

Micellar enhanced ultrafiltration and activated carbon fibre hybrid processes for copper removal from wastewater

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Abstract—Several series of experiments were conducted to investigate copper removal from artificial suspension in micellar enhanced ultrafiltration (MEUF) and activated carbon fibre (ACF) hybrid processes. Sodium dodecyl sulphate (SDS) was used as a surfactant. Copper removal increased with the increase of molar ratio of copper to SDS, operating retentate pressure and initial permeate flux. Permeate flux decreased with the increase of molar ratio of copper to SDS. Specific and relative fluxes declined, respectively, with the increase of retentate pressure and initial permeate flux. Based on removal efficiency and permeate flux, initial permeate flux of 1.05 m³/m²/day, copper to SDS molar ratio of 1 : 30 (9.44 mM of SDS), and operating retentate pressure of 1.4 bar were found to be the optimum operating parameters for 0.5 mM or less initial copper concentration. Average copper removal at the optimised condition was 98% and the corresponding permeate copper concentration was less than 1 mg/L. Adsorptive capacity of activated carbon fibre (ACF) for SDS was 170 mg/g. Langmuir isotherm equation gives a better fit with the experimental results compared to the Freundlich isotherm equation. Overall SDS removal efficiency of two sets of ACF unit in series was 85%.

Key words: Micelle Enhanced Ultrafiltration, Copper, Surfactant, Activated Carbon Fibre

INTRODUCTION

Copper is a widely used heavy metal in various industries such as electroplating, electric wire and cable, textile, and insecticide industries. Compounds generally used in the industrial system are cupric chloride and copper acetate. When wastewater containing higher concentration of copper is discharged into the natural water courses it affects the aquatic life and is destructive to the environment. It also inhibits biological processes if it is discharged into the municipal wastewater treatment system [1-3]. People exposed to copper for a long time may suffer from kidney and liver disorders. If this element can be separated from the industrial wastewater, economic, health and environmental benefits can be achieved.

Micellar enhanced ultrafiltration (MEUF) is a process in which low molecular weight substances are separated by ultrafiltration after surfactant is added to the polluted water. It combines the high selectivity of reverse osmosis (RO) and high flux of ultrafiltration (UF) [4-6]. Thus, it has higher efficiency and lower cost. Surfactant is the key component for the removal of pollutants in this process [7]. The prime principle of this process is to increase the size of pollutant molecules by forming a complex of pollutant molecules and surfactant molecules. Surfactant forms micelle at the critical micelle concentration (CMC). The micelle has high electrical potential on surface, where charged hydrophilic groups are located. After binding of metals on micelle the solution is passed through UF membrane, on the surface of which the metal molecules along with micelle are retained. Previous researchers reported that there was about 99.9% removal of ferricyanide, nitrate and chromate from the feed solution depending upon surfactant concentration,

molecular weight cut off (MWCO) of membrane, retentate pressure, initial permeate flux and the concentration of pollutant in the solution [8]. Rejection coefficient of higher than 99% was achieved while cetyl tri methyl ammonium bromide (CTABr) and CPC were used [9]. Ferricyanide removal of 99% and over 95% of nitrate were removed by using CPC [10]. Similarly, removal efficiency of at least 96% was shown for cadmium, zinc, copper and calcium [11]. Removal of metal ions was not significantly affected by the presence of organics due to its different mechanism of interaction with micelle. Simultaneous removal of metal ion mixture and organic from solution gave the idea of application of MEUF for industrial applications [3,11]. The leakage of surfactant to permeate also creates a secondary problem. With the increase of sodium dodecyl sulphate (SDS) in feed solution, permeate SDS concentration increased gradually, but after reaching 0.2 M it increased rapidly [12].

The main difficulty in using this system is foulant, which results in reduced performance, several flux decline, high energy consumption, and frequent membrane cleaning or replacement [9,13-15]. The performance of a membrane is determined either by its flux or by a given transmembrane pressure. Several researchers [10,16-18] reported that various factors such as concentration polarisation, fouling, gel layer formation, and pore plugging had effects on flux. It can be minimized by using optimum operating parameters. It was reported [19] that organic matter is the most detrimental foulant on ultrafilters for its fouling. Control of fouling is the most important factor while operating a membrane process [20,21]. Depending upon the reversibility or irreversibility of foulant, backwashing with clean water or cleaning with chemicals such as alkaline, acid and sodium hypochlorite can be applied to regenerate its performance [10,22,23].

