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# Micellar-enhanced ultrafiltration of zinc in synthetic wastewater using spiral-wound membrane

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#### ABSTRACT

In the present study, micellar-enhanced ultrafiltration (MEUF) was used to remove  $Zn^{2+}$  from synthetic wastewater by the spiral-wound ultrafiltration membrane. The effects of different operating conditions on the separation performance of membrane were investigated. It was found that the transmembrane pressure has the largest influence on the permeate flux, but it has negligible effect on the rejection coefficient. Furthermore, sodium dodecyl sulfate (SDS) feed concentrations, SDS–Brij35 mixed micelles concentration and solution pH have a major influence on the rejection coefficient and negative effect on the permeate flux due to concentration polarization layer formation. Also, the results showed that the permeate flux and removal efficiency of zinc by anionic surfactant (SDS)–MEUF depends on the ligand-to- $Zn^{2+}$  ratio extremely. In general, MEUF by spiral-wound ultrafiltration membrane has good rejection of single anionic surfactant at relatively low concentration is more efficient than mixed surfactants and MEUF was not practical when the wastewater is intensively acidic.

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#### 1. Introduction

Many industrial wastewater streams (e.g. the metal working, refineries, battery, semiconductor and copper industries, mine wastewater) contain heavy metals. The metal ions are nonbiodegradable, highly toxic and may have a potential carcinogenic effect [1,2]. Heavy metals such as cadmium, copper, lead, mercury, nickel and zinc are included on the EPA list of priority pollutants [3]. Due to their high solubility in the aquatic phases, heavy metals can be absorbed by living organisms. Since they come into the food chain, high concentrations of heavy metals may accumulate in the human organs [4]. If the mentioned above ions directly discharged into the sewage system, they may critically damage the operation of biological treatment plants [1]. According to the Iran Department of Environment (IDE), in 2006, the electroplating industry was responsible for 85% of the direct zinc discharges in Iran.

Therefore, the development and application of effective treatment processes is necessary and several methods have been used for the control of the metal toxicants.

At present, the popular techniques for treating the wastewater containing heavy metal ions are chemical precipitation, adsorption, ions exchange, chelating, evaporation, coagulation–flocculation, flotation, electro-deposition, liquid–liquid extraction, and so on. However, these techniques have of their own deficiencies, such as secondary pollution of deposition, inconvenient operation, high cost, difficulty of recycling metal ions and so on [5–7].

Membrane processes have been applied in various types of industries such as the separation, concentration and purification in food industry, biotechnology and petrochemical operations, as well as water and wastewater treatment [8]. Recently, membrane separation has been increasingly used for the treatment of inorganic effluent, because of its convenience and high efficiencies [4]. Membrane separation processes of different types of membranes show great promises in commercial application. Using of high pressure membrane operations, i.e. reverse osmosis (RO) or nanofiltration (NF) is limited in wastewater treatment applications due to high pressure requirements and low water permeabilites. Microfiltration and ultrafiltration on the other hand have low rejection potentials [9].

To overcome the problems, a surfactant-based ultrafiltration (UF) process known as micellar-enhanced ultrafiltration (MEUF) has been proposed. A surfactant is a substance composed of hydrophilic head and hydrophobic tail. Above the critical micelle concentration (CMC), the surfactant monomers form a spherical or cylindrical aggregate, called a micelle [10]. Heavy metal ions bind electro statically on the surface of opposite-charged micelles (Fig. 1). Then it can be retained by an UF membrane which has higher flux and lower energy consumption than NF or RO due to less pressure difference [3].

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Nomenclature					
EPA	Environmental Protection Agency				
$P_{\mathrm{f}}$	feed stream pressure (bar)				
$P_{\rm p}$	permeate side pressure (bar)				
$P_{\rm r}$	retentate side pressure (bar)				
Q	permeate rate (m <sup>3</sup> /s)				
TMP	transmembrane pressure (bar)				
Α	area of membrane (m <sup>2</sup> )				
$C_{\rm f}$	concentration of $Zn^{2+}$ (mg/L) in the feed solution				
	(mM)				
Cp	concentration of Zn <sup>2+</sup> in the permeate (mg/L)				
ά	mole fraction of surfactant				
С	CMCs of the single surfactants (mM)				
f	activity coefficient				

In fact, MEUF combines the high selectivity of RO and the high flux of UF [11]. MEUF can be used to remove single metal ion or several kinds of metal ions simultaneously, whose removal efficiency is high [12]. Further, MEUF may be applied for the recovery of valuable compounds, thus improving the chemical industry's sustainability [13].

