

## Effect of groups difference in surfactant on solubilization of aqueous phenol using MEUF

Fang Luo, Guang-Ming Zeng\*, Jin-Hui Huang, Chang Zhang, Yao-Yao Fang, Yun-Huan Qu, Xue Li, Dan Lin, Chun-Fei Zhou

College of Environmental Science and Engineering, Hunan University, 410082 Changsha, Hunan, PR China

### ARTICLE INFO

#### Article history:

Received 27 March 2009  
Received in revised form 24 August 2009  
Accepted 25 August 2009  
Available online 31 August 2009

#### Keywords:

Micellar-enhanced ultrafiltration (MEUF)  
Phenol  
Surfactant  
Groups difference

### ABSTRACT

Micellar-enhanced ultrafiltration (MEUF) was used to remove phenol from simulant aqueous solutions. The effect of groups difference of cationic surfactant on the solubilization of phenol was investigated through orthogonal experiment, namely, surfactants with the same length of hydrocarbon chain but different hydrophilic head group and vice versa. The effects on the solubilization of phenol of various operating parameters in the practical application of MEUF with OTAB were studied, including surfactant concentration, electrolyte concentration, feed phenol concentration, operating pressure, temperature, respectively. The results showed that the rejection of phenol increased in the order as follows: cetyltrimethylammonium bromide (CTAB) < octadecyl trimethyl ammonium bromide (OTAB) < cetylpyridinium chloride (CPC). With the introduction of feed surfactant concentration, the retention recovery of phenol increased. Electrolyte concentration, feed phenol concentration, operating pressure and temperature all had a slight influence on the retention of phenol.

© 2009 Published by Elsevier B.V.

### 1. Introduction

The wastewater containing phenol discharges into environment and creates serious problems due to its impact on human health and environmental contamination. At present, some technologies such as adsorption, chemical oxidation, precipitation, biodegradation are extensively applied for removal of phenols from wastewater [1,2]. These methods, however, possess significant and inherent disadvantages. For example, adsorption is widely used but it is a slow process and its performance is limited by the equilibrium; Chemical oxidation is a technology with high cost and stringent running conditions; Precipitation is of low efficiency and biodegradation is susceptible to water temperature and so on. Otherwise, they are not feasible in the case of low molecular weight (LMW) solutes such as phenol, and they are also ineffective to the aqueous solutions containing trace amounts and low levels of phenol [3]. Thereafter, a novel and promising technology MEUF (micellar-enhanced ultrafiltration) which exhibits low energy consumption, high removal efficiency, small space requirement, economical characteristics for removing trace amounts and low levels of organic pollutants appears [3–9]. When a surfactant is added into polluted aqueous streams, it forms large amphiphilic, transparent

micelles at a concentration higher than its critical micellar concentration (CMC), then the micelles containing solubilized solutes are separated subsequently by a filtration membrane with pore sizes smaller than the diameter of micelles [10].

In MEUF, organic contaminants are removed by virtue of solubilizing within the palisade layer or interior of micelles. Heavy metal and inorganic pollutants, however, are rejected through different mechanism that bound on the surface of the opposite-charged micelles via electrostatic interactions [11–14]. However, when the bulk solution has less than one CMC of surfactant, the removal of solutes may take place because of the influences of adsorption and concentration polarization [15]. So the aqueous stream that in the co-presence of organic and inorganic pollutants [16] /organic pollutants and heavy metals can also be disposed of using MEUF distinctly. Many literatures in recent years are published concerning removal of single phenol/phenol and heavy metals such as investigate the effect of CTAB upon ultrafiltration of oxyethylated methyl dodecanoate solutions and separation of phenol, 4-nitrophenol and 4-methylphenol [17]; study the effect of the pollutant and the presence of salts on permeation during micellar-enhanced ultrafiltration (MEUF) with different surfactants (CTAB, SDS, OMD, APG) [18]; determination of equilibrium distribution constants of phenol between surfactant micelles and water using ultrafiltering centrifuge tubes [19]; simultaneous removal of phenols and  $\text{Cr}^{3+}$  using MEUF [5]; removal of  $\text{Cu}^{2+}$  and dissolved phenol from water using MEUF with mixed surfactants [20]; MEUF of nitrobenzene

\* Corresponding author. Tel.: +86 731 8822754; fax: +86 731 8823701.  
E-mail address: [zgming@hnu.net.cn](mailto:zgming@hnu.net.cn) (G.-M. Zeng).

and 4-nitrophenol [4]; micellar-enhanced ultrafiltration of phenolic derivatives from their mixtures [6]; MEUF of phenol in synthetic wastewater using polysulfone spiral membrane [8] and so on. To make the MEUF system more economical, it is also necessary to recycle the surfactant molecules that are present in the permeate and retentate stream before final disposal. For example, the use of foam fractionation to recover valuable surfactant (SDS) in the permeate of micellar-enhanced ultrafiltration (MEUF) [21]; Free CPC surfactants molecules presented in the permeate are recovered by a two-step chemical treatment procedure [22]. Several researches have studied phenol removal from MEUF in terms of retention, however, the optimum kind of surfactant and the effect of groups difference on the solubilization of phenol is hardly monitored.

In this present work, the aim of the work is to examine the removal efficiency of phenol during micellar-enhanced ultrafiltration in the presence of different cationic surfactants such as CPC, CTAB or OTAB. We utilize orthogonal design experiment to analyze the effect of groups difference on the removal efficiency of phenol. Some various operational parameters such as surfactant concentration, electrolyte concentration, feed phenol concentration, transmembrane pressure and temperature are investigated, respectively in the single factor test.