Adsorption kinetics has been found to be an economical and efficient method for removing trace heavy metals and organics [17,18]. Previous works have shown that the adsorptive capacity of activated

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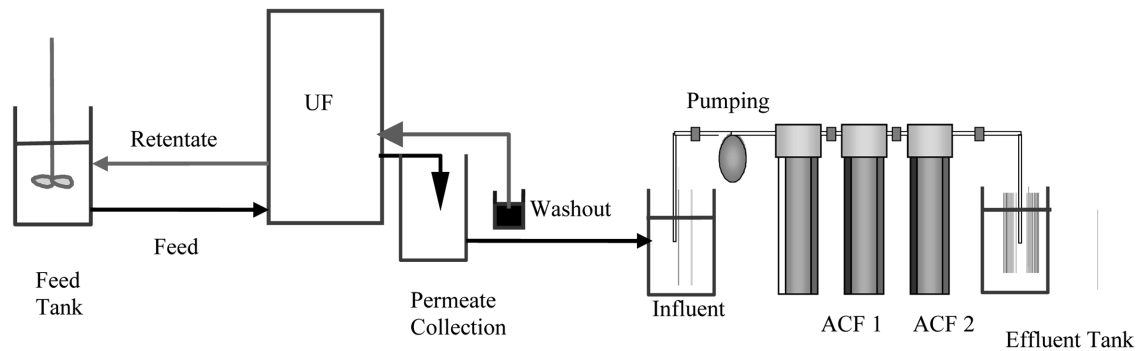


Fig. 1. MEUF combined with ACF for copper removal from wastewater.

carbon fiber (ACF) was twenty to hundred times higher than granular activated carbon (GAC). ACF has a uniform micropore structure, faster adsorption kinetics and a lower pressure drop than GAC [16,19]. The interaction between activated carbon surface chemistry and adsorbate hydrophobicity contributes to the adsorption performance of SDS surfactant. More hydrophobic entity of SDS led to faster external mass transfer rate [24].

Several studies have been done by previous researchers on inorganic removal from MEUF process [3,4,6,9,25,26]. Few researchers have focused on copper removal from the process [3]. And the optimum operation condition was not monitored in terms of permeate flux and copper removal. No study has been conducted for the removal of surfactants contained in the permeate. As activated carbon has proved to be a good adsorbent for organic removal, the coupling of MEUF with ACF has the potential to overcome the problems caused by excessive surfactant concentration [27,28]. The main objective of this study was to investigate the performance of MEUF in copper removal from synthetic wastewater and to identify the optimum operational conditions for the MEUF-ACF hybrid process.

MATERIALS AND METHODS

In this study, cupric chloride (CuCl_2) and sodium dodecyl sulphate (SDS) were used as a source of copper and surfactant, respectively, to form a complex of micelle and copper. Characteristics of membrane and ACF used in the experiment are as shown in Table 1.

Adsorptive capacity of ACF was calculated by using the Freundlich and Langmuir isotherm equations as follows:

Freundlich equation

$$\log q = \log k + n \log C_e \quad (2)$$

Table 1. Characteristics of membrane and ACF

Membrane material	Polyacrylonitrile
Membrane type	Hollow fibre
Flow direction	Inside to outside
Membrane diameter (inside/outside)	0.8/1.4 mm
Flow type	Cross flow
Effective surface area	0.055 m ²
BET surface area of ACF	1,000 m ² /g
Weight of ACF/cartridge	30 g

