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Study on solubilization capability of various Gemini micelles in micellar-enhanced ultrafiltration of phenol-contaminated waters

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ABSTRACT

A systematic study has been conducted to have an insight into the separation efficiency of phenol with the help of Gemini surfactants and conventional nonionic surfactant in their single and mixed systems using micellar-enhanced ultrafiltration (MEUF). A flat sheet membrane with a total effective area of $0.08 \,\mathrm{m}^2$ and a molecular weight cut-off of 10 kDa, was selected in this investigate. The effects of feed component (surfactant concentration for single surfactant system and mixed ratio for mixed surfactant system) on solubilization and filtration efficiency were researched. Some related parameters were used to estimate the performance of various surfactant systems, such as distribution coefficient (D), the phenol concentration in micellar phase (P_m) , the surfactant concentration in micellar phase (S_m) , the micelle loading (L_m) , and the equilibrium distribution constant (K). With the increase of feed surfactant concentration or the addition of nonionic surfactant, the degree of solubilization of phenol enhances, leading to the decrease of permeate concentration and the augment of retentate concentration. Consequently, D, P_m , and S_m increases. The addition of nonionic surfactant has positive effects to recounterbalance the interior structure and improve the micellar solubilization power for phenol. Both the single and mixed C₁₂₋₂₋₁₆ systems have higher D, P_m , and S_m values than these of $C_{12-2-12}$, due to the longer length alkyl chain and more optimized structure. L_m and K are the significant indicators for evaluating the effectiveness of dissolving phenol. Irreversible fouling was almost eliminated with a series of cleaning solution in a short time. There results from the laboratory-scale experiments could be very useful in selection of the suitable surfactant systems for raising efficiency and could serve as valuable guide for MEUF in industrial application.

Keywords: Gemini surfactant; Micellar-enhanced ultrafiltration; Distribution; Phenol; Membrane fouling cleaning

1. Introduction

Industrial processes such as chemical and petrochemical processes often produce effluents containing phenol which cause serious adverse effects on environment and human health [1,2]. There are many conventional separation methods which have been used to treat the organic wastewater, such as chemical oxidation, biological treatment, adsorption, and UV

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oxidation [3,4]. Nevertheless, these methods have inherent deficiencies, owing to their ineffectiveness for eliminating the dissolved low molecular weight organics from wastewater [5]. Their inferior selection, high cost, and inconvenient operation have limited their wide applications. Therefore, developing a low energy and highly effective separation technique has been become a pressing problem [4].

As a novel and promising separation process, micellar-enhanced ultrafiltration (MEUF) is suitable for removing small and toxic organic molecules or heavy metals ions from wastewater [6]. Although this method exhibit such advantages as simple operating, highly separation efficiency, and low-press, the concentration polarization and the membrane fouling which could decrease the filtration efficiency have shown to be the primary defectiveness for restricting its extensive application in engineering [7–9]. In micellar process, as the source of micelles, the proper surfactants are added to the pollution water and mixed evenly. When the surfactant concentration is above its critical micellar concentration (CMC), numerous micelles which contain about 50-150 molecules will be formed and their average size is larger than the average pore size of the membrane. The micelles consist of three parts-out layer (formed by hydrophilic groups), inner core (formed by hydrophobic groups), and palisade layer (formed by CH₂ groups) [3,7,10]. Due to the rule of similarity, the organics tend to dissolve in the micelles. Furthermore, the more hydrophobic the pollutant matters are, the more they could be soluble in the micelles [9,11-13]. In the process of ultrafiltration, micelles are intercepted by the ultrafiltration membrane with proper molecular weight cut-off and the permeate stream is almost totally free from impurities. The main drawbacks of this process are the membrane fouling which is brought about by the adsorption of surfactant gelation and the convective transport of surfactant molecules through the membrane which could maintain equilibrium with the micelles in water phase [14]. Therefore, the selection of surfactants plays a highly crucial role for overcoming these shortcomings.