Nowadays, more and more spiral-wound membranes are applied in various industries due to their advantages, such as compact structure and low cost. The application in wastewater treatment of spiral membrane is promising and feasible [14].

In the present study, MEUF was used to remove Zn<sup>2+</sup> from synthetic wastewater using the regenerated cellulose spiral-wound ultrafiltration membrane. The spiral-wound UF module was operated in two arrangements namely, linear continuous and cross-flow mode which have vigorously higher flux and membrane effective area than conventional batch cell system.

According to our knowledge, in literature very few papers have discussed the MEUF processes with spiral-wound module for removing metal ions. In this study, the effects of some important parameters on metal removal efficiency and permeate flux were investigated, including operating time, the concentration of SDS, Table 1

Analysis of the real wastewater sample before and after UF step.

Parameters	Units	Before membrane	After membrane
Total hardness	ppm	542	344
Ca <sup>2+</sup> hardness	ppm	311	197
Mg <sup>2+</sup> hardness	ppm	231	147
COD	ppm	16	14
BOD <sub>5</sub>	ppm	11	9
Total N	ppm	7.61	7.48
TSS	ppm	6	1
TDS	ppm	245	184
pН	ppm	7.8	7.5
Conductivity	μS/cm	374	370
Alkalinity	ppm	205	78

the operating pressure, the concentration of ligand (EDTA), solution pH and the mixture of SDS and Brij35 added into the solution. These results can be helpful to achieve the practical application of this technique.

#### 2. Experimental

#### 2.1. Chemicals

The analysis of real sample wastewater from mashhad electroplating industry (Mashhad, Iran) was used in this experiments. The analysis of the wastewater according to ASTM [15] is reported in Table 1. Distilled water was used for making model solutions containing salts.

All agents were analytical pure grade (99%) and used as received. The anionic surfactant sodium dodecylsulfate (SDS), whose structure is  $C_{12}H_{25}OSO_3Na$ , with a molecular weight of 288.38, The nonionic surfactant polyoxyethyleneglycol dodecyl ether (Brij35), whose structure is  $C_{12}H_{25}$  ( $C_2H_4O$ )<sub>23</sub>OH, with a molecular weight of 1189, zinc chloride (ZnCl<sub>2</sub>, extra pure 99.99%), with a molecular weight of 136.28, EDTA ethylenediaminete-traacetic ( $C_{10}H_{14}N_2NO_2O_8\cdot 2H_2O$ ), with a molecular weight of 372.24 were obtained from Merck Company. The critical micelle concentrations (CMC) of SDS and Brij35 are 8.15 and 0.36 mM,



Fig. 1. A schematic diagram illustrating micellar-enhanced ultrafiltration for the removal of metal ions.

0

respectively. Distilled water produced by a water purification system (Labconco, Iran) was used in all of the experiments. HCl and NaOH, both having concentration of 1 N, were used for pH adjustment.

#### 2.2. Membrane

UF spiral-wound membranes of Amicon regenerated cellulose (PL series, Millipore) with 20 kDa molecular weight cut off (MWCO) and membrane effective area of  $0.5 \text{ m}^2$  were used.

#### 2.3. Apparatus and experimental methods

The applied experimental set up for this research is shown in Fig. 2. All of the experiments were carried out at room temperature. By considering the Kraft point of the SDS is 14 °C, the temperature maintained at  $25 \pm 2$  °C to avoid any SDS precipitations. The feed tank was initially filled with 10 L of feed solution. ZnCl<sub>2</sub> was added into the distillated water to produce the synthetic wastewater with  $Zn^{2+}$  concentration of 100 mg/L. The SDS with concentration predetermined was added into the synthetic wastewater. The solution was mixed using a stirring bar driven by a magnetic motor at 300 rpm. If necessary, the solution pH was adjusted by adding a small amount of HCl or NaOH. After being fully mixed, the solution was fed into the membrane module in continuous and cross-flow ultrafiltration by the Centrifugal pump. For large-scale, industrial membrane filtration, cross-flow or tangential-flow filtration is commonly employed. Two manometers were utilized to indicate the pressure before and after the membrane module. The permeate and retentate solutions were not recycled into the system. All the experiments were carried out in the steady state conditions. Such conditions were achieved after about 20 min period of operation.

