

Application of micellar enhanced ultrafiltration and activated carbon fiber hybrid processes for lead removal from an aqueous solution

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Abstract—Micellar enhanced ultrafiltration (MEUF) and activated carbon fiber (ACF) hybrid processes were used to investigate the removal condition of lead ions and surfactant sodium dodecyl sulfate (SDS) from an aqueous solution. Lead removal efficiency increased with the increase of initial surfactant concentration. Molar ratio of lead to SDS up to 1 : 5 has shown over 90% removal efficiency of lead, and the optimum molar ratio of lead to SDS was found to be 1 : 5. Lead removal efficiency increased with the increase of pH, while it was maintained below 30% without surfactant. Lead removal was mainly due to the adsorption mechanism and no secondary layer was formed to reduce the flux. Lower molecular weight cut-off (MWCO) membrane has shown higher removal efficiency than higher MWCO one. Permeate flux decreased with the increase of molar ratio of lead to SDS. Flux decline was mainly due to the accumulation of micelles on the membrane surface. The presence of copper as a co-existing heavy metal highly affected the lead removal while nickel did not. Two sets of ACF unit in series were able to remove SDS surfactant effectively from the effluents of MEUF process.

Key words: Ultrafiltration Membrane, Micellar Enhanced Ultrafiltration, Lead, Sodium Dodecyl Sulfate, Activated Carbon Fiber

INTRODUCTION

Heavy metals are widely used in various industries and are harmful to both human and aquatic life [1]. They are present in soluble form in the aqueous phase over a wide range of pH values and quite mobile in the natural environment [2]. When wastewater containing higher concentration of heavy metals is discharged into the natural water courses, it affects aquatic life and is destructive to the environment. Lead is used in many industries such as acid battery manufacturing, metal plating and finishing, ammunition, ceramic and glass industries. People exposed to lead for a long time may suffer from damage to the kidneys, nervous system, reproductive system, liver and brain [3-5]. Micellar-enhanced ultrafiltration (MEUF) processes have been employed to remove heavy metals or toxic organic compounds for the past decades [6-10]. Micellar-enhanced ultrafiltration (MEUF) is an established research field for the separation of organic and inorganic pollutants present in trace amounts in aqueous stream [11]. It has proven to be a promising technology that employs surfactant micelles to solubilize inorganic and organic contaminants from the aqueous stream [12]. In the MEUF process, low molecular weight substances are separated by ultrafiltration after a surfactant is added to the polluted water. It combines the high selectivity of reverse osmosis (RO) and high flux of ultrafiltration (UF) [13-15]. Thus, it has higher efficiency and lower cost [16]. The surfactant is the key component for the removal of pollutants in this process [17]. The removal mechanism is thought to be the adsorption of contaminants onto micelles of the surfactant, which form when the surfactant concentration is higher than its critical micelle

concentration (CMC) [18]. In the MEUF process, a surfactant having a charge opposite to the target ions is added to the effluent stream containing the metal ions at a concentration greater than the critical micelle concentration (CMC), so that they form aggregates of around 50-150 of monomer molecules, called micelles [19]. Micelles, being larger, can be removed along with the solubilized organic contaminants by using a relatively porous membrane at lower operating pressure. Most of the solute molecules are solubilized in the micelles. The micelles are subsequently removed by ultrafiltration [18].

Several researchers have studied various types of heavy metal removal in MEUF, but few studies have been conducted on the removal of surfactant in the permeate flux [2,20-23]. Adsorption is an economical and effective method for the removal of trace heavy metals and organics from wastewater [24]. Activated carbon powdered activated carbon (PAC) and granular activated carbon (GAC) were normally used for them in the past [25]. Activated carbon fiber (ACF) is a new type of activated carbon (AC) that has been proven to be a good process for surfactant removal. Coupling of MEUF with ACF can overcome the problem caused by surfactant concentration. Previous works have shown that the adsorptive capacity of ACF is twenty to hundred times higher than GAC. ACF has a uniform micropore structure, faster adsorption kinetics and a lower pressure drop than GAC [26]. The main objective of this study is to investigate the performance of MEUF-ACF hybrid processes for lead and SDS surfactant removals, and to find the optimum operational condition of the proposed hybrid process.

