



A Review of Studies on Micellar Enhanced Ultrafiltration for Heavy Metals Removal from Wastewater

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ABSTRACT

Micellar enhanced ultrafiltration (MEUF) process has been used for the removal of copper, chromate, zinc, nickel, cadmium, selenite, arsenate and organics like phenol, o-cresol. This paper reviews various factors such as operating pressure, surfactant concentration, pH of solution, temperature, presence of non-ionic surfactant and salt, membrane type and its pore size and some inhibiting additives, competing metals on heavy metals and surfactants removals in the MEUF process. In this process, heavy metals removal reached over 99% at the initial concentration of up to 1 mM. Metals removal was enhanced by combining the MEUF treatment with electrolysis or with powdered activated carbon (PAC). Cetylperidinium Chloride (CPC) and Sodium dodecyl sulphate (SDS) surfactants removal from the MEUF permeate was also enhanced by the MEUF-ACF (activated carbon fibre) combined treatment. Surfactant has been recovered from the MEUF retentate solution by treating the retentate with HNO₃, H₂SO₄, HCl, NaOH solution but retentate solution needs further treatment. Electrolysis was found better in the separation of metal and surfactant from the MEUF retentate solution. Further study on MEUF process is required for prolonging the experimental period for the heavy metals removal from wastewater. Investigation is also needed to treat highly concentrated solution, and to treat real wastewater.

Keywords: Critical micelle concentration, Heavy metals, Hydrophilic and hydrophobic membrane, Micellar enhanced ultrafiltration, Surfactant

1.0 INTRODUCTION

Micellar enhanced ultrafiltration (MEUF) has been used for the removal of various organic and/or inorganic pollutant from aqueous phase (Baek and Yang, 2003a; Ghosh and Bhattacharya, 2006; Gzara and Dhahbi, 2001; Purkait et al., 2004). This process utilizes the high efficiency of reverse osmosis (RO) and high permeates flux of ultrafilter membrane (UF) (Baek et al., 2003a). The main principle of this process is to increase the size of pollutant molecules by forming a complex with

surfactant. Cationic or anionic surfactants are used for the removal of inorganic pollutants. In this system, the surfactant forms micelles at critical micelle concentration (cmc). The aggregation number ranges from 50 to 100. Micelle (cationic or anionic) has high electrical potential on its surface where anionic or cationic pollutants can be bounded depending upon the charge characteristic of the pollutants. When the solution containing micelle is passed to the ultrafilter membrane, micelle retains on the membrane surface. Unbound ions and surfactant monomers pass through the ultrafilter membrane to the permeate side. In the MEUF process, solute rejection efficiency and permeate flux depend on the cha-

racteristics of solutes and membrane, and various operating conditions.

MEUF study on heavy metals removal has been conducted by various researchers. But, till now there is no review paper on MEUF process indicating affecting factors on MEUF process. Therefore, this study focuses on review of different operating parameters that affect the heavy metals removal in the MEUF process.

2.0 FACTORS AFFECTING EFFICIENCY OF MEUF PROCESS

Efficiency of MEUF process on heavy metals removal depends upon various operating factors, such as operating pressure, types and concentration of surfactants, pH of solution, presence of additives, membrane type and its pore size, and presence of non ionic surfactant and salt. Effects of various parameters on the removal efficiency of MEUF are summarized below.

2.1 Effect of Operating Pressure

Various researchers reported the effect of operating pressure on the removal efficiency of MEUF for various inorganic and organic pollutants. Juang et al. (2003) found no such significant effect of pressure on metal removal. But, metal concentration in the permeate was reduced by increasing the pressure (Purkait et al., 2004). It was mainly due to increase of micelle aggregation layer (MAL) (Ghosh and Bhattacharya, 2006). Bade et al. (2007) demonstrated that chromate removal from larger pore sized membrane increased with the increase of retentate pressure. At the higher pressure the micelle-layer gets compacted causing further retention of broken micelle (Purkait et al., 2004). Urbanski et al. (2002) reported that the resistance of the membrane increased faster by increasing the input pressure. CPC leaching was also reduced due to

maximized concentration polarization and interaction of hydrophilic part of cetylperidinium chloride (CPC) monomers with the membrane (Beolchini et al., 2007). Syamal et al. (1997) reported that micelle becomes compacted with the increase of the pressure as a result the amount of heavy metals on its surface was reduced.

Permeate flux increased with increased transmembrane pressure (TMP) and cross-flow rate (Park et al., 1997; Purkait et al., 2005). Ahmad et al. (2007) reported that more concentrated solutes provide the higher osmotic pressure on the permeate resulting in the reduction in the permeate flux. It was also explained that at constant TMP, permeate flux increased with the increased of inlet pressure without affecting the permeate concentration (Aoudia et al., 2003; Fillipi et al., 1999; Ghosh and Bhattacharya, 2006; Gwicana et al., 2006).