Initially, the membrane is contacted to distillated water at a pressure of 3 bar for 1 h, and then the water flow rate through membrane was measured at 2 bar. After UF experiments carried out, the membranes were immediately flushed with distillated water and were used again only if the deviation of clean water fluxes at 2 bar was less than 5%.

Following each run, the membrane was successively washed in %1 NaOH, distillated water, 0.1 M HCl, distillated water, and finally in distillated water until the pH of the permeate became neutral. Then distillated water was filtered to determine the permeate flux in order to check the permeability of membrane.

TMP is the transmembrane pressure or operating pressure which can be calculated by the following equation:

$$TMP = \frac{1}{2}(P_{i} + P_{o}) - P_{p}$$
(1)

where  $P_i$ ,  $P_o$  and  $P_p$  are inlet, outlet and permeate pressures, respectively.

The permeation flux of the UF membrane is defined as:

$$J_{\rm p} = \frac{Q}{At} \tag{2}$$

 $J_p$  is the permeation flux (L/m<sup>2</sup> min); Q is the permeate volume (L); t is the operating time (min) and A is the area of the membrane (m<sup>2</sup>).

The rejection factor is defined as:

$$R = 1 - \frac{C_{\rm p}}{C_{\rm f}} \tag{3}$$

 $C_{\rm f}$  is the concentration of  $Zn^{2+}$  (mg/L) in the feed solution;  $C_{\rm p}$  (mg/L) is the concentration of  $Zn^{2+}$  in the permeate (mg/L).

For the standard deviation (SD) of each trial the following formula can be used:

$$SD = \sqrt{\frac{\sum (x - \bar{x})^2}{(n-1)}}$$

where  $\bar{x}$  sample mean average and n is the sample size.

#### 2.4. Analyses

The permeate flux was measured continuously and gravimetrically. The cumulative weights are converted to cumulative volumes and from the slope of the cumulative volume versus time curve, the permeate flux is obtained as a function of operating time according to Equation (2). The  $Zn^{2+}$  ion concentration in permeate was analyzed by atomic absorption spectrometry (GBC, 908AA Model) at 228.8 nm.

Each experiment was repeated for each model solution, three measurements for metal ion concentrations in permeate and flux rate were made and the results were averaged. The uncertainty in ion concentration measurements were estimated as  $\pm 0^{-2}$  ppm,  $\pm 0.05$  L/m<sup>2</sup> min for rejection factor and permeate flux respectively. A 95% confidence interval was used in both cases.

#### 3. Results and discussion

### 3.1. Effect of operating time on the permeate flux and the rejection factor

At the beginning of the experiment, the distilled water was processed at the operating pressure of 2 bar and the permeate flux was measured about  $3 L/m^2$  min. As shown in Fig. 3, the initial permeate flux is less than distillated water permeation flux due to the membrane pore blocking. The effect of operating time on permeate flux was investigated at the 6 mM concentration of SDS and 100 ppm Zn<sup>2+</sup> concentration. (The concentration of zinc which is used in experiments, is the representative of real situation separation problems in Iran.) It can be found that SDS concentration in polarization layer is higher than that of bulk solution. So, SDS bulk concentration is considered less than CMC of SDS (8.15 mM).



Fig. 2. MEUF experimental setup: (1) feed reservoir, (2) bypass line, (3) centefiugal pump, (4) heat exchanger, (5) monometer, (6) spiral-wound ultrafiltration module, (7) pressure control valve, (8) permeate stream, (9) retentate stream.



**Fig. 3.** Effect of operating time on permeate flux in different transmembrane pressure.  $[Zn^{2+}] = 100$  ppm, [SDS] 6 mM, T = 25 °C, TMP is transmembrane pressure.

