



Simulation of micellar enhanced ultrafiltration by multiple solute model

S.M. Manchalwar, V.A. Anthati, K.V. Marathe*

Department of Chemical Engineering, Institute of Chemical Technology, Mumbai 400019, India

ARTICLE INFO

Article history:

Received 6 January 2010
Received in revised form 10 August 2010
Accepted 13 August 2010
Available online 22 August 2010

Keywords:

Micellar enhanced ultra filtration
Modeling
Multiple solutes
Selective separation

ABSTRACT

Multiple solute ultrafiltration models in micellar enhanced ultra filtration (MEUF) have been studied, for experimental results of selective separation of Cu (II) and Co (II) with anionic surfactant, sodium dodecyl sulfate (SDS) and imino diacetic acid (IDA) as chelating agent using synthetic waste water. This model is based on mass balance analysis coupled with the filtration theory, resistance-in-series model and gel polarization model. This model is characterized by the parameters, membrane resistance R_m , membrane permeability P_m , back transport coefficient K_b , K_{bi} and mass transfer coefficient k_i . These parameters are estimated by using the Levenberg–Marquardt method coupled with the Gauss–Newton algorithm.

Due to cross currents caused by the superficial velocity, some solutes are removed from the membrane surface and go into the bulk known as back transport effect. Hence back transport coefficient plays significant role in explaining the extent of micellization. The simulation results show a good agreement with the experimental data of permeate quality and flux. The consideration of negligible gel thickness is suitable for dilute solutions.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Micellar enhanced ultrafiltration (MEUF) [1] is one of the surfactant enhanced non-classical extraction process [2] and is an established research field for separation of organic and inorganic pollutants present in trace amount in aqueous stream. Recent advances in this field are the removal of heavy metals and organics solutes from the dilute industrial waste, simultaneously and selectively, when coupled with other enhanced ultrafiltration process. In the light of full-scale application of MEUF in waste water treatment industries, it is necessary to predict the performance of this process mathematically, so as to proceed towards the commercializing step.

A number of engineering models are available today for analyzing the performance of classical ultrafiltration process. The key factor determining the performance of the ultrafiltration membranes is the gel polarization where the rejected solutes get deposited on the membrane surface. The gel polarization causes membrane fouling and leads to the drop in permeate flux. The most common model used in describing the performance of ultrafiltration is the resistance-in-series model [3–6]. The resistance-in-series model assumes that the flux of permeate is proportional to the transmembrane pressure and inversely proportional to the viscosity of the suspending solution where the parameter of hydraulic resistance is being introduced. The hydraulic resistance is the total resistance exerted by the mem-

brane and solutes. Damak et al. [7] developed a fluid dynamic model for the cross-flow filtration tubular membranes. A method of coupling the Navier–Stokes and Darcy equations, using a finite difference technique to simulate laminar fluid flow in the tube and in the porous wall was presented.

The models proposed in the literature are only suitable to predict the performance of ultrafiltration with the single solute system [8–12]. When multiple solutes system is used, these models can only predict the total permeate concentration of the system. In the industrial application multiple solutes systems are often encountered and the mass transport of each solute in the multiple solutes system is important. But till date very few of them are applied for studies in the performance analysis of MEUF. Chhatre and Marathe [8,9] have done the performance analysis of MEUF in batch mode using the combination of equilibrium model, mass transfer model and resistance-in-series model. This model was further extended to study the binary mixture of solutes by Das et al. [10]. Further Kamble and Marathe [11] did the membrane characteristics and fouling study in MEUF. Jadhav et al. [12] developed a mathematical model to study the separation of organic solutes by MEUF. All the above-mentioned studies were done on the dead-end system of MEUF. Changing trends suggests that the cross-flow mode of MEUF is more popular than the dead-end mode, but negligible amount of modeling or simulation work has been done in cross-flow MEUF.

Copper and cobalt may coexist in the waste streams from the metal winning and electroplating industries. Moreover, these metals are very close in the transition metal series of periodic table. The experimental and simulation results obtained in this study would be generic in nature for the selective separation of other heavy met-

* Corresponding author. Tel.: +91 22 33611001; fax: +91 22 33611002.
E-mail address: kv.marathe@ictmumbai.edu.in (K.V. Marathe).

Nomenclature

a	constant in Eq. (13), defined by Eqs. (14)–(16)
A	effective area for filtration (m^2)
C_b	total concentration of solutes in the bulk (kg/m^3)
C_g	total concentration of solutes in the gel layer (kg/m^3)
C_p	total concentration of solutes in the permeate (kg/m^3)
H	effective filtration thickness (m)
J_v	volume flux of permeate ($\text{m}^3/\text{m}^2 \text{ s}$)
$J_{v,ss}$	volume flux of permeate at the steady-state condition ($\text{m}^3/\text{m}^2 \text{ s}$)
k	mass transport coefficient (m/s)
K_b	total back transport coefficient (m^2)
M_{bt}	total back transport mass up to time t (kg)
n	total number of solutes
N	number of parameters
P_m	permeability coefficient (m^2)
q	constant in Eq. (28)
r^2	coefficient of determination
R	true rejection
R_g	gel layer resistance (m^{-1})
R_H	hydraulic resistance (m^{-1})
R_m	resistances due to the membrane (m^{-1})
R_o	observed rejection
t	filtration time (s)
v	superficial velocity (m/s)

als using MEUF. When the waste stream contains Cu^{2+} and Co^{2+} ; by the addition of surfactant to the solution it results in simultaneous removal of both the metals by ultrafiltration. When chelating agent (IDA) is added to the same solution it selectively forms metal chelate with Cu^{2+} only, and this complex, which is smaller in size, passes through the membrane, while Co^{2+} which electro statically binds with surfactant micelle is retained by the membrane resulting in selective separation of copper and cobalt.

Thus the measurable objectives in the present study are:

- (1) To select an appropriate model for predicting the performance of MEUF.
- (2) To estimate the parameters of the model from the experimental data obtained from selective separation of Cu^{2+} and Co^{2+} with anionic surfactant.
- (3) To validate the mathematical model by comparing the simulation results with the experimental data.

