Chapter 5

Nanofiltration Mediated by Surfactant Micelles: Micellar-Enhanced Ultrafiltration

Senay Taşcıoğlu

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.75775

Abstract

Surfactant micelle-assisted removal of ions and organic solutes from aqueous media by micellar enhanced ultrafiltration (MEUF), which is a membrane separation technique, is discussed in detail. Following general information about micellar structure, counterion binding, substrate solubilization, and medium effect functions of micelles which enable separation of cationic or anionic ions and organic molecules from aqueous media by MEUF are explained in a comprehensive manner. Some of the recent studies on removing pollutants from wastewater effluents of industrial plants by MEUF, and their results have been summarized to inform about the factors affecting the removal efficiency of this technique. Methods for recovery of surfactant and contaminants from retentate or permeate solutions are also given. Selective separation of metal ions of the same charge from multicomponent solutions is another topic of this chapter. In this context, the last part of the chapter provides an overview on every aspects of ligand modified MEUF (LM-MEUF) process. This report comprises a comprehensive review of MEUF and LM-MEUF studies in the literature.

Keywords: surfactant micelles, micellar-enhanced ultrafiltration, removal of metal ions, removal of organic solutes, selective removal, separation of ions, pre-concentration, recovery, ligand modified micellar-enhanced ultrafiltration

1. Introduction

The topic of this chapter is the function of surfactant micelles in removal of ions and organics from aqueous solutions by membrane filtration. It is necessary to know about the micellar structure and properties to understand the function of micelles in this separation process.

Therefore, this chapter starts with the information about micellar structure and the mechanism of micellar effects.

It is well established that all the features of chemical reactions (rate, mechanism, pathway, product distribution, regio- and stereochemistry) can be altered by performing reactions in micellar media instead of pure bulk solvents. These alterations occur by the virtue of the medium effect of micelles. As a result of the medium effect, micelles can concentrate the reactants within their small volumes and mediate reactions, stabilize and orient substrates, intermediates, or products, so that ionization potentials and oxidation-reduction properties, dissociation constants, physical properties, quantum efficiencies and reactivities are changed. On this basis, micelles are called as "nanoreactors." Micelles act as mediators for reactions such that reactions of polar substances in apolar media or reactions of apolar substances in polar media can be realized in the presence of surfactant micelles [1].

Counterion binding and solubilization functions of micelles play a role in micellar-enhanced ultrafiltration (MEUF). On the other hand, medium effect of micelles is the main factor in ligand modified micellar-enhanced ultrafiltration (LM-MEUF) process. Therefore, two main processes that play the most important roles in removal of ions and organic solutes from aqueous media by MEUF, i.e., substrate solubilization and reactive counterion binding to micelles, as well as the medium effect of micelles which enables selective separation of ions and organics by LM-MEUF have been described in this section.

1.1. Micellar structure

Micelles are dynamic colloidal aggregates formed by surfactant molecules. Such molecules are amphiphilic in character, i.e., there are both hydrophilic and hydrophobic regions in their molecules. They have a long hydrocarbon tail and a small polar head group. Surfactant molecules are called as ionic (cationic and anionic), zwitterionic, or non-ionic, depending on the nature of their head groups. Their micelles are classified in the same way.

Surfactant molecules exist individually in the medium in dilute solutions. Such solutions have completely ideal physical and chemical properties. As surfactant concentration increases, their properties deviate gradually from ideality and at the concentration where aggregation of monomers into micelles occurs, a pronounced change is observed. This concentration is called the critical micellization concentration (CMC) [1].

CMC is experimentally determined by plotting a graph of a physical property of the surfactant solution as a function of concentration. A remarkable change is observed in the slope of the graph around the CMC.

Surfactants have characteristic CMC values under given conditions. However, small differences can be observed between the CMC values determined by different methods. Micellar aggregates have highly dynamic molecular structures. Therefore micelles in solution do not have a certain aggregation number and micellar solutions are polydisperse. Ion pairs or submicellar aggregates of surfactant molecules can form at concentrations below the CMC.

CMC values are affected by some factors such as temperature, the length of the hydrocarbon tail, the nature of the head groups and counterions, and by the existence of salts and organics in the medium.

The substances solubilized in the medium lead to a change in monomer-micelle equilibrium. Thus, CMC of the surfactant to be used in MEUF is changed in the feed solution (solute micellization concentration, SCMC). Therefore, it should be determined in the presence of other solutes in the feed solution such as the target ions, organic solutes, or ligands. But some researchers disregard this fact. They do not determine the SCMC of the surfactant in the presence of the other substances existing in the medium and discuss the results assuming that the CMC of the surfactant in the feed, retentate or permeate solutions is the same as that in deionized water.

Surfactants are used in MEUF and LM-MEUF processes in higher concentrations than their SCMCs, to ensure that the surfactant exists in the medium in concentrations high enough to form micelles.

In polar solvents such as water, surfactant monomers assemble to form a micelle in such a way that their hydrocarbon tails cluster in the core of the micelle such that they are shielded from water and polar head groups project outward into the polar bulk solution. Electrical charge on a micelle is neutralized in a large extent by counterions in the electrical double layer around it.

Micelles are small and spherical, rarely spheroidal, at concentrations close to CMC. As the surfactant concentration increases they increase in size, elongate, and become rod-like micelles when concentration exceeds the second CMC (about 7 CMC). This facilitates the passage of micelles through the membrane during MEUF process and causes to higher surfactant concentrations in permeate.

Aggregates can also form in apolar solvents. In such cases, head groups of surfactant molecules locate inside to form a polar core and hydrocarbon tails are directed toward the bulk solvent. This kind of micelle is called reversed (reverse) or inverted (inverse) micelle.

In this review, the term “micelle” stands for micelles in aqueous solutions (normal micelles) not for reversed micelles.

1.2. Mechanism of micellar effects exerted in MEUF and LM-MEUF

Micellar effects which play a role in MEUF and LM-MEUF processes can be classified as “concentration” and “medium” effects.

1.2.1. Concentration effect

Concentration effect arises from counterion binding and solubilization functions of micelles. As mentioned before, these are the main functions which enable the removal of ions and organic solutes from aqueous media by MEUF. Besides, increments in rates of reactions occurred in micelle nanoreactors are provided by the virtue of this effect. Reactive ions in the bulk solution electrostatically attracted to micelle and micellar solubilized substrate are brought into proximity within small volume of micelle. Thus, reactions occur between the micellar solubilized substrate and the bound counterions in the Stern layer. The frequency of molecular collisions increases as a consequence of close association of two reacting species at the micellar interface. This results in rate enhancement.

Reaction rates in micellar solutions are affected by all the factors affecting the extent of substrate solubilization and reactive counterion binding [1].

1.2.1.1. Counterion binding

One of the most important processes exerting micellar effects in both MEUF and LM-MEUF is the counterion binding to micelles. Micelles can either attract the ions in the medium or repel them depending on the electrical charge of their head groups. Sometimes, even reactive molecules are bound to micelles as their counterions.

Head groups of ionic micelles are generally about 30% ionized, i.e., 70% neutralized by the counterions in the Stem layer, at the CMC. The degree of counterion binding depends on several factors. There are values between 10 and 70% for ionization degree of micelles reported in the literature.

Micelles can bind the other ions in the medium beyond 30%, since there is a competition between the surfactant counterions that already exist in the solution and the other ions added to the medium, for the ionic head groups of micelles. Thus, displacements can occur depending on the nature of counterions and the other ions. The affinity of ions for the head groups increases with increasing ionic charge.

Counterions interact with the head groups not only electrostatically but also hydrophobically. Bulkier ions are preferentially bound by micelles. Some series have been reported for the relative affinities of ions to various micelles [1].

1.2.1.2. Micellar solubilization

Another fundamental process that plays a role in removal of substances from aqueous media by MEUF is their solubilization in micellar interiors. It is possible to solubilize the water-insoluble substances in aqueous micellar solutions.

They penetrate toward the hydrocarbon-like cores of the micelles. Since the solvent molecules penetrate beyond the polar head groups, solute in the solvent phase can interact both with the nonpolar chains of the surfactant molecules and with their polar head groups. Micellar core containing the hydrocarbon tails of surfactant molecules behaves like an organic phase. Therefore, hydrophobic forces play an important role in the solubilization process in micellar interior.

The opposite holds for reverse micelles, i.e., polar substances can be solubilized in reversed micellar media or in microemulsions that contain a water pool surrounded by polar head groups in the central region of reversed micellar aggregates.

One can utilize from solubilization of polar substances in reverse micelles to extract polar substances, even selectively, from their aqueous solutions in contact with an organic phase containing surfactant micelles. Conversely, water insoluble substances can be extracted from organic solvents into aqueous micellar solutions. These processes are called carrier-facilitated transport, where the micelle is the carrier.

Solubilized molecules interact with the polar head groups of a micelle and penetrate toward the core. They reside in the inner core, outer core, and palisade layer or between the polar head groups.

Sometimes micellar effects can also be observed as a result of the stabilization of molecules as counterions, i.e., without solubilization, with the substances not hydrophobic enough to be solubilized in the micellar interior [1].

1.2.1.2.1. Solubilization sites in micelles

Both electrostatic and hydrophobic factors play a role in determining the binding site of solute to the micelle. Therefore, both the structures of the surfactant and the solute are of great importance in determining the extent of solubilization and the penetration of solute into the micelles. If the hydrophobicity of one partner increases, the association constant of the solute increases and the solute penetrates deeper into the micelle.

Micellar-bound polar solutes reside largely in the Stern layer at the micellar surface. If the compound has both a polar and a hydrophobic end, i.e., if it is amphipathic like as the ligands used in LM-MEUF, the polar region orientates itself toward the head groups of the surfactant molecules, while the other end becomes involved with the hydrocarbon tails in the interior of micelle. For example, aromatic anions situate near the micelle/water interface. The aromatic section of the molecule is embedded in the palisade layer, while the charged parts are located near the micellar interface.

1.2.1.2.2. Factors affecting solubilization

The most important factor is the hydrophobicity of the surfactant and the solute. The more hydrophobic the solute, the higher the value of binding constant and deeper the penetration into the micelle occurs. The molecular weight of the solute, chain length and head group structure of the surfactant, temperature, and the existence of added ions in the medium are the other factors. The concentration of the solute and the pH of the bulk phase also affect the quantity solubilized [1–4].

1.2.2. Medium effect

This effect arises from a combination of charge, cage, preorientation, microviscosity and polarity effects. Selective removal of ions with similar properties by LM-MEUF process is provided by the virtue of this effect which can change properties of ligands associated with micelles via hydrophobic or electrostatic forces and so all the features of their complexation reactions.

Charge effect: surfactant micelles attract the ions of opposite charge and repel the ions of the same charge electrostatically. As mentioned above, when micelles attract, oppositely charged reactive ions mediate and catalyze a reaction. Conversely, in cases where micelles solubilize the substrate but repel the reactive ions of the same charge, the reactants are separated and, as a result, the reactions are inhibited. The ions which are attracted by micelles are retained by the membrane, while the ions repelled by micelles permeate through the membrane and pass into permeate during a MEUF process.

Cage effect: micelles can hold two reactive species together for a longer period of time than homogeneous solutions. As a result, the probability of reactions and hence the reactivity are increased.

Preorientational effect: the capability of micelles to solubilize substances in specific orientations is one of the most important factors that facilitates the reactions and provides control over regio- and stereoselectivity. A favorable location and the orientation of the substrate in micelles lead to an increase in its reactivity. Charged substrates reside in micelles with their charged groups directed toward the micellar interface. This location brings the substrate into close proximity with micellar bound reactive ions providing a favorable orientation to react with them.

Microviscosity effect: substrate molecules incorporated in micelles have less translational and rotational freedom, since microviscosity of micellar interior is much higher than the viscosity of homogeneous bulk solvent. This reflects in their reactivity, and in regio-, stereo- and product selectivity.

Polarity effect: for both bimolecular and unimolecular reactions, micellar environment leads to a reduction in the free energy difference between the ground state and transition state and can stabilize intermediates electrostatically, relative to the ground state. Low-polarity environment in a cationic micelle can decrease the free energy of a bulky anionic transition state with more delocalized charge, relative to that of the ground state such that the reactions are catalyzed. An anionic micelle can impose the opposite effect. For some reactions, electrostatic and hydrophobic interactions between the substrate and micelle may contribute to activation energies. Micelles that catalyze a reaction decrease the activation energy and entropy, while the inhibitory ones increase them [1].

2. Micellar-enhanced ultrafiltration

MEUF is such a technique that enables nanofiltration (NF) by use of ultrafiltration (UF) membranes. Drawbacks of NF and reverse osmosis (RO) high-pressure membrane processes which are used for removal of small ions and molecules from aqueous media can be overcome by MEUF. This is because MEUF does not require thick and expensive membranes, frequent replacement of membranes due to irreversible membrane fouling, application of high transmembrane pressure due to low water permeability of membranes, high energy consumption and accordingly high operational cost. Advantages of MEUF compared to NF and RO stems from the use of larger pore-sized UF membranes. Higher permeate flux can be achieved by UF membranes and, therefore, MEUF can be applied under low to moderate transmembrane pressures, membrane fouling is less problematic and can be overcome since fouling is mostly reversible. Pore sizes of UF membranes are too large to filter inorganic ions and small molecules but if they are combined with surfactant micelles, they can be filtered through UF filters with pore sizes small enough to reject micellar aggregates. This is the basic principle of MEUF.

MEUF is mostly applied for removal of heavy metal ion and organic pollutants from industrial wastewater streams, which are hazardous to human health and aquatic biota. Removal of pollutants from industrial wastewaters requires techniques applicable to large volumes of contaminated water. Various methods have been developed for this purpose. Of these, surfactant-based separation (SBS) processes have superiorities in simplicity and low cost compared to the other methods. MEUF is the most preferred SBS technique for removal of heavy metal ions and organics from wastewaters. It enables to treat large amount of wastewater which contains pollutants in considerably low concentrations. MEUF is applied in analytical and environmental science and also as a pre-concentration and recovery method.

This physicochemical technique which is highly effective in removing pollutants was first applied in the early 1980s [5]. It can also be utilized as a recovery method for pollutants since their concentrations in retentate are increased during MEUF process.

MEUF is based on binding of target ions and solubilization of organic pollutants by surfactant micelles. Therefore, a surfactant is added to polluted water in such an amount that it exists in the medium in concentrations higher than its CMC to ensure micelle formation prior to UFs. Micellar bound ions and apolar organics are removed by an ultrafiltration process carried out with membrane filters of low porosity that can retain micelles. Thus, the target ions and organic solutes which can normally permeate through ultrafiltration (UF) membranes are retained in the feed solution (retentate) during MEUF process since micelles with which they are associated cannot pass through the UF membrane pores.

The properties and concentrations of target ions and surfactants, solution pH, ionic strength, surfactant to pollutant mole ratio, filtration pressure, stirring speed, flow rate, and pore size and material of membrane are the factors which affect the removal efficiency of MEUF. The kind of surfactant to be used in MEUF depends on the nature of target ions. Anionic surfactants are used for removing cations, while on the other hand, anions can be removed using cationic surfactants.

The use of binary mixtures of surfactants in MEUF process can improve the retention of pollutants. Functionalities of surfactants can be increased by addition of another surfactant to the medium, i.e., by using a mixed micelle system. When two amphiphiles coexist in the same solution, mixed micelles or comicelles can form as a result of mutual solubilization. Ionic surfactants of like charges and nonionic surfactants form stable mixed micelles over a wide range of ratios. However, reversely charged surfactants can also form mixed micelles but only at certain ratios. Usually mixtures of ionic and nonionic surfactants are used in MEUF experiments. The presence of a nonionic surfactant in the medium leads to a decrease in the CMC of the ionic surfactant and accordingly to an increase in the number of micelles which are to bind the contaminant ions or molecules. Besides, micellar size is increased and micelles have a more rigid structure on mixed micelle formation. Thus, added nonionic surfactants enhance retention of target ions and organics during MEUF and may especially be suitable for use in MEUF studies carried out for simultaneous removal of ions and organics. Use of a nonionic surfactant may also lower the cost of MEUF process since they are cheaper than ionic, especially cationic ones. They also reduce the amount of surfactant monomers leaked through the membrane, by decreasing the surfactant concentration in the feed solution due to CMC lowering, and accordingly reduce secondary pollution by discharged permeates. On the other hand, concomitant use of nonionic surfactants with ionic ones may result in enhanced membrane fouling.

MEUF can be applied as a continuous process in ındustrial scale so as to handle larger volumes of effluents.

The retention factor R is the measure of the filtration efficiency in removing the target ion from the feed solution.

$$R\,(\%) = \left(1 - \frac{C_p}{C_0}\right) \times 100 \tag{1}$$

C_0 and C_p are the initial concentrations of the target ion in the feed solution and in permeate, respectively.

2.1. Removal of organics by MEUF

MEUF can be utilized in removal of organic pollutants discharged by industrial plants, which are all health hazards for living organisms. This can be provided by the virtue of solubilization function of micelles (Section 1.2.1.2). As mentioned in Section 1.1, hydrocarbon tails of surfactant molecules huddle in the core of a spherical micelle during micelle formation. As a result, micellar core which involves the hydrocarbon tails behaves as a hydrocarbon solvent. This enables solubilization of apolar substances in aqueous media by surfactant micelles via hydrophobic forces. Thus, organics incorporated into micelles in this way are not allowed to permeate through the MEUF membrane which retains micelles. Some examples of recent studies on the removal of organic solutes from industrial effluents by MEUF have been given below.

Phenolic compounds are the most studied organic pollutants in MEUF studies. Their main sources are petrochemical industry plants effluents besides those of many other industries such as petroleum refining, gashouse cooking, drug, plastic, paper and edible oil industry.

Olive mill wastewater (OMW) has a high organic content, mainly polyphenols. The main ingredient in OMW is hydroxytyrosol, it is followed by cinnamic, vanillic and protocatechuic acids and by the others. Polyphenols give phytotoxic, antibacterial, antioxidant, anti-inflammatory, anti-tumor and antiangiogenic properties to OMW. Therefore, besides solving an environmental problem; recovery of phenolic compounds from OMW to be used in food, cosmetics and drug industries has of importance but there appear only very few report in the literature in this field.

El-Abbassi et al. studied the efficiency of MEUF for the removal of polyphenols from OMW using sodium dodecyl sulfate (SDS) as the surfactant and hydrophobic poly(vinylidene fuoride) (PVDF) membrane. The rejection of polyphenols was between 5 and 28% by UF, but it reached 74% in the presence of SDS micelles at pH 2. Permeate from MEUF required 4.33% less chemical oxygen demand (COD) for oxidation than the initial COD and exhibited a color reduced more than 87%. The optimum conditions were 10 CMC SDS concentration, 4 bar transmembrane pressure (TMP) and pH 2 [6].

Huang et al. used polyethersulfone membrane and five kinds of surfactants with different hydrophobic tail length and hydrophilic head groups namely cetyltrimethylammonium bromide (CTAB), p-tert-octyl-phenoxy (9.5) polyethylene ether (TX100), octadecyldimethylammonium bromide (OTAB), cetylpyridinium chloride (CPC) and SDS. Cationic surfactants were found to be more effective than SDS and TX100, with very close efficiencies in the order OTAB > CTAB > CPC. Opposite order was valid for permeate flux.

Rejection of phenol with OTAB, CTAB and CPC micelles were 71.8, 68.9 and 61.5%, respectively, in the presence of 10 mM surfactant. Rejection increased up to 99% in the presence of 30 mM OTAB [7].