Recently, numerous investigations about MEUF have been devoted to the choice of surfactants with excellent properties to treat the relevant wastewater. Luo used cetylpyridinium chloride (CPC), cetyltrimethylammonium bromide, and octadecyl trimethyl ammonium bromide to remove phenol from synthetic water and found CPC had better solubility for phenol [7]; Li studied the simultaneous removal of heavy metal ion (cadmium ions) and organic pollutant (phenol) with MEUF using single surfactant system SDS and mixed surfactants systems [15]; Yenphan reported the synergistic interaction of the mixed nonionic surfactant (iso-octyl phenoxy polyethoxy ethanol, TX-100, and polyoxyethylene nonylphenyl ether, NP12) and anionic surfactant (sodium dodecyl sulfate, SDS) for the treatment of Pb²⁺ wastewater by MEUF [10]. In general, the structure of surfactant is the dominated element that affects the operational efficiency of MEUF. However, most previous investigations on MEUF were about the removal of pollutant using single conventional surfactant system [6,16]. Researching and developing a novelty and effective surfactant systems is highly necessary for improving the operational efficiency and realizing its engineering application.

As the third-generation surfactant, Gemini surfactants include two hydrophilic headgroups and two hydrophobic chains which were connected at or near the headgroups by a relatively short spacer group [17]. In comparing with conventional surfactants groups, Gemini surfactants possess numerous superior properties, such as much lower CMC, mildness to skin, excellent foaming, and better wetting properties [18,19]. Moreover, the toxicity of Gemini surfactants is highly low, owing to the structure of strong hydrophobic groups at or near the stretched spacer which could decrease their accessibility [20,21]. They have been widely reported and applied in the fields of drug entrapment, gene therapy, enhanced oil recovery, soil remediation, MEUF, and cosmetic/pharmaceutical/ household products preparations [18,19,22]. Gemini surfactant is usually regarded to m-s-n surfactant, where s is the carbon number present in the polymethylene group in spacer, m and n represent the carbon numbers of alkyl chains, respectively. In authors' previous study, Gemini surfactant systems own greater solubilization capacity for phenol and have better efficiency for the treatment of organic wastewater than the conventional surfactant using MEUF [19,23]. Nevertheless, the estimating and selection of an efficient and excellent surfactant system among a number of Gemini surfactant systems is highly significant for the removal of organic pollutant and reduces the membrane fouling in MEUF. In addition, to our knowledge, there is no literature on the assessment and judgment of the separation efficiency and solubilization capacity for MEUF between numerous surfactant systems.

In this work, the aim is to investigate and estimate the separation efficiency and solubilization capacity of various single/mixed Gemini surfactant systems with different hydrophobic tail length. Some related parameters, including distribution coefficient (*D*), the phenol concentration in micellar phase (P_m), the surfactant concentration in micellar phase (S_m), the micelle loading (L_m), and equilibrium distribution constant (*K*), are used to assess the performance of various surfactant systems in MEUF. D could stand for the degree of the attractive power between the organic matters and micelles, thus it is a crucial parameter to evaluate the solubilization capacity of the selected surfactant system. The higher value of D reflects that this surfactant system has greater volume for dissolving the organic pollutant from wastewater, which could increase the removal efficiency. P_m and S_m is conducive to understand the proportional distributions of surfactant and organic matters between micellar phase and water phase. L_m which is defined as the number of moles of phenol solubilized by one mole of micellized surfactant contributes to measure the effectiveness of a specific surfactant in dissolving organic matters. K is the distribution of a mole fraction of phenol between water phase and micellar phase, reflecting the solubilization power of this surfactant system. Furthermore, these parameters also elucidate the distributions of surfactant and organic matters in the permeate stream and retentate stream, thus will be help to reduce the secondary pollution and recover the surfactants. In addition, after each experimental run and cleaning, the permeate flux of pure water was measured and was used to calculate the recover permeability, which could contribute to estimate the effect of a series of cleaning solution. These analyses could provide sufficient proofs to explore an efficient and optimized surfactant system for MEUF process.

Table 1The physicochemical properties of surfactants and phenol in experiment

2. Experimental section

2.1. Materials

Phenol was selected as a model of wastewater with organic matters. It is of analysis purity and obtained from Beijing Chemical Reagent Company, China. Two kinds of Gemini surfactants ($C_{12-2-12}$ and $C_{12-2-16}$, all purity >98%) were supplied by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Science. The nonionic surfactant (Brij35, purity 98%) was purchased from Sigma–Aldrich. The molecular structures and properties of organic compounds and the chosen surfactants are given in Table 1. All reagents were not further purified. The experimental synthetic wastewaters were prepared by dissolving pre-calculated phenol and the relevant surfactants in deionized water.