2. Materials and methods

2.1. Chemicals

The surfactant sodium dodecyl sulfate (SDS) and chelating agent imino diacetic acid were received from Merck Ltd., Mumbai, India were used as received without further purification. Copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and Cobalt (II) sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) were procured from Merck Ltd., Mumbai, India were used as source of metal ions. Feed solution pH was adjusted by using 0.5 N KOH and 0.5 N HCl. KOH and HCl were procured from S.D. fine chemicals Ltd., Mumbai, India. Deionized water was used in all experimental runs. For the analysis of metals, oxalic acid was used as eluent, 4-(2-Pyridylazo) resorcinol monosodium salt indicator (PAR), acetic acid (CH_3COOH) and 25% ammonia solution (NH_4OH) were used in post column reagent preparation, and were received from S.D. fine chemicals Ltd., Mumbai, India. For the anal-

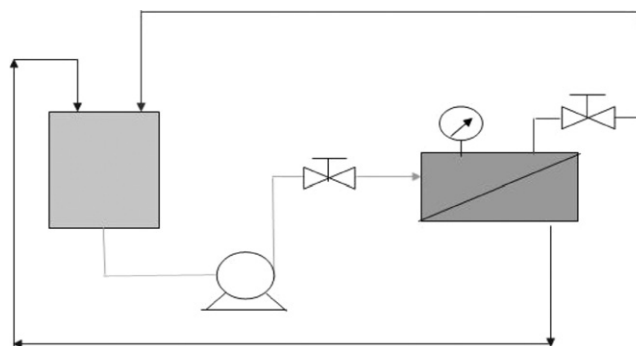


Fig. 1. Schematic presentation of the continuous cross-flow ultrafiltration.

ysis of SDS, sodium phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$), chloroform (CCl_4), sulfuric acid (H_2SO_4) and methylene blue were procured from S.D. fine chemicals Ltd., Mumbai, India. All the chemicals used were of analytical grade and had an assay of $\geq 98.5\%$.

2.2. Membrane

The membrane used in all experiments was polyethersulfone (PES) having 30 kDa molecular weight cutoff (MWCO) and 0.02 m^2 effective membrane area was purchased from Sartorius (Germany). PES membranes are hydrophobic in nature, and these can withstand a wide pH range of 1–14, compatible to almost all chemicals and it can sustain up to 75°C temperature.

2.3. Ultrafiltration setup

Ultrafiltration experiments were carried out in a cross-flow continuous mode system, from Sartorius, Germany. The micellar solution with solutes was placed in a feed tank of 500 ml capacity. 200 ml feed solution was taken for each run. The feed solution was continuously stirred by magnetic stirrer to maintain uniform concentration in the feed tank. A peristaltic pump was used to feed the solution in the cell. Retentate and permeate streams were recycled to feed tank to make the process continuous. Fig. 1 shows the schematic of the continuous cross-flow ultrafiltration. There are three pressure sensors for measuring the inlet pressure, retentate pressure and permeate pressure. Time of filtration, inlet, retentate, permeate pressures and transmembrane pressure (TMP) were continuously recorded on a computer. 1.5 ml of sample was taken from permeate stream for the analysis purpose.

2.4. Experimental procedure

Synthetic wastewater was produced by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ salts in deionized (DI) water. 50 mM concentration of surfactant, chelating agent, Cu^{2+} and Co^{2+} stock solutions were prepared and all solutions of desired concentrations were prepared by diluting stock solution with DI water. Before each experimental run DI water flux was measured to check the membrane permeability. 200 ml of feed solution was taken for each experimental run and pH was adjusted by using 0.5 N KOH or 0.5 N HCl. After each experimental run membrane was back flushed thoroughly with DI water, and then again water flux was measured to ensure uniform membrane permeability. All the experiments were carried out at constant TMP of 49 kPa and at room temperature of $27 \pm 2^\circ\text{C}$. 1.5 ml of samples were taken from permeate side for analysis purpose and permeate flux was measured. All the experiments were carried out at standard experimental conditions (Table 1) unless otherwise mentioned.

Table 1
Standard experimental conditions.

Feed solution volume	200 ml
Cu ²⁺ concentration in feed	1 mM
Co ²⁺ concentration in feed	1 mM
Cross-flow rate	100 ml/min
pH of feed solution	3.4
Surfactant to metal ratio (S/M)	7.0
Chelating agent to metal ratio (C/M)	1.0
Transmembrane pressure (TMP)	49 kPa
Temperature	27 ± 2 °C

2.5. Analysis

The concentration of Cu²⁺ and Co²⁺ in permeate samples were analyzed by “High Performance Ion chromatography” (HPIC), Dionex, USA with UV absorbance detector. The column used for the analysis was “ION Pac CS5A” with 50 mM oxalic acid of pH 4.8 as mobile phase. By using post column reagent (0.4 mM PAR/1 M CH₃COOH/3 M NH₄OH) ppb level concentrations of metals were detected on UV absorbance detector at λ_{max} = 520 nm. Retentate concentration of metals was calculated by using mass balance. The retentate concentration was calculated by the following equation

$$C_R = \frac{(V_F C_F - V_P C_P)}{V_R} \quad (1)$$

where C_R, C_F and C_P represent the metal ion concentration in the retentate, in the feed initially, and in permeate, respectively. V_F, V_P and V_R are the initial feed, the permeate and the retentate volume, respectively. % Rejection for copper and cobalt are calculated by using following formula.

$$\% \text{Rejection of Cu}^{2+} = \% \text{Rof Cu}^{2+} = 1 - [Cu^{2+}]_p / [Cu^{2+}]_R \quad (2)$$

$$\% \text{Rejection of Co}^{2+} = \% \text{Rof Co}^{2+} = 1 - [Co^{2+}]_p / [Co^{2+}]_R \quad (3)$$

where the subscript p and R indicate corresponding quantity as measured in permeate and retentate solutions, respectively.

The concentration of SDS in permeate was analyzed on UV–visible spectrophotometer at λ_{max} of 658 nm by adding methylene blue indicator and chloroform to the samples. The concentration of SDS in retentate was calculated by using mass balance.