2.2 Effect of Surfactant Concentration

Effectiveness of MEUF process highly depends upon the surfactant concentration in the feed solution. Cationic surfactants have been used for anionic metal removal. Baek et al. (2004d) demonstrated that at the molar ratio of 1:5, 98% of chromate removal was achieved but when the cpc concentration was too high it decreased due to the increased Cl (Ghosh et al., 2000). Chromate removal was increased from 98% to over 99% when the molar ratio of chromate to cpc was increased from 1:5 and 1:10 in UF membrane of 10,000 MWCO (molecular weight cutoff) (Baek et al., 2004b). Chromate removal increased with the increase of CPC in the feed solution but the percent retention slightly decreased due to preferential adsorption of chloride when CPC concentration in the feed was too high. Significant chromate removal was also observed with cetyltrimethyl ammonium bromide (CTAB) (Keskinler et al., 1997). CPC was

found effective in arsenate removal (removal efficiency = 86% to 94%) at the CPC concentration ranging from 5 to 10 mM (Iqbal et al., 2007). CPC concentration at the membrane surface reaches cmc due to concentration polarization (CP) even the feed solution concentration was less than cmc. It resulted in higher surfactant removal efficiency (Ghosh and Bhattacharya, 2006; Gzara and Dhahbi, 2001; Li. et al., 2006). Landaburu-Aguirre et al. (2010) explained that the Zn and Cd removal from MEUF depends upon sodium dodecyl sulphate (SDS) and the heavy metals concentration in the feed solution. Huang et al. (2010) reported that Cd^{2+}/Zn^{2+} concentration decreased from 50 mg/L to less than 1 mg/L at the SDS dosage of 2.15 mg/L (cmc of SDS). They explained that the adsorption is a spontaneous endothermic process, by which opposite charges were attracted. The presence of these metals enhanced the surface activity of the SDS ions (DS^-) enhancing the reduction of the cmc of the SDS micelle.

Various researchers used anionic surfactants such as SDS and sodium dodecyl benzoate sulphonate (SDBS) for cationic heavy metals removal. Molar ratio of SDS to copper of 5 and SDS concentration equal to cmc was efficient for copper removal (Liu and Li, 2005). They reported copper removal efficiency of 93% at 8.5 mM of SDS concentration. An efficient arsenic (V) removal was also achieved with the larger molecular weight cut-off (MWCO) membrane at the feed CPC concentration of 1-3 mM (Beolchini, et al., 2007), the removal efficiency reached to 98%. Aoudia et al. (2003) reported that feed SDS concentration of less than cmc has Cr^{3+} removal efficiency of 33%, but 99% removal was observed at cmc. At the lower SDS concentration zinc removal was also not effective. The removal was only 46% and 53% at SDS concentration of 1 mM and 3.4 mM. Huang et al. (2007) reported 97% of zinc

removal at the molar ratio of SDS to zinc of 24.4. They reported the gel layer concentration of CTAB and CPC were 0.6 M and 0.53 M, respectively. Comparing efficiency of SDS and SDBS, SDBS was found to be more efficient for heavy metals as well as organics removal (Chai et al., 2007; Huang et al., 2005). Gold removal efficiency was found 100%, 99.9%, and 89%, respectively using CPC, POESA, PONPE10 surfactants (Akita et al., 1997). Akita et al. (1999) mentioned an effective removal of cobalt (90%) over nickel (50%) with anionic surfactant PONPE10 and extractant EHPNA.

Ghosh and Bhattacharya (2006) explained that permeate flux reduced due to the formation of micelle aggregation layer (MAL) on the membrane surface. With a view of the permeation flux, cmc of SDS (8 mM) was the appropriate SDS concentration (Xu et al., 2007). Permeate flux reduction was higher at the lower SDS concentration ($<$ cmc) than higher SDS concentration ($>$ cmc) due to the adsorption phenomenon and the interaction between ionic species and membrane with opposite charge.

The size of micelle has an important role in the removal efficiency. Xu et al. (2007) reported that at cmc of SDS the micelle has normal size of 5.07 nm. But beyond the cmc value the size of micelle decreases and shape of it also changes. Linear molecule passes through a membrane whereas globular molecules of the same molecular weight may be retained (Trivunac and Stevanovic, 2006). CMC of surfactant can be affected by the changes in temperature, pH, presence of non ionic surfactant and inorganic salt. In aqueous medium, ionic surfactants have much higher cmc than non-ionic surfactant containing equivalent hydrophobic groups (Rosen, 1978). CMC of some of surfactants is presented in Table 1.