## 2. Material and methods

### 2.1. Chemicals

Cetylpyridinium chloride (CPC, purity 99%) was obtained from Shanghai Sinopharm Chemical Reagent Company, China. Hexadecyltrimethylammonium bromide (CTAB, analysis purity) was supplied by Shanghai Pushan Chemical Reagent Company, China. Octadecyl trimethyl ammonium bromide (OTAB, analysis purity) was purchased from Xiamen Pioneer Technological Company, China. Electrolytes of KCl,  $K_2SO_4$  were purchased from Shanghai Pushan Chemical Reagent Company, China.  $K_2CO_3$  was delivered by Shanghai Sinopharm Chemical Reagent Company, China. KSCN was purchased from Tianjin Fushen Chemical Reagent Company, China, respectively. Phenol (analysis purity) was purchased from Tianjin Fushen Chemical Reagent Company, China. All reagents were used without further purification. Distilled water was used for solution preparation.

### 2.2. Ultrafiltration

Ultrafiltration was carried out using a cross-flow unit purchased from Dalian Yidong Membrane Engineering Equipment Company, China. It is made of polysulfone which is hydrophobic in nature with an effective area of  $0.4\text{ m}^2$  and compatible in the pH range of 2–13. The pore size of membrane was 6K of molecular weight cut-off (MWCO). A schematic diagram of the ultrafiltration is presented in Fig. 1.

Feed solution for each experiment was prepared by weighing specific amounts of phenol, surfactant and electrolyte and dissolving them in 1000 mL distilled water, then the solution was mixed round adequately to ensure that the solutes are evenly distributed in the feed solution. Ultrafiltration was a cross-flow type in which the retentate was recirculated to the feed tank and permeate solution was collected in a separate tank, process was stopped when about 700 mL aqueous streams were taken as permeate, corresponding to retentate volume of about 300 mL. After each run, tap water was filtered without pressure to rinse out the exterior of membrane within 30 min, then the distilled water of about  $40^\circ\text{C}$  was recycled at 0.05 MPa for 20 min. At last, the membrane permeability of the initial measured value was determined.

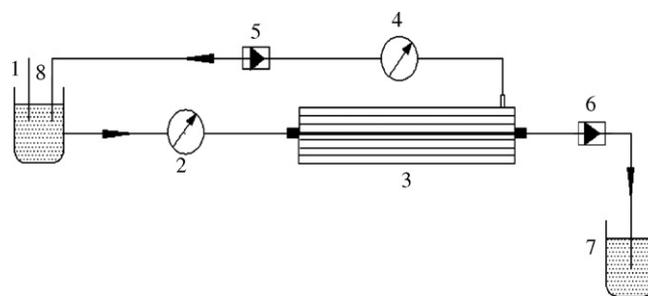


Fig. 1. Schematic diagram of the ultrafiltration unit: (1) feed solution, (2) peristaltic pump, (3) polysulfone membrane, (4) manometer, (5) retentate rotameter, (6) permeate rotameter, (7) permeate and (8) retentate.

Two sets of experiments were carried out. In the first one, orthogonal experiment was conducted, the variations of surfactant (CPC, CTAB, OTAB) concentration were in the range of 5–30 mM, and operating temperatures were from  $20^\circ\text{C}$  to  $50^\circ\text{C}$ , transmembrane pressures were from 0.05 MPa to 0.2 MPa, the electrolytes were KCl, KSCN,  $K_2SO_4$ ,  $K_2CO_3$ . The feed concentration of phenol in the first series was kept a constant value of 1 mM. In the second series, single factor test was conducted, but only OTAB was adopted as the surfactant in view of removal efficiency and economical feasibility.

### 2.3. Analysis

The concentration of CPC and phenol were analyzed by Extinction Coefficients method [23] with Shimadzu UV-2550(P/N206-55501-93) spectrophotometer from Japan. In the synthetic solution of CTAB/OTAB and phenol, the concentration of phenol was measured by UV absorption at a wavelength of 270 nm with a UV-2550 spectrophotometer (Shimadzu). CTAB and OTAB were determined by Congo red spectrophotometric method. The apparent hydrodynamic diameter ( $d_{app}$ ) of the micelle was determined by DLS (Dynamic light scattering) with Zetasizer Nano instrument (Model ZEN3600, made by Malvern Instruments Ltd., England).

### 2.4. Calculations

The rejection of an organic pollutant is the ultimate goal of MEUF. This is conditioned by two parameters: the rejection of surfactant and the relative affinities of the organic for the micelles and for water [24,25].

The efficiency of the ultrafiltration process (rejection,  $R$  and enrichment ratio,  $E$ ) are defined by the classical factor:

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100$$

$$E = \frac{C_f}{C_i}$$

where  $C_i$  and  $C_e$  are the surfactants or organics concentrations (mg/L) in the feed solution and permeate streams, respectively, and  $C_f$  is the surfactant or organics concentration in the retentate solution (mg/L).

The second parameter has often been quantified through an equilibrium distribution constant,  $K_s$ , which has been defined in several ways. One definition is

$$K_s = \frac{O_m}{S_m \cdot O_w}$$

where  $S_m$  is the concentration of surfactant present as micelles,  $O_w$  and  $O_m$  are the concentrations of organic pollutant dissolved in the bulk water and in the micelles, respectively [19].