3. Model formulation

The factors, one has to consider, to select an appropriate model are system dependent. They are number of solutes, concentration of solute, operating regime (pressure controlled/mass transfer controlled), mode of operation (dead-end/cross-flow).

In the present system for selective separation of Cu²⁺ and Co²⁺ the total numbers of solutes present are four, i.e. Cu²⁺, Co²⁺, SDS (sodium dodecyl sulfate), IDA (Iminodiacetic acid). As can be seen from Table 2 all the experiments were carried out in dilute range of concentration. The transmembrane pressure of the system was kept constant at 49 kPa for all the experiments, suggesting the system is mass transfer controlled. All the MEUF experiments were carried out on cross-flow ultrafiltration membrane module.

Considering the above factors, the model based on the mass balance analysis coupled with the filtration theory (Darcy’s law), resistance-in-series and gel polarization models, applicable to multiple solute systems [13] was selected.

3.1. Details of model

During filtration process, the solvent is transported by pressure-driven convective flow through the pores. Separation occurs because the solvent is filtered through some of the pores in the membrane. The membrane continuously rejects the solutes and

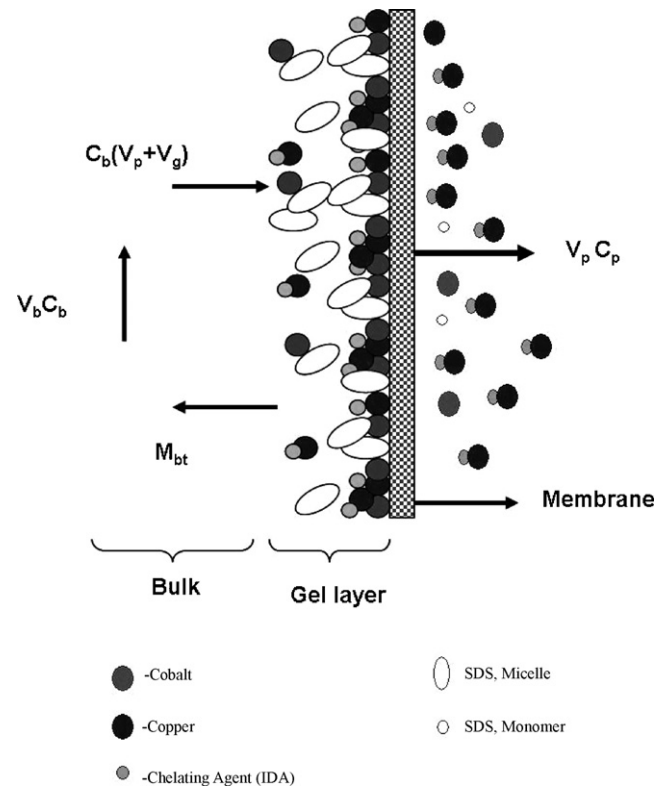


Fig. 2. Overall mass balance, over the multiple solutes system of continuous cross-flow ultra filtration.

the rejected solutes are deposited on the membrane surface. At the same time due to cross currents and stirring action caused by the superficial velocity, some solutes are removed from the membrane surface and go into the bulk (back transport effect). Thus, in the multiple solutes system of continuous cross-flow ultra filtration, the assumptions include:

1. The membrane rejects the multiple solutes by sieving action and the solute–solute interactions are neglected.
2. Since the solute–solute interactions are neglected, the concentration of each solute can be obtained by mass balance analysis with the consideration of back transport effect.
3. In the gel layer, each solute will have its independent value of diffusion, mass transfer and back transport coefficient.

Basis of the above assumptions can be found in Ahmed et al. [13].

In the multiple solutes system of continuous cross-flow ultra filtration with n solutes ($i = 1, 2, 3, \dots, n$) in a solvent, the boundary layer is first formed over the membrane within a very short period of time (within 1 s). Subsequently, the buildup of extra resistances caused due to the deposition of solutes over the membrane surface, results in the flux decline. The deposited layer over the membrane is termed as “gel layer” and the concentration of each solute in the gel layer is termed as “gel concentration”.

Now, consider the overall mass balance over the multiple solutes system of continuous cross-flow ultra filtration as shown in Fig. 2. During the filtration process, some of the solutes in the bulk are transported into the permeate stream through the boundary layer and gel layer. However, for the simplicity of the model, the mass balance analysis in the boundary layer is ignored by assuming that the total mass of solute obtained in the boundary layer is negligible compared to the total mass of solute obtained in the gel layer. This assumption is applicable for the system operated under convection

Table 2
Parameter values of feed properties and rejection coefficients of Co and Cu.

Run	Flow rate (ml/min)	Feed properties					% R Co ²⁺	% R Cu ²⁺
		pH	Co ²⁺ (mM)	Cu ²⁺ (mM)	SDS (mM)	IDA (mM)		
1	250	4.8	1	1	14	3	85.56	29.27
2	200	4.8	1	1	14	3	93.99	31.79
3	150	4.8	1	1	14	3	98.69	34.10
4	100	4.8	1	1	14	3	99.10	48.82
5	100	4.8	1	1	10	3	84.95	5.11
6	100	4.8	1	1	12	3	90.43	6.48
7	100	4.8	1	1	16	3	97.28	8.70
8	100	4.8	1	1	14	1	98.72	17.96
9	100	4.8	1	1	14	2	95.90	16.38
10	100	4.8	1	1	14	4	83.02	3.06
11	100	4.8	1	1	14	5	81.92	11.32
12	100	2.8	1	1	14	3	97.54	90.47
13	100	3	1	1	14	3	98.10	86.02
14	100	3.2	1	1	14	3	98.80	82.64
15	100	3.4	1	1	14	3	98.74	77.99
16	100	3.6	1	1	14	3	97.68	55.60
17	100	3.8	1	1	14	3	97.30	41.32
18	100	4	1	1	14	3	96.82	25.04
19	100	4.2	1	1	14	3	97.52	12.95
20	100	4.4	1	1	14	3	97.60	7.65
21	100	4.6	1	1	14	3	96.85	5.93
22	100	5	1	1	14	3	95.61	4.04
23	100	5.2	1	1	14	3	92.37	6.57
24	100	5.6	1	1	14	3	87.79	4.29

current created by cross-flow velocity or stirring action. After filtration time, t , the total solutes rejected by the membrane result in the solutes concentration rise in the gel layer and the remainder is being transported back into the bulk by convection current created by the superficial velocity.