Gemini surfactants are also used for phenol removal. Gemini surfactants are a new class of self-assembling molecules. Gemini surfactants contain two hydrophilic head groups and two hydrophobic tails in their structure. The head groups are linked by a spacer. Their polarity depends on the structure of the linker. Spacer can be short (2 methylene groups) or long (12 methylene groups); rigid (stilbene) or flexible (methylene chain); and polar or nonpolar. They are characterized by very low CMC and surface tension values. Thereby they have excellent foaming and wetting properties. CMC values of gemini surfactants are lower up to hundred times than those of corresponding monomeric surfactants. Low CMC values of Gemini surfactants render them more efficient since the number of micelles formed at a certain concentration is higher than those of other surfactants. Thus, they enable to lower the surfactant concentration in the feed and thereby in the filtrate in a MEUF process. Besides, they interact with counterions more effectively compared to conventional ionic surfactants since they bear much more charged moieties in their structure. MEUF carried out using Gemini surfactants are designated as “GMEUF” in the literature.

Zhang et al. investigated the efficiency of cationic Gemini surfactant (CG), N1-dodecyl-N1,N1,N2,N2-tetramethyl-N2-octylethane-1,2-diaminium bromide and nonionic Brij-35 on phenol removal. Phenol retention increased with increasing surfactant concentration and reached a limiting value (90.8%) over 6 mM. They also studied effect of mixtures of CG and Brij-35 with fixed CG concentration (6 mM) and varying concentrations of Brij-35. Brij-35 decreased the CMC of CG and exerted a positive effect on separation performance. Phenol retention increased with increasing Brij-35/CG mole ratio (α). Phenol retention was increased with increasing Brij-35 content to R value of 96 at α value of 1.2. They also reported that the presence of a salt (Na_2CO_3) had a negative effect on phenol retention [8].

El-Abbassi et al. studied MEUF of different phenolic compounds namely p-coumaric acid (PCA), vanillic acid and tyrosol using SDS as the surfactant and polyethersulfone (PES) membranes (20 and 50 kDa molecular weight cut-off (MWCO)). They also studied recovery of SDS by precipitation with salts. R values increased with increasing SDS concentration reaching to the values 67, 66 and 51% for PCA, vanillic acid and tyrosol, respectively, at 10 CMC using a 50 kDa PES membrane. There is no data on R values that could be obtained by using 20 kDa membrane filters in the paper. SDS was recovered from the retentate by precipitating with KCl and $CaCl_2$ in the presence of p-coumaric acid. Effect of the concentration of these salts on the amount of precipitation was investigated by electrical conductivity measurements. Removal of SDS by precipitation did not lead to decreases in amounts of phenolics in the retentate. Not any % value for SDS recovery is given [9].

In another study of Huang et al., removal of p-nitrophenol (PNP), p-chlorophenol (PCP), p-cresol (PC) and phenol (P) was investigated in the presence of cationic, anionic and nonionic surfactants.

As expected, the best result was obtained with cationic CPC. The separation efficiency and distribution coefficient of phenolic compounds in micelles was in the order PNP > PCP > PC > P. Their values increased in the order CPC > sodium dodecylbenzene sulfonate (SDBS) > TX100. In the presence of 4 mM CPC, removal efficiency of PNP was about 75% [10].

Liu et al. studied MEUF of phenolic compounds resorcinol, phenol and 1-naphthol which have high solubility in aqueous media, using a mono-rhamnolipid anionic biosurfactant and a hollow fiber polysulfone membrane with 10 kDa MWCO. Retentate concentration of these compounds increased with increasing pH, transmembrane pressure and surfactant concentration following the order resorcinol > phenol >1-naphthol. Dependence of their permeate concentrations on these parameters followed the reverse order [11].

Biosurfactants are environmentally compatible, biodegradable, non-toxic and economic surfactants effective at very low concentrations. They were shown to absorb metal ions and solubilize organics and can be used over a wide range of pH and temperature. It was also shown that they can be recovered from MEUF retentate. Secondary pollution problem which arises with synthetic surfactants because of the leakage of surfactant molecules into permeate, can be solved with their use in MEUF.

Removal and recovery of phenolic compounds from the effluent of olive oil plants was studied by Víctor-Ortega and his collaborates. They used cationic Esterquat, anionic dodecylbenzenesulfonic acid (DBSS) and nonionic Lutensol AO7. A cationic surfactant was used for the first time in MEUF of OMW and they achieved best retention (>90%) in the presence of Esterquat micelles at 5 CMC and 4 bar TMP. They investigated effect of some other factors on R values for a phenolic mixture composed of 3,4,5-trimethoxybenzoic, 4-hydroxybenzoic, gallic, siringic, vanillic and trans-cinnamic acids; besides the nature of the surfactant; such as transmembrane pressure, pH, surfactant concentration, mole fraction of Lutensol AO7 in its mixtures with ionic surfactants. Addition of nonionic surfactant had no remarkable effect on R value except for a small increase about 4% due to decreasing of CMC of the cationic surfactant [12].

Husein et al. compared the performance of TiO_2 ceramic ultrafiltration membranes with 8, 15 and 50 kDa porosity in removal and recovery of four acyclic naphthenic acids and a mixture of cyclic and acyclic naphthenic acids (NAs) with carbon number ranging from 11 to 18, by MEUF, with that of polymeric PAN membrane using CPC as the surfactant. Ceramic membranes could be preferable in MEUF process due to their stable performance at elevated temperatures and resistance toward the corrosive chemicals. But they observed lower permeate flux and recovery values with ceramic membrane compared to polymeric membrane. On the other hand, ceramic membranes exhibited very good performance in terms of concentration polarization and fouling layer resistances [13].

Tortora et al. studied removal of tetramethylammonium hydroxide from synthetic wastewater of electronic industry.by MEUF. They used two tubular ceramic membranes with different porosity. They achieved 99.75% R value with 1 kDa MWCO membrane [14].

Dyes are also organic pollutants. Removal of dyes is one of the most studied research topic of MEUF. Main source of dyes leading to environmental pollution is textile industry. All the other industries in which dyes are used contribute to environmental pollution. Dyes are not biodegradable because of the complicated aromatic nature of their structures and there are health hazards. Therefore their removal from wastewaters is of vital importance.

There appear a number of MEUF studies in the literature, carried out for removal of cationic dye methylene blue (MB). MB is used in paint production, wool dyeing, microbiology, and as a sensitizer in photo-oxidation of organic pollutants. Khosa et al. studied MB removal using SDS, CTAB, TX100 surfactants and regenerated cellulose membrane filters. They achieved 99% R in the presence of SDS micelles [15]. They reported R values of 98.8, 13 and 53 for anionic alizarin red S (ARS) removal in MEUF processes carried out following a complexation-precipitation process with Cu(II) salt; in the presence of CTAB, SDS and TX100, respectively [16]. Khosa and Shah also investigated the effects of cationic surfactants CTAB and CPC on removal of anionic reactive black 5 (RB-5) using 5,000, 10,000 and 30,000 MWCO membranes under 1 and 1.5 bar TMP. They reported that CTAB was more effective than CPC and provided R value of 98% under 1.5 TMP [17].

Huang et al. carried out several studies to remove MB by MEUF. They used polysulfone hollow fiber membranes in the experiments. They studied the effects of dye and surfactant concentrations, temperature and additional salts. They reported that the addition of NaCl improved the dye and SDS concentrations in the retentate and reduced their concentrations in permeate significantly [18].

Textile plants also discharge heavy metals to the environment. Both heavy metals and dyes are very toxic to living organisms. They are reported even to be carcinogenic. On the other hand, the presence of inorganic ions in the medium enhances the rejection of dyes during MEUF process by lowering the CMC of the surfactant, which results in increased micelle concentration. In addition, metallic ions can form water insoluble complexes with dye molecules. These complexes can be filtered through a filter paper. Thus, a significant amount of dye can be removed by precipitation. Therefore, sometimes, metal ions which form complexes with dye molecules are added to dye solution prior to MEUF process.

Khosa et al. investigated the removal of MB, RB-5 and ARS depending on the nature and concentration of surfactant and membrane MWCO. They reported 99% removal of MB in the presence of SDS micelles, 99% removal of RB-5 and 98.6% removal of ARS in the presence of CTAB. Following addition of Zn(II) ions, they could remove 47% of ARS by the filtration of precipitated ARS-Zn complex. On the other hand, they could remove 98% of ARS by MEUF carried out in the presence of CTAB utilizing from micellar solubilization of ARS-Zn complex [19].

In another research of Huang et al., simultaneous removal of MB and Cd(II) ions were studied with mixed surfactant systems composed of SDS and TX100. They observed that the addition of TX100 enhanced the retentions of both MB and Cd(II) ions and the presence of MB enhanced the Cd(II) rejection [20].

Hussain et al. investigated the removal of reactive blue 19 (RB-19) in the presence of two cationic surfactants (CTAB and ethyl hexadecyl dimethyl ammonium bromide (EHAB)) and with membranes of different MWCOs (5, 10 and 30 kDa). The highest R value was obtained in the presence of CTAB. The higher R values were obtained with the membrane of 5 kDa MWCO because of the retention of large RB-19 molecules by the membrane itself. Micellar effect could be observed with the membranes of larger MWCOs. The role of surfactant micelles in removal could be observed with membranes of 10 and 30 kDa MWCOs. The retention was 39.61 and 96.85% in the absence and presence of surfactant, respectively, with membrane of 30 kDa MWCO. They suggested use of a membrane with MWCO of 10 kDa. İncreasing the membrane MWCO exerted a negative effect on rejection. They achieved the larger R value in the presence of CTAB (99.62%) under 1.5 TMP [21].

Batik wastewater contains reactive dyes such as remazol, indigosol, napthol, benzene, rapid and phenol in high concentrations, sodium salts, wax, chrome, ammonia and solid content. Aryanti et al. investigated decontamination of batik wastewater using CPC as the surfactant. They compared the performances of ultrafiltration (UF) and MEUF and showed the superiority of MEUF in the removal of ammonia and showed that MEUF decreased the chemical oxygen demand indicative of dye-micelle binding. MEUF was found to be superior to UF also in terms of decreasing the total suspended solids [22].

In another study of Hussain et al., the removal of anionic sunset yellow (SY) was investigated in the presence of CTAB and EHAB. They suggested use of a membrane with 10 kDa MWCO and CTAB (R = 99.94) under 1.5 TMP [23].

2.2. Removal of heavy metals

Heavy metals are the elements with high atomic weights which exist at third and higher numbered periods of the periodic table. "Heavy" term stems from their high-specific gravities which are larger than five times of that of water, i.e., larger than 5 g/cm^3. They are environmental pollutants widely distributed to the environment because of their use in many kinds of industrial (fertilizer, paper, pesticide, tannery, etc.), technological, medical, mining, smelting, domestic and agricultural applications. Environmental pollution problems are caused by mainly lead, cadmium, mercury, arsenic, chromium, silver, platinum group elements, iron, zinc, nickel and cobalt. They can reduce the quality of life or even cause death depending on their concentrations in water. When their concentrations exceed the limits, health problems arises. Though some of them are essential for living organisms in very low concentrations, heavy metals are mostly regarded as toxic elements and included in the US EPA (US Environmental Protection Agency) priority pollutant list. They are hazardous to man's health and aquatic biota over concentration limits mainly because they are potent enzyme inhibitors and exert toxic effects on organisms. They compete with essential metals, which are necessary and functional for human health, for binding sites of proteins and thereby for those of enzymes which are of protein structure. Therefore, water which is of vital importance for survival of human beings and for other living organisms should be purged of heavy metals. Arsenic, mercury, cadmium, lead and chromium are the most toxic ones. These cause organ damages even at low exposure. The US EPA and the International Agency for Research on Cancer reports these metals also as carcinogens. Heavy metals are not biodegradable and cannot be discharged from organisms by metabolic route. Therefore, they accumulate in organs, i.e., they are bioaccumulative.

The most preferred technique to remove heavy metals from industrial wastewaters is MEUF. MEUF is carried out by using anionic surfactants, so that counterion binding function provided by the charge effect of micelles can be utilized to bind metal ions to micelles. However, metal cations can be removed also by the use of cationic surfactants, via LM-MEUF process.

Liu and Li studied the removal of Cu(II) ions by MEUF using SDS + TX100 mixed surfactant system and a hydrophilic membrane of 10 kDa porosity. They could remove 94% of Cu(II) content at TX100 concentrations higher than its CMC. TX100 favored micelle formation by decreasing CMC of SDS and lead to increase in micelle size by incorporating into micelle structure. As a result, SDS concentration in permeate was minimized. TX100-enhanced membrane fouling but it was reversible and could be cleaned easily by ultrasonication in water [24].

Rahmanian et al. studied MEUF of zinc(II) using regenerated cellulose spiral-wound membrane with 20 kDa MWCO. Spiral wound membranes are used in various industries because of its compact structure and low cost. The use of spiral wound membranes in MEUF has been shown to be feasible. Spiral wound UF module can be operated in linear continuous and cross-flow modes which have higher flux and membrane effective area compared to batch cell system. They achieved 98% Zn rejection in the presence of SDS in a concentration of 6 mM under 2 bar TMP. Such a high retention can be attributed to the decrement in CMC of SDS in water, caused by the presence of Zn(II) ions. They also carried out MEUF experiments in the presence of SDS-Brij35 mixed surfactant system, and in the presence of EDTA with the consideration that electroplating industry effluents contain ligands, mainly EDTA. They reported an optimum Brij35/SDS mole ratio of 0.5 to achieve maximum Zn(II) rejection to prevent membrane fouling and further decrements in permeate flux. They also reported that ligand imposed a negative effect on Zn(II) rejection [25]. The presence of EDTA could be turned into an advantage by using a cationic surfactant such that MEUF was carried out as LM-MEUF.

El Zefatwy and Mulligan used a rhamnolipid biosurfactant (JBR 425) for simultaneous removal of copper, zinc, nickel, lead and cadmium from six effluents of metal-refining industries using hollow-fiber ultrafiltration cartridges containing polysulfone membrane tubules with MWCO of 10 and 30 kDa. They determined optimum conditions by the response surface methodology and validation experiments as 69 ± 2 kPa TMP, 25 ± 1°C, pH 6.9 ± 0.1, and the surfactant: metal ion mole ratios as 2.5:1 (Cu), 2.6:1 (Zn), 2.3:1 (Ni) and 4.3:1 (Cd). They could achieve >99% rejection under optimum conditions. MWCO of the membranes did not affect the rejections practically indicating that the sizes of rhamnolipid micelles were larger than 30 kDa [26].

Landaburu et al. studied simultaneous removal of Cu(II) and Cd(II) ions from phosphorosus rich synthetic wastewater containing phosphorous, zinc and nickel using 10 kDa regenerated cellulose membranes. Existence of zinc and nickel had no effect but pH and feed concentrations of SDS and phosphorous affected the MEUF results. In the absence of phosphorous, R values over 98% were achieved. Phosphorous affected negatively rejection of both metal ions being more remarkable for Cu due to complex formation at high pHs. Experimental and theoretical results suited quite well [27]. In a similar study which they carried out later, R values of 87.1, 85.1, 84.3 and 75.0 were achieved for Zn(II), Ni(II), Cd(II) and Cu(II), respectively [28].

Simultaneous removal of Cu(II) and Cd(II) ions from phosphorous-containing wastewaters of a fertilizer plant was also studied by Hayrynen et al., in a cross-flow semi-pilot scale equipment using a 10 kDa spiral-wound PES membrane. They achieved rejections around 86 and 80% for Cd(II) and Cu(II) ions, respectively [29].

Oxyethylated fatty acid methyl esters are environmentally safe surfactants obtained from renewable natural sources. The fact that they have low CMC values imposes positive effect on R values. Staszak et al. studied removal of Cr(III) ions by MEUF using anionic SDS and nonionic Rofam 10 which is a product obtained by ethoxylation of methyl esters of rape-seed oil fatty acids, and their mixtures as the surfactants. Cellulose acetate, PES and polyvinylidene fluoride membranes were used. They compared the results of UF and MEUF experiments. R values obtained from UF experiments were below 25 for all three membranes, while R values between 90 and 95 were obtained in MEUF experiments depending on the SDS concentration, regardless of the membrane type. SDS was much more effective than nonionic surfactant. However, higher R values could be obtained by use of SDS-Rofam 10 mixture: they could achieve R values close to 100 [30].

In a study of Abbasi-Garravand and Mulligan, a rhamnolipid (JBR 425) was used as a biosurfactant and a reducing agent, using a polysulfone hollow fiber membrane with 10 kDa MWCO to remove Cr(III) and Cr(VI) ions. Chromium is utilized in many industries such as electroplating, leather tanning, metal finishing, nuclear power and textile plants. From the point of view of environmental pollution, Cr(VI) is more toxic than Cr(III) and it has a high oxidation potential. They reduced Cr(VI) to Cr(III) with rhamnolipid surfactant at different pHs prior to MEUF. They reported pH 6 as the optimum pH for reduction of Cr(VI) both in the presence and absence of rhamnolipid. The highest rejection (96.2%) was achieved at rhamnolipid/Cr(III) molar ratio of 36:1 [31].

Schwarze et al. used nonaoxyethylene oleylether carboxylic acid R090 as the surfactant, which can be anionic or nonionic depending on the pH of the medium and has a lower CMC than that of SDS. It formed larger micelles than SDS, which can be filtered with membranes MWCO of ≥10 kDa. Regenerated cellulose, PES and polysulfone membranes with different MWCO porosities were used. They achieved >95% removal efficiency for six metal ions, R values being in the order $Fe^{2+} \sim Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Mg^{2+}$. They reported the optimum R090 to metal ion molar ratio as 10 ± 1 [32].

Tortora et al. studied removal of nickel, cobalt, chromium, and zinc ions by MEUF using a monotubular ceramic membrane (zirconium oxide) of 210 kDa MWCO and SDS. Ceramic membrane was chosen because of its durable structure. They carried out the MEUF experiments in a tangential flow laboratory pilot plant. They stated that the highest R values (Co(II): 88, Ni(II): 87, Cr(III): 80, Zn(II): 79) was obtained below CMC, but 4 mM is a concentration higher than the CMC of SDS in the presence of metallic ions. One of the reasons for low R values may be high porosity of the membrane [33].

Huang et al. studied pH effect on removal of Pb(II), Cd(II), Zn(II) and Cu(II) by MEUF. They used a hydrophilic polyethersulfone membrane (10 kDa) and SDS (8 mM). The visual MINTEQ ver. 3 was used for theoretical calculations. Higher R values were obtained at pHs between 3 and 12 for Cu (II) and Cd(II), while the optimum range was 3–10 for Zn(II) and Pb(II). At high pHs, hydroxide formation and precipitation contributed to R values while removal efficiency of MEUF was decreased. In the presence of Pb(II), Na^+ counterions were replaced by Pb^{2+} ions and DS-Pb(II) salt precipitation was also observed. R values for Cu(II), Cd(II) and Zn(II) ions decreased with increasing metal ion concentration. On the other hand, the effect of increments in Pb(II) concentration depended on Pb(II) concentration. They reported optimum Cu(II) and Zn(II) feed concentration to be 150 mg/L while optimum feed concentrations of Cd(II) and Pb(II) were reported to be 300 mg/L [34].

2.3. Simultaneous removal of organics and heavy metals

Wastewaters from chemical and petrochemical industries such as textile, dye, paint, coal refining, fuel processing, battery, metal finishing and electroplating contain both organic and heavy metals. Coexistence of heavy metals and phenolic compounds in industrial effluents is the most encountered case. Heavy metals and organic solutes in the medium affect the removal efficiencies of each others in a MEUF process [35].