2.2. Experimental setup and membranes

Ultrafiltration was carried out by an experimental setup (UFP4-01) which has been designed and built by XiaMen Tianquanxin Membrane Technology Co. Ltd., China (see Fig. 1). In this study, a flat sheet membrane was purchased from Advanced Membrane Corporation, America. The membrane material is hydrophobic in nature and its characteristic is given in Table 2. The properties and parameters of the pump are presented in Table 3.

Surfactant	Structure	MW $(g mol^{-1})$	CMC ^a (mM)	<i>S_w</i> (20 °C)	$\log K_w$
Phenol		94.11		$8.3 \mathrm{g} \mathrm{L}^{-1}$	1.46 [15]
C ₁₂₋₂₋₁₂	N* 2Br	614.67	0.8 [24]		
C ₁₂₋₂₋₁₆	N*	672.03	0.2 [19]		
Brij35	$CH_3 \longrightarrow CH_2 \xrightarrow{111} O \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow OH$	1,200	0.065 [15]		

^aError limits of CMCs are ±4%.



Fig. 1. A schematic of ultrafiltration experimental setup.

2.3. Experimental procedure

According to the experimental design which is the same as our early studies [14,23], the model phenol wastewater was prepared by mixed the pre-calculative amount of surfactant and phenol into deionized water and ensure that the solutes evenly mix before entering the membrane module. The volume of feed tank was initially filled with 4.0 L solution. The pressures and the retentate flow rates were kept constant at 0.30 MPa and 5 Lmin^{-1} through all experiments. Then, the feed solution was delivered to the membrane module. The retentate stream and the permeate stream were recvcled back to the feed tank. The experiments were working for 0.5 h. The permeate fluxes and the retentate fluxes were recorded and it was observed that the fluxes were almost kept constant. The concentrations of surfactant and phenol in the permeate stream and retentate stream were determined. All the reported values were recorded three times and averaged for the

ultimate results. After each experiment run, the membrane was washed by tap water with 0.25 MPa for 20 min and the distilled water was filtered to rinse out most of deposited phenol and surfactants, then 0.1 M NaOH, distilled water, 0.1 M HNO₃, and finally distilled water were used to clean the membrane. In the end, the membrane permeability was measured by distilled water to ensure that it recovered to the initial water flux within 95%.

2.4. Analytical methods

The concentration of phenol was measured with UV-2102 PCS spectrophotometer [12,24,25]. The concentrations of $C_{12-2-12}$ and $C_{12-2-16}$ were analyzed by a titrating method [26]. The viscosities of solutions were measured by a viscometer (NDJ-5S/8S) [27]. All these analytical methods were repeated three times, and all experimental errors were less than 5%.

2.5. Calculated parameters

We assume that only the monomeric molecules of phenol and surfactant can traverse the membrane and all the micelles present in the feed solution are rejected by the membrane, thus the concentrations of surfactant and phenol in the permeate water phase are the same as that in the retentate stream [28–30]. The performance of various micellar systems in MEUF can be assessed from distribution coefficient (*D*), the phenol concentration in micellar phase (P_m), the surfactant concentration in micellar phase (S_m), the micelle loading (L_m), and equilibrium distribution constant (*K*).

According to the law of mass action, one definition of *D* is defined as:

$$D = [PH]_R / [PH]_n \tag{1}$$

Table 2			
Characteristics o	f the used	flat sheet	membrane

Туре	Material	MWCO (Da)	Effective of membrane (m ²)	Max operating pressure (MPa)	pH operating range	Operating temperature (°C)
PES10	Polyethersulfone	10 K	0.06	0.4	1–14	5–45

Table 3 Characteristics of the used pump

Туре	Production	Head	Power	Flow
TP10-20 peristaltic pump	Tianjin MOTIMO membrane technology Co. Ltd.	40 m	1.1 KW	$2 \text{ m}^3 \text{ h}^{-1}$

 P_m is given by:

$$P_m = [PH]_R - [PH]_p \tag{2}$$

 S_m can be calculated by the following equations:

$$S_m = [S]_R - [S]_n$$
(3)

 L_m can be written as:

$$L_m(\text{mol/mol}) = \frac{[PH]_M}{[S]_M} = \frac{[PH]_R - [PH]_P}{[S]_R - [S]_P}$$
(4)

K is represented as:

$$K(\text{mol}^{-1}) = \frac{[PH]_M}{[PH]_P[S]_M} = \frac{[PH]_R - [PH]_P}{[PH]_P\{[S]_R - [S]_P\}}$$
(5)

where $[PH]_R$ and $[S]_R$ denote the concentration of phenol and surfactant in the retention stream; $[PH]_P$ and $[S]_P$ represent the phenol and surfactant concentration in the permeate stream, respectively; $[PH]_M$ and $[S]_M$ are the phenol and surfactant concentration in the micellar phase.