As shown in Fig. 2, copper forms chelate with IDA and transported in the permeate stream, whereas cobalt is micellized with SDS and retained by the membrane. The unbound monomer species are also collected in permeate.

The mass of the total solutes in the gel layer at any filtration time, t , is

$$V_g C_g = (V_p + V_g) C_b - V_p C_p - M_{bt} \quad (4)$$

where V_g : is the total volume of gel layer up to time t ; C_g : is the total concentration of solutes in the gel layer; V_p : is the total volume of permeate up to time t ; C_b : is the total concentration of solutes in the bulk; C_p : is the total concentration of solutes in the permeate; M_{bt} : is the total back transport mass up to time t .

The total mass balance of the system is the summation of mass balances of each individual solute. Therefore, Eq. (4) can also be written in terms of concentration of solute i in the gel layer (C_{gi}), concentration of solutes i in the permeate (C_{pi}), concentration of solute i in the bulk (C_{bi}) and back transport mass of solute i (M_{bti}) up to time t .

$$V_g \sum_{i=1}^n C_{gi} = (V_p + V_g) \sum_{i=1}^n C_{bi} - V_p \sum_{i=1}^n C_{pi} - \sum_{i=1}^n M_{bti} \quad \text{for } i = 1, 2, 3, \dots, n \quad (5)$$

It has been assumed that the rate of back transport mass for each solute i is proportional to the superficial velocity, ν , and the concentration of the solute in the gel layer C_{gi} .

$$\frac{dM_{bti}}{dt} \propto \nu C_{gi} \quad (6)$$

Bhattacharjee and Datta [6] have introduced the back transport coefficient for solute i (K_{bi}), Integrate Eq. (6) with initial conditions

of $t=0$ and $M_{bti}=0$, then

$$M_{bti} = K_{bi} \nu C_{gi} t \quad (7)$$

Substituting Eq. (7) into Eq. (5) and rearranging in terms of total volume of permeate,

$$V_p \sum_{i=1}^n (C_{bi} - C_{pi}) = V_g \sum_{i=1}^n (C_{gi} - C_{bi}) + \nu t \sum_{i=1}^n (K_{bi} - C_{gi}) \quad (8)$$

Rearranging Eq. (8) in terms of gel layer thickness, Z , with $V_g = A \times Z$ as substitution, where A is the effective area for filtration, the equation gives

$$Z = \frac{V_p \sum_{i=1}^n (C_{bi} - C_{pi})}{A \sum_{i=1}^n (C_{gi} - C_{bi})} - \frac{\sum_{i=1}^n K_{bi} - C_{gi}}{A \sum_{i=1}^n (C_{gi} - C_{bi})} \nu t \quad (9)$$

This equation implies that the gel layer thickness reduces with time as the back transport coefficient increases due to more transport of the deposited species into the bulk solution.

The total volume flux of permeate, J_v , can be calculated by using the osmotic pressure model [14]. Kumar et al. [4] have proposed that hydraulic resistance, R_H is the sum of the membrane resistance, R_m and the gel layer resistance, R_g . Thus the total volume flux of permeate is

$$J_v = \frac{1}{A} \frac{dV_p}{dt} = \frac{\Delta P - \Delta \pi}{\mu(R_H)} = \frac{\Delta P - \Delta \pi}{\mu(R_m + R_g)} \quad (10)$$

where ΔP is the transmembrane pressure, $\Delta \pi$ is the osmotic pressure difference across the membrane, μ is the viscosity of the bulk.

The total volume flux of permeate can also be calculated by Darcy's law [6]:

$$J_v = \frac{1}{A} \frac{dV_p}{dt} = P_m \left(\frac{\Delta P_c}{\mu H} \right) \quad (11)$$

where ΔP_c is the pressure drop across the gel layer, P_m is the permeability coefficient and H is the effective filtration thickness. Thus the resistance-in-series model can be obtained by combining Eqs. (10) and (11):

$$J_v = \frac{\Delta P - \Delta \pi}{\mu(R_m + (Z/P_m))} \quad (12)$$

Substitution of Z from Eq. (9) into Eq. (12) and rearrangement in terms of $1/J_v$ gives

$$\frac{1}{J_v} = a_1 + a_2 V_p - a_3 t \quad (13)$$

where

$$a_1 = \frac{\mu R_m}{\Delta P - \Delta \pi} \quad (14)$$

$$a_2 = \frac{\mu}{AP_m(\Delta P - \Delta \pi)} \frac{\sum_{i=1}^n (C_{bi} - C_{pi})}{\sum_{i=1}^n (C_{gi} - C_{bi})} \quad (15)$$

$$a_3 = \frac{\mu v}{AP_m(\Delta P - \Delta \pi)} \frac{\sum_{i=1}^n K_{bi} C_{gi}}{\sum_{i=1}^n (C_{gi} - C_{bi})} \quad (16)$$

Eqs. (13)–(16) represent the volume flux of permeate in the multiple solutes system of the continuous cross-flow ultra filtration with n solutes ($i = 1, 2, 3, \dots, n$) in a solvent.