Langmuir isotherm equation

$$1/q = 1/q_m + 1/(k \cdot q_m \cdot C_e) \quad (3)$$

Where,

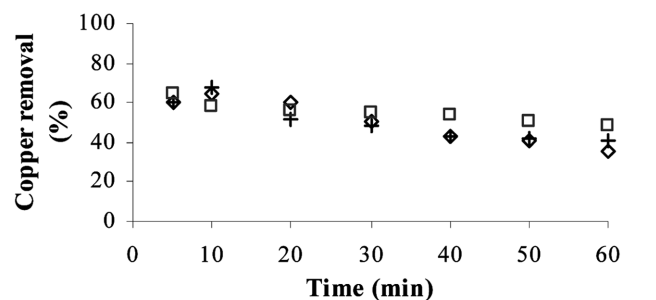
q = adsorbate adsorbed per unit weight of adsorbent (mg/g)

C_e = final concentration of adsorbate in solution (mg/L)

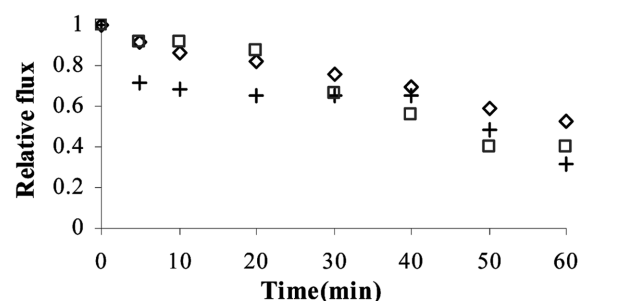
q_m = max. adsorption at monolayer coverage (mg/g)

k = adsorption equilibrium constant related (mg/g) to energy of adsorption (L/mg)

n = constant representing the adsorption intensity (dimensionless)



(a) Copper removal with time



(b) Change in relative flux

Fig. 2. Effect of permeate flux rate (Retentate pressure=1.4 bar, molar ratio of copper to SDS=1 : 2, initial conc. of copper=20 mg/L, MWCO of membrane=100,000 Dalton).

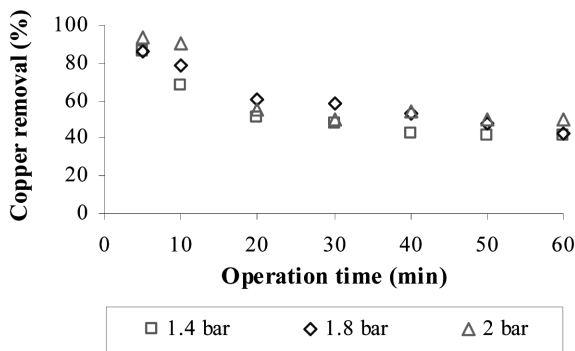
RESULTS AND DISCUSSION

1. Effect of Flux on Copper Removal

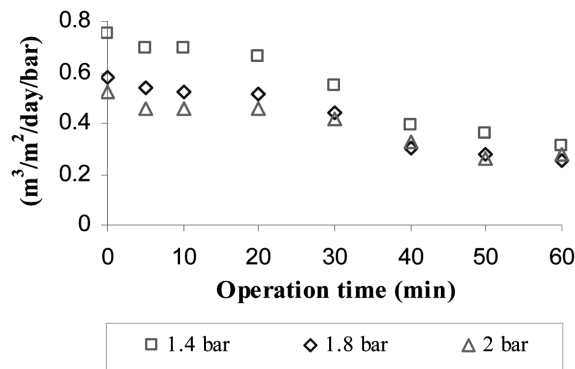
A series of experiments were carried out by varying initial permeate flux. Removal characteristics of copper are shown in Fig. 2. Average copper removal was 55% at a permeate flux of $1.31 \text{ m}^3/\text{m}^2/\text{day}$, while it was 51% and 54%, respectively, for initial permeate flux of $0.79 \text{ m}^3/\text{m}^2/\text{day}$ and $1.05 \text{ m}^3/\text{m}^2/\text{day}$. It implies that within the operation range the removal increases with the increase of flux. At the higher flux, concentration polarisation and secondary gel layer formation accelerated. In the membrane filtration process some percentage of pollutants are adsorbed on the membrane surface and its pores [9]. Further proceeding in the operation, some of the adsorbed copper starts to creep towards the permeate. It leads to an increase of copper concentration at the permeate. In surfactant based ultrafiltration (UF), flux decline is the main bottleneck of the process. It is caused by concentration polarisation, fouling and adsorption.