MATERIALS AND METHODS

In this study, 98% purity of lead(II) acetate trihydrate (molecular weight of 207.2) was obtained from Shinyo Pure Chemical, Ltd.,

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Table 1. Details of MEUF experimental set-up

Retentate pressure, bar	1.4
pH	5, 7, 9
Initial lead concentration, mg/L	20
Molar ratio of lead to SDS	1 : 0.5 to 1 : 200
Sampling time, min	0, 5, 10, 20, 30, 40, 50, 60
Initial flux (distilled water), L/m ² h	43.6

Japan. Anionic surfactant, 99% purity of sodium dodecyl sulfate (SDS, molecular weight of 288.38) was procured from Acros Organic, Ltd., USA. The surfactant was used without any further treatment. All the solutions were prepared using distilled water. They were prepared by mixing stoichiometric amounts of SDS surfactant and lead in eight liters of distilled water for two hours. Mixing speed was kept at 500 rpm. Hollow fiber membrane having three kinds of MWCO size produced from Chemicore, Ltd., Korea were used for the entire experiment. Ultrafiltration is a cross flow type in which the rejection of permeate is recirculated into the feed tank and permeate water is collected at the separation tank. Details of the experimental condition are summarized in Table 1.

The experimental module consisted of a feed tank, ultrafiltration membrane, wash out and permeate tank. As shown in Fig. 1, ACF unit consisted of a cartridge filter (CF) which was connected with a feed tank to prolong the life span of the ACF. Deviation of adsorption capacity of this ACF was found to be 1.97 and 2.72 mg/g for Langmuir and Freundlich isotherms, respectively. Based on the isotherm equilibrium the correlation coefficients for Langmuir and Freundlich equations were 0.99 and 0.98, respectively. Langmuir isotherm equation fitted better than the Freundlich isotherm one. Characteristics of the membrane used in this process are presented in Table 2.

Following the CF, two set of ACF cartridge units in series are connected. ACF was purchased from ACF Korea Ltd., whose cartridge code no. is FC-B. Bulk density and iodine number of ACF was 0.2 kg/m³ and 1,500 mg/g, respectively. After each series of experiments was completed, UF membrane was flushed and back-washed with distilled water, and cleaned with 0.1 M NaOH and 0.5% HCl. CF and ACF were cleaned with distilled water before soaking into 0.1 M NaOH and 2% HCl for a day.

Lead was measured using inductively coupled plasma (ICP, Varian OES-720) with a wave length of 283.3 nm. Samples of MEUF were

Table 2. Characteristics of MEUF membrane and ACF unit

Membrane material	Polyacrylonitrile
Membrane type	Hollow fiber
Flow direction	Inside to outside
Flow type	Cross-flow
Effective surface area, m ²	0.055
Membrane diameter (inside/outside), mm	0.8/1.4
Molecular weight cut-off (MWCO)	10000, 100000, 300000
ACF BET surface area, m ² /g	1000
Weight of ACF, g/cartridge	30

pretreated according to the Standard Methods for the Examination of Water and Wastewater [27]. SDS was measured using chemical oxygen demand (COD) according to the Standard Methods. There was a close correlation between COD and SDS concentration ($r^2=0.99$) [28]. Lead and SDS removal efficiencies were calculated using Eq. (1).

$$R = \left(1 - \frac{C_p}{C_i}\right) * 100 \quad (1)$$

Where,

R=Rejection (%)

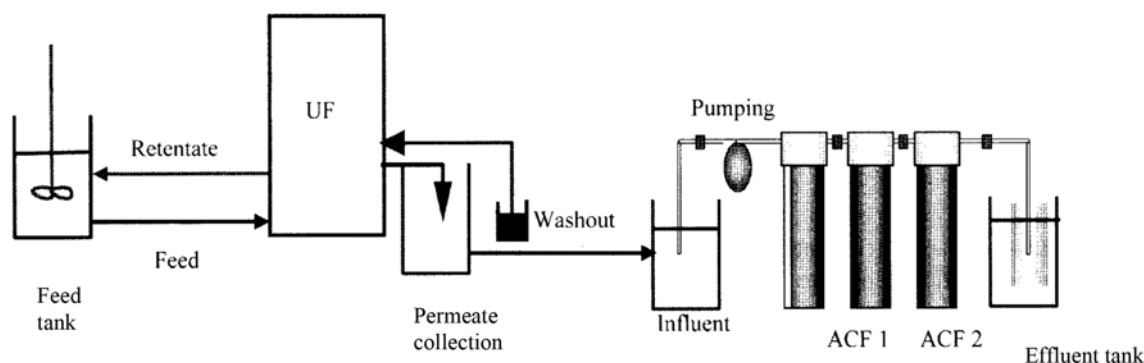
C_p =Permeate concentration (mg/L)