In order to estimate the concentrations of each solute in the permeate of the multiple solutes system of the continuous cross-flow ultra filtration, the mass of solute i where $i = 1, 2, 3$ and 4 in the gel layer at filtration time, t , can be written as

$$V_g C_{gi} = (V_p + V_g) C_{bi} - V_p C_{pi} - M_{bti} \quad (17)$$

Substituting Eq. (7) into Eq. (17) and rearranging in terms of total permeate volume up to time t gives

$$V_p (C_{bi} - C_{pi}) = AZ (C_{gi} - C_{bi}) + K_{bi} v C_{gi} t \quad (18)$$

Differentiation of Eq. (14) with respect to time t gives

$$(C_{bi} - C_{pi}) J_v = \frac{dZ}{dt} (C_{gi} - C_{bi}) + \frac{K_{bi} v C_{gi}}{A} \quad (19)$$

During steady-state filtration, the rate of solutes deposition over the membrane is equivalent to the rate of solutes being transported back to the membrane [6]. Thus, at constant volume and constant concentrations the gel layer thickness will remain constant and the rate of solutes deposition over the membrane can be written as

$$\frac{dZ}{dt} = 0 \quad (20)$$

Substituting of Eq. (20) into Eq. (19) and rearrangement in terms of concentration of solutes i in the permeate, C_{pi} , gives

$$C_{pi} = C_{bi} - \frac{K_{bi} v C_{gi}}{A J_{v,ss}} \quad \text{for } i = 1, 2, 3, 4, \dots, n \quad (21)$$

where the symbol $J_{v,ss}$ is the volume flux of permeate at the steady-state condition. In order to calculate the concentration of solute i in permeate, the concentration of solute i in the gel layer, C_{gi} , must be known. The concentration of solute i in the gel layer can be estimated by using the gel layer model [6]:

$$\frac{(C_{gi} - C_{pi})}{(C_{bi} - C_{pi})} = \exp\left(\frac{J_{v,ss}}{k_i}\right) \quad (22)$$

4. Algorithm for the solution of model

Eqs. (13)–(16), (21) and (22) are solved using the software package of Mat lab 7.0 following the algorithm as shown in Fig. 3.

1. The feed concentration of each solute and the parameters, operating pressure, feed flow rate are generally fixed in the experiment. The membrane parameters, which are R_m , $\Delta \pi$, P_m , μ , K_{bi} , k_i are obtained from the experimental data using the parameter estimation method.
2. Since the procedure is iterative, the initial estimation of the concentrations of each solute in permeate and the volume flux of permeate at steady state are needed. The concentrations of each

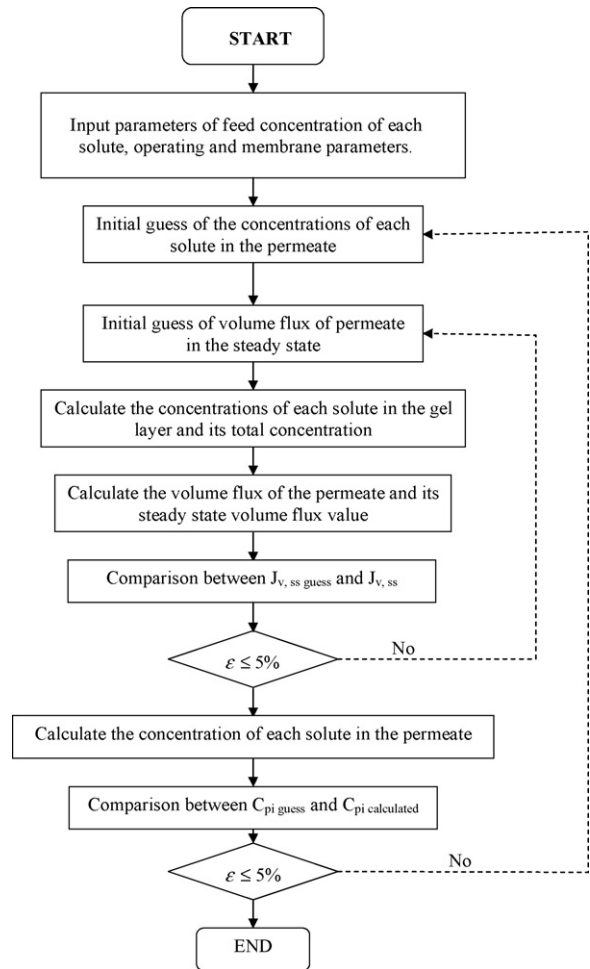


Fig. 3. Algorithm for the solution of the model.

solute in the gel layer are obtained from the gel polarization model (Eq. (22)).

3. The volume flux of permeate is estimated by solving Eqs. (13)–(16) simultaneously. The total permeate volume collected up to time t can be obtained by integrating Eq. (13) in the form of first order ordinary differential equation (ODE) as below:

$$\frac{dV_p}{dt} = \frac{A}{a_1 + a_2 V_p - a_3 t} \quad (23)$$

The V_p can be obtained by numerical integration of Eq. (23) using the higher-order Runge–Kutta method at equipaced time interval [15]. The volume flux of permeate at steady state is obtained when the calculated value of volume flux of permeate remained constant over a period of time.

4. The concentrations of each solute in the permeate is calculated from Eq. (21) when the comparison between the calculated value and the initial guess of volume flux of permeate at steady state show an error less than 5%.
5. The calculation is terminated when the error between the initial guess of the concentrations of each solute in permeate and the calculated value is less than 5%.

4.1. Parameter estimation method

Consider the multiple solutes system of continuous cross-flow ultra filtration with n solutes ($i = 1, 2, 3, \dots, n$) in a solvent. The number of parameters needed to be estimated is determined as

follows:

$$N = 4 + 2n \quad (24)$$

where N is the number of parameters to be determined in the system.

The slope in the linear plot of pure water flux (J_v) versus increasing transmembrane pressure (ΔP) indicates the value of membrane resistance (R_m). The mass transfer coefficients (k_i) of each solute can be estimated using the velocity variation method [16]. This is done by linearization of gel polarization model Eq. (22), which yields,

$$\ln\left(\frac{1}{R_{oi}} - 1\right) = \frac{1}{q} \left(\frac{J_{v,ss}}{v^\eta}\right) + \ln\left(\frac{1}{R_i} - 1\right) \quad (25)$$

The term R_{oi} is the observed rejection of solute i and is defined as

$$R_{oi} = 1 - \frac{C_{pi}}{C_{bi}} \quad (26)$$

The term R_i is the true rejection of solute i and is defined as

$$R_i = 1 - \frac{C_{pi}}{C_{gi}} \quad (27)$$

η is a constant whose value initially is assumed to be 0.8 for turbulent flow and 0.33 for laminar flow. The true rejection can be held constant by measuring the change in observed rejection with varying flow velocity at constant volumetric flux, J_v . The permeate flux can be simply held constant by maintaining a constant operating pressure, high enough to neglect minor osmotic back-pressure effects. The coefficient q and η are obtained from the best linear fit of data and the intercept of y -axis is the true rejection expression and the mass transfer coefficients can be expressed in term of superficial velocity, v :

$$k_i = qv^\eta \quad (28)$$

K_{bi} (back transport coefficient) can be determined from the linear plot of C_{pi} versus $vC_{gi}/AJ_{v,ss}$. The value of K_{bi} can be obtained from the slope.