Separate and simultaneous removal of MB and Cd(II) ions was studied by Zeng et al. using SDS and hydrophobic polysulfone hollow fiber membrane with MWCO of 10 kDa. They reported R values of 99.2 and 99.9 for Cd(II) and MB, respectively, for single component solutions. Higher R values for Cd(II) was achieved in the presence of MB when SDS concentration was below 1.0 CMC, but removal efficiency of Cd(II) decreased above this SDS concentration. Maximum R value for Cd(II) in the presence of MB was 98.4. R value for MB decreased to 96.5 in the presence of Cd(II) ions. Cd(II) removal from binary solutions increased sharply with increasing pH, but a remarkable effect of pH on MB removal was not observed. R value for MB increased at pHs > 7 [36].

Li et al. studied simultaneous removal of Cd(II) ions and phenol using SDS and its mixtures with TritonX100 as the surfactants. They used polysulfone hollow fiber membrane with MWCO of 10 kDa and a cross-flow ultrafiltration unit. In the presence of 8.0 mM SDS, R values were 97.0 and 40.0 for Cd(II) and phenol, respectively, in simultaneous removal. In the mixed SDS/TX100 systems, R values depended on the mole ratios of surfactants. Maximum R value for Cd(II) was 91.3, while a R value of 42.4 could be achieved for phenol. Permeate surfactant concentration was found to be lower than that observed when SDS was alone in the medium [37].

Tanhanei et al. reported simultaneous removal of aniline and Ni(II) ions which coexist in dying ındustry effluents, by MEUF carried out in the presence of SDS, using polysulfone UFX5 (5 kDa), PES NP010 (1 kDa) and another polysulfone (PS) membrane prepared by the authors. They reported the best R values for aniline and nickel as 97 and 70, respectively, with UFX5-pHt membrane. They studied the effect of membrane size on R values and permeate flux. They observed that coexistence of nickel ions enhanced aniline rejection regardless of SDS concentration while the presence of aniline enhanced nickel rejection in low SDS concentrations but decreased at SDS concentrations over 4.8 mM. They reported that both aniline and nickel caused to increase in micellar dimensions. They could achieve R values of 99 and 64 for nickel and aniline, respectively, in SDS-Brij35 mixed surfactant solution. R values over 90 were achieved using NP010 membrane in the presence of 16 mM SDS. The reason why the highest R values were obtained with NP010 membrane may be its smaller pore size [38].

Verma and Sarkar studied simultaneous removal of Cd(II) and p-Cresol by MEUF using a rhamnolipid biosurfactant and 10 kDa flat sheet PES membrane. The process was optimized using the response surface methodology. Maximum R values were 98.8 and 25 for Cd(II) ions and p-Cresol, respectively, in the presence of 370 mg/L surfactant at pH 7.8. The R value of p-Cresol in single component solution was 23. On the other hand, the presence of p-Cresol did not affect the R values of Cd(II) ions. They compared the results with those obtained in the presence of SDS. The experiments gave slightly higher rejections of both Cd(II) and p-Cresol with R values of 99.4 and 23.9, respectively [39].

2.4. Removal of anions

Cationic surfactants are used for the removal of anions by MEUF so that charge effect of surfactant micelles can be utilized.

Gzara and Dhabbi studied the removal of chromate anions (CrO_4^{2-}) from aqueous streams using CTAB and CPC, and 10 kDa polysulfone membranes in a tangential cell. Rejection was found to depend on ionic strength and pH of the medium besides surfactant concentration and TMP. Increase in ionic strength caused to decrease the retention of CrO_4^{2-} ions and permeate surfactant concentration. They could achieve 99.98% retention in the presence of CTAB at 3 TMP [40].

Baek et al. explored simultaneous removal of ferricyanide and nitrate ions as a function of surfactant to anion mole ratio, using 3 and 10 kDa MWCO regenerated cellulose membranes and CPC under 2 TMP. Cyanides are used in a number of chemical synthesis and metallurgical processes. They readily form ferricyanide or ferrocyanide in the presence of iron. Since they are highly toxic, they must be removed from wastewaters prior to discharge. Nitrate ion is a potential health hazard to human beings since it can convert into nitrite ion. In single solutions, rejections of ferricyanide and nitrate anions increased with increasing CPC concentration to the R values of >99.9 and 93; respectively. CPC concentration imposed a similar effect in binary solutions of these anions. For ferricyanide:nitrate:CPC mole ratio of 1:1:10, rejections of ferricyanide and nitrate were >99.9 and 78%, respectively [41].

Chlorine in gas form (Cl_2), chlorine dioxide (ClO_2), and sodium hypochlorite (NaOCl) are incorporated in the municipal and industrial waters and wastewaters at high concentrations to prevent biological growth of microorganisms. All forms of chlorine are highly corrosive, toxic and carcinogenic to living organisms even at low concentrations. Therefore, the removal of chlorine from wastewaters is crucial. Rahmati et al. studied removal of free active chlorine (FAC) using PES/TiO_2 nanocomposite membranes with different PES/TiO_2 ratios prepared by the authors. Hypochloride rejection decreased with increasing pH and feed chlorine concentration, and increased by increasing TMP and TiO_2 content of the membranes. R value for FAC was found to be around 75 between pHs 2 and 4 [42].

2.5. Use of MEUF as a pre-concentration and recovery technique

Expense for surfactant accounts for a large portion of the operating costs of MEUF. Heavy metals and organics also are of economic value. Therefore, recovery and reuse of surfactants, heavy metals and organics from retentate or permeate, following a MEUF process, is of importance. This also prevents a secondary environmental pollution which will be caused by disposal of retentate and permeate. Retentates contain surfactant, heavy metal ions or organics in high concentrations since surfactants and pollutants are concentrated during MEUF. Therefore, in some cases, MEUF is used as a pre-concentration method for recovery of metals and organics from wastewaters.

Pollutants should be separated from micelles with which they are associated, so that both the surfactant and the pollutant can be recovered. For this purpose, the surfactant can be precipitated as its salts [9] or in its protonated form by addition of salts or strong acids, respectively, or by the addition of their mixtures. Thus metal ions leave micellar surfaces as a result of ionic competition, move to bulk solution and pass from the membrane into permeate during UF.

Another way to separate micelles and metal ions is the addition of a chelating agent to the medium which forms a complex with metal ions of the same charge with micelles. In such a case, metal ions are repelled by micellar surfaces and permeate through UF membrane while micelles are retained.

Metal ions can be recovered from retentate also by electrolysis. Electrolysis process detaches metal ions from micellar surfaces and they are electroplated onto the cathode as solid metal as a result of reduction. Thus, micelles becomes capable of retaining further metal ions entering the reactor and MEUF can be applied as a continuous hybrid process comprising MEUF and electrolysis.

Precipitation of metallic ions as their hydroxides is another method for metal recovery.

Other alternatives are to destroy the micelles such that surfactant undergoes phase separation or precipitation by increasing the temperature above its cloud point or by decreasing the temperature below its Krafft point, respectively.

Removal and recovery of surfactant in permeate can also be provided by foam fractionation carried out in foam fractioners. Surface active and inactive substances in permeate can be separated by this simple and low-cost method. Surface active surfactants are adsorbed onto gas bubbles formed by a strong air flow and migrate to surface with the bubbles rising up to form the foam.

Purkait et al. studied the removal of aromatic alcohols para nitro phenol, meta nitro phenol, beta napthol, and ortho chloro phenol by MEUF. They achieved maximum retention of solutes at surfactant (CPC) to solute ratio of 1:10. Following the MEUF carried out with such a high surfactant content, CPC in the retentate and permeate was recovered by a two-step chemical treatment process. Following precipitation of the surfactant with potassium iodide as its iodide salt (CPI), CPC was recovered from the precipitate by the addition of cupric chloride to convert CPI into soluble CPC [43].

Lui and Li determined optimum conditions to recover Cu(II) ions from the retentate of a MEUF process. Cu(II) ions bound to SDS micelles are accumulated on a cathode by electrolysis such that SDS micelles becomes free from metallic ions and can be reused to bind further ions in the incoming waste stream in a continuous process [44].

Kim et al. compared the efficiencies of three methods for recovery of heavy metals from simulated MEUF retentate. The tested methods were acidification followed by UF (1), use of a chelating agent followed by UF (2) and precipitation by ferricyanide and ferrocyanide followed by centrifugation (3). Copper and cadmium were completely separated from surfactant solution at strong acidic pHs by the method 1. HNO_3 was more effective than H_2SO_4 and HCl. They used EDTA, iminodiacetic acid and citric acid as ligands and provided 100 and 75.5%

separation efficiency by the method 2 for copper and cadmium, respectively. About 84% of SDS was recovered by acidification. 0n the other hand, 100% SDS recovery was achieved by centrifugation after complexation. They pointed out that successive precipitations are required for complete separation of SDS by acidification and that this will increase the ionic strength and acidity of the medium too much. They suggested the use of ferricyanide because of rapid precipitation of metal ions and selectivity [45].

Ghezzi et al. studied removal and recovery of Pd(II) ions from $PdCl_4^{2-}$ solutions by MEUF. They achieved 99% rejection using a cationic surfactant (DTAC) and a regenerated cellulose membrane of 30 kDa MWCO. They could recover 66% of Pd(II) by the addition of 0.8 M $MgCl_2$ salt to the medium [46].

Qu et al. recovered SDS and Cd(II) from MEUF permeate using a continuous foam fractioner. They could recover 52% of SDS and 99.35% of Cd(II) by applying various optimized process parameters such as air and liquid flow rates, the heights of liquid and foam, and the temperature. They could obtain an effluent with Cd(II) concentration lower than 0.1 mg/L, which meets the wastewater discharge standards in China [47].

Ghezzi et al. studied Cd(II) removal and recovery using pyridine-2-azo-*p*-dimethylaniline (PADA) as the ligand and regenerated cellulose 3 kDa MWCO membrane in SDS micellar media. They concluded that 90% of Cd(II) forms complex with PADA, and Cd(II) ions bind to micelles also as free Cd(II) ions providing a rejection of 98%. The retentate containing micelles associated with Cd(II) complex was treated with hydrochloric acid. H^+ ions bound to micellar surface caused to dissociation of the complex and replaced with Cd(II) ions bound to micelles as counterions. Thus, Cd(II) ions were released and separated from micellar surfaces. Protonated ligand remained within the micellar pseudophase. Recovery of Cd(II) ions increased with increasing acidity but since H^+ ions in concentrations higher than 1 M are hazardous for environment and damage the membrane, NaCl was also added to the medium to increase the ionic strength. They achieved more than 80% metal recovery at $3 \geq pH$ in the presence of 0.5 M NaCl (stripping solution). The existence of Mg(II) ions did not affect the Cd(II) recovery since Mg(II) ions did not form a complex with PADA. This result reveals that the presence of Mg(II) ions will not affect heavy metal recovery from sea water. They also studied Cd(II) rejection and recovery in the presence of Zn(II) ions. Both of the metal ions were rejected with R values >95%, but 83 and 76% Cd(II) and Zn(II) could be recovered, respectively, from binary solutions with acidic salt stripping solution [48].

Li et al. determined the optimum conditions for recoveries of SDS and Cd(II) and Zn(II) ions by UF under 0.15 MPa TMP. They used hollow fiber polyethersulfone UF membrane with MWCO of 6 kDa. They applied two methods: chelation followed by UF, and acidification followed by UF. Chelating agents they used were EDTA, citric acid and tartaric acid. They used sulfuric, nitric and hydrochloric acids in 3 mol/L concentration for acidification. The feed metal and SDS concentrations of simulated MEUF retentate solution were 100 mg/L and 3 CMC. Efficiency sequence of the acids in terms of both Cd(II) and Zn(II) separation was $H_2SO_4 > HNO_3 > HCl$ with small differences. They could recover 98.0% Cd(II) and 96.1% Zn(II) by acidification at pH 1, corresponding recoveries obtained using reclaimed SDS were 88.1 and 87.8%, respectively. SDS recoveries were 58.1 for SDS-Cd(II), and 54.3% for SDS—Zn(II) binary solutions at pH 1. EDTA was found to be more efficient compared to citric and tartaric acids. Chelation-UF method provided better results than those from acidification-UF experiments except for Cd(II) recovery. They reported 67.3 and 72.9% SDS recoveries from SDS-Cd(II) and SDS-Zn(II) binary solutions, and 95.8 and 96.8% recoveries for Cd(II) and Zn(II), respectively; by the chelation-UF method at pH 3. Corresponding recoveries obtained using reclaimed SDS for Cd(II) and Zn(II) were 90.3 and 89.6%, respectively [49].

Geanta et al. determined the optimum conditions for the removal of lactic and citric acids from beet molasses previously pretreated with activated charcoal at pH 3 by continuous cross-flow MEUF. Simultaneous recovery of acids and removal of SDS for reuse were achieved by treatment of the retentate with NaOH and subsequent phase separation below the Kraft temperature of SDS. After the phase separation process, 79.34% of lactic acid and 55.6% of citric acid were recovered from the SDS-free supernatant. About 95% of SDS was recovered from the solid phase [50].

Schwarze et al. used a surfactant with a very low CMC (1–20 μmol/L, depending on pH and counterion), which can be nonionic (at low pHs) or ionic (at high pHs) depending on the pH of the medium, namely nonaoxyethylene oleylether carboxylic acid Akypo RO90 VG (R90VG). They used a cellulose membrane of 5 kDa MWCO. They removed Cu(II) ions almost quantitatively at basic pHs and recovered more than 90% Cu(II) ions from the retentate by cloud point extraction. They compared the performance of R090 in copper removal with that of SDS. Copper removal was carried out at pH 6.5 to exclude hydroxide formation. Though the CMC of R090 was quite low from that of SDS, SDS provided the same rejections in lower concentrations. Cloud point extraction was carried out at 50°C and at $pH < 2$, so that degree of ionization of micelles is almost zero [51].

Aydinoglu et al. could recover 85% of gold from the retentate by a stripping process using a $NaCl/NH_3$ mixture as the stripping agent, followed by UF. NaCl reduced the surface potential of micelles such that electrostatic attraction between DTAC micellar surface and $AuCl_4^-$ ions is reduced. On the other hand, NH_3 converted $AuCl_4^-$ ions into positively charged $Au(NH_3)_4^{3+}$ complex so that it is repelled into the aqueous phase by cationic DTAC micelles [52].

Huang et al. investigated feasibility of repeated recovery and reuse of SDS in MEUF retentate containing Cd(II), by acidification followed by UF. The authors reported that the maximum SDS and Cd(II) recoveries were attained at pH 1 and 0.5, respectively. They did not suggest working at pH 0.5 since the solution became too sticky. 94.38% Cd(II) could be removed by recycled SDS at pH 2. Optimum conditions for SDS recovery and reuse were initial SDS concentration 2 CMC, pH 1, use of sulfuric acid and volume of the acidified concentrated solution 0.2 L. They recovered and reused SDS three times and stated that this does not provide economic profit but solves the problem of secondary environmental pollution substantially caused by concentrated retentate solution [53].

2.6. Selective separation by MEUF

There are some reports on selective separation of heavy metal ions by MEUF in the literature. In these studies, two ions to be separated have quite different chemical and physical properties such as Cu(II) and Ca(II), Cu(II) and Co(II) or Cu(II) and Pb(II).

Das et al. studied feasibility of selective separation of Cu(II) and Ca(II) ions by cross-flow MEUF. They compared experimental and calculated fractional counterion binding constants for these ions and Na^+ ions which are inherent counterions of SDS in both single component and binary solutions. Binding constant of calcium ions to the micelles was larger than that of Cu(II) ions implying that competition of these ions for micellar surfaces will result in an ion exchange between sodium and calcium ions rendering selective separation of these ions feasible in a MEUF process, such that micellar bound calcium ions are retained in the retentate and most of the copper ions, released from micellar surfaces, pass through the membrane into the permeate [54].

Anthati and Marathe investigated the performance of continuous cross-flow MEUF for selective separation of Cu(II) and Co(II) ions using SDS as the surfactant and iminodiacetic acid (IDA) as the chelating agent. They compared the retentions of both metal ions by UF and MEUF. At optimal conditions, 96% selective separation of copper ions was achieved. Cobalt ions remained in the retentate. They also studied recovery of SDS from the retentate. About 75 and 84% of SDS was recovered by acidification followed by UF and addition of a ligand followed by UF methods, respectively. Cobalt ions passed through the membrane into permeate by the second method. If they used a membrane with smaller MWCO than 30 kDa, they could possibly achieve higher recovery results [55].

2.7. Membrane fouling

Membrane fouling is a major problem in membrane separation processes which results in decline of permeate flux [54, 56, 57]. It is an undesirable phenomenon which slows down MEUF process. Membrane fouling may be reversible or irreversible. Reversible fouling occurs as a result of concentration polarization which leads to accumulation of surfactant or any other solute aggregates forming a layer of gel structure over the membrane surface. This layer can be removed from membrane surface by a washing process including backflushing in the UF cell under pressure. In case of irreversible fouling, pores of the membrane are clogged partially or completely in an irreversible manner. Membrane fouling is generally characterized by the results of flux decline experiments.

PES is a thermoresistant polymer with good mechanical strength. These properties make this polymer preferable as a membrane material. But its hydrophobic character makes its fouling by adsorption easy. Pozniak et al. modified PES membrane to decrease its fouling during MEUF. For this purpose, they formed porous asymmetric ion exchange membranes by various methods: phase inversion, sulfonation (cation exchange membrane), and chloromethylation followed by aminolysis (anion exchange membrane) of PES (neutral membrane). Sulfonated PES (SPES) increased the rejection of Cr(III) ions by SDS micelles and aminated PES increased the rejection of Cr(VI) ions by CPC micelles. Charged membranes decreased membrane fouling and thereby increased the flux rate. Reduction of SDS concentration increased the permeate flux [58].

Huang et al. investigated the effects of feed surfactant concentration, recycling of retentate to the feed tank and TMP on membrane fouling; in a continuous cross-flow MEUF process carried out to remove Cd(II) ions. They concluded that fouling becomes a big problem at SDS concentrations over 5 CMC. The effect of TMP was found to depend on the stage of MEUF at which

TMP decreased or increased. They suggested the use of low- and high-concentrated surfactant solutions and different TMPs consecutively to remove the gel layer on the membrane [59].

Effects of SDS feed concentration, TMP and hydraulic flushing on permeate flux were investigated in another research of Huang et al. They carried out both experimental and theoretical studies. SDS rejection increased with increasing SDS concentration, but at 10 CMC, SDS rejection decreased and the biggest fouling resistance and lowest permeate flux were observed. They studied the effects of three kinds of hydraulic flushing methods for membrane cleaning: periodic forward flushing, periodic backwashing and forward flushing followed by backwashing. They stated that backflushing can dislodge the particles in the cake layer blocking the membrane pores but might damage the membrane. Forward flushing could easily remove the layer on membrane by means of cross-flow rinse. They suggested consecutive use of both methods to provide more effective cleaning [60].

Miller compared membrane fouling at constant flux and TMP considering that many industrial UF applications operate at constant permeate flux. They studied emulsified soybean oil fouling of 20 kDa PS ultrafiltration membranes at constant permeate flux and transmembrane pressure. Constant flux fouling was studied at fluxes below and above the threshold flux (the flux at which the rate of fouling begins to increase rapidly, TH flux). Modest increases in TMP were observed below TH flux while fouling, TMP and rejection were increased substantially above TH flux [61].

Zhang et al. studied fouling caused by Gemini micelles in MEUF of phenol containing water. They used two kinds of Gemini surfactant and Brij35 as the surfactants. They recycled retentate and permeate solutions back to the feed tank. They investigated the dependency of TH flux and limiting flux on feed surfactant concentration, TMP and on the nature of surfactants. TH flux decreased with increasing feed concentration due to increased irreversible fouling. They discussed fouling mechanism in MEUF [62].