As shown in Fig. 2, relative flux decreased from 1.0 to 0.6, 0.45, and 0.35, respectively, for initial permeate flux of $0.79 \text{ m}^3/\text{m}^2/\text{day}$, $1.05 \text{ m}^3/\text{m}^2/\text{day}$ and $1.05 \text{ m}^3/\text{m}^2/\text{day}$. Higher recovery rate resulted in higher reduction in permeate flux. Gel layer formation on membrane surface reduced the flux at higher recovery rate [9,15]. Based on copper removal and relative flux, initial permeate flux of $1.05 \text{ m}^3/\text{m}^2/\text{day}$ was found to be the optimum initial permeate flux.

2. Effect of Retentate Pressure



(a) Copper removal with time

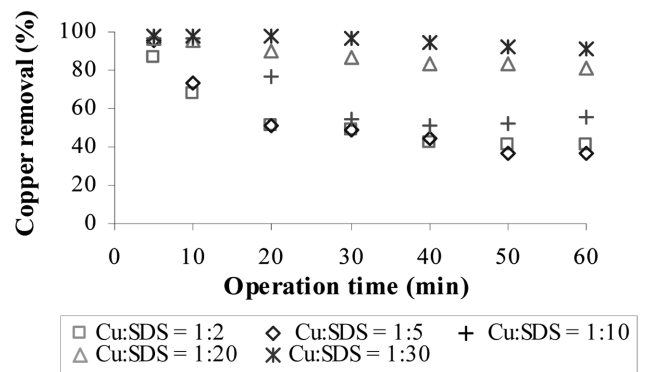


(b) Change in specific flux

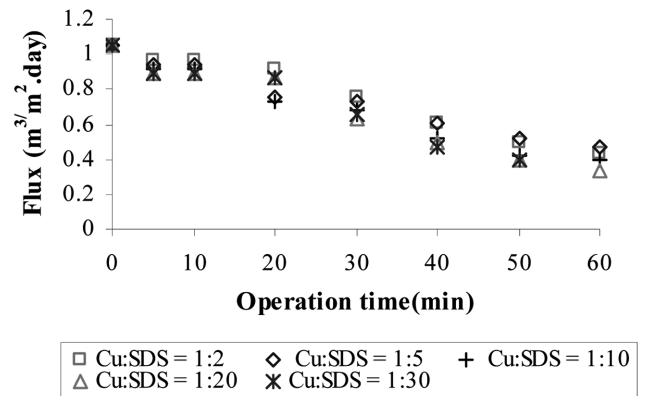
Fig. 3. Effect of initial retentate pressure (Flux rate= $1.05 \text{ m}^3/\text{m}^2/\text{day}$, molar ratio of copper to SDS=1 : 2, initial conc. of copper= 20 mg/L , MWCO of membrane= $100,000 \text{ Dalton}$).

A series of experiments were carried out for copper removal from synthetic wastewater at various initial retentate pressures. Fig. 3 shows copper removal as a function of retentate pressure. Average copper removal was found 54% for 1.4 bar retentate pressure, whereas it was 61% and 63%, respectively, for 1.8 bar and 2.0 bar retentate pressure. Copper removal increased with the increase of initial retentate pressure. Similar result was achieved on chromate [Gargi and Bhattacharya, 2006,9]. Increase of pressure increases the gel layer thickness, which results in increase in the rejection of micelle-copper complex.

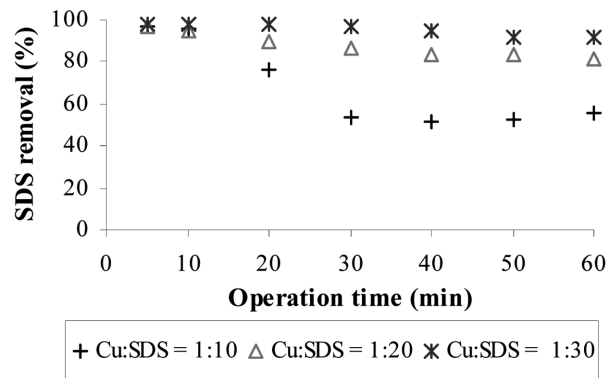
Fig. 3b shows the effect of retentate pressure on specific flux.



