Influence of micelle properties on micellar-enhanced ultrafiltration for chromium recovery

Hau Thi Nguyen, Wen-Shing Chang, Nguyen Cong Nguyen, Shiao-Shing Chen and Hau-Ming Chang

ABSTRACT

An investigation of micelle properties on the recovery of chromium for micellar enhanced ultrafiltration (MEUF) process was conducted using cationic surfactant of cetyltrimethylammonium bromide (CTAB). The relationship between degree of ionization, micellar sizes and chromium removal were determined in this study. The results showed that the complete ionization for CTA^+ and Br^- was observed for CTAB lower than 0.72 mM and aggregation initiated at concentration of CTAB higher than 0.72 mM to yield attraction of counterion. The micellar sizes increased with increase in concentration of CTAB (higher than 4.02 mM) to generate micron-sized micelles. The distribution of micellar sizes was used to estimate the molecular weight cutoff of membrane used in the MEUF process. As chromium was added into aqueous CTAB solution, the chromate was dominant and bound on the micellar surface instead of Br^-. Moreover, the presence of micelle formed a gel-layer to slightly shrink the membrane pore, therefore, UF membrane of 30k Da molecular weight cutoff (pore size ≈ 7.9 nm) was selected in the MEUF process to achieve the removal efficiency of Cr(VI) higher than 95%.

Key words | cetyltrimethylammonium bromide, chromium, micellar-enhanced ultrafiltration, micellar size

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INTRODUCTION

The micellar enhanced ultrafiltration (MEUF) process has been studied for removal of various pollutants from aqueous phase which include organic and inorganic compounds (Baek & Yang 2004; Liu *et al.* 2004; Li *et al.* 2006; Witek *et al.* 2006; Landaburu-Aguirre *et al.* 2011; Zeng *et al.* 2011; Chang *et al.* 2015). The mechanism of this process is to sieve out the pollutants by using a membrane due to the increased size of the micelle complex. Surfactant is acted as an essential role in MEUF process and the characteristic of surfactant is usually amphiphilic organic compounds, which contain both hydrophobic tails and hydrophilic heads. Surfactants are generally classified as cationic, anionic and nonionic surfactants and micelle is formed at critical micelle concentration (CMC). Micellization is accounted for by various free-energy contributions associated with assembling the charged micelle from its constituent surfactant ions which are released by the surfactant heads or added electrolytes to bind onto the micelle surface, inducing a partial reduction of the micelle surface charge (Srinivasan & Blankschtein 2003; Liu & Li 2005). Conversely, the performance of polymeric porous membranes is strongly dependent on the pore size, distribution and porosity. Moreover, the intrinsic permeation of the UF membrane is affected by the operating conditions, i.e. mass transfer resistance, gel layer formation, fouling phenomena, and interaction between solutes and the membrane solid matrix (Issid *et al.* 1992). The growth and structure of micelle have been reported as functions of chain length of surfactant monomer, surfactant concentration, operating temperature and salt concentration to evaluate the hydrodynamic radius, which is related to the chain length or grown from small spherical aggregates into long spherocylindrical micelles under high concentration (Missel *et al.* 1983). In addition, the electrical charge of added salt should be opposite to the micellar surface charge, since the electrolytes in the surfactant solution can be exhibited by both salt effect and magnetic effect in micellar system, which influences the strength of micellar surface binding (Lei *et al.* 1992). For micelle shape, different effects were observed for different surfactants with various pH values (Singh *et al.* 2013).

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Much literature has reported the effect for microenvironment in reverse micellar system. The size of synthesized micellar complex particles can be strongly changed by several parameters such as water content, reagent concentration and the intermicellar interactions, which is probably due to the change in the microenvironment, such as redox potentials and various interactions between reagents, the interface, the adsorption of salts and other molecules (Lisiecki & Pileni 1993; Pileni 2003; Rupp *et al.* 2010). Moreover, the aggregation and micellization have been studied by the operating temperature, concentration of surfactant, and polymer and electrolyte (Huang *et al.* 2012b; Kumar *et al.* 2013; Chauhan *et al.* 2014). Furthermore, the performance of MEUF process is determined by the target pollutant rejection efficiency and the permeate flux, which are affected by the characteristics of micellar system, membrane properties and operating conditions. For micellar system, degree of ionization, ionic strength, Debye length, and aggregation number are related to the micellar size, which are the crucial factors in affecting the entrapping capacity for the target pollutant.