2.8. Hybrid processes

Some researchers combined MEUF with some other processes to increase removal and/or recovery efficiency. Various auxiliary techniques have been applied prior to or during MEUF to reduce the surfactant and energy consumptions as well as membrane fouling and to shorten the process time.

Liu and Li compared the results of four kinds of processes for Cu(II) removal: UF, electrolysis-UF, MEUF and electrolysis-MEUF using SDS and 10 kDa PS membrane. The best results were obtained with the latter. Before starting, 17 mM SDS was put into the reactor. The copper removal efficiency at the steady-state condition depended on the balance between Cu(II) amount entering the reactor and Cu(II) amount removed by the electrolysis. Copper removal efficiencies were 64.6 and 90% for MEUF and electrolysis-MEUF processes, respectively, for an input SDS concentration of 5.56 mM. Higher R values could be obtained at higher SDS input concentrations. They chose 5.56 mM as the working concentration with the consideration that it was lower than CMC of SDS. But in fact, it is higher than CMC of SDS in the presence of Cu(II) ions (SCMC), which is between 1.5 and 2.2 mM, depending on the purity of SDS and Cu(II) concentration [44].

Sometimes metal salts are added to dye solutions to precipitate vast amount of dye molecules prior to MEUF. Ahmad and Puasa combined coagulation followed by filtration as a pre-treatment method prior to MEUF for the removal of C.I. Reactive Black 5 (RB5) and C.I. Reactive Orange 16 (RO16) dyes. Thus, the dye content of aqueous solution could be reduced substantially before MEUF process. The concentrations of dyes were reduced by pre-treatment from 0.5 to 0.0219 g/L (95.61% removal) and 0.1031 g/L (79.39% removal) for RB5 and RO16, respectively. They could achieve 99.75 and 99.98% R values for RB5 and RO16, respectively, using a commercial cationic coagulant and CPC as the surfactant [63].

Bade et al. combined adsorption of pollutant on activated carbon filter (ACF) and cross-flow MEUF processes for removal of chromate anions using CPC. They also removed CPC in permeate using ACF. Chromate (initial concentration 20 mg/L) removal efficiencies were 98.6 and 99.5% at 1:5 and 1:10 chromate to CPC molar ratios, respectively [64].

Venkataganesh et al. studied the effects of various parameters, including external electric field application, on removal of naphthenic acid (NA) by MEUF, using 10 kDa MWCO PES membrane and SDS. They applied electric field in two modes: in mode 1, a stepwise electric field was applied such that the operating field strength across the membrane increased stepwise; and in mode 2, a fixed electric field was applied throughout the experiment. Application of an external electric field had no effect on NA rejection. R value for NA was 98. On the other hand, electric field accelerated the filtration. Mode 2 increased the flux 24% while step 1 provided 14% increment [65].

Rafique and Lee also used MEUF-ACF hybrid process in the removal of Cd(II) from aqueous solution using SDS and hollow fiber polyacrylonitrile membranes of 100 and 300 kDa MWCO. MEUF was carried out with cross-flow type filtration. The rejected permeate was re-circulated into the feed tank and permeate water was collected at the separation tank. R values for Cd(II) removal (initial concentration 0.065 mM) by MEUF were 68.5 and 36.4 using 100 and 300 kDa membranes, respectively. Corresponding R values were 99.6 and 99.5 with combined ACF-MEUF process [66].

3. Ligand-modified micellar-enhanced ultrafiltration

MEUF has a drawback that it cannot provide high selectivity in removing ions of the same charge. It can be effective in selective separation of metal ions with quite dissimilar properties, such as Cu(II) and Ca(II) or Cu(II) and Pb(II). On the other hand, selective separation of ions can effectively be provided by use of a ligand which undergoes selective complexation with one of the target ions. The complex is solubilized in micelles via hydrophobic forces between the ligand and micellar interior, so it is retained during MEUF providing metal ion rejection. This process is called ligand-modified MEUF (LM-MEUF). The use of a ligand in MEUF process was first applied in the late 1980s [67, 68]. A number of LM-MEUF studies were carried out in 1990s in which LM-MEUF and MEUF techniques were compared and superiority of LM-MEUF to MEUF in terms of removal of metallic ions was shown. It was also shown that cationic surfactants were more effective in metal ion removal by LM-MEUF compared to anionic ones.

The ligands chosen are generally of very low solubility in water, so that leakage of free ligand molecules to permeate is minimized. Therefore, complex formation occurs at the micellar surface mainly between the amphiphilic ligand molecules solubilized in micelles and metal ions in the bulk phase. Thus, micelles behave as nanoreactors and bring close together two reactants in their small volumes (concentration effect of micelles, see Section 1.2.1). Micelles can also solubilize any metal complex molecule formed in the bulk phase (see Section 1.2.1.2). Micellar size is increased and micelles have a more compact structure as a result of complex solubilization. Accordingly, rejection of metal ion-bearing micelles is enhanced.

The efficiency of LM-MEUF process depends on the pH of the sample solution since complex formation is pH-dependent. The other factors are the ligand to metal ion and surfactant to metal ion mole ratios and the natures of the ligand and the surfactant. The working pH is generally between 3 and 7 which can be achieved easily with waste waters.

Ions of similar chemical properties are expected to interact with complexing agents in the same way under the same conditions. Nevertheless, their complexation behaviors can be differentiated in micellar media by the virtue of the “medium effect” of surfactant micelles mentioned in Section 1.2.2. Medium effect arises from the fact that microenvironments in which micellar bound reactants reside have quite different properties from those of the bulk phase. As a consequence, ionization equilibria of ligands interacting with micelles and thereby the stability constants and even the stoichiometry of their complexes to be formed are changed [1, 69, 70]. That the complexation behaviors of two ions with the same complexing agent are differentiated by micelles make selective separation of these ions by MEUF possible.

Superiority of LM-MEUF to MEUF in terms of metal ion removal efficiency has been reported in a number of papers. Pozniak et al. compared the results of MEUF and LM-MEUF experiments in which EDTA was used as the ligand. The presence of ligand in the medium decreased the SDS concentration two times to provide 99% removal of Cr(III) ions with SPES membrane. They attributed this to the fact that EDTA decreased CMC of SDS, and that more rigid structures of ligand-surfactant mixed micelles facilitated the rejection of micelles by the membrane, without referring to increased incorporation of Cr(III) ions to micelles by complex formation [58]. Decrease in SDS feed concentration provided by LM-MEUF enabled higher permeate flux and lower SDS concentration in permeate.

Reuse of a catalyst used in homogeneous catalysis provides economic benefit, but it is not easy to remove and recover it as it is in case of separation of a heterogen catalyst from a reaction system. Schwarze et al. studied the recovery of a catalyzer to enable reuse of rhodium-based homogeneous hydrogenation catalyst precursor, in the absence and presence of triphenylphosphine ligand (TPP) using nonylphenol ethoxylate (Marlopen NP9) nonionic surfactant. They used regenerated cellulose (C) and PES membranes of 5 kDa MWCO. In the absence of ligand, they could achieve retentions below 30%, while the micelle retention was almost 100% with both kinds of membranes in the presence of TPP. This enhancement attributed to formation of a highly hydrophobic complex with TPP, which incorporates into micelles more effectively than catalyst molecules alone. They achieved better results with membrane C [71].

The separation of hydrophilic small molecules, such as sugars, from aqueous solutions is another current field of research. Mehling et al. studied recovery of some sugars (arabinose, cellobiose, glucose and sucrose) from their solutions by MEUF for the first time and compared the results with those of extraction with organic solvents. Cationic CTAB and TX100/Aliquat 336 nonionic-cationic mixture was used as the surfactants. Phenylboronic acid (PBA) ligand was used as a carrier to solubilize sugars in micelles. They obtained better results than those obtained by extraction [72].

There is a limited number of LM-MEUF study performed for removal of copper. Şahin and Taşcıoğlu explored the effects of 20 azo compounds as complexing agents, on removal of Cu(II) ions from single component solutions. They compared the results of MEUF and LM-MEUF studies carried out at pHs 3, 5 and 7. The most effective ligand was found to be 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ), at pH 5. 6.6×10^{-8} mol/L TPTZ provided complete removal of 5.0×10^{-4} mol/L Cu(II) ions in the presence of SDS with two times lower concentration than that required for complete removal of Cu(II) ions by MEUF. They observed that SDS concentration required for complete removal of Cu(II) ions by LM-MEUF decreased with increase in TPTZ concentration implying that SDS feed concentration can be lowered to a concentration close to SCMC by increasing TPTZ concentration, without any concern of increased TPTZ leakage into permeate since TPTZ-Cu(II) complex is positively charged and TPTZ is sparingly soluble in water [73].

There are some reports in the literature on selective removal of metal ions by LM-MEUF. They obtained much better results for ions with quite dissimilar properties such as Cu(II)-Ca(II) or Cu(II)-Pb(II) than those obtained by MEUF studies. Most of these studies were carried out in the late 1980s and1990s.

Simmons et al. used various ligands and surfactants comprising CPC, CTAB, N, N-dimethyl= dodecylamine-N-oxide (DDAO) and polyoxyethylenenonyl phenyl ether ($NP(EO)_{10}$) for selective separation of Cu(II) and Ca(II) ions. N-(n-hexadecyl)-di-2-picolylamine ligand provided Cu(II) rejections of 99.9, 99.8, 99.7, 97.7 and 98.9% using SDS, CPC, CTAB, DDAO and (NP(EO)10), respectively; with no rejection of Ca(II) [74].

Pramauro et al. studied pre-concentration and selective removal of U(VI), Sr(II) and Cd(II) cations. Radioactive strontium is a fission product which should be separated from uranium. Cadmium originates from some other sources such as vessels exposed to acids. They used TX100 and HTAB as the surfactants. Derivatives of 4-aminosalicylic acid (PAS) and of 1-(2-pyridylazo)-2-naphthol (PAN), rendered hydrophobic by tuning alkyl chains, were used as chelating agents. They formed mixed micelles with surfactants (chelating micelles). Selective recovery of uranyl ions was possible via the multi-step UF approach with PAN derivatives in acidic medium. Effective uranyl retention could be obtained with salicylates only in neutral and basic media. Retention was only 3–5% with TX100 micelles in the absence of ligand. 91% U(VI) ions, 21% Cd(II) and 15% Sr(II) could be rejected from single component solutions in the presence of PAS-C8 derivative at pH 5.5 indicating to a selective complexation of uranyl ions with this ligand. Cd(II) and Sr(II) rejections may be resulted largely from adsorption by the membrane. 99% of uranium ions could be recovered in the presence of PAN-C8 and the authors reported that quantitative separation of uranyl ions from both Sr(II) and Cd(II) ions could be feasible at pH 3 with repeated UF processes [75].

Roach et al. reported that Pb(II) ions can be selectively separated from aqueous solutions containing equimolar Ca(II) ions almost completely in the presence of nitrilotriacetic acid (NTA) derivatives as chelating agents [69].

Ghezzi et al studied Cd(II) removal and recovery from binary solutions containing Mg(II) ions in high concentrations and concluded that Cd(II) ions bind to SDS micelles as Cd-PADA complex, and the presence of Mg(II) ions does not affect heavy metal removal from sea water since they do not complex with PADA [48].

There is only one report in the literature on selective separation of Cu(II) and Cd(II) cations which have quite similar properties. Şahin and Taşcıoğlu explored the feasibility of LM-MEUF as a method for selective removal of 0.5 mM Cu(II) ions from 0.5 mM Cd(II) containing solutions at pH 5 and showed that metal ions of similar properties can be separated simply by an UF process. Cu(II) and Cd(II) ions are expected to interact with complexing agents in the same way under the same conditions, since they have similar chemical and physical properties. But the authors showed that complexation behaviors of these cations with the same ligand can be differentiated in micellar media by the virtue of the "medium effect" of surfactant micelles [1]. On this basis, complexation behaviors of 20 azo compounds with Cu (II) and Cd(II) ions were investigated in SDS micellar medium to determine the ligands which could provide selective removal of Cu(II) ions. The selected ligands were used in LM-MEUF experiments. The most effective ligand in selective separation was found to be TPTZ. Complete removal of Cu(II) ions could be achieved with Cd(II) rejections lower than 10% in the presence of this ligand. Selective separation could be provided at SDS feed concentrations much lower than that required for removal of Cu(II) ions from single component solutions by MEUF. Feed concentration of SDS could be lowered to the values close to the SCMC by increasing the TPTZ concentration. A small rejection of Cd(II) was attributed to adsorption on membrane since Cd(II) was observed not to form complex with TPTZ in SDS micellar media [73].

Patil and Marathe studied selective separation of Ni(II) and Co(II) cations from aqueous stream using SDS and SDS/TX100 mixed surfactant system, and iminodiacetic acid (IDA) as the chelating agent, in a cross-flow UF unit. Under the optimum conditions and in SDS micellar system, 94% cobalt could be rejected while 92% Ni permeated across the membrane. TX100 exerted a negative effect on cobalt rejection such that 84% Co(II) retained in the retentate and 93% Ni(II) was in the permeate in mixed micellar system [76].

Aydinoglu et al. studied extraction and recovery of Au(III). They also investigated feasibility of gold/copper separation. Complete extraction of gold (as $AuCl_4^-$ ions) could be achieved in cationic DTAC micellar medium by electrostatic and hydrophobic interactions in the absence and presence of pyridine-2-azo-p-dimethylaniline (PADA), respectively. $AuCl_4^-$ ions were not retained by negatively charged SDS micelles. But it was possible to provide complete rejection of gold in SDS micellar medium in the presence of PADA due to hydrophobic forces between PADA and micelles and the positive charge of Au(III)-PADA complex. Cu(II) removal could not be achieved by cationic DTAC micelles. But they could provide gold-copper separation by MEUF to a large extent utilizing charge effect of SDS micelles: oppositely charged Cu(II) ions bound to micelles retained on the membrane, while $AuCl_4^-$ ions of the same charge with micelles passed through the permeate [52].

Şahin and Taşcıoğlu explored the feasibility of Cu(II)–Cd(II) separation by LM-MEUF, using the same ligands which they used in Ref. [73] but in the presence of CTAB and TX100 micelles [77]. TX100 was not found to be effective in selective separation. Interestingly, the most effective ligand in removal of Cu(II) ions from single component solutions in the presence of cationic CTAB was TPTZ as it was also the case in the presence of anionic SDS. TPTZ was also the most effective ligand in removal of Cu(II) ions from two component solutions but the authors suggested the use of 2-hydroxy-1-(2-hydroxy-4-sülfo-1-naphthylazo)naphtelene-3-carboxylic acid (CALCA) for selective separation. CALCA provided the lowest R value (6.4%) for Cd(II) ions at complete removal of Cu(II) ions at pH 5. Cd (II) rejection in such a small extent was attributed to the adsorption of Cd(II) ions by the membrane itself, since CTAB micelles cannot bind positively charged Cd(II) ions and CALCA were found not to undergo complexation with Cd(II) ions in CTAB micellar medium. The results obtained in the presence of anionic [73], cationic and nonionic [77] micelles provided evidences for the mechanism of Cu(II) removal by LM-MEUF.

Notes

***Both MEUF and LM-MEUF are research areas which require more interest. There is still much to do to determine the optimum conditions for the removal of ions or organics from aqueous media by these simple and economic techniques. There are a large number of parameters and their combinations that can be altered and optimized while conducting MEUF or LM-MEUF studies.

***It should be noted here that in the majority of MEUF and LM-MEUF studies, the SCMC values of the surfactants have not been determined. Most of the researchers take the CMC values of surfactants in deionized water as a basis, wrongly, while conducting a study and discussing the results. Therefore, the surfactant concentrations given in articles should be evaluated in terms of micelle formation, taking into consideration that surfactants exist in the medium as micellar aggregates in concentrations over SCMC, and the concentrations given in CMC unit such as "2 CMC" should be checked if CMC stands for "SCMC".

Author details

Senay Taşcıoğlu

Address all correspondence to: senaytas@gazi.edu.tr

Department of Chemistry, Faculty of Science, Gazi University, Ankara, Turkey

References

[1] Taşcıoğlu S. Micellar solutions as reacfion media. Tetrahedron. 1996;**52**(34):11113-11152

[2] Roach JD, Premjee MM, Buddhavarapu S, Hassib A. A study of the partitioning of haloacetates into cetylpyridinium chloride micelles using semiequlibrium dialysis and ultrafiltration. Journal of Colloid and Interface Science. 2013;**394**:293-300. DOI: 10.1016/j.jcis.2012.11.065

[3] Mondal S, Ghosh S, De S. Atomistic level molecular dynamics simulation on the solubilization mechanism of aromatic molecules in anionic micelles. RSC Advances. 2015; **5**:104493-104501. DOI: 10.1039/c5ra20855f

[4] Sarker AK, Cashin PJ, Balakrishnan VK, Exall K, Chung HK, Buncel E, Brown RS. Determining binding of sulfonamide antibiotics to CTABr micelles using semi-equilibrium dialysis. Separation and Purification Technology. 2016;**162**:134-141. DOI: 10.1016/j.seppur.2016.02.021

[5] Dunn RO, Scamehorn JF, Christian SD. Use of micellar-enhanced ultrafiltration to remove dissolved organics from aqueous streams. Separation Science and Technology. 1985;**20**(4):257-284. DOI: 10.1080/01496398508060679

[6] El-Abbassi A, Khayet M, Hafidi A. Micellar enhanced ultrafiltration process for the treatment of olive mill wastewater. Water Research. 2011;**45**:4522-4530. DOI: 10.1016/j.watres.2011.05.044

[7] Huang J-H, Xiong Y-L, Zeng G-M, Guo S-H, Xie G-X, Zhang D-M, Tang X-J, Liu Z-F. Separation of phenol from various micellar solutions using MEUF. Separation and Purification Technology. 2012;**98**:1-6. DOI: 10.1016/j.seppur.2012.06.037

[8] Zhang W, Huang G, Wei J, Yan D. Gemini micellar enhanced ultrafiltration (GMEUF) process for the treatment of phenol wastewater. Desalination. 2013;**311**:31-36. DOI: 10.1016/j.desal.2012.10.030

[9] El-Abbassi A, Kiai H, Hoinkis J, Hafidi A. Removal of phenolic compounds by micellar enhanced ultrafiltration using an anionic surfactant. Journal of Materials and Environmental Science. 2014;**5**(1):57-66

[10] Huang J-H, Zhao Y, Zeng G-M, Peng L, Li X, Liu L-X, Li F, Shi L-X, Yuan F. Micellar-enhanced ultrafiltration for the solubilization of various phenolic compounds with differen surfactants. Water Science and Technology. 2015;**72**(4):623-631. DOI: 10.2166/wst.2015.257

[11] Liu Z, Yu M, Zeng G, Li M, Zhang J, Zhong H, Liu Y, Shao B, Li Z, Wang Z, Liu G, Yang X. Investigation on the reaction of phenolic pollutions to mono-rhamnolipid micelles using MEUF. Environemental Science and Pollution Research. 2017;**24**:1230-1240. DOI: 10.1007/s11356-016-7851-2

[12] Victor-Ortega MD, Martins RC, Gando-Ferreira LM, Quinta-Ferrira RM. Recovery of phenolic compounds from wastewaters through micellar enhanced ultrafiltration. Colloid Surface A. 2017;**531**:18-24. DOI: 10.1016/j.colsurfa.2017.07.080

[13] Husein MM, Deriszadeh A, Harding TG. Experimental and modeling study of MEUF removal of naphthenic acids. Desalination. 2011;**273**:352-358. DOI: 10.1016/j.desal.2011.01.046