Table 1 Critical micelle concentration of surfactants

Charge	Trade name	CMC (mM)	Mol. weight	References
Cationic	Benzalkonium chloride (BC)	5.0	329.30	Iqbal et al. (2006)
Cationic	Hexadecylpyridinium chloride (CPC)	0.90	358.01	Baek and Yang (2004d)
Cationic	Hexavalent trimethyl ammonium bromide (CTAB)	0.92	364.46	Iqbal et al. (2006)
Cationic	Octadecylamine acetate (ODA)	0.90	329.05	Baek et al. (2003)
Anionic	Sodium dodecyl sulfate (SDS)	8.27		Liu et al. (2005)
Anionic	Sodium hexadecyl diphenyl oxidized-sulfonate (Calfax 16)	0.601		Yang et al.(2005)
Anionic	Sodium dodecylbenzene sulfonate(SDBS)	1.5	348.48	Zhang et al. (1999)
Non-ionic	Brij	0.28	229	Xu et al. (2006)
Non-ionic	Glucopon 215 CS UP	0.427		Urbanski et al. (2002)
Non-ionic	OP10	1 g/L		Yurlova et al. (2002)
Non-ionic	Plantcare 2000 UP	0.026		Yang et al. (2005)
Non-ionic	Tergitol NP 10	0.027		Fillipi et al.(1999)
Non-ionic	Tergitol NP 40	0.045		Fillipi et al. (1999)
Non-ionic	Triton X-100	0.28		Xiarchos and Doulia (2006)
Non-ionic	Triton X-102	0.37	756	Xiarchos and Doulia (2006)
Non-ionic	Triton X-114	0.265	555	Xiarchos and Doulia (2006)
Non-ionic	Tween 80	0.03	1310	Lee et al. (2005)

Boelchini et al. (2006) explained that larger pore sized UF membrane did not have any negative effect of interaction of CPC charge with negative membrane charge. Iqbal et al. (2007) reported that octadecylamine (ODA) had higher tendency to lower the flux than CPC, CTAB, ODA and BC (benzalkonium chloride).

Geocol et al. (2004) reported that cmc of CPC changed with the change in the As (V) concentration in the solution (Table 3). They

reported that at As(V) concentration of 0-250 mg/L, cmc of CPC was 0.96 -0.92 (for pH= 5.5) and 0.95-0.90 (for pH =8).

2.3 Effect of pH

Various researchers have demonstrated significant effect of pH on heavy metal removal. Juang et al. (2003) reported that cationic heavy metals (Mn^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} , and Cr^{3+}) removal reached over 80% with SDS as

the pH increased from 2 to 12. At the lower pH lower heavy metals removal efficiency was due to the competition between H^+ ions and cationic metal ions to get adsorbed on the anionic micelle surface of SDS. But, there was no effect of pH on the removal efficiency for Sr^{2+} and Cr^{3+} . Cadmium rejection increased from 83% to 99% when pH increased from 3 to 11 in the feed solution containing cadmium (100 mg/L) and SDS (8 mM) (Xu et al., 2007). Viera et al. (2001) reported that Ca, Mg and Fe removal efficiencies were 55%, 53%, and 74%, respectively at the pH of 4-5 with PEI membrane. But, the removal efficiencies were reduced by 10% over or below this pH range.

Geocol et al. (2004) expressed different view on the effect of pH. In CPC enhanced ultrafiltration, with the increase of pH (5.5-8.0) arsenic leaching decreased (0.02 mg/L - 0 mg/L) when 10 KDa Polysulfonate (PS) membrane was used with 0.221 mg/L of initial arsenic concentration. The increase in the removal was mainly due to the formation of di-anionic arsenic at the higher pH. The less removal at the low pH was mainly due to the arsenic in the mono-ionic form. But the flux decreased with the increase of removal due to concentration polarization. Similar effect of pH on arsenate removal was observed for cationic surfactants CPC, CTAB and Octadecylamine acetate (ODA) (Iqbal et al., 2007). But at higher surfactant concentration due to the availability of larger number of binding sites the removal was not significantly reduced even the pH was low. Cadmium removal increased sharply at pH less than 9 and increased to 99% at pH 11 with 8 mM SDS (Xu et al., 2007). Copper removal sharply dropped at the lower pH (Bade and Lee, 2007). Various researchers presented similar trend of effect of pH on zinc, cadmium (Kim et al., 2005; Trivunac et al., 2006); cobalt (Baek and Yang, 2005) removal.

2.4 Effect of Temperature

CMC of surfactant is a function of temperature (Kowalska et al., 2006). CMC of SDS increased with the increase of temperature due to the de-micellization process because of the disruption of the palisade layer of the micelle. Thus, surfactant ions start detaching from micellar bulks. At the temperature of 25°C, 40°C, and 45°C cmc of SDS was 2,257 mg/L, 2,445 mg/L, and 2,706 mg/L, respectively (Kowalska et al., 2006). If the cmc exceeds the solubility of the surfactant at a particular temperature, then the minimum surface tension will be achieved at the point of maximum solubility, rather than at cmc. The temperature at which the solubility of an ionic surfactant becomes equal to the cmc is known as the kraft point (Rosen, 1978). Resistance of surfactants increased with the kraft point. Urbanski et al. (2002) reported that SDS showed higher additional resistance compared with Cetyl Tri ammonium Bromide (CTAB) and APG. It is because of higher kraft point for CTAB. They reported the kraft point of 25°C and 21°C for CTAB and CPC, respectively.