**Table 1**  
Factor and level.

Level	Factor			
	Surfactant concentration (A) (mM)	Temperature (B) (°C)	Pressure (C) (MPa)	Electrolyte (D)
1	5	20	0.05	K <sub>2</sub> CO <sub>3</sub>
2	10	30	0.1	K <sub>2</sub> SO <sub>4</sub>
3	20	40	0.15	KSCN
4	30	50	0.2	KCl

### 3. Results and discussion

#### 3.1. Orthogonal design experiment

The variations of phenol rejection with orthogonal experiment for different surfactants concentrations, various temperatures, pressures and different electrolytes are presented in Tables 1 and 2.

It is clearly observed that the optimal rejection of phenol increases in the order as follows: CTAB (85.9%) < OTAB (92.4%) < CPC (93.8%). This obviously indicates that the surfactant with hydrophilic pyridinium head group has better effect on solubilization of phenol in micelles. In the case of surfactant with the same hydrophilic head group, the surfactant with longer hydrophobic tail does better influence on the solubilization of phenol, which is explained as follows: the increase of hydrophobic alkyl chain of surfactant results in the decrease of CMC of surfactant so as to enhance the solubilization capability. The effect of surfactant with pyridinium head group on the phenol solubilization is better compared with other surfactants selected, which may be attributed to the rule of similarity and intermiscibility, because CPC and phenol all possess an aromatic ring. The same phenomenon is also obtained in the solubilization of dichloroethane (DCE) on the CTACI micelle [26]. In the range of factors observed, the most important factors

**Table 2**  
Rejection of phenol after solubilization in micelles.

SN	A	B	C	D	R <sub>CPC</sub> (%)	R <sub>CTAB</sub> (%)	R <sub>OTAB</sub> (%)
1	5	20	0.05	K <sub>2</sub> CO <sub>3</sub>	74.8	71.6	75.5
2	5	30	0.1	K <sub>2</sub> SO <sub>4</sub>	44.3	66.9	63.7
3	5	40	0.15	KSCN	10.7	64.7	×
4	5	50	0.2	KCl	23.9	57.1	61.1
5	10	20	0.1	KSCN	47.1	66.4	×
6	10	30	0.05	KCl	68.7	64.9	67.4
7	10	40	0.2	K <sub>2</sub> CO <sub>3</sub>	83.2	76.3	80.7
8	10	50	0.15	K <sub>2</sub> SO <sub>4</sub>	57.3	66.1	69.7
9	20	20	0.15	KCl	78.9	78.3	78.9
10	20	30	0.2	KSCN	75.9	82.5	×
11	20	40	0.05	K <sub>2</sub> SO <sub>4</sub>	79.1	76.6	74.7
12	20	50	0.1	K <sub>2</sub> CO <sub>3</sub>	90.9	82.7	86.9
13	30	20	0.2	K <sub>2</sub> SO <sub>4</sub>	85.6	80.9	79.9
14	30	30	0.15	K <sub>2</sub> CO <sub>3</sub>	93.8	85.9	92.4
15	30	40	0.1	KCl	83.9	79.6	75.9
16	30	50	0.05	KSCN	75.9	74.1	×
I	153.7	286.4	298.5	342.7			
II	256.3	282.7	266.2	266.3			
III	324.8	256.9	240.7	209.6			
IV	339.2	248	268.6	255.4			
R(CPC)	185.5	38.4	57.8	133.1			
I	260.3	297.2	287.2	316.5			
II	273.7	300.2	295.6	290.5			
III	320.1	297.2	295	287.7			
IV	320.5	280	296.8	279.9			
R(CTAB)	60.2	20.2	9.6	36.6			
I	200.3	234.3	217.6	335.5			
II	217.8	223.5	180.8	288			
III	240.5	235.3	221.3	×			
IV	248.2	217.7	201.7	283.3			
R(OTAB)	47.9	17.6	40.5	×			

Due to the fact that the mixture of KSCN and OTAB is a flocculent material, the KSCN in the OTAB is wiped off.

**Table 3**  
Particles size of surfactant micelles.

Kind of surfactant	Particles size
CPC + K <sub>2</sub> CO <sub>3</sub>	4.19 nm
CTAB + K <sub>2</sub> CO <sub>3</sub>	4.57 nm
OTAB + K <sub>2</sub> CO <sub>3</sub>	5.68 nm
CPC + K <sub>2</sub> CO <sub>3</sub> + Phenol	4.20 nm
CTAB + K <sub>2</sub> CO <sub>3</sub> + Phenol	4.78 nm
OTAB + K <sub>2</sub> CO <sub>3</sub> + Phenol	5.96 nm

that based on range analysis are surfactant concentration, kinds of electrolyte. The optimal experimental conditions of solubilizing of CPC on phenol are surfactant concentration of 30 mM, electrolyte of K<sub>2</sub>CO<sub>3</sub>, pressure of 0.05 MPa, temperature of 20 °C, and to CTAB and OTAB are surfactant concentration of 30 mM, 30 mM, electrolyte of K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, pressure of 0.2 MPa, 0.15 MPa, temperature of 30 °C, 40 °C, respectively. Furthermore, in view of removal efficiency and economical feasibility, OTAB is preferential to solubilize phenol of stimulant aqueous stream in the following single factor test.

$K_{sCPC} = 0.076 \text{ mM}^{-1}$ ,  $K_{sOTAB} = 0.056 \text{ mM}^{-1}$ ,  $K_{sCTAB} = 0.045 \text{ mM}^{-1}$ . The higher the  $K_s$  value, the larger the affinity of the organic compound for the micelles, which improves the efficiency of the MEUF process.  $K_s$  is usually considered to be independent of, or slightly dependent on, the surfactant/phenol ratio and independent of the operation variables.  $X_m$  is the mole fraction of the organic compound in the micelles.  $X_{mCTAB} = 0.023$ ,  $X_{mOTAB} = 0.041$ ,  $X_{mCPC} = 0.07$ . It showed that  $X_m$  increases as  $K_s$  increases.