(a) Copper removal with time



(b) Change in flux



(c) SDS in permeate

Fig. 4. Effect of molar ratio (Flux rate= $1.05 \text{ m}^3/\text{m}^2/\text{day}$, initial conc. of copper= 20 mg/L , retentate pressure= 1.4 bar , MWCO of membrane= $100,000 \text{ Dalton}$).

Among the applied retentate pressures, the highest average specific flux of $0.52 \text{ m}^3/\text{m}^2/\text{day}/\text{bar}$ was observed when the retentate pressure was 1.4 bar. At the higher retentate pressure, compared to the energy applied, the flux reduction was found higher due to faster gel layer formation on membrane surface. Based on permeate flux, retentate pressure of 1.4 bar was the optimized retentate pressure.

3. Effect of Molar Ratio of Copper to SDS

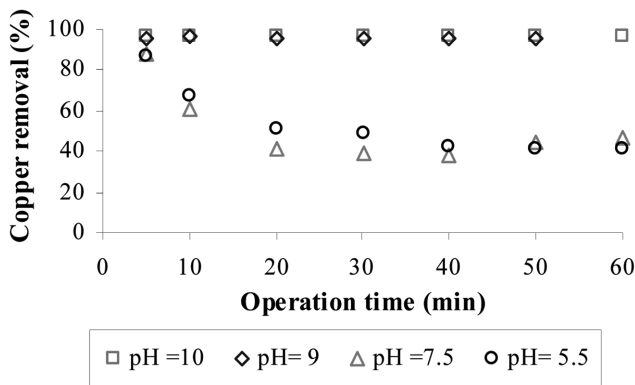
To observe the influence of SDS concentration on copper removal, another series of experiments were performed at various molar ratios of copper to SDS as shown in Fig. 4. Copper removal was 95% for molar ratio of 1 : 30, while it was 88% and 69% for the molar ratio of 1 : 20 and 1 : 10, respectively. Copper removal increases with the increase of molar ratio of copper to SDS. Similar result was achieved in chromate [4,9]. After surfactant concentration reaches to critical micelle concentration (CMC), all the surfactant added converts to micelle, which provides more surface area available for electrostatic attraction on micelle. As a result, a higher quantity of copper was removed together with the micelle.

Permeate flux decreased from initial flux of $1.05 \text{ m}^3/\text{m}^2/\text{day}$ to $0.65 \text{ m}^3/\text{m}^2/\text{day}$ and $0.64 \text{ m}^3/\text{m}^2/\text{day}$, respectively, for molar ratio of copper to SDS of 1 : 10 and 1 : 30. The reduction in flux could be due to the increased solution viscosity, osmotic pressure and pore blocking resistance [12]. Fig. 4c shows that the concentration of

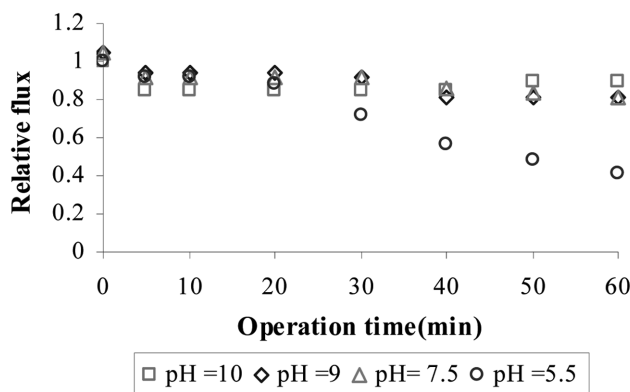
surfactant in permeate increased with the increase of initial concentration of surfactant (higher molar ratio). SDS removal increased from 81% to 92% when copper to SDS molar ratio increased from 1 : 10 to 1 : 30 in feed solution. Since the bulk monomer concentration is maintained at CMC level, extra surfactant monomers contribute towards the growth of several smaller size micelles. It may also break the micelles into dimmers and trimmers which pass through the membrane [26]. The increase in the concentration of surfactant at permeate is due to the creeping effect and the passing of some of the monomer surfactant to the effluent. The increase in the concentration of SDS at rejection was mainly due to the increase in the concentration of micelle in the bulk solution. The result is in line with previous study on anionic removal [4]. Copper to SDS molar ratio of 1 : 30 (9.44 mM SDS concentration) was the optimum condition to keep copper concentration less than 1 mg/L in permeate. For efficient removal of copper from the feed solution, optimum concentration of SDS was found at a molar ratio of copper to SDS of 1 : 30 with at least 1 CMC of SDS.