To estimate the unknown parameters in Eqs. (13)–(16), several experimental data with V_p and t as independent variables and $1/J_v$ as dependent variable are collected. This data are fitted in to Eqs. (13)–(16) and the parameters are estimated using Levenberg–Marquardt with Gauss–Newton algorithm. Once the a_1 , a_2 , a_3 values are known, the unknown parameters $\Delta\pi$, P_m can be determined from Eqs. (14)–(16), respectively, when the viscosity of the bulk is obtained experimentally.

5. Results and discussion

The viscosity (μ) of the aqueous solution as 8.55×10^{-4} Pa s was found to be slightly less than the viscosity of water (8.7790×10^{-4} Pa s) due to the presence of surfactant in the aqueous stream. The value of R_m ($6.4137 \times 10^{-7} \text{ m}^{-1}$) is calculated from Eq. (14). The permeability coefficient (P_m) of the system depends on the type of solutes and the type of membrane used and was found to be $1.35 \times 10^{-8} \text{ m}^2$.

The typical value of back transport coefficient (K_{bi}) of every solute estimated in the present study was 0.035–0.0035 m^2 (Table 3). The deviation of the value shows that the turbulence created by continuous cross-flow ultra filtration resulted in higher back transport of the solutes compared to the turbulence created by stirred ultra filtration. The value of K_{bi} for Cu^{2+} and SDS was much greater than the value of Co^{2+} and SDS; this is because micellized species forms higher molecular weight complexes than non micellized species.

The mass transfer coefficient (k_i), value has the similar order of magnitude (10^{-6} m/s) with the volume flux of permeate

Table 3
Estimated parameters for the model.

Parameter	Value			
μ ($\times 10^{-4}$ Pa s)	8.7790			
M_r ($\times 10^{-7} \text{ m}^{-1}$)	6.4137			
P_m ($\times 10^{-8} \text{ m}^2$)	1.3582			
	Co^{2+}	Cu^{2+}	SDS	IDA
K_{bi}	0.026	0.0034	0.035	0.0035
k_i ($\times 10^{-6} \text{ m/s}$)	5.99	1.68	1.087	2.91

(10^{-6} m/s). Therefore, with the calculation of transport parameters, the gel polarization effect taken into consideration in the present study was valid. The estimated values are in good agreement with the typical value obtained by classical mass transfer models [11].

5.1. Comparison of simulation and experimental results for effect of feed flow rate

At standard experimental conditions the inlet flow rate was varied from 100 ml/min, to 250 ml/min. As shown in Fig. 4, at 100 ml/min, 50% of Cu^{2+} and nearly 100% of Co^{2+} was rejected. As flow rate increases, percentage rejection of Cu^{2+} decreases, simultaneously percentage rejection of Co^{2+} also decreases. The drop in rejection beyond 100 ml/min flow rate may be attributed to the fact that some of the Cu^{2+} chelates are forcibly pumped through the membrane pores and simultaneously some of the micelles in which Co^{2+} was bound electrostatically were also forcibly pumped through the membrane pores along with monomeric surfactant and unbound metals. It was observed that as inlet flow rate increases the permeate flux also increases which is in agreement with Cheryan 1998 [17]. Since the present study aims at selective separation of Cu^{2+} from Co^{2+} , the flow rate was empirically optimized at 100 ml/min, which gives maximum separation. The simulation results are in good agreement with the experimental data. The coefficients of determination (r^2) are more than 0.93 for the feed flow rate of 100–250 ml.

5.2. Comparison of simulation and experimental results for effect of surfactant to metal ratio (S/M)

The effect of surfactant to metal ratio on selective separation of Cu^{2+} from Co^{2+} was studied by varying S/M ratio from 5 to 8. From

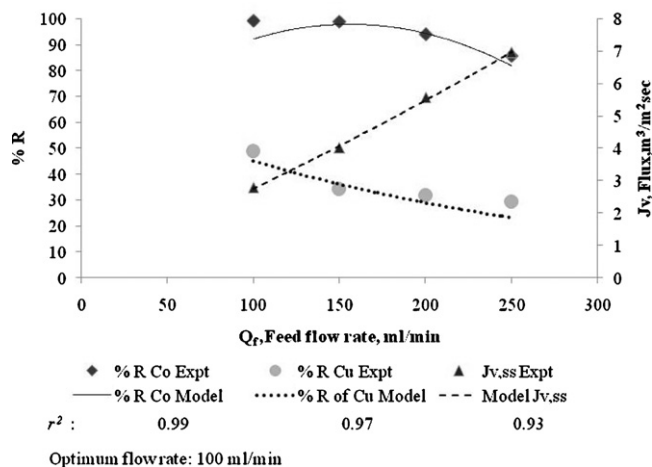


Fig. 4. Comparison of simulation and experimental results for effect of feed flow rate on percentage rejection and flux.

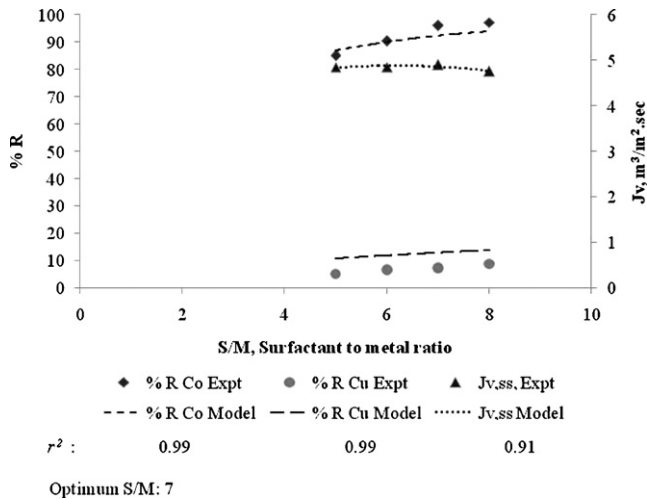


Fig. 5. Comparison of simulation and experimental results for effect of surfactant to metal ratio on percentage rejection and flux.