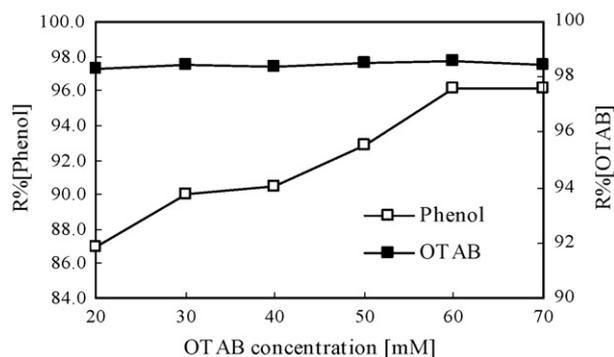
#### 3.2. Micellization of surfactants

The apparent hydrodynamic diameters of the micelles in the presence and absence of phenol are reported in Table 3. It is observed that the apparent hydrodynamic diameters of micelles in the presence of phenol are larger than that of in the absence of phenol, and the particle diameter of OTAB (6.48 nm) is the biggest of three kinds of surfactants due to the longest hydrophobic tail. The increase of particles diameters with the increase of hydrophobic tail can be explained as follows: the CMC of surfactant diminishes with the increase of hydrophobic tail extent, so the solubilization of surfactant micelle on the phenol is enhanced and lead to the increase of micelle size, which have been elucidated in aforementioned Section 3.1. CPC with the smallest micelle size of three surfactants, however, has the best solubilization on phenol, which is shown in the Orthogonal design experiment. So we can know that the decrease of micelle size has no influence on the rejection of phenol in the investigated range of conditions, which indicated that the pore size of membrane used were smaller than all surfactant micelles size selected.

#### 3.3. Single factor test

##### 3.3.1. Effect of OTAB concentration

The effects of feed surfactant concentration on the separation efficiency of phenol and OTAB are reported in Figs. 2 and 3. With the introduction of surfactant OTAB continuously, the corresponding retention of phenol increases from 86.9% to 96.1%, and then the slope levels off. So the effect of OTAB addition becomes less significant when the feed OTAB concentration is higher than 60 mM, since feed OTAB concentration is increased, and the micelle concentration in the solution increases, which results in more solubilization of phenol on OTAB micelles, and then the solubilization of phenol on OTAB micelles is saturated, which compares well with the phenomenon in the work that flux and retention analysis during micellar-enhanced ultrafiltration for the removal of phenol and aniline [3]. The permeate concentration of OTAB goes up from 135 mg/L to 430.75 mg/L upon the addition of OTAB in feed solu-



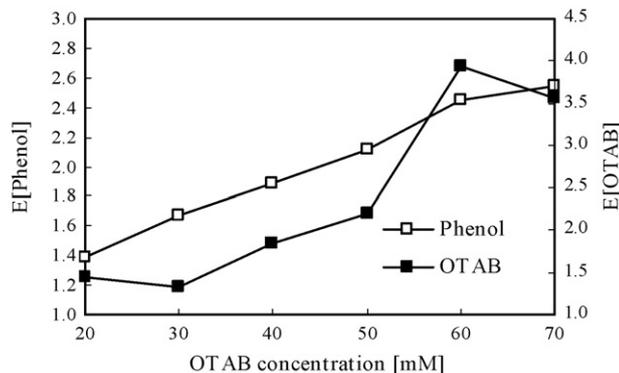
**Fig. 2.** Effect of feed OTAB concentration on rejection of phenol and OTAB. Operating pressure, 0.15 MPa; feed concentration of phenol and  $K_2CO_3$ , 1 and 10 mM; temperature, 40 °C.

tion stream, the OTAB that penetrate into the permeate ascend distinctly, however, the rejection of OTAB nearly keeps constant (about 98%), which is explained as follows: Though the feed concentration of OTAB increases, the pores of ultrafiltration membrane is greatly less than the sizes of OTAB micelles, so feed concentration had little effect on OTAB rejection.

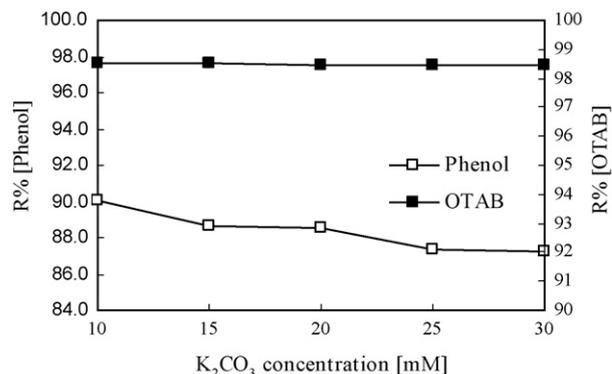
Fig. 3 describes the enrichment ratio of Phenol and OTAB with different feed surfactant concentrations. With the addition of surfactant concentration, the enrichment ratio of phenol keeps increasing from 1.39 to 2.55, while that of OTAB increases with feed surfactant concentration increasing, then decrease sharply when OTAB concentration is above 60 mM, which is reasonable. It is worth nothing that in the ultrafiltration process, the retention of micelles by membrane results in the concentration polarization and the deposition of micelles on the membrane surface or membrane pore [8]. Consequently, the free OTAB monomers which are retained in the retentate solution decrease and enrichment ratio diminishes accordingly.