4. Effect of pH

Fig. 5 shows copper removal with respect to pH of feed solution. Copper removal was below 60% for feed solution pH of 5.5 and 7.5, while it was up to 96% for pH of 9 and 10. Copper removal increases with the increase of pH in feed solution. At the lower pH, copper needs to compete with H^+ ions to get the micelle sur-

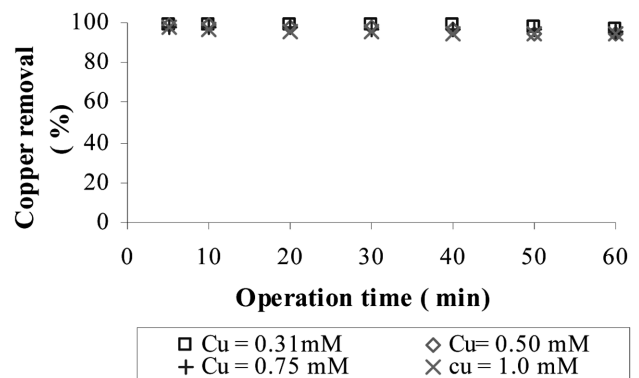


(a) Copper removal with time

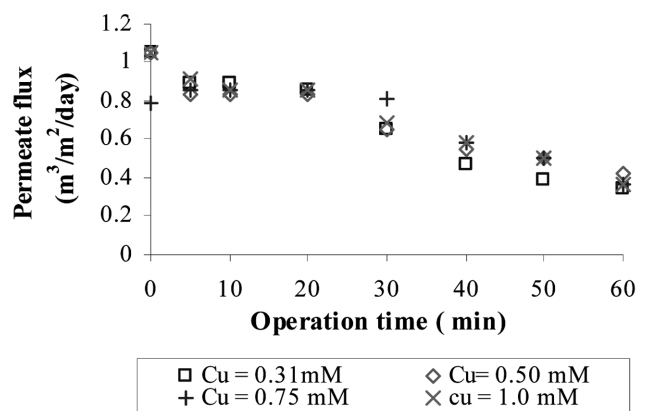


(b) Change in relative flux

Fig. 5. Effect of pH variation (Flux rate= $1.05 \text{ m}^3/\text{m}^2/\text{day}$, copper to SDS molar ratio=1 : 2, initial conc. of copper=20 mg/L, retentate pressure=1.4 bar, MWCO of membrane=100,000 Dalton).



(a) Copper removal with time



(b) Change in permeate flux

Fig. 6. Effect of initial concentration of copper (Flux rate= $1.05 \text{ m}^3/\text{m}^2/\text{day}$, SDS concentration=9.44 mM, retentate pressure=1.4 bar, MWCO of membrane=100,000 Dalton).

face. In acidic conditions due to the competition with H^+ ions, less copper was adsorbed on the micelle surface, which leads to the reduction of copper removal. Flux increases with the increase of pH feed solution as shown in Fig. 5. Previous researchers have shown that chromate removal increased with the increase of acidity in feed solution [9]. The effect of pH depends upon the type of metal used in the solution whether H^+ ions compete with metal or not during the electrostatic adsorption on micelle.

5. Effect of Initial Concentration of Copper

Another series of experiments were performed with initial SDS surfactant concentration of 9.44 mM at various initial copper concentration in feed solution as shown in Fig. 6. Copper removal efficiency was 98% for initial copper concentration of 0.31 mM while 96% for 1 mM concentration. For initial copper concentration of 0.31 mM and 0.5 mM, the permeate copper concentration was less than 1 mg/L, whereas 1.4 mg/L and 2.7 mg/L, respectively, for copper concentration of 0.75 mM and 1 mM. Copper concentration in permeate increased with the increase of initial copper concentration mainly due to less micelle surface area available for the electrostatic adsorption of higher copper concentration. Average permeate flux remained almost the same for the given surfactant concentration [9]. The charge surface available for copper on micelle surface remained constant for constant initial surfactant concentration. It results in the lower removal of copper at its higher concentration.