Fig. 3 represents the variation of permeate flux with the operating time. It shows that with the increase of operating time, permeate flux decreases. This phenomenon is attributed to the fact that the surfactant accumulation on membrane surface increases with the operating time increasing. This behavior is known as the concentration polarization. The concentration polarization is caused by the accumulation of retained solutes such as micelles on the membrane surface in a short period of time, where their concentration will gradually increase [2,12]. The micelles retained on the membrane surface generate a deposited layer on the membrane surface which results in the increase of resistance enhancement against the solvent flux and consequently, decreases the permeate flux [15]. The accumulation of the micelles over the membrane can continue until a gel layer concentration  $(C_{\sigma})$  is formed. This gel layer formed by the rejected surfactant on membrane surface may operate as an additional resistance to permeate. Therefore, the permeate flux was declined and rejection factor was increased as the operating time extended [7].

According to our knowledge and pervious published papers [11,16] when the SDS concentration exceeded its CMC, the rejection variations were small (98–99%). We started with a SDS concentration of 6 mM due to reduction of surfactant usage and surfactant loss that may decrease the cost of the separation process. On the other hand, in high SDS concentration the surfactant monomers certainly leaked into the permeate through the ultrafiltration membrane and produced secondary pollution.

# 3.2. Effect of SDS concentration on permeation flux and the rejection factor

The effect of feed SDS concentration on  $Zn^{2+}$  rejection was investigated at the  $Zn^{2+}$  concentration of 100 ppm and operating pressure of 2 bar. The results are shown in Fig. 4.

The rejection factor increased with increase of the feed SDS concentration Fig. 4 shows that an immediate rise in the rejection of  $Zn^{2+}$  with the increasing feed SDS concentration. No significant enhancements of rejection factor can be seen at higher SDS concentrations because of efficient binding sites do not increase anymore. Theoretically, there are no micelles formed at surfactant concentrations below the CMC and therefore, there is not any metal ion rejection, but according to our results, the  $Zn^{2+}$  rejection was observed when the SDS concentrations are below the CMC. This behavior can be demonstrated due to the concentration polarization effect which hinders the ions permeation through the membrane pores. The concentration polarization is an important



**Fig. 4.** Effect of feed surfactant concentration on the permeate flux and  $Zn^{2+}$  rejection.  $[Zn^{2+}] = 100$  ppm, TMP = 2 bar,  $T = 25 \degree C$ .

characteristic of all ultrafiltration systems. Some level of concentration polarization may have a beneficial effect in terms of permeate and rejection. When the SDS concentration reaches the CMC level at the concentration polarization layer, many SDS monomers begin to form large numbers of big-size micelles at the concentration polarization layer. Furthermore, the surfactant concentration in the layer adjacent to the membrane surface was higher than that of the bulk solution.

Actually, at the constant  $Zn^{2+}$  concentrations, the true rejection of the solute do not depend on the initial SDS concentration in the bulk solution while it is a function of the SDS concentration at the concentration polarization layer.

Also, the  $Zn^{2+}$  rejection which is observed at surfactant concentration below the CMC may be explained from the fact that ions reduce the CMC of anionic surfactants and formation of micelles to bind metal ions is possible. As shown in Fig. 4, it can be seen that the rejection factor can reach to 98% when feed SDS concentration is 6 mM.

As depicted in Fig. 4, the permeation flux decreases with the increase of the feed SDS concentration. When the feed SDS concentration is below the CMC, all the SDS molecules exist as free monomers, whose size is much smaller than the UF pore diameter. Under these conditions, monomers can easily pass through membrane. So, the permeation flux is high [12]. The initial decrease can be explained due to the membrane fouling, the adsorption of surfactant on the membrane surface and concentration polarization phenomena. Since, the apparent diameters of micelles at high SDS concentrations were smaller than the ones at low concentration, further decrease in permeate flux can occur as the result of the membrane pore plugging [5]. Similar justification has been reported by Fang el al. in the case of cadmium ion. When increasing the SDS feed concentration, a higher fraction of surfactants will be in micellar form and, consequently, more zinc will be trapped on the micelles, resulting in lower permeation flux [13].