Fig. 5, by increasing surfactant to metal ratio, percentage rejection of Cu²⁺ was increased whereas in case of Co²⁺ at first increased up to S/M = 7 and then it was constant. It may be because at low S/M ratios complexation between Cu²⁺ and chelating agent was high resulting in less rejection of Cu²⁺, whereas in case of Co²⁺ at low S/M ratio, fewer sites are available for binding of Co²⁺ with the surfactant resulting in low rejection of Co²⁺. As S/M ratio increases more surfactant is available to bind electrostatically with metals that is why percentage rejection of metals increases which means that selective separation increases up to S/M = 7, after that still Cu²⁺ rejection increases but Co²⁺ rejection was constant means selective separation was decreased. Flux was constant up to S/M = 7, after that it decreases, because increase in surfactant concentration may cause gel layer formation which causes decrease in flux. Thus S/M ratio was optimized at 7 experimentally. The simulation results are in good agreement with the experimental data. The coefficients of determination (r²) are more than 0.99 for S/M ratio 5–8. Thus S/M ratio was optimized at 7 by statistical analysis also.

5.3. Comparison of simulation and experimental results for effect of chelating agent to metal ratio (C/M)

Fig. 6 shows that, after increasing chelating agent to metal ratio, percentage rejection of Cu²⁺ decreased at first up to C/M = 2 and then increases whereas in case of Co²⁺ rejection was decreased. It may be because at low C/M ratios complexation between metal and chelating agent was low, and metals bind with surfactant electrostatically that may be the reason for high rejection of Cu²⁺ and Co²⁺. As C/M increases up to 2.0 complexation between metals and chelating agent increases, percentage rejection of Cu²⁺ was decreased faster than percentage rejection of Co²⁺, which means selective separation increases up to 1.5 and further decreases. Above C/M ratio 2.0 percentage rejection of Cu²⁺ was increased whereas in case of Co²⁺ it was constant which means selective separation decreases it can be explained that at higher concentration of IDA, there is an interaction between surfactant and chelating agent [18]. Due to this the binding sites of the surfactant are blocked causing decrease in rejection of Co²⁺. Also from Fig. 6 steady-state flux value remains almost constant for all C/M ratios at constant feed flow rate. The simulation results are in good agreement with the experimental data. The coefficients of determination (r²) are more than 0.71 for C/M ratio 0.5–4.5. Thus from the simulation results the C/M ratio is optimized at 1.5.

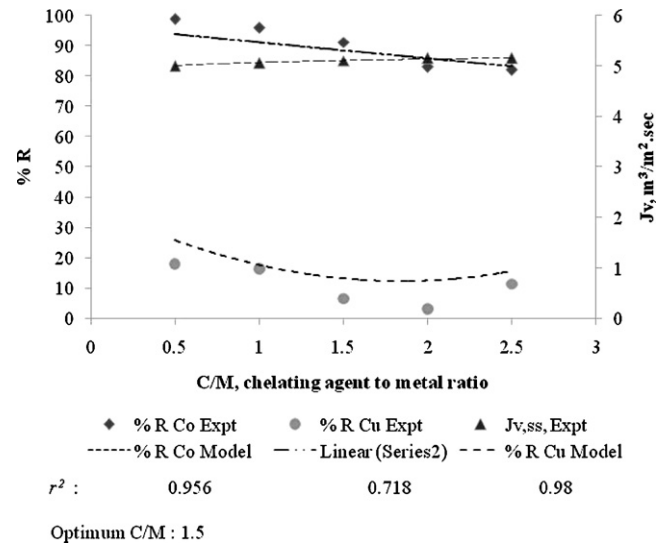


Fig. 6. Comparison of simulation and experimental results for effect of chelating agent to metal ratio on percentage rejection and flux.

5.4. Comparison of simulation and experimental results for effect of pH on selective separation

From Fig. 7 we can say that increasing pH of the feed solution the percentage rejection of Cu²⁺ decreases at first up to 4.8 pH and then it was nearly constant, whereas in case of Co²⁺ rejection was constant up to 4.8 and then it started decreasing. Therefore it can be concluded that as increasing pH of the feed solution at first selective separation was increased up to 4.8 and further increment of pH above 5.0 decreases in selective separation was observed. The flux was constant throughout. Complexation between Cu²⁺ and IDA (pK_a = 2.98) forms by the displacement of one or more weak acidic protons of the chelating agent by a metal. As the pH of the solution decreases to strong acidic region nearly 2.8 the deprotonation of complexing agent does not occur, therefore Cu²⁺ electrostatically binds with SDS and rejection was high. When pH of solution is higher nearly 4.8–5.0, the carboxylic group of complexing agent is deprotonated [18]; therefore, there will be more complexation between Cu²⁺ and IDA. Metal complex is small in size, which can easily pass through the membrane pores. Above pH 5.0, the

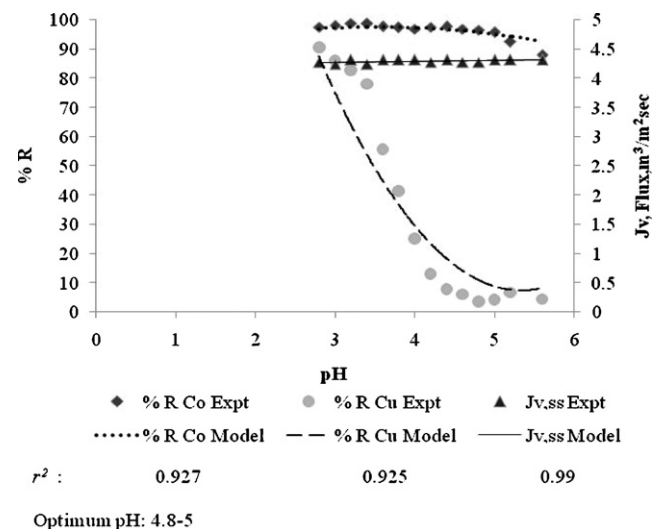


Fig. 7. Comparison of simulation and experimental results for effect of pH on percentage rejection and flux.