3. Results and discussion

3.1. Effect of feed surfactant concentration on the phenol concentration in permeate stream and retentate stream, distribution coefficient, and the phenol concentration in micellar phase

The variations of distribution coefficient D and the phenol concentration in micellar phase for phenol P_m are plotted as a function of the feed surfactant concentration (0.5, 1, 2, 4, 6, and 8 mM) and the Brij35/CG molar ratio α (0, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2), as shown in Figs. 2 and 3, respectively. The distributions for the phenol between the micellar phases and water phases in the permeate and retentate stream are in equilibrium. D is an indicator of the distribution ratio for the phenol between the permeate stream and retentate stream [23,31]. P_m is a significant parameter, which is closely related to the phenol's distributions between water phase and micellar phases [23]. The values of D and P_m for all surfactant systems studied herein rise continuously with the incremental concentrations of single surfactant systems and the addition of Brij35. Obviously, the size of micelles and the aggregation number enhance with the increasing concentration of surfactant and the Brij35/CG molar ratio α , namely, the number of surfactant molecules or in the micellar phase increase, and more binding sites between phenol and surfactant micelles enlarge [3,32– 36], which could be observed from higher *D* in Fig. 2. These results cause more phenol molecules that were solubilized into the micelles (higher P_m).

It is evident that the optimal D and P_m of phenol is following the order: $C_{12-2-16} + Brij35 > C_{12-2-12} + Brij35$ $>C_{12-2-16}>C_{12-2-12}$ for all selected surfactant systems. Comparing with C₁₂₋₂₋₁₂ systems, C₁₂₋₂₋₁₆ systems have more excellent solubilization power at selected surfactant concentrations, which is due to two facts: Firstly, owing to the larger inner cores of C₁₂₋₂₋₁₆ systems for dissolving greater number of the organic molecules, organic matters are easier to solubilized in their micelles with larger volume [15]; secondly, for the C_{12} -2-16 systems, the longer length of alkyl chain decrease their hydrophilicity, leading to the accretion of the number of binding sites [26], which indicates that C₁₂₋ 2-16 systems' relative affinity for phenol is larger and their binding locations are deeper in the C12-2-16 micelles, thereby in the long run, C₁₂₋₂₋₁₆ systems which has a longer alkyl chain would have stronger solubilizing power. Besides, the CMC of $C_{12-2-16}$ systems is much lower and larger micelles formed by C₁₂₋₂₋₁₆ systems more easily occur at a lower concentration, bringing about the accretion of phenol concentration in micelles.

With respect to the single surfactant system, mixed surfactant systems have higher D and P_{m} value. In the pure surfatant solution, the electrostatic repulsive forces for the hydrophilic head groups could impede the production of micelles [14]. When Brij35 molecules were added into the solution, the ethylene oxygen group (C_2H_4O) inserts the micelles, then the charge of their hydrophilic groups is recounterbalance, and the electrical repulsion between the micelles' Stern layer decreases, which would lead to the reduction of the charge density on the surface of micelles [1,15]. In addition, the strong effect between two head groups of Gemini surfactant and aromatic organics and the stability micelles could elevate their solubilization power. As a consequence, all above efforts could excites the shape of micelles, the promotion of the size of micelles, and the aggregation number [37,38], thus more phenol would be dissolved in micelles and can be observed from the higher *D* and P_m values in the Fig. 2.

3.2. Effect of feed surfactant concentration on the surfactant concentration in permeate stream and retentate stream and the surfactant concentration in micellar phase

Fig. 4 presents surfactant concentration in micellar phase (S_m) at various surfactant concentrations or various Brij35/CG molar ratios α . Phenol concentration



Fig. 2. The distribution coefficient with the feed surfactant concentration.



