compartments normally by cellophane or ion-exchange membranes. Meanwhile, an additional rinsing cycle can be used within each compartment to wash away electrolysis products and prevent particle deposition at the electrodes.

A typical design with separate compartment of electrodes and rinsing cycle is displayed in **Figure 6**. If the feed solution is negatively charged, a cation-exchange membrane could be put on the cathode side and an anion-exchange membrane on the anode side in order to avoid

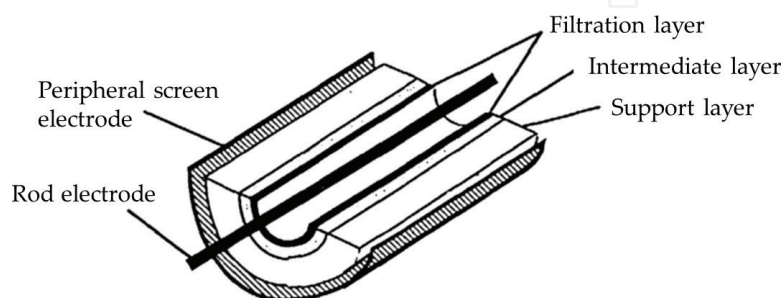


Figure 4. Typical tubular electrically assisted NF membrane module design.

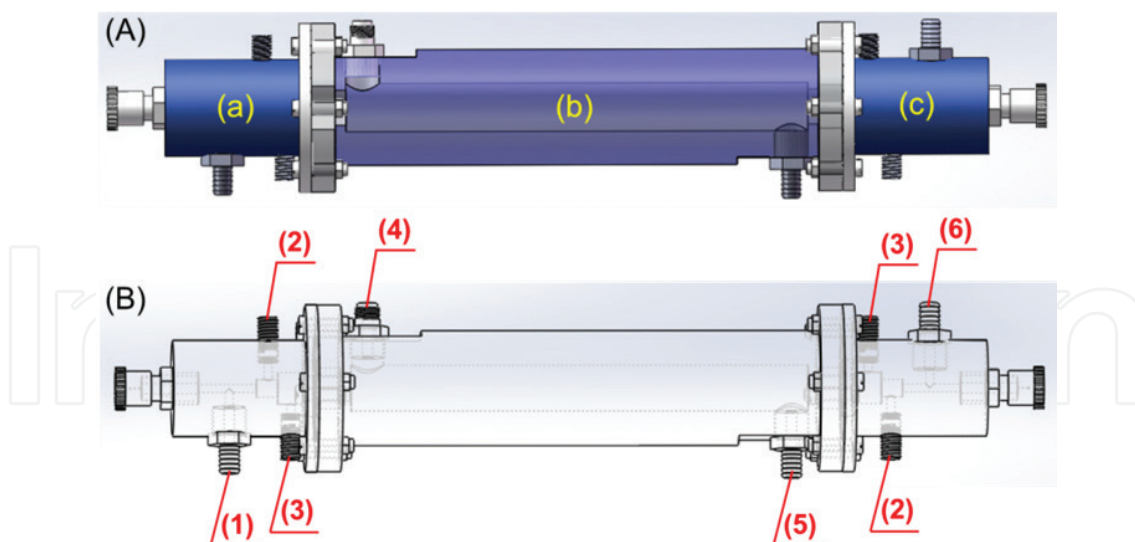


Figure 5. Three-dimensional (A) and perspective view (B) of (a) tubular membrane module with electric contact for inner and outer membrane surface, (b) compartment used for permeate collection, (c) symmetrical compartments for the flow of feed solution and retentate. (1) Inlet opening for feed solution, (2) electricity connectors in contact with the inner surface, (3) electricity connectors in contact with the outer surface, (4) pressure gauge connector in the permeate side, (5) opening for permeate, (6) outlet opening for retentate [18] (reproduced with permission).