### 3.3. Effect of the operating pressure on permeation flux and $Zn^{2+}$ rejection factor

Fig. 5 shows the variation of permeate flux with the Zn<sup>2+</sup> concentration of 100 mg/L and the SDS concentration of 6 mM in different operating pressures.

Ultrafiltration is a pressure-driven membrane separation process. Generally, higher the operating pressure gives higher the permeate flux. At low pressures, the flux increases with increasing pressure. However, flux may not increase proportionally with



**Fig. 5.** Effect of operating pressure on the permeate flux and the  $Zn^{2+}$  rejection.  $[Zn^{2+}] = 100$  ppm, [SDS] = 6 mM bar,  $T = 25 \degree C$ .

pressure at high pressures and so the flux reaches a plateau level. This behavior is usually explained by the reason that high operating pressures can lead to more micelle deposition on the membrane surface. Consequently, it enhances the concentration polarization and the gel layer compression [12].

Therefore, it can be noticed that the very high operating pressure is not necessary for a high permeate flux. Higher operating pressures needs higher investments in equipment and also higher operational costs. For commercial applications, the recommended operating pressure for this UF membrane separation system is below the 1.5 MPa. By considering Fig. 5, after pressure difference of 3 bar, no meaningful effect can be seen on the permeate flux. This finding is in agreement with other studies on UF [2].

Fig. 5 shows that the operating pressure has no significant effect on the  $Zn^{2+}$  rejection. The reason is that the MEUF process cannot reject free ions at any operating pressure and only, the variation of the surfactant concentration can alter the removal efficiency. This fact implies that micelle and micelle-ion hybrid formation are the more important characters in the ion rejection from the feed solution by MEUF process.

### 3.4. Effect of SDS–Brij35 mixed micelles concentration on permeation flux and the $Zn^{2+}$ rejection efficiency

Traditionally, the large quantities of anionic surfactant are necessary for attaining the appropriate rejection factor and this leads to higher cost of MEUF membrane separation process. Also high level of residual surfactants can diffuse through the membrane pores and they accumulate in the permeate without participation in the separation. Lowering the CMC of anionic surfactant by adding nonionic surfactant has been demonstrated and applied in the MEUF processes for treating metal ions [5,17].

According to Rubbing's regular solution theory for mixed micelles, the mixed CMC ( $C_{12}$ ) for  $C_{12}E_m$  + metal dodecyl sulfates system obtained by mixing the two surfactants is given by Eq. (4)

$$\frac{1}{C_{12}} = \frac{\alpha_1}{f_1 C_1} + \frac{1 - \alpha_1}{f_2 C_2} \tag{4}$$

where  $\alpha_1$  is the mole fraction of surfactant 1 in the total mixed solution and  $f_1$  and  $f_2$  are the activity coefficients of surfactant 1 and 2 in mixed micelle.  $C_1$  and  $C_2$  are the CMCs of the single surfactants 1 and 2, respectively.

In the case of ideal behavior,  $f_1 = f_2 = 1$  and hence Eq. (1) reduces to the form:

$$\frac{1}{C_{12}} = \frac{\alpha_1}{C_1} + \frac{1 - \alpha_1}{C_2}$$
(5)

As proposed by Clint for ideal mixed micelles [19,20].



**Fig. 6.** Effect of Brij35–SDS mixed micelles on permeate flux and the  $Zn^{2+}$  rejection.  $[Zn^{2+}] = 100 \text{ ppm}, [TMP] = 2 \text{ bar}, [SDS] = 5 \text{ mM}, T = 25 \circ \text{C}.$ 

Synergistic behaviors of mixed surfactant systems may be exploited to reduce the total amount of surfactant used in particular applications resulting in reduction of cost and environment impact The mixed system almost invariably yields enhanced interfacial properties (e.g. decreased CMC, higher surface activity) with respect to the individual surfactants, in what is termed synergism [21].

As shown in Fig. 6, the rejection of  $Zn^{2+}$  increases when the Brij35/SDS molar ratio increases from 0 to 0.5 at a fixed SDS concentration of 5 mM. The  $Zn^{2+}$  rejection efficiency increases with an increase of Brij35 nonionic surfactant. The increase of the rejection factor is due to that increase of the nonionic surfactant dosage causes a decrease in the CMC and more SDS molecules participate in micelle formation thus resulting in higher  $Zn^{2+}$  rejection.