Fig. 3. The phenol concentration in micellar phase with the feed surfactant concentration.

keeps constant at 1 mM. It can be observed that the values of S_m of the single surfactant systems rise linearly with the increment of the feed surfactant concentration. It could be explained as followed: when the feed surfactant concentration increased, more micelles formed in the solution [32–36], which means the number of surfactant molecules entered the micellar phase (higher S_m), thus the free phenol in the water phase accordingly reduced. As for the mixed surfactant system, the right figure showed that S_m values are approximate to each other and enhance slowly when the Brij35/CG molar ratios α varies from 0 to 1.2. As mentioned above, with the addition of nonionic surfactant, the aggregation number increase and more surfactant

molecules join the micellar phase, due to the reduction of electrostatic repulsive forces [15] by the insert of the ethylene oxygen group (C_2H_4O).

It is seen from Fig. 4 that S_m values of $C_{12-2-16}$ are higher than these of $C_{12-2-12}$ for both single and mixed surfactant systems, which is reasonable. With lower CMC, the micelles of $C_{12-2-16}$ own larger amount of micelle [19,23], and leading to the high concentration of $C_{12-2-16}$ in micellar phase. Moreover, the large size of $C_{12-2-16}$ micelles is easier to retain by ultrafiltration membrane and recycle into the feed tank, thus causing the accretion of surfactant concentration in the retentate stream. Owing to the stronger hydrophobic interaction [22], micelles of $C_{12-2-16}$ despite on



Fig. 4. The surfactant concentration in micellar phase (S_m) with the feed surfactant concentration.

membrane pores or the membrane surface more easily, which can decrease the surfactant concentration in retentate stream and P_m values. However, these efforts may be not enough to impact the S_m values.

3.3. The micelle loading and the equilibrium distribution constant

The micelle loading of phenol (L_m) is used to measure the effectiveness of a particular surfactant system for dissolving a given solute in the ultrafiltration experiment. When other organic matters exist in feed solution, the separation efficiencies depend on the micelles capacity for solubilizing organic matters. The other organic matters could access micelles, if these micelles have power to solubilize more other organic matters. Otherwise, due to the existence of other organic matters, their solubilization capacity for phenol may reduce while the micelles cannot dissolve more organic matters [14]. As shown in Fig. 5, it is observed that L_m of $C_{12-2-12}$ and $C_{12-2-16}$ decrease from 0.76 and 0.84 at 0.5 mM to 0.11 and 0.12 at 8 mM for the single surfactant system, respectively. With the augment of feed surfactant concentration, the number of micelles increase and their solubilization capacity for phenol enhances [7], thus one mole of micellized surfactant could solubilize fewer moles of phenol.

The right figure is the L_m of the Brij35/C₁₂₋₂₋₁₂ system and Brij35/C₁₂₋₂₋₁₆ system. The values of L_m nearly keep constant (about 0.156 and 0.155). It is well known that the synergistic effect of nonionic surfactant/cationic surfactant could improve their solubilization capacity by the means of optimizing

micellar structure [23]. However, the feed phenol concentration is fixed at 1 mM, therefore the solubilization volume of phenol for micelles is hard to increase and the L_m almost remain unchanged. In the single surfactant system, L_m of C₁₂₋₂₋₁₆ is higher than that of C₁₂₋₂₋₁₂. Whereas, this is reverse of what happens in the mixed surfactant system. A conclusion could be received that the micelles of C₁₂₋₂₋₁₂ have more potential solubilization power for other organic matters than that of C₁₂₋₂₋₁₆ has better capability of binding more other organic matters than that of Brij35/C₁₂₋₂₋₁₆ has better than that of Brij35/C₁₂₋₂₋₁₈.

The equilibrium distribution constant (K) is used to characterize the effectiveness of solubilization power of phenol ulteriorly. It is described as the mole fraction of phenol between surfactant micelles and the water phase [14]. Effects of feed surfactant concentration and the Brij35/CG molar ratios α on the equilibrium distribution constant (K) are shown in Fig. 6. It is observed that the equilibrium distribution constant of $C_{12-2-12}$ and $C_{12-2-16}$ decrease from 1.19 and 1.44 mol⁻¹ at 0.5 mM to 0.48 mol^{-1} and 0.75 mol^{-1} at 2 mM, then increase sharply to 1.31 and 1.62 mol⁻¹ at 8 mM. It is found K values decrease firstly, and then increase with the increasing of the feed surfactant concentration, which is attributed to the enhancement of the retentate surfactant concentration, the decrease of permeate phenol concentration, and the augment of the retentate phenol concentration. When the surfactant concentration is 1, 2, and 4 mM, the extent of increment of the retentate surfactant concentration is bigger than this of the retentate phenol concentration and the diminution of permeate phenol concentration, thus the K values



Fig. 5. The micelle loading with the feed surfactant concentration.