[14] Tortora F, Innocenzi V, Prisciandaro M, Michelis ID, Veglio F, Mazziotti di Celso G. Removal of tetramethyl ammonium hydroxide from synthetic liquid wastes of electronic industry through micellar enhanced ultrafiltration. Journal of Dispersion Science and Technology. 2017:1-7. DOI: 10.1080/01932691.2017.1307760

[15] Khosa MA, Shah SS, Nazar MF. Application of micellar enhanced ultrafiltration for the removal of methylene blue from aqueous solution. Journal of Dispersion Science and Technology. 2011;**32**:260-264. DOI: 10.1080/01932691003659171

[16] Khosa MA, Shah SS, Nazar MF. UV-visible spectrometric study and micellar enhanced ultrafiltration of alizarin red S dye. Journal of Dispersion Science and Technology. 2011;**32**:1634-1640. DOI: 10.1080/01932691.2010.528338

[17] Khosa MA, Shah SS. Micellar enhanced ultrafiltration of reactive black 5 from aqueous solution by cationic surfactants. Journal of Dispersion Science and Technology. 2011;**32**:1002-1007. DOI: 10.1080/01932691.2010.497428

[18] Huang J-H, Zhou C-F, Zeng G-M, Li X, Huang H-J, Niu J, Li F, Shi L-J, He S-B. Studies on the solubilization of aqueous methylene blue in surfactant using MEUF. Separation and Purification Technology. 2012;**98**:497-502. DOI: 10.1016/j.seppur.2012.08.012

[19] Khosa MA, Shah SS, Feng X. Micellar enhanced ultrafiltration of organic dyes. Separation Science and Technology. 2013;**48**:1315-1323. DOI: 10.1080/01496395.2012.740124

[20] Huang J, Peng L, Zeng G, Li X, Zhao Y, Liu L, Li F, Chai Q. Evaluation of micellar enhanced ultrafiltration for removing methylene blue and cadmium ion simultaneously with mixed surfactants. Separation and Purification Technology. 2014;**125**:83-89. DOI: 10.1016/j.seppur.2014.01.020

[21] Hussain KI, Usman M, Siddiq M, Rasool N, Bokhari TH, İbrahim M, Rana UA, Khan SU-D. Application of micellar enhanced ultrafiltration for the removal of reactive blue 19 from aqueous media. Journal of Dispersion Science and Technology. 2015;**36**:1208-1215. DOI: 10.1080/01932691.2014.971368

[22] Aryanti N, Pramudono B, Prawira CNP, Renardi R, Ika S FK. Micellar enhanced ultrafiltration membrane (MEUF) of batik wastewater using cetylpyridinium chloride surfactant. In: American Institute of Physics, AIP Conference Proceedings. Vol. 1699. 2015. pp. s060002-1-06002-9. DOI: 10.1063/1.4938356

[23] Hussain KI, Usman M, Siddiq M, Rasool N, Nazar MF, Ahmad I, Holder AA, Altaf AA. Application of micellar enhanced ultrafiltration for the removal of sunset yellow from aqueous media. Journal of Dispersion Science and Technology. 2017;**38**:139-144. DOI: 10.1080/01932691.2016.1146616

[24] Li C-W, Liu C-K, Yen W-S. Micellar-enhanced ultrafiltration (MEUF) with mixed surfactants for removing Cu(II) ions. Chemosphere. 2006;**63**:353-358. DOI: 10.1016/j.chemosphere.2005.07.017

[25] Rahmanian B, Pakizeh M, Maskooki A. Micellar-enhanced ultrafiltration of zinc in synthetic wastewater using spiral-wound membrane. Journal of Hazardous Materials. 2010;**184**:261-267. DOI: 10.1016/j.jhazmat.2010.08.031

[26] ElZeftawy MAM, Mulligan CN. Use of rhamnolipid to remove heavy metals from wastewater by micellar-enhanced ultrafiltration. Separation and Purification Technology. 2011; **77**:120-127. DOI: 10.1016/j.seppur.2010.11.030

[27] Landaburu-Aguirre J, Pongracz E, Keiski RL. Separation of cadmium and copper from phosphorous rich synthetic waters by micellar-enhanced ultrafiltration. Separation and Purification Technology. 2011;**81**:41-48. DOI: 10.1016/j.seppur.2011.06.040

[28] Landaburu-Aguirre J, Pongracz E, Sarpola A, Keiski RL. Simultaneous removal of heavy metals from phosphorous rich real wastewaters by micellar-enhanced ultrafiltration. Separation and Purification Technology. 2012;**88**:130-137. DOI: 10.1016/j.seppur.2011.12.025

[29] Hayrynen P, Landaburu-Aguirre J, Pongracz E, Keiski RL. Study of permeate flux in micellar-enhanced ultrafiltration on a semi-pilot scale: Simultaneous removal of heavy metals from phosphorous rich real wastewaters. Separation and Purification Technology. 2012;**93**:59-66. DOI: 10.1016/j.seppur.2012.03.029

[30] Staszak K, Konopczynska B, Prochaska K. Micellar enhanced ultrafiltration as a method of removal of chromium(III) ions from aqueous solutions. Separation Science and Technology. 2012;**47**:802-810. DOI: 10.1080/01496395.2011.644613

[31] Abbasi-Garravand E, Mulligan CN. Using micellar enhanced ultrafiltration and reduction techniques for removal of Cr(VI) and Cr(III) from water. Separation and Purification Technology. 2014;**132**:505-512. DOI: 10.1016/j.seppur.2014.06.010

[32] Schwarze M, Groβ M, Buchner G, Kapitzki L, Chiappisi L, Gradzielski M. Micellar enhanced ultrafiltration (MEUF) of metal cations with oleylethoxycarboxylate. Journal of Membrane Science. 2015;**478**:140-147. DOI: 10.1016/j.memsci.2015.01.010

[33] Tortora F, Innocenzi V, Prisciandaro M, Veglio F, Mazziotti di Celso G. Heavy metal removal from liquid wastes by using micellar-enhanced ultrafitration. Water, Air, & Soil Pollution. 2016;**227**:240-250. DOI: 10.1007/s11270-016-2935-7

[34] Huang J, Yuan F, Zeng G, Li X, Gu Y, Shi L, Liu W, Shi Y. Influence of pH on heavy metal speciation and removal from wastewater using micellar-enhanced ultrafiltration. Chemosphere. 2017;**173**:199-206. DOI: 10.1016/j.chemosphere.2016.12.137

[35] Li F, Li X, Zhang JD, Peng L, Liu CY. Removal of organic matter and heavy metals of low concentration from wastewater via micellar-enhanced ultrafiltration: An overview. IOP Conference Series: Earth and Environmental Science. 2017;**52**:1-7. DOI: 10.1088/1755-1315/52/1/012077

[36] Zeng G-M, Li X, Huang J-H, Zhang C, Zhou C-F, Niu J, Shi L-J, He S-B, Li F. Micellar-enhanced ultrafiltration of cadmium and methylene blue in synthetic wastewater using SDS. Journal of Hazardous Materials. 2011;**185**:1304-1310. DOI: 10.1016/j.jhazmat.2010.10.046

[37] Li X, Zeng G-M, Huang J-H, Zhang D-M, Shi L-J, He S-B, Ruan M. Simultaneous removal of cadmium ions and phenol with MEUF using SDS and mixed surfactants. Desalination. 2011;**276**:136-141. DOI: 10.1016/j.desal.2011.03.041

[38] Tanhanei B, Chenar MP, Saghatoleslami N, Hesampour M, Laakso T, Kallioinen M, Sillenpaa M, Manttari M. Simultaneous removal of aniline and nickel from water

by micellar-enhanced ultrafiltration with different molecular weight cut-off membranes. Separation and Purification Technology. 2014;**124**:26-35. DOI: 10.1016/j.seppur.2014.01.009

[39] Verma SP, Sarkar B. Rhamnolipid based micellar enhanced ultrafiltration for simultaneous removal of Cd(II) and phenolic compound from wastewater. Chemical Engineering Journal. 2017;**319**:131-142. DOI: 10.1016/j.cej.2017.03.009

[40] Gzara L, Dhahbi M. Removal of chromate anions by micellar-enhanced ultrafiltration using cationic surfactants. Desalination. 2001;**137**:241-250

[41] Baek K, Lee H-H, Yang J-W. Micellar-enhanced ultrafiltration for simultaneous removal of ferricyanide and nitrate. Desalination. 2003;**158**:157-166

[42] Rahmati NO, Chenar MP, Namaghi HA. Removal of free active chlorine from synthethic wastewater by MEUF process using polyethersulfone/titania nanocomposite membrane. Separation and Purification Technology. 2017;**181**:213-222. DOI: 10.1016/j.seppur.2017.03.030

[43] Purkait MK, DasGupta S, De S. Separation of aromatic alcohols using micellar-enhanced ultrafiltration and recovery of surfactant. Journal of Membrane Science. 2005;**250**:47-59. DOI: 10.1016/j.memsci.2004.10.014

[44] Liu C-K, Li C-W. Combined electrolysis and micellar enhanced ultrafiltration (MEUF) process for metal removal. Separation and Purification Technology. 2005;**43**:25-31. DOI: 10.1016/j.seppur.2004.09.010

[45] Kim H, Baek K, Lee J, Iqbal J, Yang J-W. Comparison of separation methods of heavy metal from micellar solutions for the recovery of surfactant. Desalination. 2006;**191**:186-192. DOI: 10.1016/j.desal.2005.09.013

[46] Ghezzi L, Robinson BH, Secco F, Tine MR, Venturini M. Removal and recovery of palladium(II) ions from water using micellar-enhanced ultrafiltration with a cationic surfactant. Colloid Surface A. 2008;**329**:12-17. DOI: 10.1016/j.colsurfa.2008.06.037

[47] Qu Y-H, Zeng G-M, Huang J-H, Xu K, Fang Y-Y, Li X, Liu H-L. Recovery of surfactant SDS and Cd^{2+} from permeate in MEUF using a continuous foam fractionator. Journal of Hazardous Materials. 2008;**155**:32-38. DOI: 10.1016/j.jhazmat.2007.11.024

[48] Ghezzi L, Monteleone G, Robinson B, Secco F, Tine MR, Venturini M. Metal extraction in water/micelle systems: Complex formation, stripping and recovery of Cd(II). Colloid Surface A. 2008;**317**:717-721. DOI: 10.1016/j.colsurfa.2007.12.008

[49] Li X, Zeng G-M, Huang J-H, Zhang C, Fang Y-Y, Qu Y-H, Luo F, Lin D, Liu H-L. Recovery and reuse of surfactant SDS from a MEUF retentate containing Cd^{2+} or Zn^{2+} by ultrafiltration. Journal of Membrane Science. 2009;**337**:92-97. DOI: 10.1016/j.memsci.2009.03.030

[50] Geanta RM, Ruiz MO, Escudero I. Micellar-enhanced ultrafiltration for the recovery of lactic acid and citric acid from beet molasses with sodium dodecyl sulphate. Journal of Membrane Science. 2013;**430**:11-23. DOI: 10.1016/j.memsci.2012.12.006

[51] Schwarze M, Chiappisi L, Prevost S, Gradzielski M. Oleylethoxycarboxylate – An efficient surfactant for copper extraction and surfactant recycling via micellar enhanced ultrafiltration. Journal of Colloid and Interface Science. 2014;**421**:184-190. DOI: 10.1016/j.jcis.2014.01.037

[52] Aydinoglu S, Biver T, Ceccarini A, Secco F, Venturini M. Gold(III) extraction and recovery and gold(III)/copper(II) separation using micelles. Colloid Surface A. 2015;**482**:324-328. DOI: 10.1016/j.colsurfa.2015.06.024

[53] Huang J, Qi F, Zeng G, Shi L, Li X, Gu Y, Shi Y. Repeating recovery and reuse of SDS micelles from MEUF retentate containing Cd^{2+} by acidification. Colloid Surface A. 2017;**520**:361-368. DOI: 10.1016/j.colsurfa.2017.02.001

[54] Das C, DasGupta S, De S. Prediction of permeate flux and counterion binding during cross-flow micellar enhanced ultrafiltration. Colloid Surface A. 2008;**318**:125-133. DOI: 10.1016/j.colsurfa.2007.12.027

[55] Anthati VAK, Marathe KV. Selective separation of copper(II) and cobalt(II) from wastewater by using continuous cross-flow micellar-enhanced ultrafiltration and surfactant recovery from metal micellar solutions. Canadian Journal of Chemical Engineering. 2011;**89**(2):292-298. DOI: 10.1002/cjce.20380

[56] Guo W, Ngo H-H, Li J. A mini-review on membrane fouling. Bioresource Technology. 2012;**122**:27-34. DOI: 10.1016/j.biortech.2012.04.089

[57] Shi X, Tal G, Hankins NP, Gitis V. Fouling and cleaning of ultrafiltration membranes: A review. Journal of Water Process Engineering. 2014;**1**:121-138. DOI: 10.1016/j.jwpe.2014.04.003

[58] Pozniak G, Pozniak R. Modified polyethersulfone membranes for micellar enhanced ultrafiltration of chromium. In: Proceedings of European Congress of Chemical Engineering (ECCE-6); Copenhagen. September 16-20, 2007. pp. 1-7

[59] Huang J-H, Shi LJ, Zeng GM, Li X, He S-B, Li F, Xiong Y-L, Guo S-H, Zhang DM, Xie G-X. Effects of feed concentration and transmembrane pressure on membrane fouling in Cd^{2+} removal by micellar-enhanced ultrafiltration. Desalination. 2012;**294**:67-73. DOI: 10.1016/j.desal.2012.03.009

[60] Huang J, Liu L, Zeng G, Li X, Peng L, Li F, Jiang Y, Zhao Y, Huang X. Influence of feed concentration and transmembrane pressure on membrane fouling and effect of hydraulic flushing on the performance of ultrafiltration. Desalination. 2014;**335**:1-8. DOI: 10.1016/j.desal.2013.11.038

[61] Miller DJ. Comparison of membrane fouling at constant flux and constant transmembrane pressure conditions. Journal of Membrane Science. 2014;**454**:505-515. DOI: 10.1016/j.memsci.2013.12.027

[62] Zhang W, Ding L, Zhang Z, Wei J, Jaffrin MY. Threshold flux and limiting flux for micellar enhanced ultrafiltration as affected by feed water: Experimental and modeling studies. Journal of Cleaner Production. 2016;**112**:1241-1251. DOI: 10.1016/j.jclepro.2015.09.042

[63] Ahmad AL, Puasa SW. Reactive dyes decolourization from an aqueous solution by combined coagulation/micellar enhanced ultrafiltration process. Chemical Engineering Journal. 2007;**132**:257-265. DOI: 10.1016/j.cej.2007.01.005

[64] Bade R, Lee SH, Jo S, Lee H-S, Lee S-E. Micellar enhanced ultrafiltration (MEUF) and activated carbon fibre (ACF) hybrid processes for chromate removal from wastewater. Desalination. 2008;**229**:264-278. DOI: 10.1016/j.desal.2007.10.015

[65] Venkataganesh B, Maiti A, Bhattacharjee S, De S. Electric field assisted cross flow micellar enhanced ultrafiltration for removal of naphthenic acid. Separation and Purification Technology. 2012;**98**:36-45. DOI: 10.1016/j.seppur.2012.06.017

[66] Rafique RF, Lee S. Micellar enhanced ultrafiltration (MEUF) and activated carbon filter (ACF) hybrid processes for the removal of cadmium from an aqueous solution. Korean Chemical Engineering Research. 2014;**52**(6):775-780. DOI: 10.9713/kcer.2014.52.6.775

[67] Schovanec AL. Use of ligand-modified micellar-enhanced ultrafiltration to selectively remove dissolved metals from water. [PhD dissertation]. The School of Chemical Engineering and Materials Science, Graduate Colledge, University of Oklahoma. 1991

[68] Klepac J, Simmons DL, Taylor RW, Scamehorn JF, Christian SD. Use of ligand-modified micellar-enhanced ultrafiltration in the selective removal of metal ions in water. Separation Science and Technology. 1991;**26**(2):165-173. DOI: 10.1080/01496399108050464

[69] Roach JD, Christian SD, Tucker EE, Taylor RW, Scamehorn JF. Ligand-modified colloid enhanced ultrafiltration. Separation Science and Technology. 2003;**38**(9):1925-1947. DOI: 10.1081/SS-120020127

[70] Biver T, Ghezzi L, Malvaldi V, Secco F, Tine MR, Venturini M. Kinetics and equilibria of the interaction of 8-hydroxyquinoline with gallium(III) in water and sodium dodecyl sulfate solution. The Journal of Physical Chemistry. B. 2009;**113**:1598-1606

[71] Schwarze M, Schmidt M, Nguyen LAT, Drews A, Kraume M, Schomacker R. Micellar enhanced ultrafiltration of a rhodium catalyst. Journal of Membrane Science. 2012;**421-422**:165-171. DOI: 10.1016/j.memsci.2012.07.017

[72] Mehling T, Zewuhn A, Ingram T, Smirnova I. Recover of sugars from aqueous solution by micellar enhanced ultrafiltration. Separation and Purification Technology. 2012;**96**:132-138. DOI: 10.1016/j.seppur.2012.05.026

[73] Şahin D, Taşcıoğlu S. Removal of Cu(II) ions from single component and Cd(II) containing solutions by micellar enhanced ultrafiltration utilizing micellar effects on complex formation. Desalination and Water Treatment. 2016;**57**:11143-11153. DOI: 10.1080/19443994.2015.1042059

[74] Simmons DL, Schovanec AL, Scamehorn JF, Christian SD, Taylor RW. Ligand-modified micellar-enhanced ultrafiltration for metal ion separations. Use of N-alkyltriamines. ACS Symposium Series. 1992;**509**:180-193

[75] Pramauro E, Prevot AB, Zelano V, Gulmini M, Viscardi G. Selective recovery of uranium(VI) from aqueous acid solutions using micellar ultrafiltration. The Analyst. 1996;**121**:1401-1405

[76] Patil PN, Marathe KV. Selective separation of nickel(II) and cobalt(II) from waste water by using continuous cross-flow micellar-enhanced ultrafiltration with addition of chelating agent. Separation Science and Technology. 2013;**48**:547-553. DOI: 10.1080/01496395.2012.690485

[77] Şahin D, Taşcıoğlu S. Separation of Cu(II) ions from single component and Cd(II) containing solutions by LM-MEUF utilizing micellar effects of CTAB and TX100 on complex formation. Desalination and Water Treatment. Forthcoming paper

Chapter 6

Fouling of Nanofiltration Membranes

Flávio Caldeira Silva

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.75353

Abstract

Despite all promising perspectives and new research in nanofiltration, for example, in drinking water production, in wastewater treatment, the food industry, the chemical and pharmaceutical industry, and many other industries, there are still some obstacles that slow down large-scale applications. Fouling is an irreversible and time-dependent phenomenon, and it is related to the characteristics of the membrane and solute-solute and solute-membrane interactions. Therefore, an understanding of fouling mechanisms such as fouling characteristics and consequences, fouling mathematical models, and physical-chemical and processing factors affecting fouling, are very important. As a result, the aim of this chapter is to present some phenomena that contribute to fouling: physical-chemical interactions, pore mechanical blocks, and deposit of suspension material on membrane surface.

Keywords: nanofiltration, fouling, fouling membranes, fouling characteristics, membrane process

1. Introduction

Nanofiltration (NF) is defined as "a process intermediate between reverse osmosis and ultrafiltration that rejects molecules which have a size in the order of one nanometer." In general, the use of membrane process is limited by fouling, which reveals itself as a decrease in flux with time of operation. Fouling probably is the most important reason for the minimal acceptance of nanofiltration and other membrane processes in large-scale processing [1, 2].