C_i =Influent concentration (mg/L)

RESULTS AND DISCUSSION

1. Lead Removal without Surfactant

A series of experiment was conducted without surfactant in the feed solution as shown in Fig. 2. During 60 minutes of filtration time, average lead removal efficiency was found to be 28.1% at the MWCO size of 100,000. As a result, UF alone cannot remove lead ions from the feed water. In the MEUF process, removal of pollutants is mainly due to adsorption and sieving action of the membrane. In the absence of SDS, UF membrane pores are big enough to pass lead ions through membrane. Due to its smaller size, most of the lead ions passed through the membrane, while a smaller percentage was retained due to the adsorption on the wall of the membrane. Screening action of the membrane was ineffective and the rejection of them was due to the adsorption on the membrane surface and inside the pore walls [29,30]. Therefore, two assumptions can

**Fig. 1. Experimental set-up for MEUF-ACF hybrid processes.**

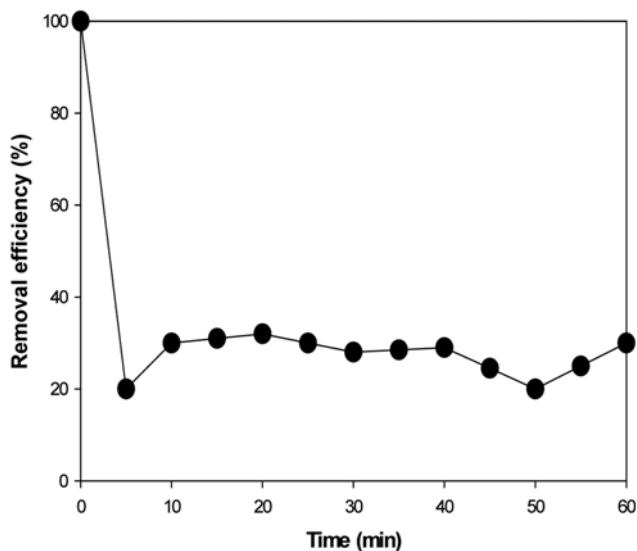


Fig. 2. Lead removal efficiency without surfactant (initial lead concentration=20 mg/L, initial retentate pressure=0.14 MPa, MWCO of the membrane=100,000 Dalton).

be made from this result. First, lead removal was mainly due to the adsorption mechanism, and, second, no secondary layer was formed to reduce flux from the membrane [25].

2. Effect of Molar Ratio of Lead to SDS

To observe the influence of SDS concentration on lead removal, another series of experiment was conducted at various molar ratios of lead to SDS. Fig. 3 shows the lead removal efficiency during 60 minutes of operational time at the lead to SDS molar ratios of 1 : 0.5 to 1 : 200. Average lead removal efficiency was 98.8% at the molar ratio of 1 : 20. Lead removal efficiency was almost constant to 99.5% and 98.6% at the molar ratio of 1 : 80 and 1 : 100, respectively. Corresponding lead removal efficiency for the molar ratio 1 : 5 and 1 : 10 was 89.6% and 93.4%, respectively. Lead removal efficiency increases with the increase of molar ratio. It means that lead removal

efficiency was higher for a higher initial SDS concentration, which produces more micelles [25]. After surfactant concentration reaches the critical micelle concentration (CMC) at 8.2 mM, all the surfactant added converts to micelle [31]. Then it provides more surface area available for electrostatic attraction. Surfactant monomer cannot form micelle unless it reaches CMC. Monomers pass through the membrane together with pollutant. It results in a larger micelle surface area available for electrostatic attraction of lead ions. As a result, a higher quantity of lead was removed together with the micelle [22]. Considering the higher lead removal efficiency, the molar ratio of 1 : 5 was found to be the most appropriate one.