Several researchers have reported the effects of operating pressure, concentration of pollutant, temperature, and concentration of surfactant on the removal efficiency and permeate flux in the MEUF process for various inorganic and organic pollutants (El Zeftawy & Mulligan 2011; Huang *et al.* 2012a; Vinder & Simoni 2012; Lee & Shrestha 2014). However, the correlations among the micellar complex size and parameters such as variations of aggregation, micellization, degree of ionization and target pollutant entrapping by micelle are not clear. Hence, the objectives of this study are focused on: (1) determination of the characteristics of cetyltrimethylammonium bromide (CTAB) micellar system without chromium and *with chromium*; (2) effect of distribution of micellar sizes on permeate flux in MEUF process; and (3) evaluation of the chromium removal efficiency in MEUF process.

EXPERIMENTAL

Materials

All chemicals were used in this study which was analytical-grade reagents, $K_2Cr_2O_7$ and CTAB were supplied by Merck and Sigma Aldrich, respectively. The thin film composite UF membrane (type: JW) manufactured by GE-Desal which possessed the molecular weight cutoff of 30 kDa and operating pH range from 1 to 11, flux(GFD)/psi of 192–207/50.

Experimental setup

Figure 1 shows the schematic diagram of experimental setup unit. Stage 1 was conducted for investigation of micellar system, and stage 2 was studied for MEUF process. In stage 1, the characteristics of micellar system were determined with and without electrolyte (chromium) by various

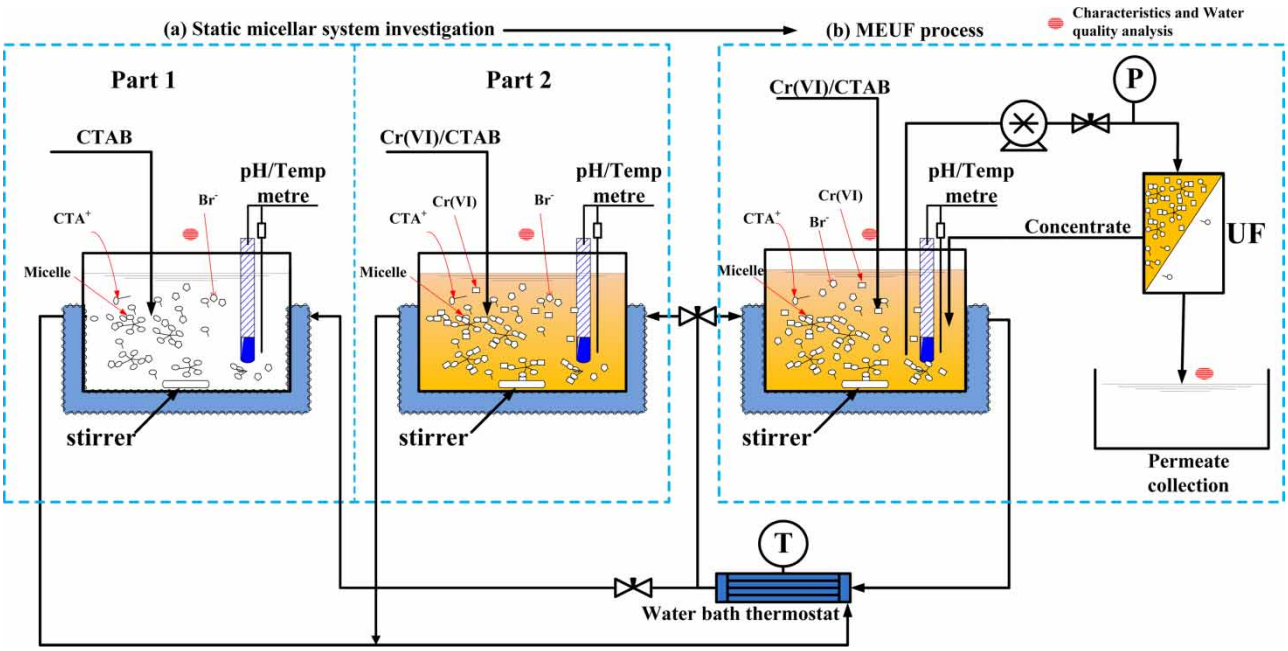

Figure 1 | Schematic diagram: (a) stage 1: static micellar system investigation; and (b) stage 2: MEUF process.