Fig. 6. The equilibrium distribution constant with the feed surfactant concentration.

decrease. For the same reason, the degrees of increment of the retentate phenol concentration and the decrease of permeate phenol concentration are greater than accretion of the retentate surfactant concentration, leading to the elevating of K. With regard to the mixed surfactant system, the K values keep slightly increasing with the addition of Brij35, which could be explained as follows: the nonionic surfactant/cationic surfactant mixed surfactants promote the solubilization power of phenol [23], bringing about the rise of the retentate phenol concentration and the diminishment of permeate phenol concentration, consequently, the results illustrate the K of the mixed surfactant systems increase. In this case, the sequence of *K* is: $C_{12-2-16} + Brij35 > C_{12-2-12} + Brij35 > C_{12-2-16} > C_{12-2-12}$, which is in tune with the order of solubilization power of various surfactant systems and are consistent with the results discussed in section 3.1.

3.4. Membrane fouling and cleaning

Membrane fouling is a serious problem which could decrease the permeate flux sharply. Finding an effective cleaning method is an important approach to offset the influence of membrane fouling by micelles. Using tap water, 0.1 mM NaOH, distilled water and 0.1 mM HNO₃



Fig. 7. The permeate flux recovery of fouled membrane with the feed surfactant concentration.

with 0.25 MPa at room temperature, the cleaning process was carried out for 20 min and the initial permeate flux could be nearly recovered. Fig. 7 shows the permeate flux recovery of fouled membranes by various micelles after cleaning. With the increase of feed surfactant concentration, more micelles exist in the stream and deposit on the membrane surface and membrane pores, then causing bigger extent of irreversible membrane fouling. The order of recovery for all selected surfactant systems is $C_{12-2-12} > C_{12-2-16} > C_{12-2-12} + Brij35 > C_{12-2-16} +$ Brij35, which can be explained by the hydrophobicity of micelles and the number of micelles. Compare with C₁₂₋₂₋₁₂, C₁₂₋₂₋₁₆ has lower CMC and bigger hydrophobicity, therefore, larger number of micelles of C₁₂₋₂₋₁₆ form. Overall, these recovery values keep at a high level, indicating that, by using a series of cleaning solution and process, membrane fouling by micelles can be removed efficiently.

4. Conclusions

The MEUF operation efficiency of various surfactant systems for separation phenol could be judged by some related parameters, including the distribution coefficient, the phenol concentration in micellar phase, the surfactant concentration in micellar phase, the micelle loading, and the equilibrium distribution constant. In this study, C₁₂₋₂₋₁₂, C₁₂₋₂₋₁₆, C₁₂₋₂₋₁₂ + Brij35 and C₁₂₋₂₋₁₆ + Brij35 were used as the micellar sources. It is found that the following the order of distribution coefficient and the phenol concentration in micellar phase is: C₁₂₋₂₋₁₆ + Brij35 > C₁₂₋₂₋₁₂ + Brij35 > C₁₂₋₂₋₁₆ > C₁₂₋₂₋₁₂, which is in tune with the solubilization power of phenol. The addition of nonionic surfactant could recounterbalance and improve the interior structure for dissolving organic matters. Furthermore, the single and mixed surfactant systems of C12-2-16 possessing longer length alkyl chain have more excellence solubilization capacity for phenol than these of $C_{12-2-12}$, respectively. With the increase of feed surfactant concentration and the addition of nonionic surfactant, the number of surfactant in the micellar phase rise, leading to the augment of the surfactant concentration in micellar phase. The micelle loading could representative the solubilization power for other organic matters. The equilibrium distribution constant is an indicator which is related to the phenol concentration and the surfactant concentration in retentate stream and permeate stream. A routine cleaning measure can rinse the foulants and recover the membrane permeability effectively. The experimental results in this study make a clear understanding of solubilization capabilities of the single Gemini surfactant system and the Gemini/conventional nonionic mixed surfactant systems and extend the selection of surfactant system used in solubilization for water contamination treatment with MEUF.