3. Effect of pH

Another series of experiments was conducted to investigate the effect of pH. Fig. 4 shows the lead removal efficiency at various lead to SDS ratios with respect to pH of feed solution. Lead removal efficiency increases with the increase of pH in feed solution at CMC. At the lower pH, lead has to compete with H^+ ions to get the micelle surface. Due to the competition with H^+ ions in acidic condition, less amount of lead was adsorbed on the micelle surface, which led to the reduction of lead removal. As a result, lower lead removal efficiency was observed at a lower pH. This type of phenomenon was also explained for SDS in copper removal [16]. Effect of pH depends upon the type of metal used in the solution whether H^+ and OH^- ions compete with metal or not during the electrostatic adsorption on micelle [16]. Up to the molar ratio of 1 : 5, lead removal efficiency decreased with the increase of pH.

4. Flux Variation

Fig. 5 shows the permeate flux variation in ultrafiltration process with various concentration of SDS. Initial flux using distilled water was $43.6 L/m^2 \cdot d$. As shown in Fig. 5, permeate flux decreased with the increase of surfactant concentration. Permeate flux sharply decreased from 43.6 to $25.1 L/m^2 \cdot d$ for 60 min at the molar ratio of 1 : 20 as shown in Fig. 5(a). Corresponding permeate flux for the molar ratio of 1 : 30 and 1 : 40 was $21.8 L/m^2 \cdot d$ and $4.9 L/m^2 \cdot d$ respectively. Up to the molar ratio of 1 : 80, flux variation was not monitored because it has very low flux during the ultrafiltration pro-

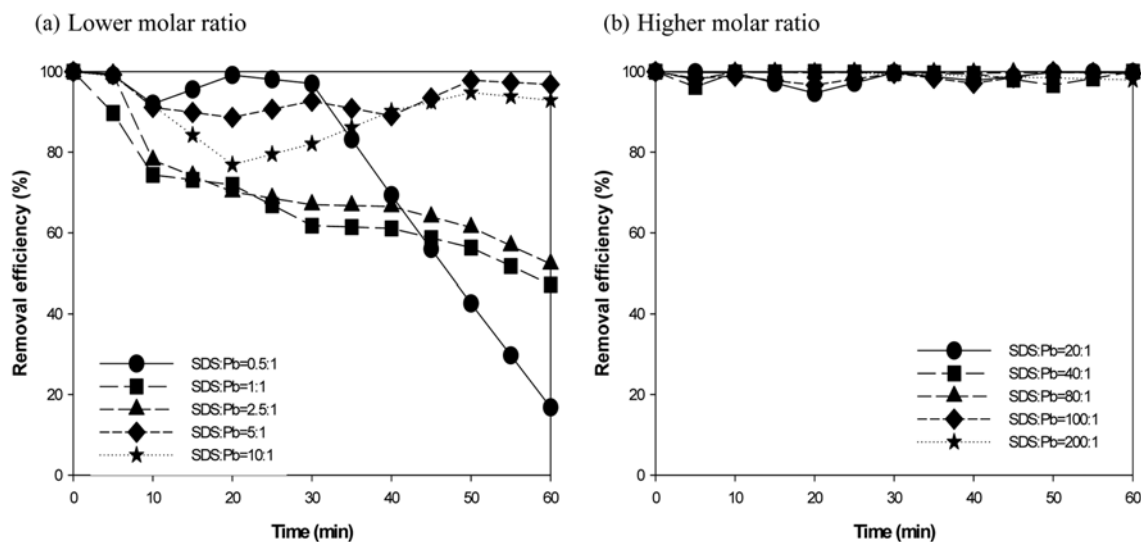


Fig. 3. Effect of the molar ratio of Lead to SDS (initial lead concentration=20 mg/L, initial retentate pressure=0.14 MPa, MWCO of the membrane=100,000 Dalton, pH=7).