concentrations of CTAB. In part 1, the concentrations of CTAB were increased from 0.1 mM to 10 mM without chromium. The CTAB aqueous solutions were prepared by deionized water and well mixed by stirring for at least 24 hours and setting for 30 minutes. In part 2, $K_2Cr_2O_7$ (chromium) with concentrations from 1 mM to 8 mM were added into CTAB solutions with concentration of 5 mM, and then the solution was mixed, stirred and set using the procedure described for part 1. In stage 2, the UF module comprised a batch tank and a UF unit, in which UF unit was fabricated with stainless outside crust and plastic membrane support. The effective membrane area was 161.5 cm^2 with adjustable feed flow and pressure. The synthetic wastewater samples of Cr(VI) and CTAB were prepared by dissolving $K_2Cr_2O_7$ and CTAB in deionized water using the procedure of stage 1–part 2. In this batch operation, concentrate stream was recirculated to the feed water tank with concentration ratio of 50% and the permeate flux was withdrawn for analysis.

Characterization of micellar system

Degree of ionization is defined by concentration of counterions in the bulk to total ion concentration and expressed using Equation (1), where the range of α is between 0 and 1 (Hsiao *et al.* 2005).

$$\alpha = \frac{C_{\text{bulk}}}{C_{\text{t}}} \tag{1}$$

where C_{bulk} is the concentration of the measured counterion (Br^- and chromium) concentration (mM), and C_t is the total counterion concentration (mM).

The ratio of forming micelle for surfactant is defined by the molar concentration ratio of micelles in the bulk to the total dissociated surfactant monomer:

$$\psi = \frac{S'}{S} \tag{2}$$

where S′ is the concentration of the measured forming micelle concentration (mM), and S is the total dissociated surfactant monomer (mM).

Micelle aggregation number is described as the number of molecules presented in a micelle. The aggregation number is given as below (Anachkov *et al.* 2012):

$$N_{\text{agg}} = \frac{Z}{\alpha} \tag{3}$$

where α is the degree of ionization, Z is the micelle charge that is derived from the ionic strength, I, Debye length, k^{-1}, and zeta potential ($\text{zeta} = 4\pi \times k^{-1} \times Z/\xi$, $k^{-1} = 0.304/\sqrt{I}$, ξ = dielectric constant) (Fuerstenau *et al.* 1985).

Analytical methods

The concentration of CTA^+ and Br^- were analyzed using ion-selective electrodes (ISE) meter (a DionexICS-90), Cr(VI) was determined by UV-Vis light spectrophotometer. The viscosity and the conductivity were determined by a Vibro Viscometer (AD Company, Japan) and a conductivity meter (Sension156, Hach, China), respectively. The pH and total dissolved solids were determined by HACH – Sension 156 meter. The micellar size was measured by Dynamic Light Scattering (DLS) method (SZ-100 (Horiba, Japan)).

RESULTS AND DISCUSSION

Characterization of CTAB micellar system without chromium

In the aqueous solution, CTAB was dissociated into CTA^+ and counterion Br^-. The degree of ionization (α), concentrations of CTA^+ and Br^-, the ratio of forming micelles (ψ), the adsorption ratios of counterions (Br^-) (ε), were measured as a function of CTAB up to 10 mM without adding electrolyte in the aqueous solution. The degree of ionization (α) was equal to 1 and kept a plateau trend with the concentration of CTAB lower than 0.72 mM, meaning the counterion (Br^-) were dissociated completely in this stage as shown in Figure 2(a). However, the value of α decreased gradually from 1.0 to 0.23 with increasing concentration of CTAB from 0.72 mM to 10.0 mM, since micellization yielded electrostatic attraction from micelle at the concentration of CTAB higher than 0.72 mM and induced partially counterions binding to micelles. Furthermore, the measured CTA^+ increased initially and dropped dramatically at the turning point of 0.92 mM of CTAB, which is the CMC as shown in Figure 2(b). With the concentration higher than CMC, the measured CTA^+ gradually decreased with increasing concentration of CTAB due to proceeded micellization. This phenomenon was also demonstrated by the variation of the ratio of forming micelles for CTA^+ (ψ). The aggregation was initiated from the concentration of CTAB of 0.72 mM and the micelle was formed at the concentration of 0.92 mM. Thereafter, there were many micelles formed and also increased the