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References

- J. Lee, J. Yang, H. Kim, K. Baek, J. Yang, Simultaneous removal of organic and inorganic contaminants by micellar enhanced ultrafiltration with mixed surfactant, Desalination 184 (2005) 395–407.
- [2] S. Rengaraj, S. Moon, R. Sivabalan, B. Arabindoo, V. Murugesan, Agricultural solid waste for the removal of organics: Adsorption of phenol from water and wastewater by palm seed coat activated carbon, Waste Manage. 22 (2002) 543–548.
- [3] G. Zeng, K. Xu, J. Huang, X. Li, Y. Fang, Y. Qu, Micellar enhanced ultrafiltration of phenol in synthetic wastewater using polysulfone spiral membrane, J. Membr. Sci. 310 (2008) 149–160.
- [4] 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) 541–557.
- [5] M.M. Husein, A. Deriszadeh, T.G. Harding, Experimental and modeling study of MEUF removal of naphthenic acids, Desalination 273 (2011) 352–358.
- [6] A. Êl-Abbassi, M. Khayet, A. Hafidi, Micellar enhanced ultrafiltration process for the treatment of olive mill wastewater, Water Res. 45 (2011) 4522–4530.
- [7] F. Luo, G. Zeng, J. Huang, C. Zhang, Y. Fang, Y. Qu, X. Li, D. Lin, C. Zhou, Effect of groups difference in surfactant on solubilization of aqueous phenol using MEUF, J. Hazard. Mater. 173 (2010) 455–461.
- [8] C. Liu, C. Li, Combined electrolysis and micellar enhanced ultrafiltration (MEUF) process for metal removal, Sep. Purif. Technol. 43 (2005) 25–31.
- [9] M.A.M. El Zeftawy, C.N. Mulligan, Use of rhamnolipid to remove heavy metals from wastewater by micellar-enhanced ultrafiltration (MEUF), Sep. Purif. Technol. 77 (2011) 120–127.
- [10] P. Yenphan, A. Chanachai, R. Jiraratananon, Experimental study on micellar-enhanced ultrafiltration (MEUF) of aqueous solution and wastewater containing lead ion with mixed surfactants, Desalination 253 (2010) 30–37.
- [11] A.L. Ahmad, S.W. Puasa, Reactive dyes decolourization from an aqueous solution by combined coagulation/micellar-enhanced ultrafiltration process, Chem. Eng. J. 132 (2007) 257–265.
- [12] 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.
- [13] J. Huang, G. Zeng, Y. Fang, Y. Qu, X. Li, Removal of cadmium ions using micellar-enhanced ultrafiltration with mixed anionic-nonionic surfactants, J. Membr. Sci. 326 (2009) 303–309.
- [14] W. Zhang, G. Huang, J. Wei, H. Li, R. Zheng, Y. Zhou, Removal of phenol from synthetic waste water using Gemini micellar-enhanced ultrafiltration (GMEUF), J. Hazard. Mater. 235–236 (2012) 128–137.
- [15] X. Li, G. Zeng, J. Huang, D. Zhang, L. Shi, S. He, M. Ruan, Simultaneous removal of cadmium ions and phenol with MEUF using SDS and mixed surfactants, Desalination 276 (2011) 136–141.
- [16] K. Xu, H. Ren, G. Zeng, L. Ding, J. Huang, Investigation of interaction between phenol and cetylpyridinium chloride micelle in the absence and in the

presence of electrolyte by 1H NMR spectroscopy, Colloids Surf., A 356 (2010) 150–155.