Huang et al. [5] indicated that when the Brij35/SDS molar ratio is more than 0.5, the rejection factor declines noticeably. This phenomenon occurs when the nonionic surfactant: SDS molar ratio is more than 0.5; the nonionic surfactant lowers the degree of counterion binding more than it lowers the CMC. Consequently, the Brij35/SDs molar ratio should be given at near 0.5 for maximum Zn<sup>2+</sup> rejection (98%) [13].

The variation of permeate flux versus the Brij35/SDS molar ratio is shown in Fig. 6. Our measurement of the permeate flux revealed that a decline occurs as molar ratio is increasing. The reason of this observation can be explained in the relation of the solution viscosity and membrane pore blocking which are attributed to the addition of nonionic surfactants, which results in the increase of hydraulic resistance against the flux.

Although, the addition of nonionic surfactants has the benefits of reducing the CMC of SDS and improving the  $Zn^{2+}$  removal efficiency, but it makes the possibility of membrane fouling undesirably. Other disadvantage of non-anionic surfactant adding is its recovery problems which is lower for anionic surfactants [16].

### 3.5. Effect of ligand concentrations on permeation flux and the $Zn^{2+}$ rejection factor

Wastewaters generated by electroplating industry usually contain a variety of ligands such as EDTA. These chelating agents are used to prevent the precipitation of metal hydroxide in the plating solution. To treat this type of wastewater with MEUF successfully, the effects of the type and concentration of the ligands on metal removal efficiency must be considered [16].

As shown in Fig. 7, the  $Zn^{2+}$  rejection efficiency at neutral pH decreases gradually with an increase in ligand concentration at



**Fig. 7.** Effect of L/M ratio on permeate flux and the  $Zn^{2+}$  rejection.  $[Zn^{2+}] = 100$  ppm, [TMP] = 2 bar, [SDS] = 6 mM,  $T = 25 \degree C$ .

fixed SDS and Zn<sup>2+</sup> concentrations of 6 mM and 100 ppm, respectively.

It is due to the competitive complexation of zinc with SDS and ligands. EDTA has much higher affinity than SDS for zinc, Furthermore many of free metal ions were not absorbed on formed micelles and consequently Zn<sup>2+</sup> rejection reduced.

According to our experiments, the variation of the EDTA ligand concentration showed a negligible effect on the permeate flux and the obtained results were identical to Fig. 4 at the fixed 6 mM SDS concentration.

# 3.6. Effect of solution pH on permeation flux and $Zn^{2+}$ the rejection factor

As shown in Fig. 8, the  $Zn^{2+}$  rejection factor increases gradually with an increase in solution pH at fixed SDS and  $Zn^{2+}$  concentrations of 6 mM and 100 ppm, respectively. This is due to the competition of H<sup>+</sup> trapped on the micelle surface with metal ions. At low pH (acidic condition), there are more H<sup>+</sup> compared with



**Fig. 8.** Effect of solution pH on permeate flux and the  $Zn^{2+}$  rejection.  $[Zn^{2+}] = 100$  ppm, [TMP] = 2 bar, [SDS] = 6 mM, T = 25 °C.

Comparison of some membranes and their treatment performance for zinc removal.

Table 2

basic condition (pH > 10). Consequently, the effective binding sites are occupied by hydrogen ions. But in solutions with high pH there is less the ions with the same charge, as a result  $Zn^{2+}$  rejection increased. However, the results show that the MEUF process is not practical when the synthetic wastewater is intensively acidic.Fig. 8 shows that the increasing the solution pH has very little effect on permeation fluxes. This phenomenon can be explained by the reason that the shape and the aggregation number of micelles changes with the increase of the feed solution pH and pore blocking can be more intense.

Table 2 summarizes the characteristics of some of the membranes and their treatment performance for zinc removal from wastewaters published in the last years and gives a comparison between those articles and present work. It is observed that NF membranes with Polymeric skin materials have a higher removal efficiency, but this type of membrane processes have inherent problems include high energy consumption and low permeate flux. In our MEUF experiments, using of low-energy requirements gives high removal efficiency like NF membrane and higher permeate flux [23,24]. On the other hand, the efficient removal of  $Zn^{2+}$  at low  $Zn^{2+}$  feed concentrations is a very important feature of MEUF. Other hybrid separation processing are practical when initial  $Zn^{2+}$ feed concentrations higher than 300 mg/L [22].