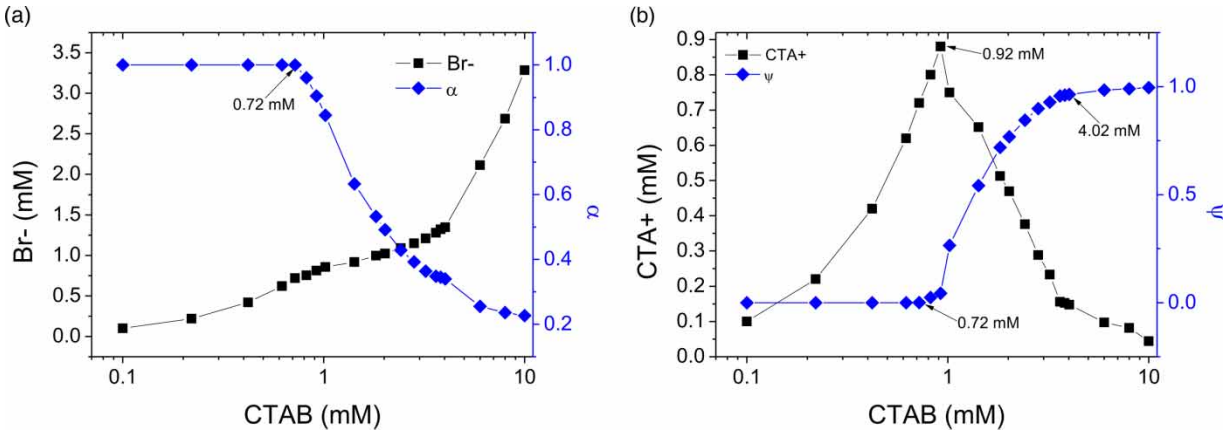

Figure 2 | (a) The effect of variation of CTAB concentrations on α and Br^-. (b) The effect of variation of CTAB concentrations on CTA^+ and ψ.

micellar sizes with increase in concentration of CTAB. When the concentration of CTAB exceeded 4.02 mM, ψ showed a plateau trend in the range of 0.96–0.99 which meant the micellization of CTA^+ was excellent at higher concentration of CTAB.

The micellar sizes increased with an increase in concentration of CTAB as shown in Figure 3, and the distribution of micellar sizes was divided into nano-size (0–999 nm) and micron-size (≥1,000 nm) particles in a polydisperse phase. However, the retained efficiency depended on the pore size of the membrane. When the UF membrane was applied in MEUF process, its molecular weight cutoff (MWCO) and pore size usually ranged from 1,000 to 10^6 Daltons (Akita *et al.* 1999; Deriszadeh *et al.* 2009; Lee & Shrestha 2014) and 1.5–42.3 nm, respectively. The pore size was estimated from diffusion coefficient, viscosity and particle diameter of molecules by the Stokes–Einstein equation (Kim *et al.* 1994). Typically, 90% rejection was used to estimate the MWCO for the membrane (Calvo *et al.* 2011), thus, the corresponding MWCO of membrane was estimated accordingly as shown in Table 1, and the estimation procedure offered an important reference for operating parameter in MEUF process.

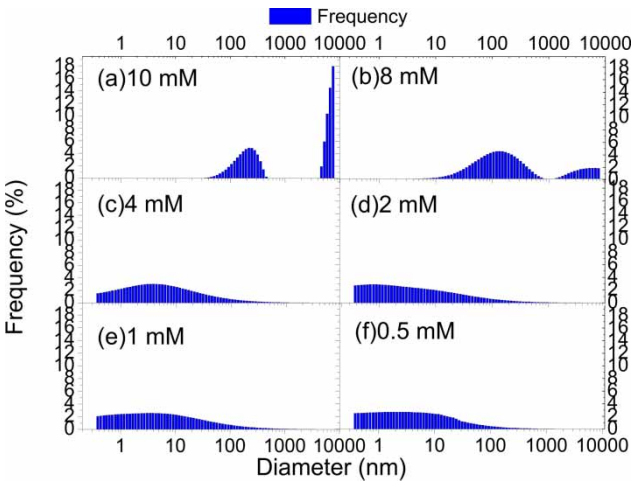

Figure 3 | The distribution of micellar sizes.