- [17] O. Zheng, J. Zhao, Solubilization of pyrene in aqueous micellar solutions of gemini surfactants C12-s-C122Br, J. Colloid Interface Sci. 300 (2006) 749–754.
- [18] W.W. Song, N.B. Li, H.Q. Luo, Gemini surfactant applied to the heparin assay at the nanogram level by resonance Rayleigh scattering method, Anal. Biochem. 422 (2012) 1–6.
- [19] J. Wei, G. Huang, L. Zhu, S. Zhao, C. An, Y. Fan, Enhanced aqueous solubility of naphthalene and pyrene by binary and ternary Gemini cationic and conventional nonionic surfactants, Chemosphere 89 (2012) 1347–1353.
- [20] A. Brun, G. Brezesinski, H. Möhwald, M. Blanzat, E. Perez, I. Rico-Lattes, Interaction between phospholipids and new Gemini catanionic surfactants having anti-HIV activity, Colloids Surf., A 228 (2003) 3–16.
- [21] H. Tan, H. Xiao, Synthesis and antimicrobial characterization of novel l-lysine gemini surfactants pended with reactive groups, Tetrahedron Lett. 49 (2008) 1759–1761.
- [22] J. Wei, G. Huang, H. Yu, C. An, Efficiency of single and mixed Gemini/conventional micelles on solubilization of phenanthrene, Chem. Eng. J. 168 (2011) 201–207.
- [23] W. Zhang, G. Huang, J. Wei, D. Yan, Gemini micellar enhanced ultrafiltration (GMEUF) process for the treatment of phenol wastewater, Desalination 311 (2013) 31–36.
- [24] Y.H. Qu, G.M. Zeng, J.H. Huang, K. Xu, Y.Y. Fang, X. Li, H.L. Liu, Recovery of surfactant SDS and Cd²₊ from permeate in MEUF using a continuous foam fractionator, J. Hazard. Mater. 155 (2008) 32–38.
- [25] J. Fan, W.B. Yang, A.M. Li, Adsorption of phenol, bisphenol A and nonylphenol ethoxylates onto hypercrosslinked and aminated adsorbents, React. Funct. Polym. 71 (2011) 994–1000.
- [26] Y. Sun, Y. Feng, H. Dong, Z. Chen, Adsorption of dissymmetric cationic gemini surfactants at silica/ water interface, Surf. Sci. 601 (2007) 1988–1995.
- [27] C. Wei, X. Huang, R. Ben Aim, K. Yamamoto, G. Amy, Critical flux and chemical cleaning-in-place during the long-term operation of a pilot-scale submerged membrane bioreactor for municipal wastewater treatment, Water Res. 45 (2011) 863–871.
- [28] P. Yenphan, A. Chanachai, R. Jiraratananon, Experimental study on micellar-enhanced ultrafiltration (MEUF) of aqueous solution and wastewater containing lead ion with mixed surfactants, Desalination 253 (2010) 30–37.
- [29] V.D. Karate, K.V. Marathe, Simultaneous removal of nickel and cobalt from aqueous stream by cross flow micellar enhanced ultrafiltration, J. Hazard. Mater. 157 (2008) 464–471.
- [30] J.H. Huang, Y.L. Xiong, G.M. Zeng, S.H. Guo, G.X. Xie, D.M. Zhang, X.J. Tang, Z.F. Liu, Separation of phenol from various micellar solutions using MEUF, Sep. Purif. Technol. 98 (2012) 1–6.
- [31] M. Bielska, J. Szymanowski, Micellar enhanced ultrafiltration of nitrobenzene and 4-nitrophenol, J. Membr. Sci. 243 (2004) 273–281.
- [32] J. Wei, G. Huang, C. An, H. Yu, Investigation on the solubilization of polycyclic aromatic hydrocarbons in the presence of single and mixed Gemini surfactants, J. Hazard. Mater. 190 (2011) 840–847.

- [33] J.N. Israelachvili, Intermolecular and Surface Forces, Academic Press, London, 1991.
- [34] R.G. Alargova, V.P. Ivanova, P.A. Kralchevsky, Growth of rod-like micelles in anionic surfactant solutions in the presence of Ca²⁺ counterions, Colloids Surf., A 142 (1998) 201–218.
- [35] K. Sakai, S. Umezawa, M. Tamura, Y. Takamatsu, K. Tsuchiya, K. Torigoe, T. Ohkubo, T. Yoshimura, K. Esumi, H. Sakai, M. Abe, Adsorption and micellization behavior of novel gluconamide-type gemini surfactants, J. Colloid Interface Sci. 318 (2008) 440–448.
- [36] Q. Zhang, M. Tian, Y. Han, C. Wu, Z. Li, Y. Wang, Synthesis, aggregation behavior and interfacial activity of branched alkylbenzenesulfonate gemini surfactants, J. Colloid Interface Sci. 362 (2011) 406–414.
- [37] P. Mukerjee, Solubilization in micellar systems, Pure Appl. Chem. 52 (1980) 1317–1321.
 [38] C.C. Hu, R.Q. Li, H. Yang, J.B. Wang, Properties of
- [38] C.C. Hu, R.Q. Li, H. Yang, J.B. Wang, Properties of binary surfactant systems of nonionic surfactants C12E10, C12E23, and C12E42 with a cationic gemini surfactant in aqueous solutions, J. Colloid Interface Sci. 356 (2011) 605–613.