6. Effect of MWCO of Membrane

To identify the effect of membrane pore size another series of experiments were conducted by varying the molar ratio of copper to SDS with ultrafiltration membrane of MWCO 300,000 Dalton. In terms of permeate flux, it increased with the increase of MWCO of membrane. Copper removal was 95%, 85%, and 66% for molar ratio of 1 : 30, 1 : 20, and 1 : 10, respectively. Corresponding removal for 100,000 MWCO membrane was 95%, 88%, and 69%, respectively. In comparison with MWCO of 100,000 Dalton for the lower molar ratio (low surfactant concentration), the removal was less in the membrane with pore size of 300,000 Dalton. For a higher molar ratio of copper to SDS, its removal efficiency was close to the MWCO

of 100,000. Similar results were presented in the previous paper on the removal of anionic pollutant through MWCO of 3,000 and 10,000 [8]. In which chromate removal was 82%, 99%, and >99% in the membrane pore size of 3,000 Dalton, while it was 67%, 95% and 98% with the membrane pore size of 10,000 Dalton at the molar ratio of chromate to CPC as 1 : 2, 1 : 5, and 1 : 10, respectively. At higher SDS concentration they were mostly in micelle forms and only a little influence of MWCO of membrane in the removal was observed.

7. Copper Removal Without Surfactant

Another set of experiments were conducted without surfactant in the feed solution as shown in Table 3. During 40 minutes of filtration the average copper removal was 23%. In the MEUF process the removal of pollutants is mainly due to adsorption and the sieving action of the membrane. In the absence of SDS, UF membrane pores are big enough to pass copper ions through it. Due to its smaller size most of copper ions passed through the membrane while a smaller percentage was retained due to adsorption on the wall of the membrane. UF alone was not enough to treat copper from the feed solution. Once the surfactant is not present in the solution, no concentration polarisation and no secondary gel layer formation exist on the membrane surface to reduce the flux. As a result, stable permeate flux was observed at the permeate.

8. Adsorption Isotherm Constants for SDS on ACF

Adsorptive capacity of ACF for SDS was identified from batch experiments. Freundlich and Langmuir isotherm equations were used to calculate the adsorptive capacity. Adsorption constants and adsorption rates are summarized in Tables 4 and 5, respectively. Adsorption capacity of ACF on SDS was 170 mg/g at initial SDS concentration of 1,200 mg/L. Langmuir isotherm equation gives a better fit with the experimental results compared to the Freundlich isotherm equation.

9. SDS Removal from ACF Filter

MEUF process can remove copper to a lower concentration, while the leakage of SDS in the permeate creates secondary pollutants. A set of experiments was carried out to study the SDS removal in ACF unit. As shown in Table 6, SDS removal was 88%, 86% and 83% at the initial concentration of SDS of 100 mg/L, 200 mg/L and 1,200

Table 2. Experimental condition

Operating parameter	Unit	
Retentate pressure	bar	1.4, 1.8, 2.0
pH		5.5, 7.5, 9.0, 10.0
Initial concentration of copper	mM	0.31, 0.50, 0.75, 1.0
Molar ratio of copper to SDS		1 : 5, 1 : 10, 1 : 20, 1 : 30
Initial permeate flux	m ³ /m ² /day	0.79, 1.05, 1.31
Membrane pore size	Dalton	100,000-300,000
ACF flux	m ³ /day	0.06

Table 3. Copper removal without surfactant

Time (min)	Concentration (mg/L)	Removal efficiency (%)	Flux (m ³ /m ² /day)
10	47.2	25.7	1.05
20	50.6	20.4	1.05
30	48.5	23.8	1.05
40	48.7	24.9	1.05