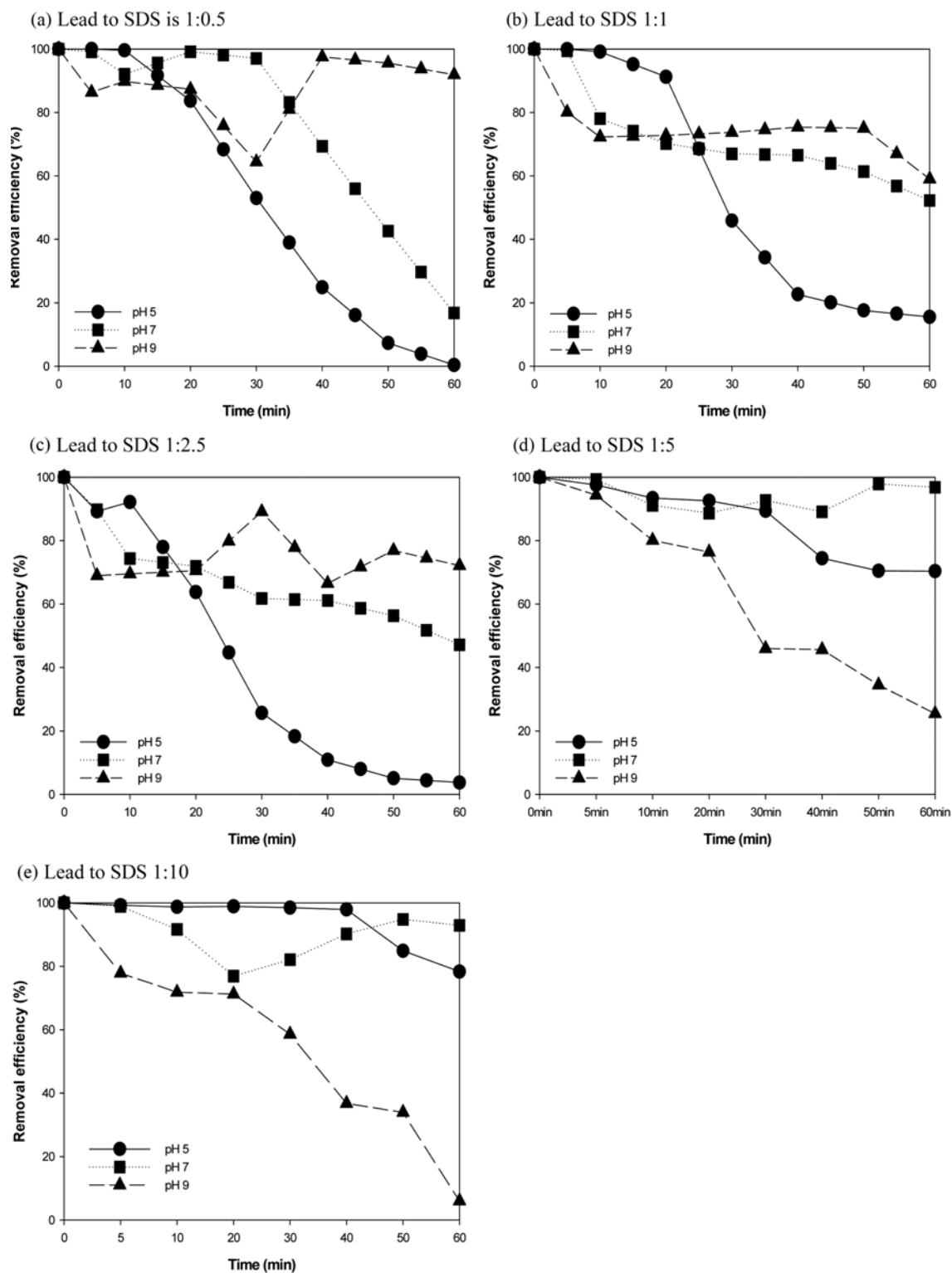


Fig. 4. Effects of pH at various lead to SDS molar ratio (initial lead concentration=20 mg/L, initial retentate pressure=0.14 MPa, MWCO of the membrane=100,000 Dalton).

cess. At higher SDS concentration, more micelles were accumulated on the membrane surface, reducing the driving force and consequently lowering the permeate flux [32]. There could have been another possibility for the partial blockage of membrane pores by micelles and/or a formation of an additional resistant layer which

may have decreased the flux [23]. Since the bulk monomer concentration is maintained at CMC level, extra surfactant monomers contribute towards the growth of separate small sized micelles or increase the size of already existing micelles. While filtering through the UF membrane, micelles were retained on the membrane sur-