Zeng et al (2007) further reported that with the increase of temperature CPC monomer increases in the solution. Thus, the hydrophobic tails of CPC monomers interact with polysulphone membrane (hydrophobic) resulting in the adsorption of CPC on the membrane surface and in its pores. They also elaborated that at the high temperature the CPC micelle gets easy to dissociate and decreases micelle number and its size. It results in the passage of more CPC monomers. Another reason of passage of CPC at the permeate was due to the thermal expansion of membrane.

With the increase of temperature permeate flux increases due to decreased viscosity and thermal expansion of membrane material. The increased flux resulted in the higher concentration polarization (Kowalska et al., 2006).

2.5 Effect of Non-Ionic Surfactant

In MEUF process, the use of surfactant in the feed solution should be minimized from economic as well as secondary pollution point of view. Use of surfactant can be reduced by reducing the cmc. One way of it is to reduce cmc of surfactant, by using non-ionic surfactant (Xu et al., 2006; Yurlova et al., 2002). In the mixture of surfactant, hydrophilic parts of non-ionic surfactant counterbalance the charge of ionic hydrophilic groups (Lee et al., 2005). It results in decrease of charge density at the surface of micelle leading to diminish of the electrical potential. Eventually, it enhances the formation of micelle at the lower cmc, but the removal efficiency decreased slightly. Chromate removal reduced from 93.7% to 84.8% with the increase of Tween 80 from 10 mM to 25 mM in CPC and chromate solution (Liu and Lee, 2004). With the increase of Brij/SDS ratio, both SDS and Cd^{2+} removal decreased (Xu et al., 2007). Similar results of decrease of Cr^{3+} removal with Nonylphenol ethoxylate (NPE) (Aoudia et al., 2003), zinc removal with NPE were observed (Fillipi et al., 1999).

In 1991 Jonsson and Jonsson compared the retention of the nonionic surfactant and ionic surfactant. They reported low removal of Triton X-100 but quite high removal of SDBS and CTAB at the SDBS and CTAB concentration below the cmc. In terms of surfactant removal the trend was opposite to that for heavy metals. CPC removal increased from 91% to 99% with Tween 80 due to formation of more micelle hence less CPC monomer passes to the permeate. Yurlova et al. (2002) reported different view that at less than cmc of SDS, the addition of OP-10 improved the removal efficiency of nickel from 88% to 96%. But at or over cmc of SDS no improvement in nickel removal was observed. Li and Liu (2006) reported that copper removal efficiency increased from 15% to 70% in the

presence of 3.01 mM of Triton-X in SDS solution of 2.15 mM (less than cmc). No significant effect on copper removal and permeate SDS concentration was observed when Triton-X concentration (cmc = 0.2 mM – 0.43 mM) was less than 0.1 mM. Copper removal efficiency decreased from 90% to 88% when non-ionic surfactant Triton X-100 was added with SDS fraction of 0.7 (Lee et al., 2005). Fillipi et al. (1999) reported that by the addition of non-ionic surfactant both Zn^{2+} and organic TBP removal efficiency was increased in the negatively charged membrane. Details of effect of some of non-ionic surfactants on metal removal efficiency are presented in Table 2.

Permeate flux decreased by non-ionic surfactant in micelle solution; it was mainly due to the higher viscosity of non ionic surfactant OP-10 (Yurlova et al., 2002). Yang et al. (2005) explained the increase of viscosity from 0.88 to 1.36 with CPC to Tween ratio of 5:25 mM. The decrease of permeate flux was mainly due to the transition of micelle configuration from spherical to cylindrical or lamellar. The viscosity of Triton-X was 240 centipose (CP) at 25°C for pure Triton-X which was 0.89 only for pure water. Increase in Triton-X concentration has bigger impact on hydraulic resistance than increase in copper concentration (Li et al., 2006). Contrarily, addition of complexing agent has no effect on flux since complex of metal and chelating passed through the ultrafiltration membrane (Kim et al., 2006).

2.6 Effect of Salt Concentration

Addition of salt in surfactant solution is another way of reducing cmc of surfactant. In general, repulsive forces between the head groups of ionic surfactants are fighting against the aggregation. In the presence of salt, the repulsive forces of head group of SDS monomer decreases due to the electrostatic shield-

ding effect resulting in the formation of micelle at less than cmc (Xu et al., 2007; Yang et al., 2005). They further explained that electrical double layer was compressed due to the increased electrolyte concentration resulting in the reduced electrostatic attraction between ions and the micelles. As(V) replaces Cl⁻ ions in CPC and arsenic solution, the As(V) binds closely with CPC ions and decrease the electrical charge on the surface and reducing cmc (Geocol et al., 2004). As a result, non-trapped metals pass through the membrane leading to the lower rejection (Geocol et al., 2004; Juang et al., 2003). Xu et al. (2007) reported that cadmium removal efficiency decreased from 95% to 75% at NaCl concentration of less than 20 mM. It could be due to the competition between Cd²⁺ and Na⁺ ions to get the micelle surface, and due to the formation of complex of Cl⁻ and metal. Gzara and Dhahbi