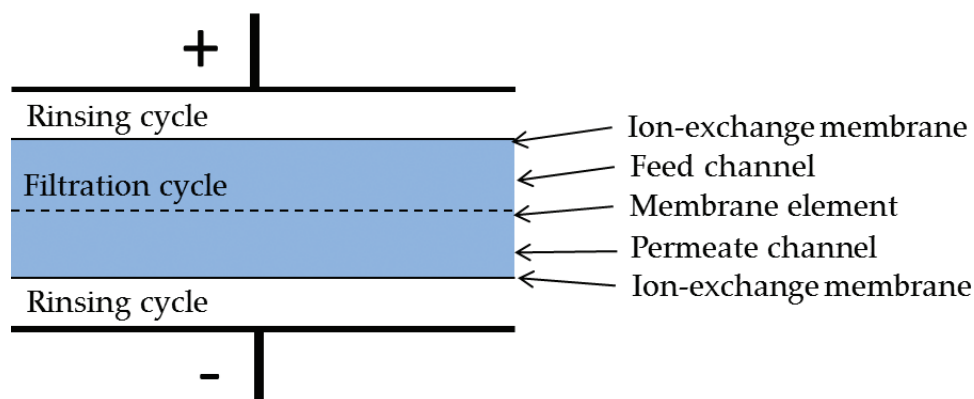


Figure 6. Membrane module design with separate compartment of electrodes and rinsing cycle.

increase of ion concentration in the filtration cycle. As reported by Weigert and coworkers, a tenfold increase of permeate flux was achieved using this process design [53].

3.4. System energy consumption

The additional energy consumed by DC power supply should be considered for the electrically or electrochemically combined NF system. The total energy consumption should include energy required for operating the pump and for electrophoresis or electrooxidation. Normally, the energy consumption is written as total specific consumption per unit volume of permeate flux, with the equation below [25]:

$$E_{total} = \frac{Q \Delta P}{JA\eta} + \frac{VI}{JA\eta_{DC}} \quad (6)$$

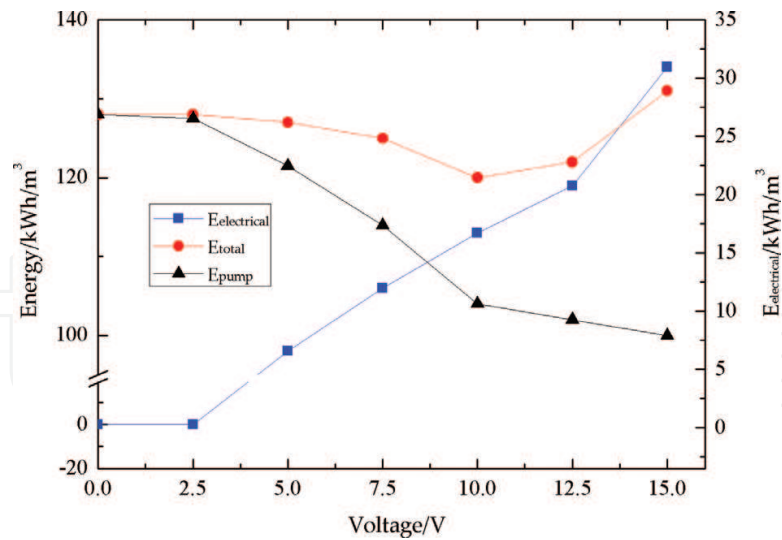


Figure 7. Variation of energy consumption per unit volume of permeate with applied potential at TMP of 0.8 MPa and CFV of $0.0258 \text{ m}\cdot\text{s}^{-1}$ [25] (reproduced with permission).

where Q was the flow velocity ($\text{m}^3\cdot\text{s}^{-1}$), ΔP the TMP (Pa), V the applied voltage (V), I the electric current (A), J the permeate flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), A the membrane area (m^2), η the efficiency of pump, and η_{DC} the efficiency of DC power supply. Despite the additional costs brought by electrooxidation or electrophoresis, total energy consumption may be reduced due to the significant increase of specific permeate flux and the decrease of required treating time or membrane surface area.

A typical graph showing individual and total energy consumptions is presented in **Figure 7**. Although the energy consumed by electrooxidation increased with applied voltage, lower energy is required for the operation (the pump energy) because of the enhancement of permeate flux. As a result, the total energy demand shows a “V” curve with the minimum value at around 10 V. At higher electric potential, the decrease in concentration polarization and fouling layer became less obvious resulting in insignificant increase in permeate flux. Therefore, the total energy increased with higher voltage [25].