A number of factors contribute to fouling and are strongly interlinked. Organic, inorganic, particulate, and biological fouling are some of the main fouling categories. Also important are metal complexes, for example, Fe, Al, Si. Despite many research traditionally focusing on one category or fouling mechanism at a time, it is well accepted that in most cases, it is not one single category that can be identified. In most real-life applications, all four types of fouling go hand in hand [2, 3]. Fouling is an irreversible and time-dependent phenomenon; it is related to the characteristics of the membrane and solute-solute and solute-membrane interactions that cause an irreversible decline in the flow of permeate, which can only be recovered by the chemical cleaning of the membrane. In addition, some process parameters like equipment design, temperature, feed concentration, flow, and pressure can also contribute to membrane fouling.

2. Nanofiltration and membranes

The singularity of these membranes is highlighted by their ability to selectively reject different dissolved salts; they have a high rejection rate of low molecular weight, dissolved components. Nanofiltration membranes with low transmembrane pressure, operating pressure of generally 5–30 bar, were developed to achieve high divalent ion rejection. It is expected that the rejected molecules can have a molecular weight of 200 $g.mol^{-1}$; this corresponds to an equivalent of Stokes diameter of approximately 1 nm [3, 4].

Nanofiltration membranes are neither entirely dense nor entirely porous, so their retention mechanisms are determined by both size exclusion (porous membranes) and sorption and diffusion (dense membranes). Also, these kinds of membranes are principally used to partially soften potable water, allowing some minerals to pass into the product water, thus increasing the stability of the water and preventing it from being aggressive to distribution piping material. Additionally, NF membranes are discovering increasing use in purifying industrial effluents and minimizing waste discharge. The key to using NF membranes for particular applications is the selection of a membrane with the appropriate rejection characteristics and the design of a suitable process. In general, NF membranes are characterized by a high charge density and pore sizes in the range of nanometers; the surface charge is most often negative and has the greatest effect on the selective passage nature of these membranes. New studies have been developed, and new membranes having unique properties, including a varying range of hardness rejection and fouling resistance manufactured [2, 4].

3. Characteristics of fouling and consequences of fouling

The efficiency of the nanofiltration process is affected by fouling on the membrane and other factors like tangential velocity, pressure, temperature, turbulence, feed particles size, concentration polarization changes in membrane properties, and membrane characteristics [2].

Fouling phenomenon is the result of the interaction between solutes adsorbed onto the membrane and solutes present in the feed flow, or even between the membrane and diverse solutes present in the solution. Fouling can be the result of three main factors or the interaction between them: the properties of the material constituting the membrane, the properties of the solute, and the operational parameters [2, 3, 5].

The interaction between solute and membrane, the interaction among molecules of solute present, and the chemical constitution of the membrane structure must be identified to understand the phenomenon of fouling. Notably, the interaction between solute and membrane will determine the fouling formed by the adsorption of solute onto the membrane surface [6, 7].

In contrast to polarization of concentration, which is considered a reversible phenomenon and independent of process time, fouling is an irreversible phenomenon and dependent on time. Fouling can be defined as a deposition or adsorption of retained particles, colloids, macromolecules, salts, etc., on the membrane surface and/or aggregation in the pores, causing partial or even total blockage of the pores, resulting in a continuous decline of flow. The different ways in which the pores become blocked are a function of the size and form of the solute in relation to the pore size distribution of the membrane. Partial blockage of the pores occurs when isolated macromolecules or groups of them partially seal the pores, with the possibility of forming a deposit on the membrane surface, increasing the resistance to permeation. When chemical species are deposited or adsorbed on the inside of the membrane pores, it reduces the volume available for passage of the permeate; there is internal blockage of the pores. Complete blockage of the pores occurs when the particles that deposit on the membrane surface are larger than the membrane pores, completely obstructing them [8, 9].

This phenomenon, related to the characteristics of the membrane and solute-solute and solute-membrane interactions, causes an irreversible decline in the flow of permeate, which is only recovered by the chemical cleaning of the membrane. **Figure 1** shows some types of blocks [2, 8, 9].

Observing and analyzing **Figure 1**, it is possible to understand the different ways in which the membrane can be blocked and compare concentration polarization. When hydrocolloids, macromolecules, or other particles with larger dimensions as compared to the diameter of the membrane pore, are rejected and accumulate on the surface of the membrane, concentration polarization occurs. An increase in resistance to solvent passage occurs by this accumulation, and consequently leads to a greater local osmotic pressure. In general, concentration polarization occurs in any selective transport process such as classical filtration and tangential filtration. In tangential flux, concentration polarization stabilizes quickly and this provokes an additional resistance to mass transfer by the membrane, and as a result a decline in flux permeate [10, 11].

The precipitation of organic solutes on the membrane surface is known as gel formation. This process usually occurs when the wall concentration due to concentration polarization exceeds the solubility of the organic solute. It is very important to consider that gel formation does not necessarily mean irreversible flux decline. The gel polarization model is based on the fact that at steady state, flux reaches a limiting value, where an increase in pressure no longer increases the flux. Conforming to the gel polarization model, at this limiting value, the solubility limit of the solute in the boundary layer is reached and a gel formed [5, 12].

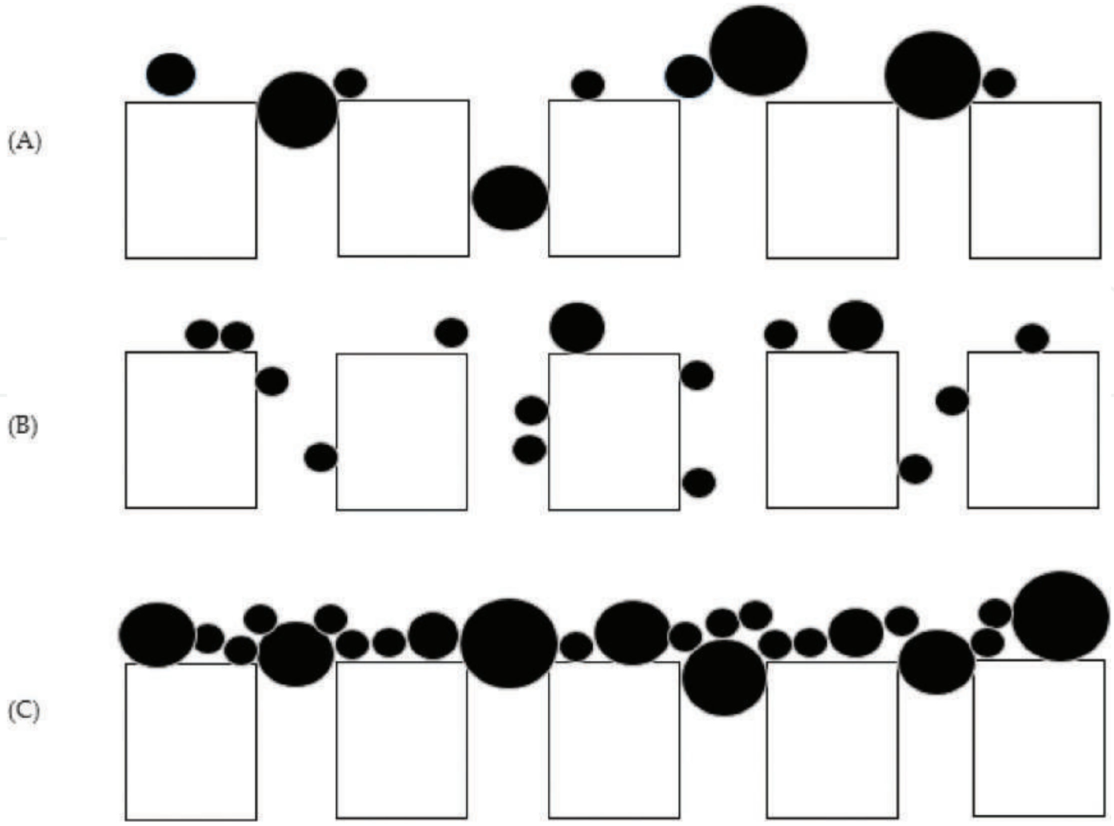

Figure 1. Inlay membrane mechanism: (A) complete blockage of pores; (B) partial (internal) blocking of pores; (C) polarized layer.

The typical permeation flux curves can be described in three different stages. The first stage (I) is characterized by a sudden drop in flux in the first minutes due to the polarization of the solutes by concentration on the surface of the membrane. At this stage, loss of flow is reversible. In the second stage (II), the flow variation decreases, varying with the pore diameter of the membrane. The precipitation of the accumulated solutes begins, which leads to the blocking of the pores and the adsorption of the components in the membrane, causing the formation of the polarized layer and the incrustation. The decrease in flow due to this latter phenomenon is irreversible. Finally, the third stage (III) is the consolidation of incrustation; in this stage, the flow decreases continuously and slowly. **Figure 2** shows each step described here [13].

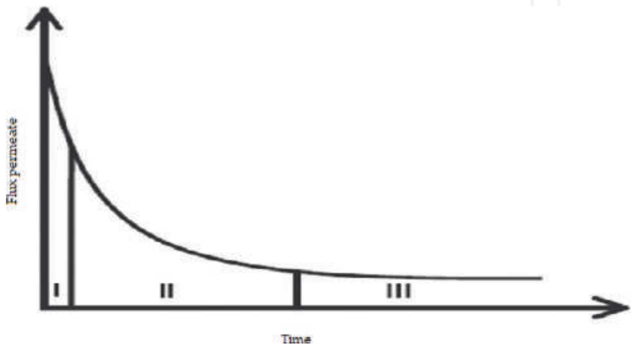

Figure 2. Typical permeation flux curves described in three different stages (adapted from Marshall and Daufin [13]).

4. Physical and chemical factors affecting fouling

Nanofiltration membranes retain substances with molar masses higher than ~300 g mol^{-1} and multivalent ions. The retention characteristics depend largely on how much free volume there is in the membranes, which can for some membranes be related to the flux. As nanofiltration membranes have characteristics of both ultrafiltration as well as reverse osmosis membranes, their fouling characteristics are also rather unique [12, 14].

It has already been discussed that fouling is initiated by solute-membrane material interactions; however, Van der Waals forces, chemical binding, and Lewis acid-base interactions are the major phenomena involved in the interactions resulting between surfaces and solutes on a molecular level. As a result, physicochemical properties of membrane surfaces are changed and this facilitates the deposition of other molecules and other aggregates. Membrane-solvent interactions can be expected to diversify with changes in the solvent properties, such as molecular size, surface tension, viscosity, and dielectric constant [11, 14, 15].

The relationship between the type of solvent, polar or non-polar, and the type of membrane, hydrophilic or hydrophobic, used in separation processes, must be judiciously analyzed. The flow rate of polar solvents is significantly higher (8–10 times) than that of non-polar solvents in processes carried out with hydrophilic membranes [9].

The relationship between the components of solute molar mass and rejection by the membrane can be observed from the results obtained in the analysis of the rejection of triacylglycerols present in *n*-hexane solution, where the percent rejection obtained was higher for larger molar masses [9].

Fouling of nanofiltration membranes has been studied very extensively up to date and many studies have tried to explain what happens in each situation. Because fouling can decrease the flux drastically, it is important to investigate what types of foulants should be avoided in NF [13].

It is necessary to identify the foulants in order to reduce or eliminate fouling. This objective can be achieved by a characterization of the fouled membrane or by fouling studies in the laboratory. Once the foulants are identified, suitable control strategies can be adapted. An overview of foulants and appropriate control strategies are summarized in **Table 1**. The strategies include a number of categories, for example: module design, operation mode and cleaning, membrane selection like non-fouling materials/coatings, feed pre-treatment, suitable surface charge, porosity, hydrophilicity chlorine compatibility, and surface roughness [5, 11].

Important factors that differentiate nanofiltration from other processes of membranes separation are as follows:

- Rejection of multivalent negative ions, such as sulfates, and phosphates;
- Rejection of sodium chloride (0–70%) in systems of complex mixtures;
- Rejection of particles without loads, dissolved materials, and positive charge ions in solution is related to the size and shape of the molecule in question.

Foulant	Fouling control
General	Hydrodynamics/shear, operation below critical flux, chemical cleaning
Inorganic (scaling)	Operate below solubility limit, pre-treatment, reduce pH to 4–6 (acid addition), low recovery, additives (antiscalants); some metals can be oxidized with oxygen
Organic	Pretreatment using biological processes, activated carbon, ion exchange, ozone, enhanced coagulation
Colloids (<0.5 μm)	Pre-treatment using coagulation and filtration, microfiltration, ultrafiltration
Biological solids	Pretreatment using disinfection (e.g., chlorination/dechlorination), filtration, coagulation, microfiltration, ultrafiltration

Adapted and modified from Fane et al. [19].

Table 1. Foulants and their control strategies in nanofiltration processes.

Therefore, the efficiency of a nanofiltration process depends on the size of the particles present in the solution and molecular loads [5].

It is also known that mineral salts have a deep influence on the fouling of ultrafiltration and nanofiltration membranes. These components can interact with the membrane directly or precipitate on the membrane and cause a reduction in flux. However, mineral salts contribute to the ionic strength of the solution, which in turn affects the conformation and dispersion of the proteins and consequently, the fouling of the nanofiltration membrane [2, 5, 6].

Many studies report the effect of pH on membrane fouling. Flux is lowest at the isoelectric point of the protein and is higher as the pH moves away from the isoelectric point. Changes in pH affect proteins in solubility, which is generally lowest at the isoelectric point and increases as pH is adjusted away from it; conformation, because of the interaction between proteins and membranes, also changes with pH membranes. Thus, these effects of pH on flux should not be unexpected, especially in view of the effect on solubility of salts [2, 6].

In general, in many industrial or laboratory test processing cases, membrane fouling may be caused by pectins, proteins, tannins, starch, cellulose, and hemicellulose. Moreover, it is very necessary to consider biofouling in membranes. Biofouling is a term used to describe all instances of fouling where biologically active organisms are involved. Whilst the different forms of chemical fouling reflect largely passive deposition of organic or inorganic materials on membrane surfaces, biofouling is a dynamic process of microbial colonization and growth, which results in the formation of microbial biofilms. Biofilms are microbial communities that grow attached to surfaces. Biofilm formation constantly precedes biofouling, which becomes an issue only when biofilms reach thicknesses and surface coverages that reduce permeability. In some cases, biofilms may cause total blockage of feedwater channels and mechanical collapse of modules by telescoping [2, 6, 15–22].

5. Processing factors affecting fouling: temperature, pressure, feed concentration, flow rate and turbulence

It is important to consider that other factors can affect fouling, and not just the complex physical-chemical interaction of feed components.

The main physical operational parameters that affect the permeate flow rate are: pressure, temperature, viscosity and density of the feed fluid, and the tangential velocity [23].

The temperature effect is not completely clear and can influence fouling in two different ways. It is possible that as temperature is increased further, the beneficial effects (lower viscosity, higher diffusivity) will outweigh the harmful effects (loss of solubility of salts) and may result in a net increase in flux. It could also result in a decrease in flux for certain feeds, due to decreases in solubility of feed components at higher temperatures. Evidently, for biological systems, too high temperature will result in protein denaturation and other heat damage, which will provoke lowering of the flux [2, 10].

An increase in feed concentration alters the viscosity, density, and diffusivity of the feed solution, causing a decrease in permeate flow rate. The permeate flow rate is directly proportional to the pressure applied and inversely proportional to the viscosity. Viscosity can be controlled by two factors: solids concentration in the feed and temperature [24, 25].

As is known, an increase in pressure results in a greater convective rate for the transport of solute to the membrane surface, increasing its concentration at the interface, causing an increase in diffusivity of the solute in the opposite direction to that of the process pressure, and thus decreasing the permeate flow rate [26–29]. It is important to emphasize that there is a linear relationship between flow rate and the inverse of the solvent viscosity for nanofiltration and ultrafiltration membranes, revealing that the main mass transport mechanism in these systems is convection [2, 30].

Moreover, an increase in tangential velocity increases the permeate flow rate by provoking greater turbulence, causing a dispersion in the solute molecules concentrated on the membrane surface, and reducing the thickness of the gel layer. High shear rates generated at the membrane surface tend to shear off deposited material thus reducing the hydraulic resistance of the fouling layer. This is one of the simplest and most effective methods to control the effect of concentration polarization. Severe decreases in flux can sometimes be observed at too low velocities [2, 6, 31].

6. Resistance and mathematical models of fouling

Because of concentration polarization and fouling, there is a reduction on flux permeate value compared with pure solvent. As a result, both represent additional resistances to mass transfer by the membrane. The kinetic that is relativity slow for some phenomes and that provokes fouling, can explain the long time it takes to reach a possible stationary state. **Figure 3** is presented as an illustration of these phenomes. Thus, the relation between permeate flux and pressure variation applied on both sides of the membrane can be expressed by Eq. (1):

$$J = \frac{1}{n\,R_T}\,\Delta P \tag{1}$$

where

$$R_T = R_m + R_a + R_b + R_g + R_{cp} \tag{2}$$

Here R_m, resistance of transport by the membrane; R_a, additional resistance due to adsorption phenomenon; R_b, additional resistance of physical pores blocks; R_g, additional resistance due to formation of gel layer on the membrane surface; R_{pc}, additional resistance due to polarization concentration phenomenon; R_T, total resistance due of mass transfer through the membrane; n, solution viscosity that permeates through the membrane.

Despite the resistance-in-series model being used frequently, in which permeation flux declines due to membrane fouling and concentration polarization resistance on the membrane surface, other mathematical models to predict the flux behavior can also be used. A number of mathematical models are available in the literature that attempt to describe the mechanism of transport of particles through membranes such as Brownian diffusion, inertial lift, shear-induced diffusion, flowing cake and surface transport, and cake layer models [32].

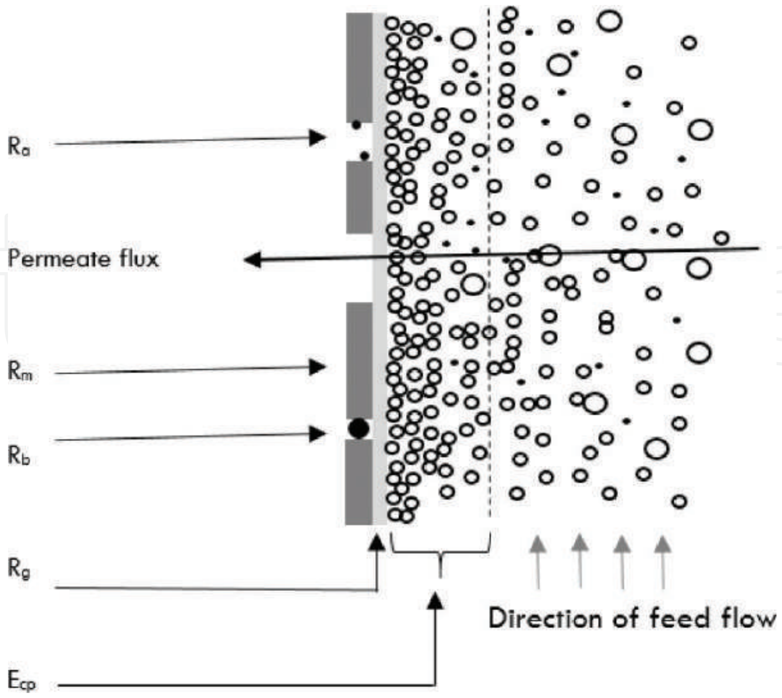

Figure 3. Resistances of mass transfer in membrane provoked by fouling and concentration polarization. Additional resistance: R_m, membrane resistance; R_a, adsorption; R_b, blocked pore; R_g, gel layer; E_{cp}, concentration polarization.