(2001) reported the decrease of chromate (CrO₄²⁻) removal from 1 to 0.15 mM when NaCl concentration increased from 1 mM to 500 mM. Aoudia et al. (2003) reported that Cr³⁺ removal was also reduced with the addition of NaCl. In contrary, the addition of NaCl has negative effect on the reduction of metal removal and the formation of metal chloride. Basar et al. (2004) explained that with the increase of NaCl from 2 mM to 100 mM, CTAB rejection increased from 68% to 98%. On the contrary, LABS rejection rate decreased slightly from 38% to 34% at the salt concentration of 2 mM and 100 mM, respectively. Sampler et al. (2009) also reported the similar result of reduction of heavy metals (Cd²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Zn²⁺) when NaCl was added in the surfactant SDS and Alkylbenzene sulfonate (LAS).

Table 2 Effect of non-ionic surfactants on heavy metal removal efficiency in MEUF process

Metal	Surfactant	Removal (%)		Non-ionic surfactant	Conc./fraction	References
		With ionic	With ionic & nonionic			
Cr ⁶⁺	CPC	93.7	84.8	Tween	80/10-25 mM	Liu and Lee (2004)
Cr ³⁺	SDS	99.5	43	NPE	0.2-0.5M	Aoudia et al. (2003)
Zn	SDS	99.2	98.5	NPE	0.2-0.6M	Fillipi et al. (1999)
Cd	SDS	88.0	96.0	OP-10	0.2 g/L	Li and Liu (2006)
Cu	SDS	90	88	Triton X-100	0.7	Lee et al. (2005)
Cu	SDS (2.15mM)	15	70	Triton X-100	3.01 mM	Lee et al. (2005)

The relative flux also decreased with the increase of salt concentration. Akita et al. (1997) reported that in the process of removal of gold by MEUF process; permeate flux reduced by the addition of NaCl however it tends to lower the surfactant leakage.

Azoug et al. (1998) reported that at the SDS concentration of less than cmc, the SDS totally dissociate into free ions, Na⁺ and DS⁻.

They further added that membrane resistance was highly influenced by free ions dodecylsulphates (DS⁻) and sodium (Na⁺), and very slightly by negatively charged spherical micelles, and weakly by rod-like aggregates.

Adamczak et al. (1999) reported that presence of NaHCO₃ reduced the permeate flux in MEUF process containing SDS and hydrophobic oxyethylated methyl dodecanodate.

Urbanski et al. (2002) further added that NaCl and NaHCO₃ caused salting out effect where as Potassium thiocyanate (KSCN) caused salting in effect. They observed increase in viscosity by 10% to 20% with the addition of NaCl or NaHCO₃ (0.5 M), whereas it increased by 50% to 230% with 0.5 M KSCN for CTAB and SDS, respectively.

2.7 Effect of Membrane Type and Pore Size

Larger pore sized membranes caused earlier development of concentration polarization and reduced the release of surfactant at the permeate (Beolchini et al., 2007). Baek et al., (2003b) observed higher rejection of CPC (> 98%) with YM3 and YM10 ultrafilter of 3000 and 10,000 MWCO at the molar ratio of 1:10 (Baek et al., 2003b). Chromate removal was higher (> 99%) with 3000 MWCO membrane than was 10,000 MWCO membrane (98%) at chromate to cpc molar ratio of 1:10 (Baek et al., 2004b). Chromate removal efficiency with 100 KD UF membrane was 98% while it was 97% with 300 KD membrane at molar ratio of chromate to CPC of 1:5 (Bade et al., 2008).

Metal rejection can vary depending upon the nature of membrane whether they are hydrophilic or hydrophobic. Kim et al. (1998) stated that polythyleneglycol (PEG) membrane increased rejection with the increase in hydrophobicity of surfactant in the hydrophilic membrane cellulose acetate (CA). Hydrophilic part of micelle or monomer tries to adsorb on the hydrophilic membrane surface compared to hydrophobic membrane surface (Juang et al., 2003). Ferella et al. (2007) further added that micelle adsorbs preferly on the hydrophilic surface of polyamide membranes rather than the hydrophobic surfaces of ceramic or polysulfone membranes. Cationic surfactant dodecylamine removal was found higher on the hydrophobic ceramic membrane due to the formation of lumps (Ferella et al.,

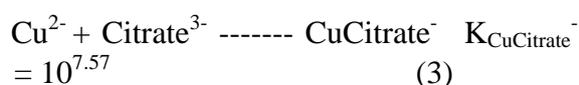
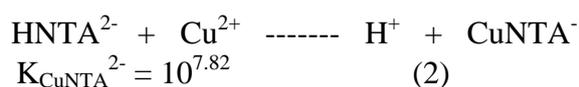
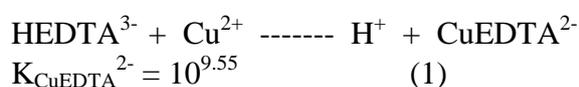
2007). Byhlin and Jonsson (2002) stated that Triton X-100 at concentration below cmc, the rejection was constant for both hydrophobic and hydrophilic membrane. But the concentration over cmc the permeation leveled off for hydrophilic membrane (Regenerated cellulose) while it still remained high for the hydrophobic (Polyether sulphone) membrane. They further explained that there was no removal of non-ionic surfactant Triton X-100 from hydrophilic material below cmc. But at or over cmc there was higher percentage removal.