4. Application

4.1. Ion separation and alteration of membrane property

Pupunat and coworkers present the first results obtained by superimposing an electric field on a classical NF operation with single salt or mixed solutions of Na_2SO_4 and NaCl (fixed Na^+ concentrations of 10 and $50 \text{ mol}\cdot\text{m}^{-3}$) over an estimated potential range from 0 to $1.9 \times 10^3 \text{ V}\cdot\text{m}^{-1}$ (0–7.5 V). The detailed experimental conditions are listed in **Table 1** with the same module design shown in **Figure 4**. The membrane was created from an α -alumina macroporous support, an intermediate mesoporous titania substrate, and a very thin microporous film of negatively charged Nafion. The anode is a stainless steel rod at the center of tubular membrane, while the cathode is a stainless steel cylindrical wire netting stuck on the membrane support. The anode was put inside in order to promote a pumping effect of Na^+

Membrane element	Anode	Cathode	Application	Conditions	Ref.
Organo-inorganic tubular membranes	Stainless steel rod	Stainless steel cylindrical wire netting	Single salt and mixed solutions of Na_2SO_4 and NaCl with fixed Na^+ concentrations of 10 and $50 \text{ mol}\cdot\text{m}^{-3}$	CFV: $3 \text{ m}\cdot\text{s}^{-1}$ TMP: 5, 10, 20, 30 bar Electric field: 0 to $1.9 \times 10^3 \text{ V}\cdot\text{m}^{-1}$	[1]
NF45 and BQ01 flat polymeric membranes	Stainless steel wire lattice	Porous, stainless-steel disk	Direct red dye with an average molecular weight of $1373 \text{ kg}\cdot\text{kmol}^{-1}$	TMP: 6.9 bar CFV: $0.5 \text{ m}\cdot\text{min}^{-1}$ Electric field: 0 to $1.5 \times 10^4 \text{ V}\cdot\text{m}^{-1}$	[41]
BQ01 flat polymeric membranes	Stainless steel wire lattice	Porous, stainless-steel disk	3.08, 17.11 and $59.88 \text{ mol}\cdot\text{m}^{-3}$ NaCl solution	TMP: 6.9 bar Electric field: 0 to $2.67 \times 10^4 \text{ V}\cdot\text{m}^{-1}$	[54]
Self-prepared negatively charged polyamide nanofiltration membrane NF-PS-3	Solid graphite	Perforated graphite plate	0–1000 ppb As (V) and As (III) solutions	TMP, 80–180 psig; CFV, $3.785 \text{ L}\cdot\text{min}^{-1}$; electric potential, 0 to 2 V	[42]
NF90 flat polymeric membrane	Mesh Ti/ $\text{SnO}_2\text{-Sb}$	Ti Mesh	$250 \text{ mg}\cdot\text{L}^{-1}$ tetracycline hydrochloride with NaCl of $0.06 \text{ mol}\cdot\text{L}^{-1}$	TMP, 0.4–1.2 MPa; CFV, $10\text{--}60 \text{ L}\cdot\text{h}^{-1}$; electric current, $10\text{--}50 \text{ mA}\cdot\text{cm}^{-2}$	[37]
Polyamide polymeric membrane	Mesh Ti/ $\text{SnO}_2\text{-Sb}_2\text{O}_3\text{-Y}$	Ti Mesh	$0.3\text{--}0.8 \text{ g}\cdot\text{L}^{-1}$ Acid Red 73 solution with $0.1 \text{ mol}\cdot\text{L}^{-1}$ Na_2SO_4	TMP, 0.4–1.2 MPa; CFV, 0.0086 to $0.043 \text{ m}\cdot\text{s}^{-1}$; electric potential, 2.5–15 V	[24]

Table 1. Summary of typical researches on electrically and electrochemically assisted NF.

through the porous medium. As expected, the experimental results clearly indicate that the electric field could strongly modify the kinetics of ionic transport through the membrane. The selectivities of $S_{\text{Na}^+/\text{Cl}^-}$ and $S_{\text{Na}^+/\text{SO}_4^{2-}}$ continuously increased with higher electrical voltage at $[\text{Na}_2\text{SO}_4]/[\text{NaCl}]$ of 1 and transmembrane pressure (TMP) of 10 bar. Meanwhile, the directions of variations of $[\text{Na}^+]$, $[\text{SO}_4^{2-}]$, and $[\text{Cl}^-]$ rejections were found to be independent of $[\text{Na}^+]$ concentration whether it was 10 or 50 mol m^{-3} . The most significant difference in NF and electrically assisted NF was observed at lower TMP. At TMP of 5 bar and voltage of 7.5 V, the rejection of $[\text{Na}^+]$ strongly decreased from 30 to -367% (minus means passage of $[\text{Na}^+]$), while the rejection of $[\text{Cl}^-]$ increased from -27 to 81% and $[\text{SO}_4^{2-}]$ from 56 to 90% [1]. This may be because the electrophoretic force was much more significant compared with the competitive hydrodynamic force [37]. However, under practical consideration, it is better to control the boundary voltage within 4 V because rapid increase in current density and strong variations of pH values were observed.