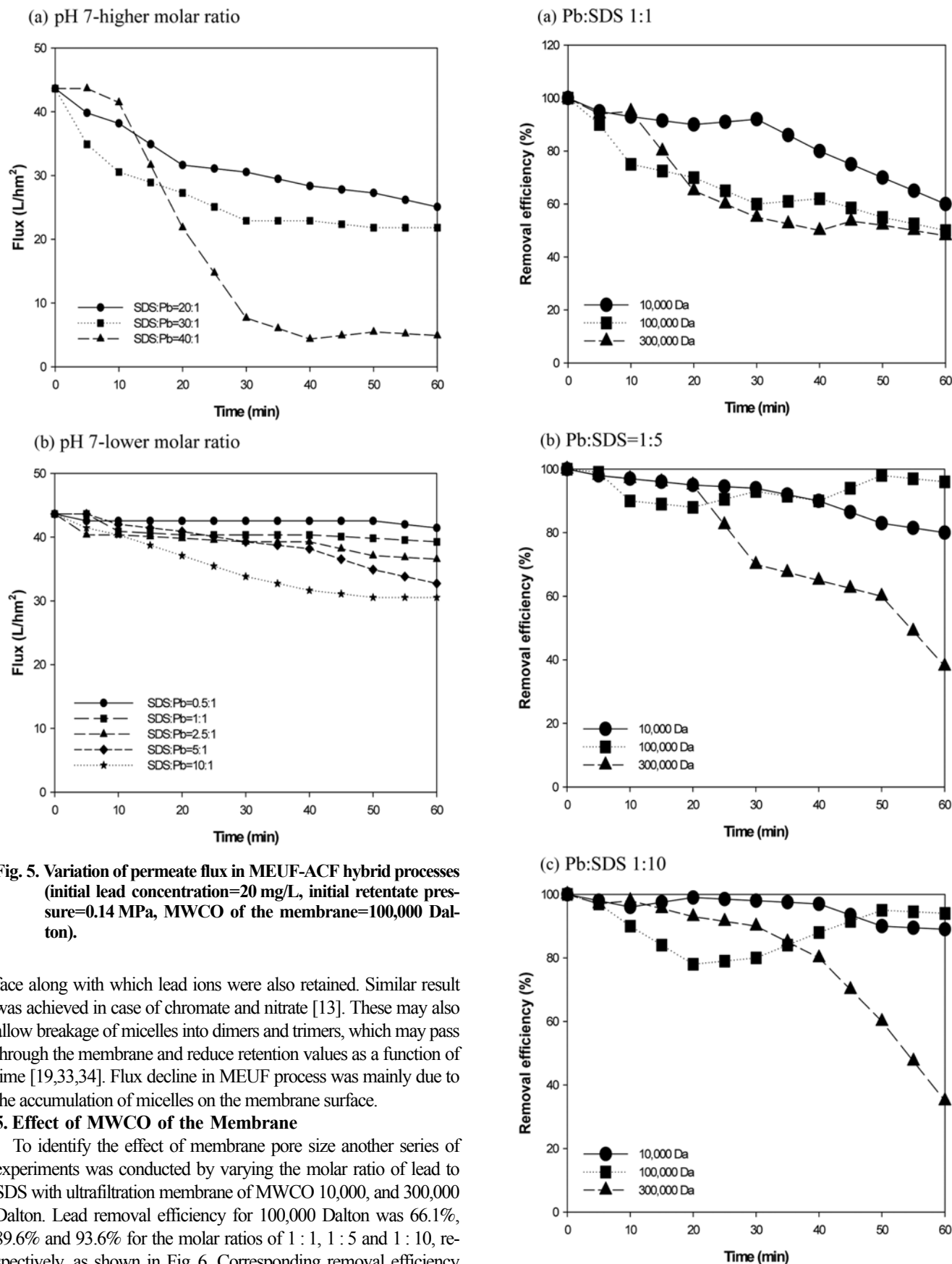


Fig. 5. Variation of permeate flux in MEUF-ACF hybrid processes (initial lead concentration=20 mg/L, initial retentate pressure=0.14 MPa, MWCO of the membrane=100,000 Dalton).

face along with which lead ions were also retained. Similar result was achieved in case of chromate and nitrate [13]. These may also allow breakage of micelles into dimers and trimers, which may pass through the membrane and reduce retention values as a function of time [19,33,34]. Flux decline in MEUF process was mainly due to the accumulation of micelles on the membrane surface.