#### 4. Statistical analysis

The Standard deviation and standard error percentage between the data in each trial for rejection factor and permeate flux are as follow: rejection factor  $\sim$ -2.15 to 3.053% and 1.24 to 1.76% and permeate flux  $\sim$ -0.25 to 0.50% and 0.15 to 0.29% respectively. The 95% prediction interval is the range in which one can expect any individual value to fall into 95% of the time.

#### 5. Conclusions

Micellar-enhanced ultrafiltration was applied to remove  $Zn^{2+}$  from synthetic wastewater using spiral-wound ultrafiltration membrane and excellent separation performance was observed. The effect of some important parameters were investigated, including operating time, the feed SDS concentration, operating pressure, the mixture of SDS and Brij, ligand–zinc ratio (L/M) and solution pH. The results indicated that the flux increased with increasing operating pressure, and cross-flow velocity. The permeate fluxes decreased while the feed SDS concentration, nonionic surfactant: SDS molar ratio increased and operating time extended, and ligand– $Zn^{2+}$  ratio (L/M) and solution pH had negligible effects on the permeate flux. Although the permeate flux of MEUF with SDS is higher than for MEUF with mixed surfactants.

The rejection of zinc increased along with increasing feed SDS concentration, Brij35/SDS molar ratio, solution pH and extending operating time, whereas the rejection of  $Zn^{2+}$  decreased along with increasing ligand concentration, and operating pressure had negligible effect on the rejection of  $Zn^{2+}$ . In general, MEUF by spiral-wound ultrafiltration membrane has good rejection of  $Zn^{2+}$  under different operating conditions, as the rejections were higher than 98.0%.

Type of application	Skin materials	Type of module	Initial Zn <sup>2+</sup> concentration (mg/L)	Zn <sup>2+</sup> rejection (R%)	Ref.
UF combined with additives of natural origin	PVDF	Hollow fibre	50-450	>90%	[22]
Nanofiltration	Polymeric	Spiral-wound	10-100	90%	[23]
Nanofiltration	Polymeric	Spiral-wound	295	96–99%	[24]
Present work	Regenerated cellulose	Spiral-wound	100	>98%	

The results show that mixed anionic–nonionic surfactant system is not very effective and economical for reducing the dosage of surfactant. Using nonionic surfactant also generates some problem for recovery of the main surfactant. When the initial SDS concentration was below the CMC (6 mM) unexpectedly high  $Zn^{2+}$  rejection (98%) was obtained due to concentration polarization occurring near the membrane–solution interface. The study demonstrates the potential practicality of the MEUF technique for the removal of heavy metal ion pollutants such as  $Zn^{2+}$  at low surfactant concentrations. Also, the MEUF process is not useful when the synthetic wastewater is intensively acidic and contains variety of ligands.

#### References

- I. Xiarchosa, A. Jaworskab, G. Zakrzewska-Trznadelb, Response surface methodology for the modelling of copper removal from aqueous solutions using micellar-enhanced ultrafiltration, J. Membr. Sci. 321 (2008) 222–231.
- [2] Y. Hea, G. Li, H. Wanga, J. Zhaoa, H. Suc, Q. Huangc, Effect of operating conditions on separation performance of reactive dye solution with membrane process, J. Membr. Sci. 321 (2008) 183–189.
- [3] H. Kim, K. Baek, J. Leec, J. Iqbala, J.W. Yang, Comparison of separation methods of heavy metal from surfactant micellar solutions for the recovery of surfactant, Desalination 191 (2006) 186–192.
- [4] T.A. Kurniawan, G.Y.S. Chan, W.H. Loa, S. Babel, Physico-chemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J. 118 (2006) 83–98.
- [5] J.H. Huang, G.M. Zeng, Y.Y. Fang, Y.H. Qu, X. Li, Removal of cadmium ions using micellar-enhanced ultrafiltration with mixed anionic–nonionic surfactants, J. Membr. Sci. 326 (2009) 303–309.
- [6] L. Yurlova, A. Kryvoruchko, B. Kornilovich, Removal of Ni(I1) ions from wastewater by micellar-enhanced ultrafiltration, Desalination 144 (2002) 255–260.
- [7] L. Aguirre, V. Garcia, E. Pongr\_acz, R.L. Keiski, The removal of zinc from synthetic wastewaters by micellar-enhanced ultrafiltration: statistical design of experiments, Desalination 240 (2009) 262–269.
- [8] J. Ren, Z. Li, F.S. Wong, A new method for the prediction of pore size distribution and MWCO of ultrafiltration membranes, J. Membr. Sci. 279 (2006) 558–569.