Different from the study of Pupunat and coworkers, a very small fractionation was obtained with applied electric field by Moël and coworkers using BQ01 membrane (polymeric membrane from Osmonics). Before the application of electricity, higher permeability was achieved

for NaCl separation (dynamic permeability) compared with pure water (pure water permeability), which was explained by the swollen effect. After electricity was applied, they found that dynamic permeability decreased. The loss in dynamic permeability increased with higher NaCl concentration but was not affected by the magnitude and polarity of electric field. The researchers suggest that the electric field could induce favorable conditions for cross-linkage on the polymeric membrane surface. The smallest electric potential of $1.33 \times 10^4 \text{ V} \cdot \text{m}^{-1}$ was sufficient to establish the polymer conformation, which explains the absence of significant variations with magnitude. The possibility of controlling pore size by an external force like an electric field represents an interesting opening in the field of NF and deserves further investigation [54].

4.2. Treatment of dye wastewater

A major problem in the textile industry is the discharge of dyehouse effluents without proper treatment, which will limit aquatic plant growth and affect the esthetic merits of water [55]. Efficient color reduction has been achieved by NF [56, 57], but the fouling issue remained to be tackled. Moël and coworkers studied the electrically assisted NF process for a textile direct dye solution with Stokes-Einstein radius of 1.2 nm and concentrations of 0.2 and 12 $\text{kg} \cdot \text{m}^{-3}$. Two types of membranes, BQ01 (polymeric membrane from Osmonics) and NF45 (polymeric membrane from Dow Chemical), were employed. Although both membranes can have 100% dye rejection, they showed different behaviors. With low red dye concentration of 0.2 $\text{kg} \cdot \text{m}^{-3}$, fouling was reversible for BQ01 but irreversible for NF45. For BQ01 membrane, a $1.25 \times 10^4 \text{ V} \cdot \text{cm}^{-1}$ electric potential is needed to avoid fouling, while for NF45, $6 \times 10^3 \text{ V} \cdot \text{cm}^{-1}$ is sufficient. With much higher red dye concentration of 12 $\text{kg} \cdot \text{m}^{-3}$, a reversible fouling is obtained using BQ01 with an electric field of $1.33 \times 10^4 \text{ V} \cdot \text{cm}^{-1}$, whereas a partially reversible fouling is observed without an electric field. The authors suggested that electric field could delay the formation of fouling layer and may interact with the structure of the red dye layer leading to a more reversible fouling [42].

Xu and coworkers developed a coupled separation process with electro-catalytic oxidation to treat C.I. Acid Red 73 wastewater [25]. Flat sheet module design was adopted with anode located in close vicinity of membrane surface to achieve electrooxidation-assisted antifouling filtration. A Ti net was fixed behind the membrane in the permeate side serving as both the cathode and the support for membrane, while a $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_3\text{-Y}$ net with electro-catalytic activity was positioned at the feed side serving as the anode. With electrical supply, dyestuff in the wastewater can be directly degraded at the anode; meanwhile, the rising of bubbles may also result in turbulence of liquid around membrane surface and enhance the antifouling performance. The authors investigated the enhanced flux from electrooxidation by coating the anode with insulating varnish. With the application of electro-catalytic oxidation reaction, both permeate flux and dye retention were improved. Besides electrooxidation, electrophoresis and electroosmosis may also account for the flux increase at relatively higher applied potential. The study revealed that the electro-catalytic permeation flux increased with applied potential, initial feed concentration, TMP, and cross-flow velocity (CFV). However, the increment became slower when the applied potential exceeded 8 V and CFV was greater than $0.035 \text{ m} \cdot \text{s}^{-1}$. The authors further quantified the individual and total energy consumption required to run

the pump and supply electric potential for electrooxidation. From their estimation, the optimal energy consumption could be obtained at 10 V, 0.6 MPa with low CFV [25].