### 3.3.2. Effect of $K_2CO_3$ concentration

It is well known that the presence of salts decreases the CMC of ionic surfactants, due to the electrostatic shielding effect: the repulsive forces between the head groups are normally fighting against the aggregation, which becomes easier in the presence of electrolyte. Consequently, the addition of small amounts of electrolyte to solutions of ionic surfactants increases the extent of solubilization of hydrocarbons and decreases that of polar compounds [27,28]. In this study,  $K_2CO_3$  (potassium carbonate) acting as an optimal electrolyte according to orthogonal design experiment was chosen to study the effect of electrolyte concentration



**Fig. 3.** Effect of feed OTAB concentration on enrichment ratio of phenol and OTAB. Operating pressure, 0.15 MPa; feed concentration of phenol and  $K_2CO_3$ , 1 and 10 mM; temperature, 40 °C.

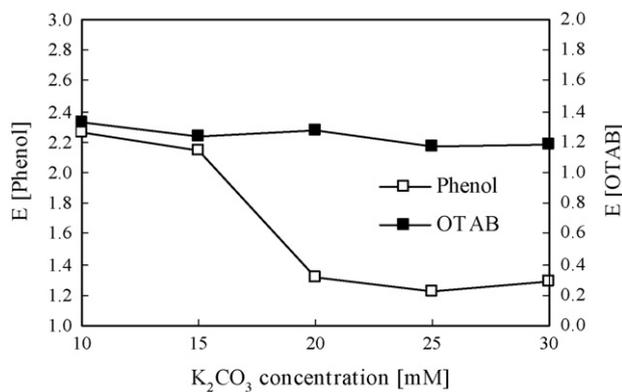


**Fig. 4.** Effect of feed  $K_2CO_3$  concentration on rejection of phenol and OTAB. Operating pressure, 0.15 MPa; feed concentration of phenol and OTAB, 1 and 30 mM; temperature, 40 °C.

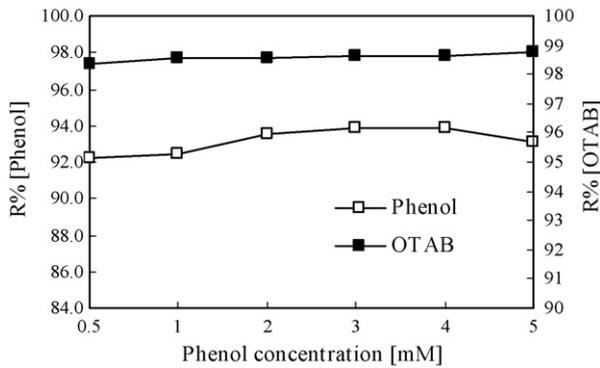
on solubilization of phenol, which are shown in Figs. 4 and 5. It is observed that the rejection of phenol decreases slightly from 90.09% to 87.26% with the addition of  $K_2CO_3$  concentration continuously. It can be explained as follows: Though the CMC of OTAB decreases upon the addition of electrolyte  $K_2CO_3$ , at higher electrolyte concentration, phenol has to compete with excessive  $CO_3^{2-}$  ions to get adsorbed on the OTAB micelle, which may be attributed to strong electrostatic force between anionic phenol and cationic OTAB micelles [3]. As a result, less rejection of phenol is observed at a higher  $K_2CO_3$  concentration. This phenomenon has also been explained for cationic surfactant CPC for phenol removal [8]. As for the rejection of OTAB, which is from 98.51% to 98.44% with electrolyte concentration. When it comes to enrichment ratio of Phenol and OTAB, phenol enrichment ratio decreases from 2.26 to 1.29 and that of OTAB decreases from 1.33 to 1.19. From the point that reducing the back contamination of OTAB and phenol, it is better to add electrolytes. However, considering of the solubilization capability of micelle and economical feasibility, the electrolyte concentration must not be high.

### 3.3.3. Effect of feed phenol concentration

Effects of feed phenol concentration on the observed separation efficiency of phenol and OTAB are shown in Figs. 6 and 7. In this case, the feed OTAB concentration was fixed at 30 mM and feed phenol concentration was varied as 0.5, 2, 3, 4 and 5 mM, and all these experiments were conducted at the operating pressure of 0.15 MPa and the temperature of 40 °C. It can be observed from the figure that the phenol rejection of about 93% has an insignificant variation for its initial concentration ranging from 0.5 mM to 5 mM. A conclu-



**Fig. 5.** Effect of feed  $K_2CO_3$  concentration on enrichment ratio of phenol and OTAB. Operating pressure, 0.15 MPa; feed concentration of phenol and OTAB, 1 and 30 mM; temperature, 40 °C.

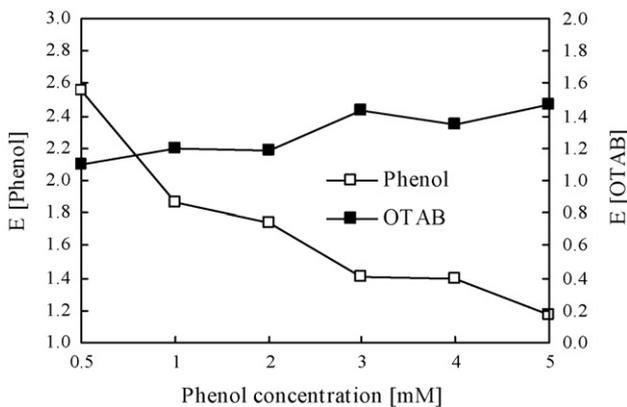


**Fig. 6.** Effect of feed phenol concentration on rejection of phenol and OTAB. Operating pressure, 0.15 MPa; feed concentration of OTAB and  $K_2CO_3$ , 30 and 10 mM; temperature, 40 °C.