- [9] M. Muthukrishnan, B.K. Guha, Heavy metal separation by using surface modified nanofiltration membrane, Desalination 200 (2006) 351–353.
- [10] F. Ferella, M. Prisciandaro, I.D. Michelis, F. Veglio, Removal of heavy metals by surfactant-enhanced ultrafiltration from wastewaters, Desalination 207 (2007) 125–133.
- [11] E. Sampera, M. Rodiguez, M.A. De la Rubiab, D. Pratsa, Removal of metal ions at low concentration by micellar-enhanced ultrafiltration (MEUF) using sodium dodecyl sulfate (SDS) and linear alkylbenzene sulfonate (LAS), Sep. Purif. Technol. 65 (2009) 337–342.
- [12] K. Xu, G.M. Zeng, J.H. Huang, J.Y. Wu, Y.Y. Fang, G. Huang, J. Li, B. Xi, H. Liu, Removal of Cd<sup>2+</sup> from synthetic wastewater using micellar-enhanced ultrafiltration with hollow fiber membrane, Colloids Surf. A: Physicochem. Eng. Aspects 294 (2007) 140–146.
- [13] Y.Y. Fang, G.M. Zeng, J.H. Huang, J.X. Liu, X.M. Xu, K. Xu, Y.H. Qu, Micellarenhanced ultrafiltration of cadmium ions with anionic–nonionic surfactants, J. Membr. Sci. 320 (2008) 514–519.
- [14] G.M. Zeng, K. Xu, J.H. Huang, X. Li, Y.Y. Fang, Y.H. Qu, Micellar enhanced ultrafiltration of phenol in synthetic wastewater using polysulfone spiral membrane, J. Membr. Sci. 310 (2008) 149–160.
- [15] Standard Methods for the Examination of Water and Wastewater, 17th ed., Ammerican Public Association/American Water Works Association/Water Environment Federation, Washington, DC, 1989.
- [16] M. Aoudia, N. Allal, A. Djennet, L. Toumib, Dynamic micellar enhanced ultrafiltration: use of anionic (SDS)-non-ionic (NPE) system to remove Cr<sup>3+</sup> at low surfactant concentration, J. Membr. Sci. 217 (2003) 181–192.
- [17] Ch.W. Li, Ch.K. Liu, W.Sh. Yen, Micellar-enhanced ultrafiltration (MEUF) with mixed surfactants for removing Cu (II) ions, Chemosphere 63 (2006) 353–358.
- [19] D.N. Rubingh, in: K.L. Mittal (Ed.), Sol. Chem. Surf., vol. 3, Plenum Press, New York, 1979, p. 337.
- [20] J.H. Clint, J. Chem. Soc., Faraday Trans. 73 (1975) 1327.
- [21] A. Khan, E.F. Marques, Synergism and polymorphism in mixed surfactant systems, Curr. Opin. Colloid Interface Sci. 4 (2000) 402–410.
- [22] E. Katsou, S. Malamis, K. Haralambous, Examination of zinc uptake in a combined system using sludge, minerals and ultrafiltration membranes, J. Hazard. Mater., in press, corrected proof.
- [23] N.B. Fares, S. Taha, G. Dorange, Influence of the operating conditions on the elimination of zinc ions by nanofiltration, Desalination 185 (2005) 245-253.
- [24] N.E. Belkhouche, M.A. Didi, S. Taha, N. Ben Fares, Zinc rejection from leachate solutions of industrial solid waste effects of pressure and concentration on nanofiltration membrane performance, Desalination 239 (2009) 58–65.