Characterization of CTAB micellar system with chromium

Figure 4(a) shows the variations of the degree of ionization (α), free Br^- and Cr(VI) in the CTAB aqueous solution at a fixed concentration of 5 mM CTAB. With the increasing concentration of chromium, α was decreased from 0.48 to 0.06, free Br^- concentration was slightly increased from 0.94 mM to 0.98 mM, and free Cr(VI) was gradually increased from 0.01 to 0.22. However, free Br^- concentration was kept a plateau trend at the chromium concentration higher than 6 mM. Figure 4(b) shows the variations of the free CTA^+ and the micelle charge in the CTAB

Table 1 | Estimated MWCO of membrane versus minimum micellar size at 90% rejection for various concentrations of CTAB

CTAB (mM)	0.5	1	2	4	8	10
Micellar size (nm)	0.62	0.62	0.8	0.8	44.72	118.74
MWCO (Da)	150	150	200	200	1,120,000	8,500,000

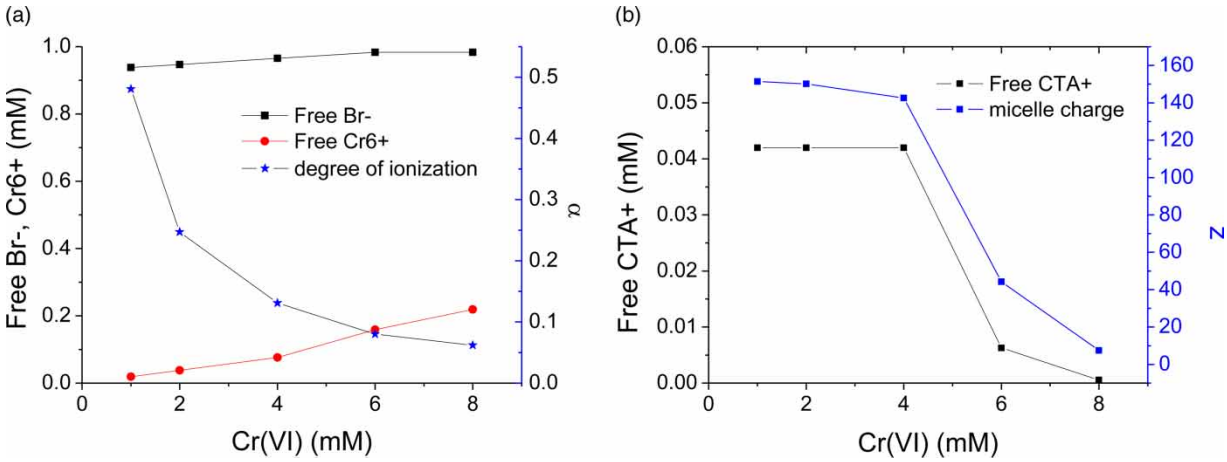

Figure 4 | (a) The variations of the degree of ionization and free Br^- as a function of concentration of chromium at 5 mM of CTAB. (b) The variations of free CTA^+ and Cr(VI) as a function of concentration of chromium at 5 mM of CTAB.

aqueous solution with various concentrations of chromium. The results showed that the free CTA^+ concentrations were stable (0.042 mM) when the concentrations of Cr(VI) increased from 1 to 4 mM, and then quickly decreased to 0.0005 mM with the concentration of Cr(VI) higher than 4 mM. The micelle charge was decreased with increasing chromium concentration since almost CTA^+ completely formed micelle and chromium was more dominant than Br^- which resulted in the decreasing α and micelle charge. Hence, micelle aggregation number was significantly prompted.

The distributions of micellar sizes were determined as a function of concentration of chromium at the concentration of CTAB of 5 mM as shown in Figure 5. The results

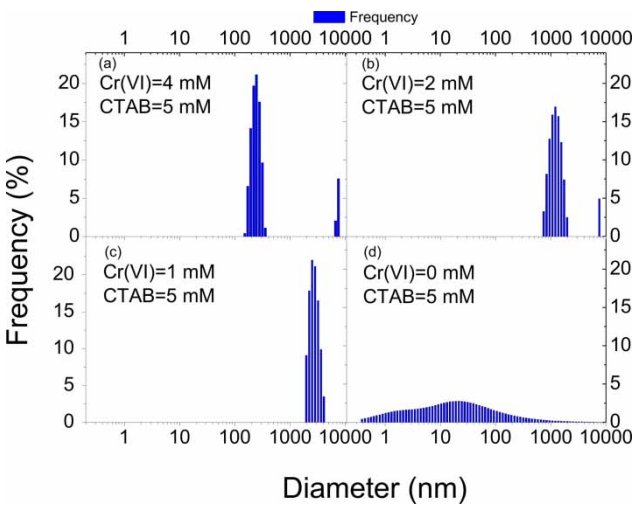

Figure 5 | The distributions of micellar sizes as a function of concentration of chromium at 5 mM of CTAB.

indicated that the presence of chromium was beneficial for prompting micellization and counterions binding onto micelles.