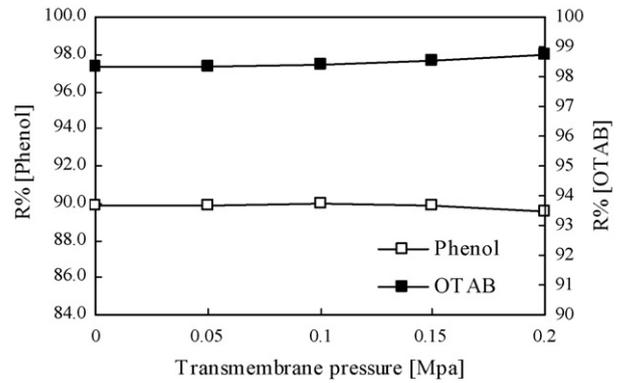
sion can be received that solubilization capability of OTAB micelle increases with the increase of feed phenol concentration: the retention of phenol, however, seems independent of the feed phenol concentration which is just comparatively in accordance with a model proposed by Mulder, 1996 (as to the low levels of contamination, the retention do not change with the feed contamination concentration.) [29]. As mentioned earlier, higher feed phenol concentration increases the concentration of solutes in the micelles, so the solubilized solutes slightly enhance the size of the micellar aggregates, which leads to the little increase of OTAB rejection, as is shown in Fig. 6. An increase in the feed Phenol concentration slightly results in changing of the enrichment ratio of OTAB, which means phenol concentration has little effect on surfactant separation efficiency ( $R\%$ ;  $E$ ) of OTAB. While Phenol concentration was adjusted from 0.5 mM to 5 mM, phenol enrichment ratio decreases from 2.56 to 1.17. It can be explained as follows: at higher phenol concentration the membrane may be polluted severely, decreasing the enrichment ratio, which needs further research in the following stage.

3.3.4. Effect of pressure

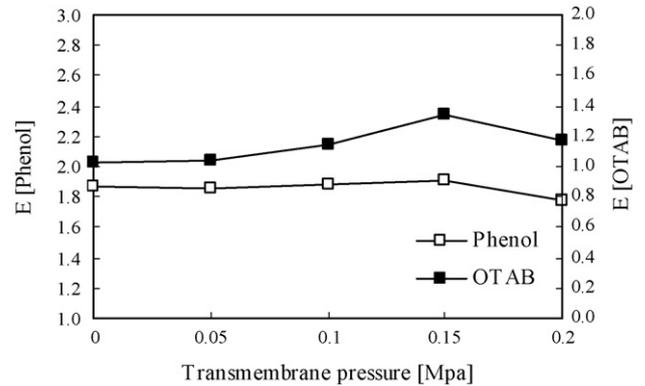
Effects of operating pressure on the observed separation efficiency are presented in Figs. 8 and 9 for phenol and OTAB. It is observed from figure that the retention of phenol remains almost independent of pressure nearly within the range of 0–0.15 MPa, however, the rejection of phenol has a slight decrease when the pressure is beyond 0.15 MPa, which is due to two facts: firstly, micelles may become compact at high pressure and therefore solubilization capability of micelles decreases [6]; secondly, at higher



**Fig. 7.** Effect of feed phenol concentration on enrichment ratio of phenol and OTAB. Operating pressure, 0.15 MPa; feed concentration of OTAB and  $K_2CO_3$ , 30 and 10 mM; temperature, 40 °C.



**Fig. 8.** Effect of transmembrane pressure on rejection of phenol and OTAB. feed concentration of phenol, OTAB and  $K_2CO_3$ , 1, 30 and 10 mM; temperature, 40 °C.

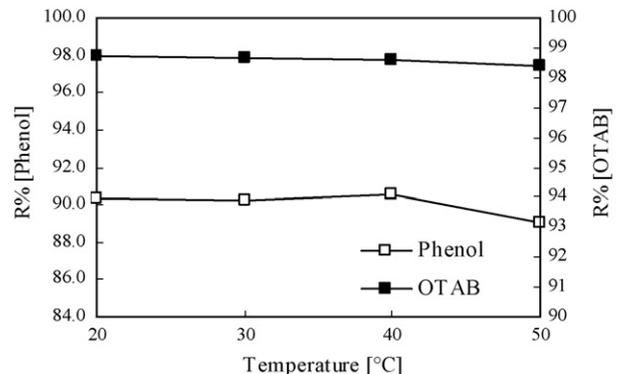


**Fig. 9.** Effect of transmembrane pressure on enrichment ratio of phenol and OTAB. feed concentration of phenol, OTAB and  $K_2CO_3$ , 1, 30 and 10 mM; temperature, 40 °C.

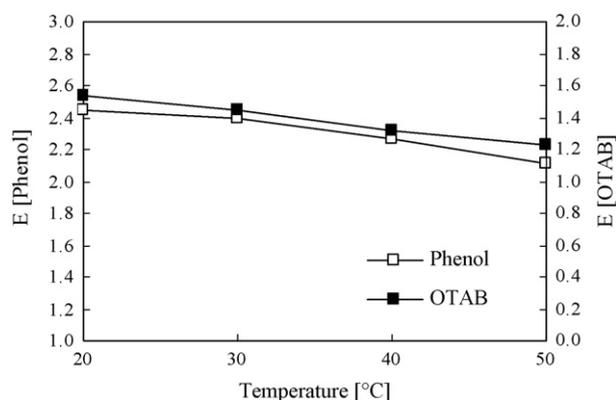
operating pressure, the convective transport of the solutes through the membrane is high leading to higher value of the permeate concentration, thereby lowering the value of observed phenol retention [30]. In the case of OTAB, the rejection insignificantly increases from 98.31% to 98.71%. As seen in Fig. 9, it is observed that the enrichment ratio of phenol decreases from 1.9 to 1.78 as the pressure increases from 0.15 MPa to 0.2 MPa, while OTAB enrichment ratio has a maximum value when pressure is 0.1 MPa, which may be attributed to an error. (Fig. 10).