5. Effect of MWCO of the Membrane

To identify the effect of membrane pore size another series of experiments was conducted by varying the molar ratio of lead to SDS with ultrafiltration membrane of MWCO 10,000, and 300,000 Dalton. Lead removal efficiency for 100,000 Dalton was 66.1%, 89.6% and 93.6% for the molar ratios of 1 : 1, 1 : 5 and 1 : 10, respectively, as shown in Fig. 6. Corresponding removal efficiency for 10,000 MWCO membrane was 82.7%, 91.7% and 96.6%, respectively. Lead removal efficiency was 66.5%, 76.7% and 79.1%

Fig. 6. Effect of MWCO of the membrane (initial lead concentration=20 mg/L, initial retentate pressure=1.4 MPa, pH=7).

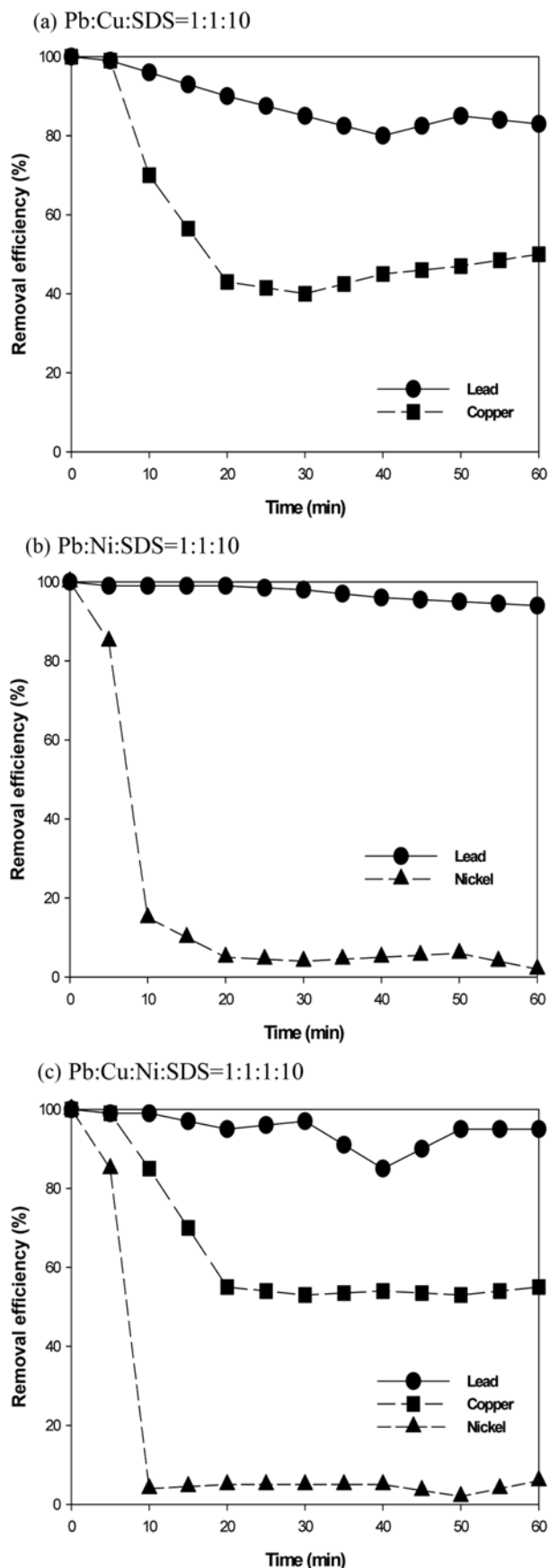


Fig. 7. Effect of co-existing heavy metals (initial retentate pressure=1.4 MPa, MWCO of the membrane=100,000 Dalton, pH=7).

in the membrane pore size of 300,000 Dalton. In comparison with MWCO of 10,000 Dalton for the lower molar ratio (low surfactant concentration), lead removal was less in the membrane with pore size of 100,000 and 300,000 Daltons. Similar results were presented in the previous paper on the removal of anionic pollutant through MWCO of 3,000 and 10,000 Daltons [2].