Permeate flux was highly influenced by the hydrophobic and hydrophilic behavior of membrane material and the adsorbate. Jonsson and Jonsson (1991) indicated that flux reduction was much higher in the hydrophobic membranes than that in hydrophilic membranes. Kim et al. (1998) also reported on the reduction of flux in hydrophobic membrane. Byhin and Jonsson (2002) further added that hydrophobic membranes reduced flux at concentration below the cmc, whereas hydrophilic membranes did not reduce the flux at below cmc of non ionic surfactant TritonX-100. They further explained that the decrease in permeate flux was more with the hydrophobic membrane than hydrophilic membrane even though the pore diameter was the same for both the membrane. The type of membrane such as hydrophilicity or hydrophobicity has higher effect on permeates flux than by transmembrane pressure (TMP). In their experiment, they found that increasing TMP by two folds there was increase in permeate flux by two times in aqueous solution whereas it was only 1.5 times with the hydrophobic membranes for non-ionic surfactant TitronX-100. Fernandez et al. (2005) reported that decrease in flux of SDS solution with CA membrane was due to interaction with the positive ions of the membrane caused by pH less than isoelectric point. Purkait et al. (2005) reported higher permeate flux for hydrophobic solutes

betanaphthol (BN), ortho chloro phenol (OCP) and solutes of lower hydrophilicity catechol (CC) and phenol (P) than strongly hydrophilic solute para nitro phenol (PNP) and meta nitro phenol (MNP).

2.8 Effect of Additives

In MEUF process presence of ligands inhibit metals and surfactant removal. In the presence of Diaminoethantetraacetic (EDTA) copper removal decreased from 95% to 40% while SDS concentration at the permeate increased over cmc (Liu et al., 2004). Due to higher affinity of EDTA with copper, it forms complexation better with EDTA rather than with SDS. No complexation forms between EDTA and SDS micelles because of similar ionic characteristics. In addition EDTA-Cu complexation is smaller in size than the pore size of the membrane hence copper ions are not removed. It was also explained that with the increase of ligand/metal ratio, copper and SDS removal decreased. They indicated that the complexation of copper with ligand depends upon its complexation constant, which was the highest for EDTA and lower for nitrilotriacetate (NTA) and citric acid. They further stated that the lower copper removal at the higher complexation constant was due to the competition with SDS. The complexation constant for those ligands are represented in Eq. (1), Eq. (2) and Eq. (3).



Humic acid and Kaolinite have negative charges which is similar in characteristics with anionic surfactant thus they form nega-

tive complexation with copper (Liu et al., 2004). In this case the addition of CPC helps in forming complexation between CPC and the Cu-ligands complexation. Copper removal was over 90% at the molar ratio of copper to CPC of 1:70. Isopropyl alcohol has tendency to increase the solubility for the surfactant resulting in the increase in permeate concentration (Yang et al., 2005b).

2.9 Effect of Competing Metals

Various researchers reported that metal removal in MEUF process was inhibited in the presence of other inorganic pollutants. Baek and Yang (2004e) reported that in the treatment of inorganic pollutants the presence of higher valence ions inhibited the removal of low valence ions. In the coexistence of multi-pollutants, the higher valence pollutant were saturated first thereafter accelerated the removal of subsequent lower valence pollutant. In their study, chromate removal was inhibited in the presence of ferricyanide while the higher valence ferricyanide removal remained unchanged in octadecylamine (ODA) solution (Baek et al., 2004b; Baek et al., 2004d). In single pollutant system the order of removal was nitrate < chromate < ferricyanide, the same was true for the multi-pollutant system (Baek and Yang, 2004a). In the coexistence of multi pollutants, the quantity of surfactant required increased compared to that in single pollutant for achieving similar removal efficiency. Iqbal et al. (2007) had shown that small quantity of nitrate and phosphate (0.01 mM) reduced arsenate removal by 7%-8% due to competition to get binding site on cationic CPC micelle. Channarong et al. (2010) explained that there was no significant effect on Zn and Ni removal in MEUF process on the co-existence of both the metals.