3.3.5. Effect of temperature

Effects of temperature on rejection of phenol and OTAB were studied at a fixed pressure of 0.15 MPa, feed OTAB concentration of 30 mM, feed phenol concentration of 1 mM, electrolyte concen-



**Fig. 10.** Effect of temperature on rejection of phenol and OTAB. Operating pressure, 0.15 MPa; feed concentration of phenol, OTAB and  $K_2CO_3$ , 1, 30 and 10 mM.



**Fig. 11.** Effect of temperature on enrichment ratio of phenol and OTAB. Operating pressure, 0.15MPa; feed concentration of phenol, OTAB and  $K_2CO_3$ , 1, 30 and 10 mM.

tration of 10 mM, respectively. It is found that the rejection of phenol decreases slightly with the increase of temperature, which can be explained as follows: with the increase of temperature, CMC of micelle increases, which leads to decreasing of aggregation number of micelles, so quantities of free phenol increase [8,31]. Besides, the increase of temperature can expand membrane pores, consequently, more OTAB and phenol molecules pass through the membrane and go into permeate. The rejection of OTAB decreases from 98.71% to 98.36% accordingly. As the temperature increases, the phenol enrichment ratio decreased from 2.44 to 2.11 (Fig. 11), and the OTAB enrichment ratio diminishes from 1.54 to 1.23.

#### 4. Conclusions

MEUF can be used to dispose of low levels of phenol from an aqueous stream. Orthogonal design experiment was adopted, and the surfactant concentration, temperature, pressure, electrolyte and four levels for each of these factors were selected as controllable factors. It was found that for solubilization of phenol, the efficiency of solubilization is in the sequence of CPC > OTAB > CTAB. The optimal experimental conditions were acquired by the range analysis, as a result, the surfactant concentration and electrolyte kind were revealed as significant factors.

OTAB was adopted as a cationic surfactant in the single factor test. The rejection of phenol increases with the feed surfactant concentration increasing and then levels off when surfactants concentration is above 60 mM ( $R$ , 96.13%). The decrease of phenol rejection with the  $K_2CO_3$  concentration is due to the competition of phenol and  $CO_3^{2-}$  on the surface of OTAB micelles at high electrolyte concentration. The retention of phenol remains almost independent of feed phenol concentration which is in the range of 0.5–5 mM and pressure which is in the range of 0–0.15 MPa, the retention of phenol, however, decreases when pressure exceeds 0.2 MPa, because of the fact that micelle may become compact at high pressure and therefore solubilization capability of micelles decreases. The decrease of rejection of phenol with the increase of temperature is attributed to the increase of CMC of OTAB and the expansion of membrane pores with the increase of temperature, and the removal fraction of OTAB is nearly higher 98% with different operational parameter. In conclusion, MEUF is a promising and advisable method for removing the low levels of and low molecular weight organic contaminants from contaminative water.

#### Acknowledgements

This work was financially supported by the Natural Science Foundation of China for Distinguished Young Scholars (No.50225926; No. 50425927); the National 863 High Technol-

ogy Research Program of China(2004AA649370); the National Basic Research Program (973 Program)(No.2005CB724203); Program for Changjiang Scholars and Innovative Research Team in University (IRT0719) and the National Natural Science Foundation of China (No.50608028; No.50708032).