Removal efficiency of chromium and ratio of relative flux in MEUF process

The results demonstrated that the presence of chromium increased the micellar size, however, the micellar size changed in the MEUF process due to spatial confinement and moderate hydrodynamic forces (Zhao *et al.* 2014). The solution behaved as a gel-alike and exhibited strong anisotropic scattering, indicating structure deformation along the flow direction in the shear-induced phase (Oda *et al.* 1997). As can be seen in Table 1, the minimum rejected micellar size at 90% rejection was 118.74 nm (corresponded membrane MWCO ≈ 8,500k Da) for 10 mM of CTAB, but the effect of structure deformation could induce the smaller micellar size in MEUF process. Moreover, a fraction of free Cr(VI) still existed in the aqueous solution and the molecular size of Cr(VI) (dichromate ion) was about 0.674 nm which could penetrate through the membrane, the presence of micelle could form a gel-layer and shrink the membrane pore. Thus, MEUF process was employed at 10 mM CTAB and UF membrane of 30 kDa MWCO (pore size ≈ 7.9 nm) to achieve higher flux and stillreach high recovery of chromium. The results in Figure 6(a) show that the concentrations of CTA^+ were gradually decreased and the concentrations of Br^- were increased with increasing chromium concentration. Figure 6(b) shows the variations of removal efficiency of Cr(VI) and the ratio of relative flux(Φ) in the MEUF process.

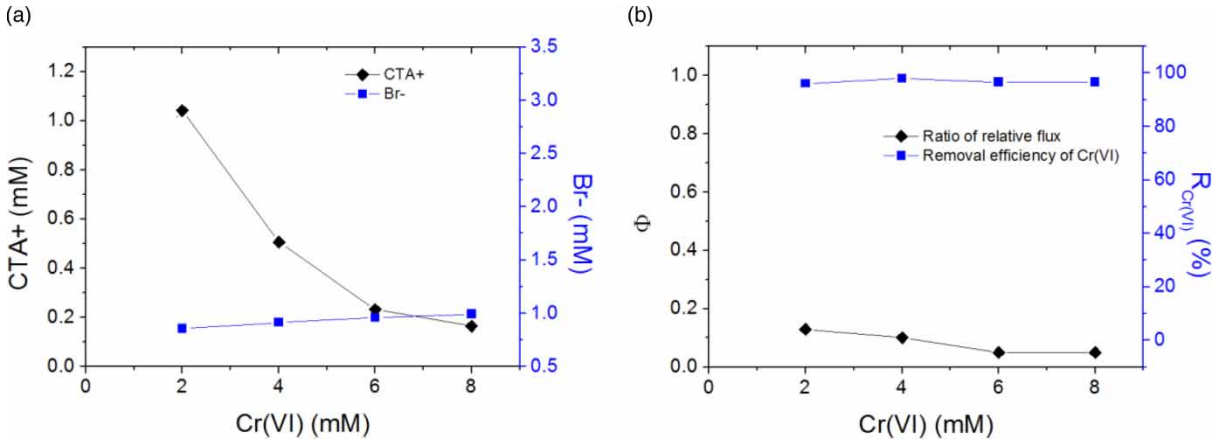

Figure 6 | (a) The variations of free CTA^+ and Br^- in permeate for MEUF process. (b) The variations of removal efficiency of Cr(VI) and the ratio of relative flux, Φ.

The results presented that the removal efficiency of Cr(VI) was higher than 95% with the increase of chromium concentration from 2 mM to 8 mM, the ratio of relative flux (Φ) was gradually decreased with increasing concentration of chromium and varied from 0.24 to 0.05 which was due to the formation of gel-layer and shrinking of the membrane pore. Therefore 30 kDa MWCO membrane was suitable to sieve out the micellar complex with acceptable flux.