2.10 Effects of Organics on Heavy Metals Removal

Various researchers presented simultaneous removal of heavy metals and volatile organics such as phenol, o-cresol and individual organics. In MEUF process, ionic surfactants are removed by the electrostatic attraction whereas hydrophobic organics by the solubilization into the micelle core (Lee et al., 2005). They stated that co-presence of Trichloroethylene (TCE) and chromate did not hinder the removal of each other due to different in removal mechanism. Zinc and phenol removal were also not inhibited in their co-presence (Dunn et al., 1989). Similarly, chromate removal was not inhibited in the presence of 1-chlorobenzene and 2-dichlorobenzene (Baek and Yang, 2004f); presence of Cr^{3+} did not influence the rejection of phenols (Witek et al., 2006). In another experiment Tung et al. (2002) found that copper removal was enhanced in the presence of phenol while phenol removal was only 27% due to its relatively hydrophilic characteristics (Tung et al., 2002). The increased removal of copper in the presence of phenol may be due to the slight reduction in the cmc of SDS in the presence of salt (Fillipi et al., 1999; Tung et al., 2002). Jung et al. (2008) reported that MEUF was also able to reduce the COD contained in the soil washing solution (about 80%). Based on the literature review, removal efficiency of MEUF for different heavy metals is summarized in Table 3.

3.0 SURFACTANT RECOVERY FROM RETENTATE

Secondary pollution generated due to the formation of highly concentrated surfactant at the retentate is one of the concerns in MEUF process (Baek et al., 2003b). MEUF process produces concentrated (over 90%) surfactant (Lipe et al., 1996). Thus, the separation of surfactant from bulk solution is one of great concerns for reuse purposes.

Carbuzares et al. (2002) mentioned the possibility of regeneration of water soluble poly-

mer by changing the pH of solution. The acid/basic behavior of the functional groups make possible for the further dissociation of already formed macromolecular complexes by their protonation. Hiraide and Itoh (2004) reported that copper in the MEUF retentate was leached from micelle with 4 mol/L of nitric acid. When pH of the aqueous medium was reduced, polymer regeneration and recovery of the metal were achieved by a second ultrafiltration process. Nitric acid, sulphuric acid or hydrochloric acid recovered 84% SDS from retentate solution and have separation efficiency over 95% for cadmium and copper after ultrafiltration (Kim et al., 2006). Juang et al. (2003) mentioned the recovery of surfactant using 6N NaOH solution until precipitation reaction occurred. They repeatedly used the remaining solution after removing the precipitates by centrifuge at 5,000 rpm. Later on, Liu et al. (2004) reported the use of slightly excess amount of Ca^{2+} counter ions to cause higher proportion of SDS to precipitate. They further stated that due to low solubility of calcium dodecyl sulphate monovalent compound it must be transferred to higher valence by the addition of Na_2CO_3 before it is re-dissolved in water for recycle. By using precipitant, SDS precipitated at the range of 45%-55%. Precipitated materials were separated by centrifuging the solution. SDS that was retained in the solution was reused for removing heavy metals in MEUF process. They reported Sr^{2+} , Mn^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} and Cr^{3+} removal of 50%-58% after reusing SDS solution.

Chelating agents can make good complexation with metal in retentate solution. After complexation the chelating agent and metal can be well separated from the solution by ultrafiltering the solution. Kim et al. (2006) added iminodiacetic acid (IDA), ethylenediaminetetraacetic (EDTA), citric acid for in the MEUF retentate solution, then filtered it through ultrafilter membrane. The membrane rejected the surfactant while 82.5%, 99.9%

and 100%, of copper were passed through the membrane, respectively for the solution IDA, EDTA, citric acid. Similarly, EDTA showed

higher removal efficiency of 75.7% for cadmium removal from the MEUF retentate solution.

Table 3 Heavy metals removal in MEUF process

Metal		Surfactant		Non-ionic surfactant/ Conc.	Inhibitor	Removal (%)	References
Species	Conc.	Type	Conc./molar ratio				
Cu(II)	0.2 mM	SDS	5.67 mM	Tritron-X/1.29		93%	
Chromate	1 mM	CPC	8-60 mM	-		99.5%	Gzara Dhahbi (2001)
Cr ⁶⁺	0.5 mM	CPC	1:10			99%	Ghosh and Bhattacharya 2001
Mn	0.91 mM	SDS	13.6			99%	Jung et al.(2003)
Cr ³⁺	0.96 mM	SDS	11			95%	Jung et al.(2003)
Zn	0.76 mM	SDS	12			> 99%	Jung et al.(2003)
Cu	0.79 mM	SDS	18.5			> 99%	Jung et al.(2003)
Sr ²⁺	0.51 mM	SDS	8.9			> 99%	Jung et al.(2003)
Cs	50 mg/L	SDS	5			40%	Jung et al.(2003)
Cu	0.71 mM	SDS	8.5		Citric acid	> 99%	Liu et al. (2004)
Cu	0.71 mM	SDS	8.5		NTA	> 99%	Liu et al. (2004)
Cu	0.71 mM	SDS	8.5		EDTA	100-50%	Liu et al. (2004)
Ni	10 mg/L	SDS	2.34			96%	Yurlova et al. 2002
As	6-10 mg/L	CTAB				94%	Iqbal et al.(2007)
As	6-10 mg/L	BC				95%	Iqbal et al.(2007)
As	6-10 mg/L	ODA				80%	Iqbal et al.(2007)
Cd	10 mg/L	SDS (8 mM)		Brij		99%	Xu et al. (2006)
Chromate ⁶⁺		CPC		Tween 80 (10-250)		93.7-84.8%	Liu and Lee 2004