6. Effect of Co-existing Heavy Metals

Copper and Nickel were added to investigate the effect of co-existing heavy metals in the removal of lead from an aqueous solution. Lead removal efficiency was affected by co-existing heavy metals as shown in Fig. 7. Copper significantly affected lead removal while Nickel did not. In this study, copper showed high removal efficiency but its presence induces the reduction of lead removal. Nickel itself was not removed well and it did not affect the lead removal. Lead has the highest atomic number and the poorest electrical conductivity compared to copper and nickel. Copper has a higher electrical and thermal conductivity than other metals. Nickel is magnetic and a naturally magnetostrictive material, meaning that in the presence of a magnetic field the material undergoes a small change in length. In the case of nickel, this change in length is negative (contraction of material), which is known as negative magnetostriction. It seems that nickel did not affect the lead removal due to the negative magnetostriction produced in this process [35]. It was reported [28] that the separation efficiency of cadmium and copper was 100% and 85.6%, respectively, when sulfuric acid was used. 94.7% of copper and 97.6% of cadmium were liberated from the surfactant micelle by hydrochloric acid. It seems that copper has higher separation rate from SDS solute with the co-existing heavy metals. Cu^{2+} removal efficiency with phenol was 90% when SDS mole fraction was 0.7 [36]. Moreover, the Cu^{2+} rejection seemed to be enhanced slightly in the presence of 1 mM phenol, which may be caused by the slight reduction of SDS CMC with the addition of an organic solute [37].

7. SDS Removal by ACF

MEUF process alone was found to be effective in the removal

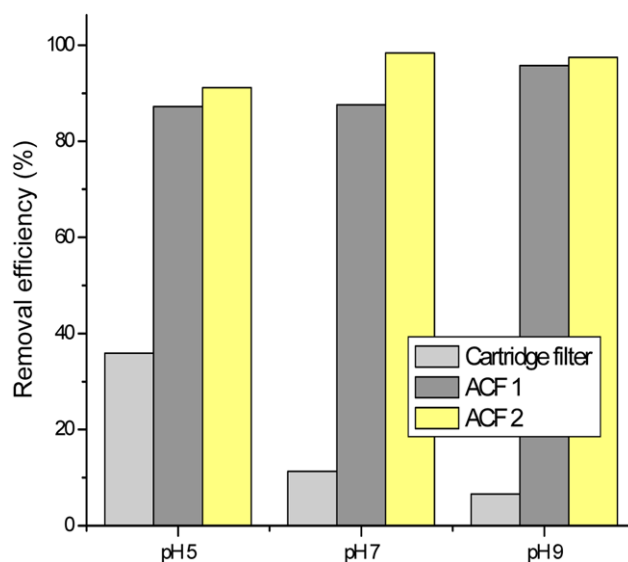


Fig. 8. Comparison of SDS removal efficiency at various ACF units (Pb : SDS=1 : 5, initial lead concentration=20 mg/L, initial retentate pressure=1.4 MPa, pH=5, 7, 9).

Table 3. Lead removal efficiency at various MWCO sizes

MWCO Ratio	10,000	100,000	300,000
1 : 1	82.7	66.1	66.5
1 : 5	91.7	89.6	76.7
1 : 10	96.6	93.6	79.1

of lead from feed solution, while the leakage of SDS in permeate creates secondary pollutants. Two series of experiments were carried out to investigate the SDS removal in ACF unit. As shown in Fig. 8, ACF has shown higher SDS removal efficiency. SDS removal efficiency was 95.6%, 98.4% and 97.8%, respectively, while cartridge filter removed SDS below 50% at the pH value of 5, 7 and 9. Pore size of cartridge filter was larger than that of SDS monomers and they can easily pass through the pore in cartridge filter.

CONCLUSIONS

Lead removal was investigated using the MEUF process and an anionic surfactant, SDS. Lead removal decreased with the decrease of the molar ratio of lead to SDS. Average lead removal efficiencies were over 95% at molar ratio of lead to SDS of 1 : 20, 1 : 40 and 1 : 100, respectively. Optimum molar ratio of lead to SDS was found to be 1 : 5. Surfactant concentration reached the critical micelle concentration (CMC) in all experiments conducted. Lead removal efficiency increased with the increase of pH while it was maintained below 30% without the surfactant. Permeate flux decreased with the increase of SDS concentration due to the accumulation of micelles on the surface of membrane. More micelles were accumulated on the membrane surface reducing the driving force, and consequently lowering the permeate flux. Lead removal efficiency was affected by co-existing heavy metal ions. Presence of copper affected the lead removal while nickel did not. A smaller MWCO membrane has shown a higher lead removal efficiency than the larger MWCO membrane. Over 95% of the SDS from the MEUF effluent was removed by two sets of ACF unit.

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