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Nanofiltration Mediated by Surfactant Micelles: Micellar-Enhanced Ultrafiltration

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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 industrial 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 dodecylbenzene-sulfonic 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, $25 \pm 1°C$, 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 bio-surfactant 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 industry 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 ≥ 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".

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