Table 4
Gel layer thickness.

Parameter		Z ($\times 10^{-6}$ m)
S/M	5	10.6
	6	8.98
	7	8.00
	8	7.32
C/M	0.5	12.8
	1.0	8.48
	1.5	7.67
	2.0	6.91
	2.5	6.13

rejection of Co^{2+} decreases resulting in to decrease in separation factor. This may be attributed to marginal complexation of Co^{2+} with IDA [18]. The simulation results are in good agreement with the experimental data. The coefficients of determination (r^2) are more than 0.92 for pH 2.8–5.6. Based on the simulation results the pH is optimized at 4.8–5.0.

5.5. Gel layer thickness

From Table 4 it can be seen that the gel layer thickness (from Eq. (9)) is of the order of few μm . Also it can be seen that, varying the concentration of surfactant or chelating agent in the feed solution results in negligible change in thickness of gel layer. From the experimental and simulation results (Figs. 5–7), we can say that variation in flux, which is a measure of fouling, is marginal or almost constant. So consideration of negligible gel thickness is suitable for dilute solutions.

6. Conclusions

Multiple solute ultrafiltration models are useful in predicting the performance of MEUF. Also the parameters estimated in present study are in good agreement with their typical values reported in literature, except for K_{bi} . As flow rate increases, percentage rejection of Cu^{2+} decreases, simultaneously percentage rejection of Co^{2+} also decreases. As inlet flow rate increases the permeate flux also increases. By increasing surfactant to metal ratio, percentage rejection of Cu^{2+} was increased, where as in case of Co^{2+} at first increased up to S/M = 7 and then it was constant. After increasing chelating agent to metal ratio, percentage rejection of Cu^{2+} decreased at first up to C/M = 2 and then increases, where as in case of Co^{2+} rejection was decreased. Increasing pH of the feed solution the percentage rejection of Cu^{2+} decreases at first up to pH 4.8 and then it was nearly constant, where as in case of Co^{2+} rejection was constant up

to 4.8 and then it starts decreasing. It was found that the value of back transport coefficient plays significant role in explaining the extent of micellization. The simulation results show a good agreement with the experimental data, both for permeate quality and flux. Consideration of negligible gel thickness is suitable for dilute solutions.

References

- [1] J.F. Scamehorn, S.D. Christian, R.T. Ellington, Use of micellar-enhanced ultrafiltration to remove multivalent metal ions from aqueous streams *Surfactant Based Separation Processes: Surfactant Science Series*, vol. 33, 1989, pp. 29–51.
- [2] H. Adamczak, K. Materna, R. Urbaniski, J. Szymanowski, Ultrafiltration of micellar solutions containing phenols, *J. Colloid Interface Sci.* 218 (1999) 359–368.
- [3] B. Tansel, W.Y. Bao, I.N. Tansel, Characterisation of fouling kinetics in ultrafiltration systems by resistance in series model, *Desalination* 129 (2000) 7.
- [4] N.S.K. Kumar, M.K. Yes, M. Cheryan, Ultrafiltration of soy protein concentrate: performance and modeling of spiral and tubular polymeric modules, *J. Membr. Sci.* 244 (2004) 235.
- [5] G. Gehlert, M. Adbulkadir, Fuhrmann, et al., Dynamic modeling of an ultra filtration module for use in a membrane bioreactor, *J. Membr. Sci.* 248 (2005) 63.
- [6] C. Bhattacharjee, S. Datta, Analysis of polarized layer resistance during ultra filtration of PEG-6000: an approach based on filtration theory, *Sep. Purif. Technol.* 33 (2003) 115.
- [7] K. Damak, A. Ayadi, B. Zeghami, P. Schmitz, A new Navier–Stokes and Darcy's law combined model for fluid flow in crossflow filtration tubular membranes, *Desalination* 161 (2004) 67–77.
- [8] A.J. Chhatre, K.V. Marathe, Dynamic analysis and optimization of surfactant dosage in micellar enhanced ultra filtration of nickel from aqueous streams, *Sep. Sci. Technol.* 41 (2006) 2755.
- [9] A.J. Chhatre, K.V. Marathe, Modeling and performance study of MEUF of divalent metal ions in aqueous streams, *Sep. Sci. Technol.* 43 (11) (2008) 3286–3304.
- [10] C. Das, S. DasGupta, S. De, Prediction of permeate flux and counterion binding during cross-flow micellar-enhanced ultra filtration, *Colloids Surf. A* 318 (2008) 125–133.
- [11] S.B. Kamble, K.V. Marathe, Membrane characteristics and fouling study in MEUF for the removal of chromate anions from aqueous streams, *Sep. Sci. Technol.* 40 (15) (2005) 3051–3070.
- [12] S.R. Jadhav, N. Verma, A. Sharma, P.K. Bhattachayra, Flux and retention analysis during micellar enhanced ultra filtration for the removal of phenol and aniline, *Sep. Purif. Technol.* 24 (2001) 541–557.
- [13] A.L. Ahmed, M.F. Chong, S. Bhatia, Ultrafiltration modeling of multiple solutes systems for continuous cross-flow process, *Chem. Eng. Sci.* 61 (2006) 5057–5069.
- [14] S.K. Karode, Unsteady state flux response: a method to determine the nature of the solute and gel layer in membrane filtration, *J. Membr. Sci.* 188 (2001) 9–20.
- [15] S.C. Chapra, R.P. Canale, *Numerical Methods for Engineers*, McGraw-Hill, New York, 1998.
- [16] A.L. Ahmed, M.F. Chong, S. Bhatia, Mathematical modeling and simulation of the multiple solutes system for nanofiltration process, *J. Membr. Sci.* 253 (2005) 103–115.
- [17] M. Cheryan, *Process Design in Ultra Filtration and Microfiltration Handbook*, Technomic Publishing Co. Inc., USA, 1998.
- [18] H. Kim, K. Baek, J. Lee, J. Iqbal, J.W. Yang, Comparison of separation methods of heavy metal from surfactant micellar solutions for the recovery of surfactant, *Desalination* 191 (2006) 186.