The most elementary type of model relates the flux to the time and volume permeated. Most of them are based on the assumption that the build-up of fouling layer is a first order reaction [2].

Decrease in permeate flux with time has been related to the volume concentration factor (VCR), defined as the initial volume divided by the retentate volume at any time (VCR = $V_0/(V_0 - V_P)$), where V_0 is the initial volume and V_P is the permeate volume [33].

In general, almost any data (flux vs. time) will adequately fit almost any of models reasonably well, but since they are semi-empirical in nature, they do not help to explain or understand the phenomenon itself [2].

7. Fouling and cleaning

According to the characteristics and factors described before, fouling reveals itself to be a decline performance, commonly a decline in flux under constant operating conditions, processing, and probable modification in the permeate properties of the membrane. The optimum way to reduce fouling will depend on the fouling process [34].

Membrane fouling problems can also be cleaning problems. For food processes, the membrane material, and all other food contact surfaces, should be compatible with normal food and food cleaners [2, 34].

Reducing membrane fouling must include an attention to the chemical nature of the membrane such as physical-chemical properties of feed stream. Some studies reported that hydrophilic membranes normally foul less than hydrophobic membranes [34].

To decide about the cleaning process, it is very important to consider the type of foulant, that is, the cleaning agents to use will depend on the material that causes the fouling. Moreover, the cleaning cycle can be incorporated into the design of nanofiltration plant as automatic cleaning operation. The membrane system is considered clean when the original water flux has been restored [2].

8. Final considerations

Nanofiltration technology has been widely applied in the desalination and concentration, separation and purification of drinking water, wastewater treatment and other industrial processes [36–41]. This process already plays an important role in a variety of cases in the water treatment, the dairy industry, biomedical processes and, so on. It is important to note that the ability of nanofiltration to separate monovalent and multivalent ions is a key feature in environmentally related processes. Operations with high pressure membranes are already established technologies for the treatment of waste water that aim at the production of purified water for recycling or reuse and recovery of valuable compounds [12, 35, 42–46].

Among these example applications, a number of factors have been contributing to the increasing interest in using membrane processes for water treatment. The essential factor is the stringent water quality regulations, which can be met to some extent, in an economically viable way, by membrane processes [5].

Furthermore, the food industry was one of the first industries to introduce membrane filtration into its commercial processes since membrane processes are potentially nondestructive, relatively energy efficient (no phase change), and even cheaper than conventional treatment [36–41]. However, nowadays, the cost of application and industrial processes by membranes is still expensive.

Researches reveal that in practice, industrial application of membranes becomes more attractive and competitive when combined processes, i.e., classical processes and membrane processes, are used together. In this way, each process acts in the most efficient part, and thus, the results are more advantageous than when applying technologies alone [5].

It is also necessary to improve the competitiveness of the process for filtration of drinking water, wastewater treatment, the food industry, the chemical and pharmaceutical industry, purification of biodiesel, and many other industries. It is important to improve the technological process and products and to reduce costs.

Fouling of membranes is important as it limits the competitiveness of the process due to an increase in costs caused by an increased energy demand, additional labor for maintenance and chemical costs for cleaning as well as a shorter lifetime of the membranes. Essential for effective fouling control is a proactive operation of the nanofiltration (NF) plant where an early indication of fouling is acted upon and a good identification of the type of fouling is carried out. On the other hand, nanofiltration technology can be applied in many industrial sectors in many different ways. The use of membrane technology appears as a relevant alternative to conventional processing in a huge variety of annexed processes.

NF membranes are also finding increasing use for purifying industrial effluents and minimizing waste discharge. The possibility of waste treatment, the preservation of compounds of importance from them, the reduction in energy consumption and of chemical products stand out among the principal advantages of NF membranes.

Author details

Flávio Caldeira Silva

Address all correspondence to: flaviocaldeira@iftm.edu.br

Instituto Federal do Triângulo Mineiro, MG, Brazil

References

[1] Ogawa N, Kimura K, Watanabe Y. Membrane fouling in nanofiltration/reverse osmosis membranes coupled with a membrane bioreactor used for municipal wastewater treatment. Desalination and Water Treatment. 2010;**18**:292-296

[2] Cheryan M. Ultrafiltration and Microfiltration Handbook. Chicago: Technomic Publ; 1998

[3] Broeckmann A, Wintgens T, Schätfer AI. Removal and fouling mechanisms in nanofiltration of polysaccharide solutions. Desalination. 2005;**178**:149-159

[4] Bartels C, Wilf M, Casey W, Campbell J. New generation of low fouling nanofiltration membranes. Desalination. 2008;**221**:158-167

[5] Schäfer AI, Fane AG, Waite TD. Nanofiltration—Principles and Applications. Great Britain: Elsevier; 2006

[6] Strathmann H. Synthetic membranes and their preparation. In: Porter MC, editor. Handbook of Industrial Membrane Technology. New Jersey: Noyes Publications; 1990

[7] Susanto H, Ulbricht M. Influence of ultrafiltration membrane characteristics on adoptive fouling with dextrans. Journal of Membrane Science. 2005;**266**:132-142

[8] Mulder MHV. Polarization phenomena and membrane fouling. In: Noble RD, Stern SA, editors. Membrane Separations Technology: Principles and Applications. Amsterdan: Elsevier; 1995. pp. 45-84

[9] Bhanushali D, Kloos S, Bhattacharyya D. Solute transport in solvent resistant nanofiltration membranes for non-aqueous systems: Experimental results and the role of solute–solvent couplin. Journal of Membrane Science. 2002;**208**:343-359

[10] Giorno L, Todisco S, Donato L, Driolo E. Study of fouling phenomena in apple juice clarification by enzyme membrane reactor. Separation Science and Technology. 1998; **33**:739-756

[11] de Morais Coutinho C, Chiu MC, Basso RC, Badan Ribeiro AP, Gonçalves LAG, Viotto LA. State of art of the application of membrane technology to vegetable oils: A review. Food Research International. 2009;**42**(5-6):536-550

[12] Halbert AC, Borges CP, Nóbrega R. Processos de separação com membranas. Rio de Janeiro: Ed. e-papers; 2006. p. 180

[13] Marshall AD, Daufin G. Physico-chemical aspects of membrane fouling by dairy fluids. In: IDF Special Issue 9504 (Ed.), Fouling and Cleaning in Pressure Driven Membranes Process. Brussels: International Dairy Federation; 1995. pp. 9-29

[14] Nyström M, Kaipia L, Luque S. Fouling and retention of nanofiltration membranes. Journal of Membrane Science. 1995;**98**:249-262

[15] Hafidi A, Pioch D, Ajana H. Adsorptive fouling of inorganic membranes during microfiltration of vegetable oils. European Journal of Lipid Science and Technology. 2003;**105**:138-148

[16] Scott K. Handbook of Industrial Membranes. Introduction to Membranes Separations. Vol. 1. Oxford, UK: Elservier. Cap; 1995. pp. 3-175

[17] Kim I, Kim J, Lee K, Tak T. Phospholipids separation (degumming) from crude vegetable oil by polyimide ultrafiltration membrane. Journal of Membrane Science. 2002;**205**:113-123

[18] Lappin-Scott HM, Costerton JW. Bacterial biofilms and surface fouling. Biofouling. 1989;**1**:323-342

[19] Fane AG, Beatson P, Li H. Membrane fouling and its control in environmental applications. Water Science Technology. 2000;**41**(10-11):303-308

[20] Ridgway HF, Flemming HC. Membrane Biofouling, in Water Treatment Membrane Processes. In: Mallevialle J, Odendaal PE, Wiesner MR, editors. New York: McGraw Hill; 1996;**6**(1-6):62

[21] Flemming H-C. Biofouling Bei Membranprozessen. Berlin: Springer; 1995

[22] Sadr Ghayeni SB, Beatson PJ, Schneider RP, Fane AG. Adhesion of waste water bacteriato reverse osmosis membranes. Journal of Membrane Science and Technology. 1997;**138**:29-42

[23] Scott K. Handbook of Industrial Membranes. Oxford: Elsevier; 2003

[24] Satyanarayana SV, Bhattacharya PK, De S. Flux decline during ultrafiltration of Kraft black liquor using different flow modules: A comparative study. Separation and Purifcation Technology. 2000;**20**:155-167

[25] Hwang ST, Kammermeyer K. Membranes in separations. In: Cheryan M, editor. Ultrafiltration and Microfiltration Handbook. Chicago: Technomic Publ; 1998. p. 526

[26] Chen V, Fane AG, Madaeni S, Wenten IG. Particle deposition during membranes filtration of colloids: Transition between concentration polarization and cake formation. Journal of Membrane Science. 1997;**125**:109-122

[27] Field RW, Wu D, Howell JA, Gupta BB. Critical flux concept for microfiltration fouling. Journal of Membrane Science. 1995;**100**:259-272

[28] Porter MC. Handbook of Industrial Membrane Technology. New Jersey: Noyes Publications; 1990

[29] Song L. A new model for the calculation of the limiting flux in ultrafiltration. Journal of Membrane Science. 1998;**144**:173-185

[30] Tsui EM, Cheryan M. Characteristics of nanofiltration membranes in aqueous ethanol. Journal of Membrane Science. 2004;**237**:61-69

[31] Cheng T, Lin CT. A study on cross flow ultrafiltration with various membrane orientations. Separation Purification Technology. 2004;**39**:13-22

[32] Wang Z, Chu J-s, Wen-juan W, Yao J-m. Study of unsteady-state flux prediction in crossflow microfiltration. Desalination. 2009;**238**:290-301

[33] Mondor M, Girard B, Oresoli CM. Modeling flux behavior for mebrane filtration of apple juice

[34] Heldman DR, Lund DB. Handbook of Food Engineering. 2nd ed. Boca Raton, FL: CRC Press; 2007

[35] Wang XL, Zhang CH, Ouyang PK. The possibility of separating saccharides from a NaCl solution by using nanofiltration in diafiltration mode. Journal of Membrane Science. 2002;**204**:271-281

[36] Wang XL, Ying AL, Wang WN. Nanofiltration of L-phenylalanine and L-aspartic acid aqueous solutions. Journal of Membrane Science. 2002;**196**:59-67

[37] Li SL, Li C, Liu YS, Wang XL, Cao ZA. Separation of L-glutamine from fermentation broth by nanofiltration. Journal of Membrane Science. 2003;**222**:191-201

[38] Wang DX, Wang XL, Tomi Y, Ando M, Shintani T. Modeling the separation performance of nanofiltration membranes for the mixed salts solution. Journal of Membrane Science. 2006;**280**:734-743

[39] Wang DX, Wu L, Liao ZD, Wang XL, Ando M, Shintani T. Modeling the separation performance of nanofiltration membranes for the mixed salts solution with Mg^{2+} and Ca^{2+}. Journal of Membrane Science. 2006;**284**:384-392

[40] Jiraratananon R, Sungpet A, Luangsowan P. Performance evaluation of nanofiltration membranes of nanofiltration membranes for treatment of effluents containing reactive dye and salt. Desalination. 2000;**130**:177-183

[41] Ducom G, Cabassud C. Interests and limitation of nanofiltration for the removal of voltaic organic compounds in drinking water production. Desalination. 1999;**124**:115-123

[42] Galanakis CM, Tonmerg E, Gekas V. Clarification of high-added value products from olive mill wastewater. Journal of Food Engineering. 2010;**99**:190-197

[43] Galanakis CM, Chasiotis S, Botsaris G, Gekas V. Separation and recovery of proteins and sugars from Halloumi cheese whey. Food Research International. 2014;**65**:477-483

[44] Muro C, Riera F, Del Carmen Diaz M. Membrane separation process in wastewater treatment of food industry. In: Valdez B, editor. Food Industrial Processes—Methods and Equipment. Rijeka, Croatia: InTech; 2012. pp. 253-280

[45] Suárez E, Lobo A, Alvarez-Blanco S, Riera FA, Álvarez R. Utilization of nanofiltration membranes for whey and milk ultrafiltration permeate demineralization. Desalination. 2006;**199**:345-347

[46] Tylkowski B, Tsibranska I, Kochanov R, Peev G, Giamberini M. Concentration of biologically active compounds extracted from Sideritis ssp. L. by nanofiltration. Food and Bioproducts Processing. 2011;**89**:307-314

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

Ping Geng and Guohua Chen

Additional information is available at the end of the chapter

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 ξ 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],

$$u_e = \frac{\zeta \varepsilon_0 \varepsilon_r}{\mu} = \frac{v_e}{E} \tag{1}$$

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

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 filed, 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.

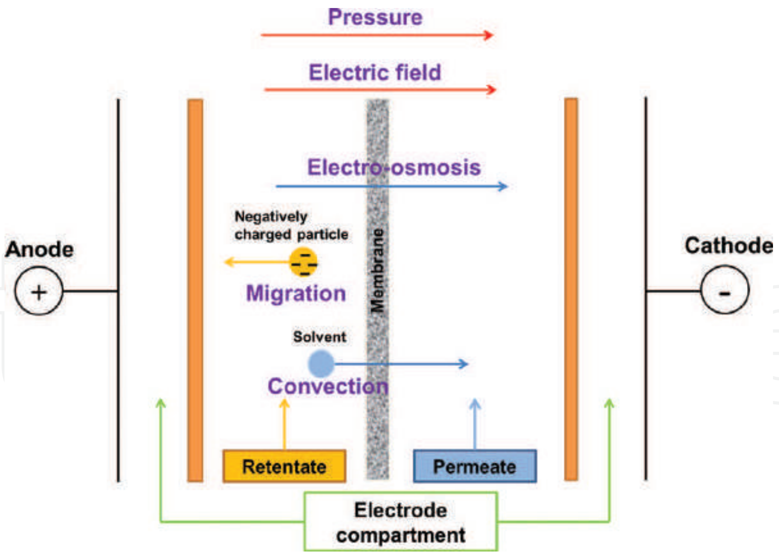

Figure 1. Schematic diagram of the electrofiltration process [18] (reproduced with permission).

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 ($MO_n{\cdot}OH{\cdot}$) or chemisorbed active oxygen (MO_{n+1}). Physisorbed oxygen reacts directly with oxidizable organic compounds acting as a source of hydroxyl radicals. β-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 $MO_n{\cdot}OH{\cdot}$ 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, ·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:

$$H_2O + MO_x \rightarrow MO_x(\cdot OH) + H^+ + e^- \quad (2)$$

$$R + MO_x(\cdot OH)_z \rightarrow CO_2 + zH^+ + ze^- + MO_x \quad (3)$$

Oxidation by chemisorbed active oxygen:

$$MO_x(\cdot OH) \rightarrow MO_{x+1} + H^+ + e^- \quad (4)$$

$$R + MO_{x+1} \rightarrow RO + MO_x \tag{5}$$

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 O_2 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]. PbO_2 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 Pb^{2+} pollution. SnO_2 has been reported to have a high overpotential of oxygen evolution. Its stability is very poor [24]. Sb-doped SnO_2 electrodes have been developed including Ti/SnO_2-Sb, Ti/SnO_2-Sb-CNT [9] and Ti/SnO_2-Sb_2O_3-Y [25]. However, the performance still needs further improvement. Although IrO_2-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 IrO_2-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, Ti_4O_7, has similarly large O_2 evolution potential to BDD electrode. With nanotube array morphology, it even possesses comparable electrochemical activity to BDD as well [35]. The preparation temperature of Ti_4O_7 is over 800°C requiring H_2 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

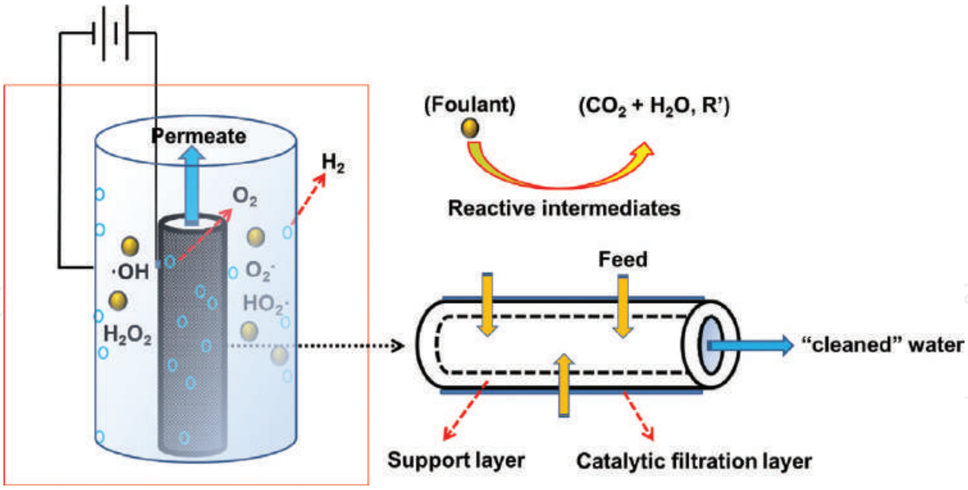

Figure 2. Schematic diagram of electrooxidation-assisted filtration [18] (reproduced with permission).

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.

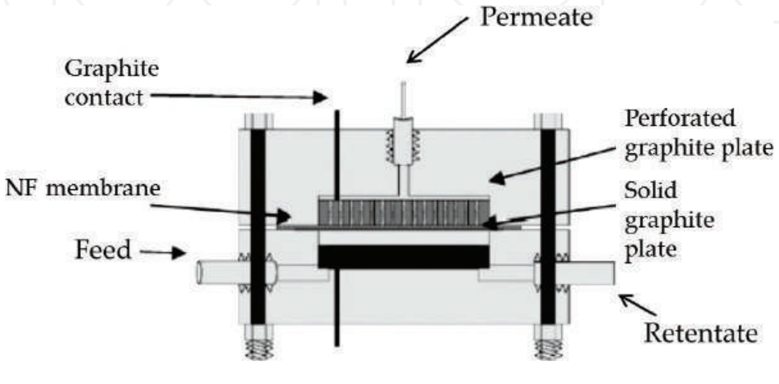

Figure 3. Flat sheet membrane module designs with electrophoresis assistance [43] (reproduced with permission).

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

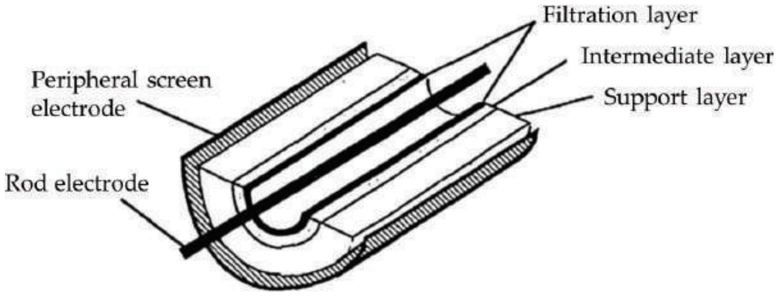

Figure 4. Typical tubular electrically assisted NF membrane module design.