#### References

- [1] X.F. Qu, J.T. Zheng, Y.Z. Zhang, Catalytic ozonation of phenolic wastewater with activated carbon fiber in a fluid bed reactor, *J. Colloid Interf. Sci.* 309 (2007) 429–435.
- [2] W.X. Zheng, M. Maurin, M.A. Tarr, Enhancement of sonochemical degradation of phenol using hydrogen atom scavengers, *Ultrason. Sonochem.* 12 (2005) 313–317.
- [3] S.R. Jadhav, N. Verma, A. Sharma, P.K. Bhattacharya, Flux and retention analysis during micellar enhanced ultrafiltration for the removal of phenol and aniline, *Sep. Purif. Technol.* 24 (2001) 541–547.
- [4] M. Bielska, J. Szymanowski, Micellar enhanced ultrafiltration of nitrobenzene and 4-nitrophenol, *J. Membr. Sci.* 243 (2004) 273–281.
- [5] A. Witek, A. Koltuniewicz, B. Kurczewski, M. Radziejowska, M. Hatalski, Simultaneous removal of phenol and  $Cr^{3+}$  using micellar-enhanced ultrafiltration process, *Desalination* 191 (2006) 111–116.
- [6] M.K. Purkait, S. DasGupta, S. De, Micellarenhanced ultrafiltration of phenolic derivatives from their mixtures, *J. Colloid Interf. Sci.* 285 (2005) 395–402.
- [7] F.I.T. Alesson, H. Adamczak, J. Szymanowski, Micellar-enhanced ultrafiltration of phenol by means of oxyethylated fatty acid methyl esters, *J. Membr. Sci.* 192 (2001) 163–195.
- [8] 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.
- [9] H. Adamczak, K. Materna, R. Urbaniński, J. Szymanowski, Ultrafiltration of Micellar Solutions Containing Phenols, *J. Colloid Interf. Sci.* 218 (1999) 359–368.
- [10] Y.Y. Fang, G.M. Zeng, J.H. Huang, K. Xu, Removal of metal ions and dissolved organic compounds in the aqueous solution via Micellar enhanced ultrafiltration, *Huanjing Kexue* 27 (2006) 641 (in Chinese).
- [11] Y.Y. Fang, G.M. Zeng, J.H. Huang, J.X. Liu, X.M. Xu, K. Xu, Y.H. Qu, Micellar-enhanced ultrafiltration of cadmium ions with anionic–nonionic surfactants, *J. Membr. Sci.* 320 (2008) 514–519.
- [12] J.H. Huang, G.M. Zeng, K. Xu, Y.Y. Fang, Removal of cadmium ions from aqueous solution via micellar-enhanced ultrafiltration, *Trans. Nonferrous Met. Soc.* 15 (2005) 184–189.
- [13] K. Xu, G.M. Zeng, J.H. Huang, J.Y. Wu, Y.Y. Fang, G.H. Huang, Removal of  $Cd^{2+}$  from synthetic wastewater using micellar-enhanced ultrafiltration with hollow fiber membrane, *Colloid Surf. A* 294 (2007) 140–146.
- [14] Z. Zhang, G.M. Zeng, J.H. Huang, Removal of zinc ions from aqueous solution using micellar-enhanced ultrafiltration at low surfactant concentrations, *Water SA* 33 (2007) 129–135.
- [15] H. Byhlin, A.S. Jonsson, Influence of adsorption and concentration polarization on membrane performance during ultrafiltration of a non-ionic surfactant, *Desalination* 151 (2002) 21–31.
- [16] J. Lee, J.S. Yang, H.J. Kim, K. Baek, J.W. Yang, Simultaneous removal of organic and inorganic contaminants by micellar enhanced ultrafiltration with mixed surfactant, *Desalination* 184 (2005) 398–407.
- [17] F.I. Talens-Alesson, R. Urbanski, J. Szymanowski, Evolution of resistance to permeation during micellar enhanced ultrafiltration of phenol and 4-nitrophenol, *Colloid Surf. A* 178 (2001) 71–77.
- [18] B. Korzystka, H. Adamczak, A. Sobczyn'ska, J. Szymanowski, Ultrafiltration characteristics of colloid solutions containing oxyethylated methyl dodecanoate, hexadecyltrimethylammonium bromide and selected phenols as pollutants, *Colloid Surf. A* 212 (2003) 175–183.
- [19] J. Sabate, M. Pujola, E. Centelles, M. Gala'n, J. Llorens, Determination of equilibrium distribution constants of phenol between surfactant micelles and water using ultrafiltering centrifuge tubes, *Colloid Surf. A* 150 (1999) 229–245.
- [20] C.C. Tung, Y.M. Yang, C.H. Chang, J.R. Maa, Removal of copper ions and dissolved phenol from water using micellar-enhanced ultrafiltration with mixed surfactants, *Waste Manage.* 22 (2002) 695–701.
- [21] Y.H. Qu, G.M. Zeng, J.H. Huang, K. Xu, Y.Y. Fang, X. Li, H.L. Liu, Recovery of surfactant SDS and  $Cd^{2+}$  from permeate in MEUF using a continuous foam fractionator, *J. Hazard. Mater.* 155 (2008) 32–38.
- [22] M.K. Purkait, S. DasGupta, S. De, Separation of aromatic alcohols using micellar-enhanced ultrafiltration and recovery of surfactant, *J. Membr. Sci.* 250 (2005) 47–59.
- [23] Y.W. Liu, Y.Z. Chi, X.N. Fei, On simultaneous determination of phenol aniline and benzoic acid by ultraviolet absorption spectrometry, *J. Safe. Environ.* 5 (2005) 72–74.
- [24] M. Krivorot, Y. Oren, Y. Talmon, Y. Schmidt, J. Gilron, Characterization of micellar systems for removal by MEUF of refractory organic from contaminated groundwater, *Desalination* 200 (2006) 718–719.
- [25] J. Sabatie, M. Pujol, J. Llorens, Comparison of Polysulfone and Ceramic Membranes for the Separation of Phenol in Micellar-Enhanced Ultrafiltration, *J. Colloid Interf. Sci.* 246 (2002) 157–163.
- [26] J.J. Yan, Research of DCE synthetic waste water using Micellar enhanced ultrafiltration, Dissertation, The Beijing University of Technology, Beijing, 2004.

- [27] N. Zaghbani, A. Hafiane, M. Dhahbi, Removal of Safranin T from wastewater using micellar-enhanced ultrafiltration, *Desalination* 222 (2008) 348–356.
- [28] N. Zaghbani, A. Hafiane, M. Dhahbi, Separation of methylene blue from aqueous solution by micellar enhanced ultrafiltration, *Sep. Purif. Technol.* 55 (2007) 117–124.
- [29] A.K. Mulder, B. Legube, S. Dard, Atrazine and simazine removal mechanisms by nanofiltration: Influence of natural organic matter concentration, *Water Res.* 30 (1996) 2535–2542.
- [30] M.K. Purkait, S. DasGupta, S. De, Removal of dye from wastewater using micellar-enhanced ultrafiltration and recovery of surfactant, *Sep. Purif. Technol.* 37 (2004) 81–92.
- [31] J.X. Xiao, Z.G. Zhao, *Applied mechanism of surfactant*, M, Chemical Industry Publishing Company, Beijing, 2003, pp. 168–169.