Table 4. Langmuir and Freundlich isotherm constants

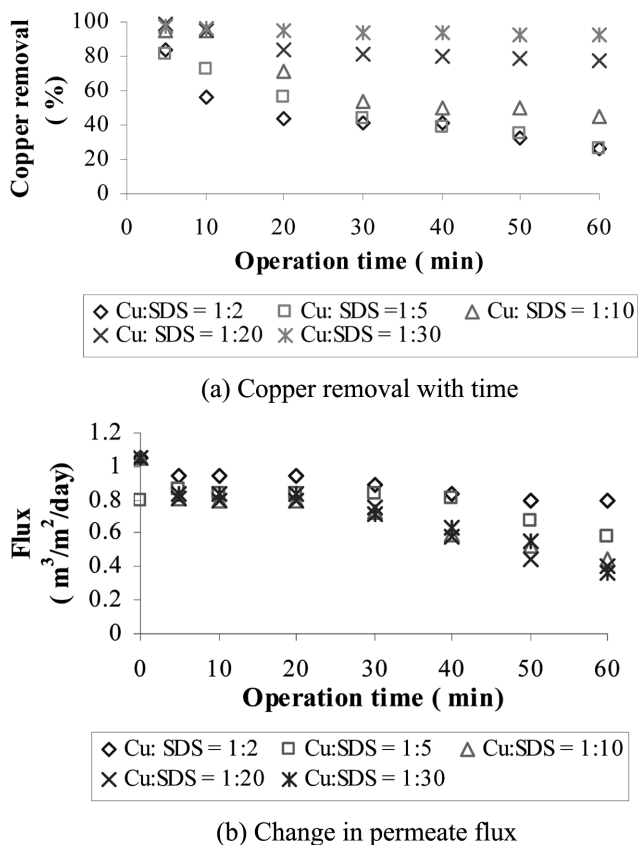
Langmuir isotherm constants		Freundlich isotherm constants	
k_a	q_m	n	k_f
0.30	222.2	0.0827	141.1

Table 5. Adsorption rate of ACF at different equilibrium concentration

Equilibrium conc. (Ce) (mg/L)	Adsorption rate (mg/g)		
	Experimental	Langmuir equation	Freundlich equation
10.7	170.6	169.3	215.8
124.9	204.6	216.5	219.2
187.2	242.6	218.3	222.2
400.4	217.6	220.4	220.2

Table 6. SDS removal from ACF at various initial concentrations

Average permeate surfactant concentration and removal efficiency					
1,200 mg/L		200 mg/L		100 mg/L	
C_e (mg/L)	Removal efficiency (%)	C_e (mg/L)	Removal efficiency (%)	C_e (mg/L)	Removal efficiency (%)
195.3	83.8	26.5	86.8	11.4	87.0

**Fig. 7. Effect molar ratio for membrane with 300,000 Dalton (Flux rate=1.05 m³/m²/day, retentate pressure=1.4 bar, MWCO of membrane=300,000 Dalton).**

mg/L, respectively, with the corresponding permeate SDS concentration of 11.38 mg/L, 26.49 mg/L and 195.33 mg/L. Two ACF units in series have removed SDS efficiently from the wastewater.

CONCLUSIONS

Copper removal was investigated in MEUF by using anionic surfactant SDS. Based on removal efficiency and permeate flux, the initial permeate flux of 1.05 m³/m²/day, copper to SDS molar ratio of 1 : 30 (9.44 mM of SDS concentration), and operating retentate pressure of 1.4 bar were found to be optimum operating parameters. Average copper removal was 98% for 0.5 mM or less initial copper concentration. Copper removal efficiency increased with the increase of molar ratio of copper to SDS, retentate pressure and initial permeate flux. Corresponding permeate, specific and relative fluxes were declined. Adsorptive capacity of ACF for SDS was 170 mg/g. Langmuir isotherm equation gives a better fit with the experimental results compared to the Freundlich isotherm equation. SDS

removal efficiency of the ACF unit was 85%.

ACKNOWLEDGMENT

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NOMENCLATURE

- C_e : final concentration of adsorbate in solution [mg/L]
 k : adsorption equilibrium constant related [mg/g] to energy of adsorption [L/mg]
 n : constant representing the adsorption intensity (dimensionless)
 q_m : aax. adsorption at monolayer coverage [mg/g]
 q : adsorbate adsorbed per unit weight of adsorbent [mg/g]

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