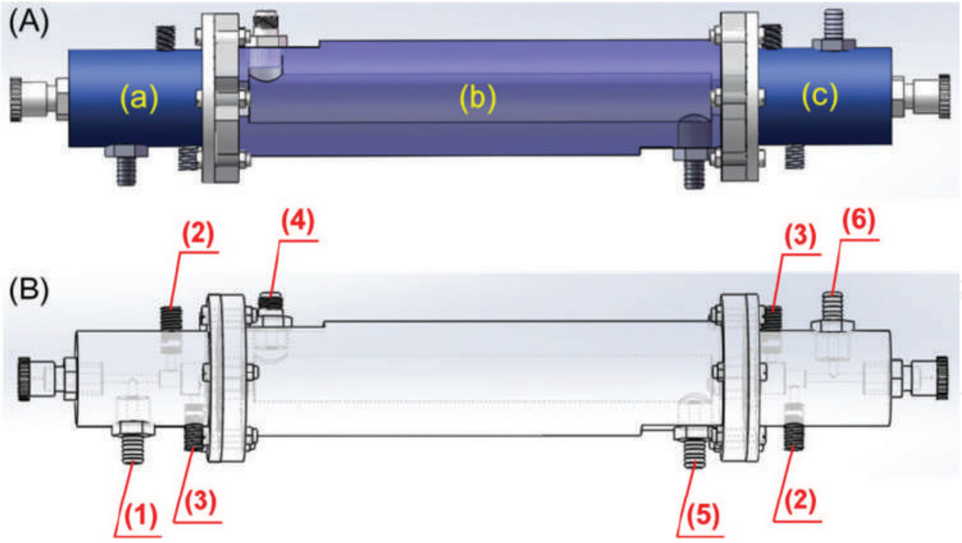

Figure 5. Three-dimensional (A) and perspective view (B) of (a) tubular membrane module with electric contact for inner and outer membrane surface, (b) compartment used for permeate collection, (c) symmetrical compartments for the flow of feed solution and retentate. (1) Inlet opening for feed solution, (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).

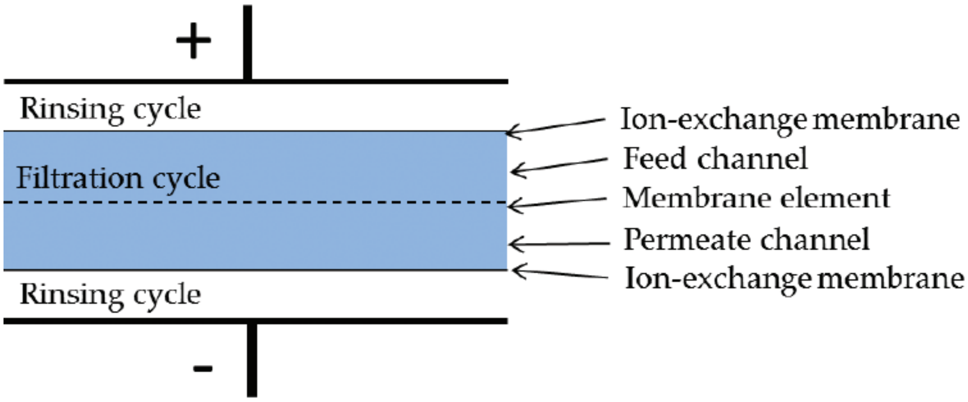

Figure 6. Membrane module design with separate compartment of electrodes and rinsing cycle.

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]:

$$E_{total} = \frac{Q\,\Delta P}{JA\eta} + \frac{VI}{JA\,\eta_{DC}} \tag{6}$$

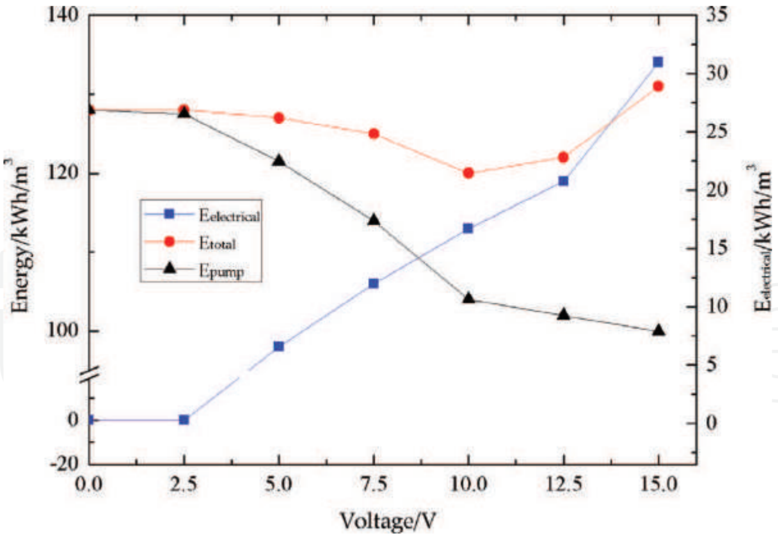

Figure 7. Variation of energy consumption per unit volume of permeate with applied potential at TMP of 0.8 MPa and CFV of 0.0258 $m \cdot s^{-1}$ [25] (reproduced with permission).

where Q was the flow velocity ($m^3 \cdot s^{-1}$), ΔP the TMP (Pa), V the applied voltage (V), I the electric current (A), J the permeate flux ($L \cdot m^{-2} \cdot s^{-1}$), 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 $mol \cdot m^{-3}$) over an estimated potential range from 0 to 1.9×10^3 $V \cdot m^{-1}$ (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 mol·m^{-3}	CFV: 3 m·s^{-1} TMP: 5, 10, 20, 30 bar Electric field: 0 to 1.9×10^3 V·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 kg·kmol^{-1}	TMP: 6.9 bar CFV: 0.5 m·min^{-1} Electric field: 0 to 1.5×10^4 V·m^{-1}	[41]
BQ01 flat polymeric membranes	Stainless steel wire lattice	Porous, stainless-steel disk	3.08, 17.11 and 59.88 mol·m^{-3} NaCl solution	TMP: 6.9 bar Electric field: 0 to 2.67×10^4 V·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 L·min^{-1}; electric potential, 0 to 2 V	[42]
NF90 flat polymeric membrane	Mesh Ti/ SnO_2-Sb	Ti Mesh	250 mg·L^{-1} tetracycline hydrochloride with NaCl of 0.06 mol·L^{-1}	TMP, 0.4–1.2 MPa; CFV, 10–60 L·h^{-1}; electric current, 10–50 mA·cm^{-2}	[37]
Polyamide polymeric membrane	Mesh Ti/ SnO_2-Sb_2O_3-Y	Ti Mesh	0.3–0.8 g·L^{-1} Acid Red 73 solution with 0.1 mol·L^{-1} Na_2SO_4	TMP, 0.4–1.2 MPa; CFV, 0.0086 to 0.043 m·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 $S_{Na+/Cl-}$ and $S_{Na+/SO42-}$ continuously increased with higher electrical voltage at $[Na_2SO_4]/[NaCl]$ of 1 and transmembrane pressure (TMP) of 10 bar. Meanwhile, the directions of variations of $[Na^+]$, $[SO_4^{2}–]$, and $[Cl^-]$ rejections were found to be independent of $[Na^+]$ 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 $[Na^+]$ strongly decreased from 30 to −367% (minus means passage of $[Na^+]$), while the rejection of $[Cl^-]$ increased from −27 to 81% and $[SO_4^{2-}]$ 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 1.33×10^4 $V \cdot m^{-1}$ 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 $kg \cdot m^{-3}$. 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 $kg \cdot m^{-3}$, fouling was reversible for BQ01 but irreversible for NF45. For BQ01 membrane, a 1.25×10^4 $V \cdot cm^{-1}$ electric potential is needed to avoid fouling, while for NF45, 6×10^3 $V \cdot cm^{-1}$ is sufficient. With much higher red dye concentration of 12 $kg \cdot m^{-3}$, a reversible fouling is obtained using BQ01 with an electric field of 1.33×10^4 $V \cdot cm^{-1}$, 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 Ti/SnO_2-Sb_2O_3-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 $m \cdot s^{-1}$. 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, pKa = 9.13; H_3AsO_4, pKa = 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 $L \cdot h^{-1}$, and current density of 20 $mA \cdot cm^{-2}$, the total filtration resistance decreased from 14.54 to 3.84×10^{13} 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 $mA \cdot cm^{-2}$. 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.

Author details

Ping Geng[1]* and Guohua Chen[2]

*Address all correspondence to: ping.geng@polyu.edu.hk

1 Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Kowloon, Hong Kong SAR, China

2 Department of Mechanical Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong SAR, China

References

[1] Pupunat L, Rios GM, Joulie R, Persin M, Pourcelly G. Electronanofiltration: A new process for ion separation. Separation Science and Technology. 1998;**33**:67-81

[2] Zydney AL, Ho C-C, Yuan W. Chapter 2 - fouling phenomena during microfiltration: Effects of pore blockage, cake filtration, and membrane morphology. In: Dibakar B, Butterfield DA, editors. Membrane Science and Technology. CRC Press, Elsevier; 2003. pp. 27-44

[3] Bier M. Electrical filtering process and device. In: U.S.P. Office, editor. United States. p. 1963

[4] Wakeman RJ, Tarleton ES. Experiments using electricity to prevent fouling in membrane filtration. Filtration & Separation. 1986;**23**:174-176

[5] Huotari HM, Huisman IH, Trägårdh G. Electrically enhanced crossflow membrane filtration of oily waste water using the membrane as a cathode. Journal of Membrane Science. 1999;**156**:49-60

[6] Wakeman RJ. Electrically enhanced microfiltration of albumin suspensions. Food and Bioproducts Processing. 1998;**76**:53-59

[7] Yang Y, Li J, Wang H, Song X, Wang T, He B, Liang X, Ngo HH. An electrocatalytic membrane reactor with self-cleaning function for industrial wastewater treatment. Angewandte Chemie International Edition. 2011;**50**:2148-2150

[8] Li XW, Li JX, Gao CY, Chang M. Surface modification of titanium membrane by chemical vapor deposition and its electrochemical self-cleaning. Applied Surface Science. 2011;**258**:489-493

[9] Zhang L, Xu L, He J, Zhang J. Preparation of Ti/SnO_2-Sb electrodes modified by carbon nanotube for anodic oxidation of dye wastewater and combination with nanofiltration. Electrochimica Acta. 2014;**117**:192-201

[10] Fan X, Zhao H, Liu Y, Quan X, Yu H, Chen S. Enhanced permeability, selectivity, and antifouling ability of CNTs/Al_2O_3 membrane under electrochemical assistance. Environmental Science & Technology. 2015;**49**:2293-2300

[11] Pabby AK, Rizvi SSH, Requena AMS. Handbook of Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications. 2nd ed. CRC Press; 2015

[12] Overbeek JTG. Thermodynamics of electrokinetic phenomena. Journal of Colloid Science. 1953;**8**:420-427

[13] Huotari HM, Trägårdh G, Huisman IH. Crossflow membrane filtration enhanced by an external DC electric field: A review. Chemical Engineering Research and Design. 1999;**77**:461-468

[14] Wakeman RJ, Tarleton ES. Membrane fouling prevention in crossflow microfiltration by the use of electric fields. Chemical Engineering Science. 1987;**42**:829-842

[15] Weng Y-H, Li K-C, Chaung-Hsieh LH, Huang CP. Removal of humic substances (HS) from water by electro-microfiltration (EMF). Water Research. 2006;**40**:1783-1794

[16] Ahmad AL, Ibrahim N. Automated electrophoretic membrane cleaning for dead-end microfiltration and ultrafiltration. Separation and Purification Technology. 2002;**29**: 105-112

[17] Lentsch S, Aimar P, Orozco JL. Enhanced separation of albumin-poly(ethylene glycol) by combination of ultrafiltration and electrophoresis. Journal of Membrane Science. 1993;**80**:221-232

[18] Geng P. Electricity-Assisted Antifouling Ceramic Membrane Modified by Magnéli Titanium Sub-Oxides for Environmental and Biological Applications, in. Hong Kong: The Hong Kong University of Science and Technology; 2015

[19] Särkkä H, Vepsäläinen M, Pulliainen M, Sillanpää M. Electrochemical inactivation of paper mill bacteria with mixed metal oxide electrode. Journal of Hazardous Materials. 2008;**156**:208-213

[20] Chen G. Electrochemical technologies in wastewater treatment. Separation and Purification Technology. 2004;**38**:11-41

[21] Comninellis C. Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment. Electrochimica Acta. 1994;**39**:1857-1862

[22] Awad YM, Abuzaid NS. Electrochemical treatment of phenolic wastewater: Efficiency, design considerations and economic evaluation. Journal of Environmental Science and Health. Part A: Environmental Science and Engineering and Toxicology. 1997;**32**:1393-1414

[23] Zhou M-H, Dai Q-Z, Lei L-C, Wu Z-C, Ma C-A, Wang D-H. Electrochemical oxidation for the degradation of organic pollutants on a novel PbO_2. Acta Physico-Chimica Sinica. 2004;**20**:871-876

[24] Chen X, Gao F, Chen G. Comparison of Ti/BDD and Ti/SnO_2–Sb_2O_5 electrodes for pollutant oxidation. Journal of Applied Electrochemistry. 2005;**35**:185-191

[25] Xu L, Zhang L, Du L, Zhang S. Electro-catalytic oxidation in treating C.I. Acid red 73 wastewater coupled with nanofiltration and energy consumption analysis. Journal of Membrane Science. 2014;**452**:1-10

[26] Hu J-M, Sun X-J, Hou Y-Y, Zhang J-Q, Cao C-N. Degradation characteristics of IrO_2-type DSA® in methanol aqueous solutions. Electrochimica Acta. 2008;**53**:3127-3138

[27] Martínez-Huitle CA, Quiroz MA, Comninellis C, Ferro S, Battisti AD. Electrochemical incineration of chloranilic acid using Ti/IrO_2, Pb/PbO_2 and Si/BDD electrodes. Electrochimica Acta. 2004;**50**:949-956

[28] Chatzisymeon E, Fierro S, Karafyllis I, Mantzavinos D, Kalogerakis N, Katsaounis A. Anodic oxidation of phenol on Ti/IrO_2 electrode: Experimental studies. Catalysis Today. 2010;**151**:185-189

[29] Chen X, Chen G, Gao F, Yue PL. High-performance Ti/BDD electrodes for pollutant oxidation. Environmental Science & Technology. 2003;**37**:5021-5026

[30] Chen X, Chen G. Anodic oxidation of orange II on Ti/BDD electrode: Variable effects. Separation and Purification Technology. 2006;**48**:45-49

[31] Chen X, Chen G, Yue PL. Anodic oxidation of dyes at novel Ti/B-diamond electrodes. Chemical Engineering Science. 2003;**58**:995-1001

[32] Chen G, Betterton EA, Arnold RG. Electrolytic oxidation of trichloroethylene using a ceramic anode. Journal of Applied Electrochemistry. 1999;**29**:961-970

[33] Bejan D, Malcolm JD, Morrison L, Bunce NJ. Mechanistic investigation of the conductive ceramic Ebonex® as an anode material. Electrochimica Acta. 2009;**54**:5548-5556

[34] Bejan D, Guinea E, Bunce NJ. On the nature of the hydroxyl radicals produced at boron-doped diamond and Ebonex® anodes. Electrochimica Acta. 2012;**69**:275-281

[35] Geng P, Su J, Miles C, Comninellis C, Chen G. Highly-ordered Magnéli Ti_4O_7 nanotube arrays as effective anodic material for electrooxidation. Electrochimica Acta. 2015;**153**: 316-324

[36] Yang B, Geng P, Chen G. One-dimensional structured IrO_2 nanorods modified membrane for electrochemical anti-fouling in filtration of oily wastewater. Separation and Purification Technology. 2015;**156**:931-941

[37] Geng P, Chen G. Electro-microfiltration concentration of whey protein using Magneli titanium sub-oxide modified ceramic membrane. In: Asia Pacific Confederation of Chemical Engineering Congress 2015: APCChE 2015, Incorporating CHEMECA 2015, Melbourne, Australia; 2015. pp. 641-650

[38] Xu L, Sun Y, Du L, Zhang J. Removal of tetracycline hydrochloride from wastewater by nanofiltration enhanced by electro-catalytic oxidation. Desalination. 2014;**352**:58-65

[39] Sarkar B, De S, DasGupta S. Pulsed electric field enhanced ultrafiltration of synthetic and fruit juice. Separation and Purification Technology. 2008;**63**:582-591

[40] Bowen WR, Ahmad AL. Pulsed electrophoretic filter-cake release in dead-end membrane processes. AICHE Journal. 1997;**43**:959-970

[41] Zumbusch P, Kulcke W, Brunner G. Use of alternating electrical fields as anti-fouling strategy in ultrafiltration of biological suspensions – Introduction of a new experimental procedure for crossflow filtration. Journal of Membrane Science. 1998;**142**:75-86

[42] Noël IM, Lebrun R, Bouchard CR. Electro-nanofiltration of a textile direct dye solution. Desalination. 2000;**129**:125-136

[43] Pérez-Sicairos S, Lin SW, Félix-Navarro RM, Espinoza-Gómez H. Rejection of As(III) and As(V) from arsenic contaminated water via electro-cross-flow negatively charged nanofiltration membrane system. Desalination. 2009;**249**:458-465

[44] Hofs B, Ogier J, Vries D, Beerendonk EF, Cornelissen ER. Comparison of ceramic and polymeric membrane permeability and fouling using surface water. Separation and Purification Technology. 2011;**79**:365-374

[45] Rueffer M, Bejan D, Bunce NJ. Graphite: An active or an inactive anode? Electrochimica Acta. 2011;**56**:2246-2253

[46] Geng P, Chen G. Magnéli Ti_4O_7 modified ceramic membrane for electrically-assisted filtration with antifouling property. Journal of Membrane Science. 2016;**498**:302-314

[47] Geng P, Chen G. Antifouling ceramic membrane electrode modified by Magnéli Ti_4O_7 for electro-microfiltration of humic acid. Separation and Purification Technology. 2017; **185**:61-71

[48] Zaky AM, Chaplin BP. Porous substoichiometric TiO_2 anodes as reactive electrochemical membranes for water treatment. Environmental Science & Technology. 2013;**47**: 6554-6563

[49] Rabah MA, Nassif N, Azim AAA. Electrochemical wear of graphite anodes during electrolysis of brine. Carbon. 1991;**29**:165-171

[50] Brisson G, Britten M, Pouliot Y. Electrically-enhanced crossflow microfiltration for separation of lactoferrin from whey protein mixtures. Journal of Membrane Science. 2007;**297**:206-216

[51] Dudchenko AV, Rolf J, Russell K, Duan W, Jassby D. Organic fouling inhibition on electrically conducting carbon nanotube-polyvinyl alcohol composite ultrafiltration membranes. Journal of Membrane Science. 2014;**468**:1-10

[52] Zhang Q, Vecitis CD. Conductive CNT-PVDF membrane for capacitive organic fouling reduction. Journal of Membrane Science. 2014;**459**:143-156

[53] Weigert T, Altmann J, Ripperger S. Crossflow electrofiltration in pilot scale. Journal of Membrane Science. 1999;**159**:253-262

[54] Noël IM, Lebrun RE, Bouchard CR. Nanofiltration of NaCl solutions using a SPPO membrane (BQ01) part 2. Membrane behavior with an electric field. Desalination. 2003; **155**:243-254

[55] Buckley CA. Membrane technology for the treatment of dyehouse effluents. Water Science and Technology. 1992;**25**:203-209

[56] Sójka-Ledakowicz J, Koprowski T, Machnowski W, Knudsen HH. Membrane filtration of textile dyehouse wastewater for technological water reuse. Desalination. 1998;**119**:1-9

[57] Xu Y, Lebrun RE, Gallo P-J, Blond P. Treatment of textile dye plant effluent by nanofiltration membrane. Separation Science and Technology. 1999;**34**:2501-2519

[58] Brandhuber P, Amy G. Arsenic removal by a charged ultrafiltration membrane — Influences of membrane operating conditions and water quality on arsenic rejection. Desalination. 2001;**140**:1-14