4.3. Treatment of arsenic-contaminated water

Arsenic is highly toxic to humans, with As (V) and As (III) most likely to be encountered in potable water solutions. The prevailing pH ranges of As (III) and As (V) are 2–9 and 7–11.5, respectively [58]. As (III) was found primarily as H_3AsO_3 and hard to be ionized, which explains the reason why As (III) was difficult to be removed from water using ordinary processes like ion-exchange and electro-cross-flow membrane system [43]. Compared with As (III), As (V) was easier to be removed (H_3AsO_3 , $\text{pK}_a = 9.13$; H_3AsO_4 , $\text{pK}_a = 2.22$), so chlorine or oxygen was usually added to treat arsenic-contaminated feed [43].

Pérez-Sicairos and coworkers found that rejection of As (V) and As (III) can be enhanced by applied potential across the electro-cross-flow NF membrane system. The module design is presented in **Figure 3**. The rejection of As (V) was increased slightly from 97.3 to 98.6% when the applied potential was increased from 0 to 2.0 V at initial As (V) concentration of 1000 ppb. The rejection of As (III) was increased from 52.3 to 70.4% when the applied potential was increased from 0 to 2.0 V at initial As (III) concentration of 1000 ppb due to enhanced dissociation of the neutral species H_3AsO_3 to form H^+ and H_2AsO_3^- . Applied pressure and type of salt in the feed under investigation did not obviously affect the rejection of arsenic by the electro-membrane system [43]. Better As (III) removal should be achieved with As (III) oxidized to As (V) prior to the electrically assisted NF process.

4.4. Treatment of wastewater containing antibiotics

Xu and coworkers applied the technique of electro-catalytic oxidation enhanced NF to reduce membrane fouling in the treatment of tetracycline hydrochloride wastewater. The mesh catalytic anode was put on the intercept side and in close vicinity of the membrane. The application of electrooxidation through the generation of hydroxyl radicals to the NF process brought obvious higher permeate flux and lower flow resistance. For instance, at TMP of 0.4 MPa, CFV of $30 \text{ L}\cdot\text{h}^{-1}$, and current density of $20 \text{ mA}\cdot\text{cm}^{-2}$, the total filtration resistance decreased from 14.54 to $3.84 \times 10^{13} \text{ m}^{-1}$ with the assistance of electrooxidation effect. The apparent retention of tetracycline hydrochloride was slightly increased as well (from over 97% to over 99%). Within the experimental range, higher permeate flux was obtained at higher TMP and higher current density. The enhancement became less obvious at TMP of over 1.2 MPa and current density of over $40 \text{ mA}\cdot\text{cm}^{-2}$. For the coupled process, the effect of CFV on permeate flux was insignificant because the concentration polarization layer was very thin. Compared with NF alone, better filtration performance could be obtained at lower TMP and CFV, indicating the process may be energy saving as well [38].

5. Concluding remarks and future perspectives

There is still a long way to go for the investigation of electrically and electrochemically assisted NF process because existing research is quite limited compared with MF and UF. The

increasing application of NF in industry will surely trigger the development of in situ cleaning technique for fouling mitigation, with the electrically and electrochemically assisted filtration process as a very important part of the technique.

Here are some areas that worth further studies. First, for most of existing research, the investigation time is less than 3 hours or even shorter. Longer time should be investigated in order to see the coupled effect in the long run. Second, more fundamental research should be conducted to investigate in depth the basic mechanism of this coupled process. Third, most developed modules are only applicable to single membrane element. In order to increase the feasibility of this coupled technique in practice, it is highly suggested to develop membrane modules with multiple membrane elements (tubes or flat sheets) compacted together, which definitely requires more complicated design of electricity connection. Fourth, more practical and compact designs of membrane modules with separate compartment of electrodes are needed because it is necessary to maintain the conditions of feed and permeate constant. Fifth, new electrode materials are still required which should possess the following qualities: electrochemically stable, corrosion resistant, economically acceptable, and electro-catalytic. It is even better if such material could be placed on the membrane surface. Moreover, energy consumption is still a key aspect to consider when determining the optimal operation condition. In order to minimize energy consumption, pulsed electric field instead of constant electric field could be used as suggested by some researchers. More research is still needed to further reduce total energy consumption from the aspects of operation condition, membrane module design, and membrane materials development.

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