4.0 COMPARATIVE REMOVAL OF HEAVY METALS AND SURFACTANT FROM COMBINED PROCESS

The combined MEUF-Electrolysis has advantages of higher metal removal efficiency and the reduction of SDS at the permeate due to lower SDS concentration at the feed (Liu and Li, 2005). Lower current consumption was also advantageous of this system. Basar et al. (2006) reported that Powder activated carbon (PAC/MF) + CTAB (90%) was more efficient than PAC/MF alone (78%). They stated that PAC size should be sufficiently bigger in size to prevent internal clogging of MF. With the increase of water soluble polymeric ligands, complexation-ultrafiltration became more efficient; it increased concentration polarization close to membrane and hence increased the metal removal (Viera et al., 2001).

MEUF process was more efficient with flocculation. By the addition of Al^{3+} as a flocculant on SDS micelle and Zn^{2+} solution, it

enhanced zinc removal by forming more micelle flocs (Hankins et al., 2005). In the adsorptive micellar filtration (AMF), with the increase of zinc the flocculation decreased due to the competition between Zn^{2+} and Al^{3+} to get the micelle surface. Care should be taken not to dissolve Al^{3+} , if its concentration is high. When Al^{3+} was added to SDS solution it leads to the suppression of electrostatic repulsion between micelles. They explained that when the ratio of cationic to anionic charge was greater than one, apparent charge inversion occurred. Binding ratio also played a role on the removal of metal (Hankins et al., 2005). Talens-Alession (2007) explained that the resistant to gelation was higher for combined Al^{3+} and SDS than unbound SDS. They also verified that partially flocculated solution and cation colloidal matter had higher fouling capacity. It is also true that this micelle flocculation prevents micelle to form larger micelle. Comparative removal efficiency of MEUF with other process is summarized in Table 4.

Table 4 Copper removal efficiency of different treatment processes

Process	Membrane only	Electrolyses and membrane	MEUF	MEUF	MEUF Electrolyses
SDS (mM)			5.5	8.5	5.56
Average copper removal (%)	28	44.5	64.4	95.8	90.4

Initial Cu conc. = 0.21 mM

Surfactant in the permeate of MEUF can cause the secondary pollution in the environment, thus surfactant concentration at the permeate should be considered during MEUF process (Baek and Yang, 2004c; Gwicana et al., 2006). Urila et al. (2006) reported that with O_3 and PAC removed SDBS efficiently. The dual mechanisms occurred in this process namely transfer of O_3 to OH radicals and adsorption of organic to PAC. Over 70% of SDBS was removed from the solution using O_3 /PAC system within 5 minutes of hydraulic

retention time (HRT). The removal was only 18% with O_3 at the SDBS concentration of 2.8×10^{-5} M. Efficiency of MEUF was found higher for the removal of heavy metals but it produced surfactant polluted permeate, which needs to be treated before discharging or recycling in industrial process. Bade and Lee (2007) had reported that almost 98% of copper was removed using SDS but the process removed only 50% of SDS. MEUF followed by ACF removed almost 98% of SDS. Similarly, Bade and Lee (2008) reported that

MEUF-ACF hybrid process removed 99.5% of chromate and over 99.5% of CPC. The hybrid process successfully removed chromate and CPC from the feed solution.

5.0 CONCLUSIONS

Micellar enhanced ultrafiltration has been used for the separation of low molecular weight substances using surfactant at the cmc. It has been used for the removal of copper, chromate, zinc, nickel, cadmium, selenium and arsenate. In this paper, detailed review study was carried out in various factors affecting on heavy metals removal in MEUF process. Operating pressure, surfactant concentration, pH of solution, temperature, presence of non-ionic surfactant and salt, membrane type and its pore size and some inhibiting additives such as EDTA, citric acid, competing metals affect on the removal of heavy metals and surfactants. Heavy metals removal increased with the increased pressure increase of ionic surfactant. CMC of surfactant was reduced by adding non-ionic surfactant or electrolyte in the micelle solution. It enhanced the surfactant removal, but, it results in negative effect such as less removal efficiency of metal and less permeate flux. Chelating agents such as EDTA, NTA, and citric acid inhibited the heavy metals removal. In the coexistence of multi-metal in the solution, higher valent metals received priority for the anionic pollutant removal.

Metal removal was enhanced in the MEUF + electrolysis or MEUF + PAC system. MEUF effluent was improved in terms of surfactant concentration by further treating the effluent with ACF. Electrolysis was effective for separating heavy metals and surfactant from the retentate. For the application of the MEUF process in the real wastewater, there are still some more works to be done in this field such as i) improving the performance in terms of permeate flux, and ii) recovering

metals, organics and surfactant from the retentate solution.

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