CONCLUSIONS

In the micellar system, the ratio of forming micelles (ψ) increased with increasing concentration of CTAB in a polydisperse phase, and the aggregation was initiated from 0.72 mM of CTAB to yield the attraction effect to counterion. The micellar sizes increased with increasing concentration of CTAB and yielded micron-sized micelles at the concentration of CTAB higher than 4.02 mM .The distribution of micellar sizes was divided into nano-size (0–999 nm) and micron-size (≥1,000 nm) in a polydisperse phase. The distribution of micellar sizes was available to estimate molecular weight cutoff of membrane. As chromium was added into aqueous CTAB solution, the chromate was dominant and bound on the micellar surface instead of Br^-. Moreover, the presence of micelle formed a gel-layer which shrinked the membrane pore. Therefore, UF membrane of 30 kDa MWCO (pore size ≈ 7.9 nm) was applied in MEUF process and achieved a removal efficiency of Cr(VI) higher than 95%.

REFERENCES

Akita, S., Castillo, L. P., Nii, S., Takahashi, K. & Takeuchi, H. 1999 Separation of Co(II)/Ni(II) via micellar-enhanced ultrafiltration using organophosphorus acid extractant solubilized by nonionic surfactant. *Journal of Membrane Science* **162** (1–2), 111–117.

Anachkov, S. E., Danov, K. D., Basheva, E. S., Kralchevsky, P. A. & Ananthapadmanabhan, K. P. 2012 Determination of the aggregation number and charge of ionic surfactant micelles from the stepwise thinning of foam films. *Advances in Colloid and Interface Science* **183–184**, 55–67.

Baek, K. & Yang, J.-W. 2004 Simultaneous removal of chlorinated aromatic hydrocarbons, nitrate, and chromate using micellar-enhanced ultrafiltration. *Chemosphere* **57** (9), 1091–1097.

Calvo, J. I., Peinador, R. I., Prádanos, P., Palacio, L., Bottino, A., Capannelli, G. & Hernández, A. 2011 Liquid–liquid displacement porometry to estimate the molecular weight cut-off of ultrafiltration membranes. *Desalination* **268** (1–3), 174–181.

Chang, W.-S., Chen, S.-S., Sie, C.-H., Nguyen, N. C., Cheng, H.-H. & Hsu, H.-T. 2015 Recovery of chromium from plastic plating wastewater by cetyltrimethylammonium bromide MEUF and electrodialysis. *Desalination and Water Treatment* **55** (9), 2408–2415.

Chauhan, S., Kaur, M., Kumar, K. & Chauhan, M. S. 2014 Study of the effect of electrolyte and temperature on the critical micelle concentration of dodecyltrimethylammonium bromide in aqueous medium. *The Journal of Chemical Thermodynamics* **78**, 175–181.

Deriszadeh, A., Harding, T. G. & Husein, M. M. 2009 Improved MEUF removal of naphthenic acids from produced water. *Journal of Membrane Science* **326** (1), 161–167.

El Zeftawy, M. A. M. & Mulligan, C. N. 2011 Use of rhamnolipid to remove heavy metals from wastewater by micellar-enhanced ultrafiltration (MEUF). *Separation and Purification Technology* **77** (1), 120–127.

Fuerstenau, M. C., Miller, J. D. & Kuhn, M. C. 1985 *Chemistry of Flotation*. SME/AIME, NewYork.

Hsiao, C. C., Wang, T. Y. & Tsao, H. K. 2005 Counterion condensation and release in micellar solutions. *Journal of Chemical Physics* **122** (14), 144702.

Huang, J.-H., Guo, S.-H., Zeng, G.-M., Xiong, Y.-L., Zhang, D.-M., Tang, X.-J. & Xie, G.-X. 2012a Prediction of fouling resistance and permeate flux in cross-flow micellar-enhanced ultrafiltration (MEUF). *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **401**, 81–89.

Huang, J.-H., Zhou, C.-F., Zeng, G.-M., Li, X., Huang, H.-J., Niu, J., Li, F., Shi, L.-J. & He, S.-B. 2012b Studies on the solubilization of aqueous methylene blue in surfactant using MEUF. *Separation and Purification Technology* **98**, 497–502.

Issid, I., Lavergne, M. & Lemordant, D. 1992 Using micelles to determine the pore size of UF membranes. *Journal of Membrane Science* **74** (3), 279–287.

Kim, K. J., Fane, A. G., Ben Aim, R., Liu, M. G., Jonsson, G., Tessaro, I. C., Broek, A. P. & Bargeman, D. 1994 A comparative study of techniques used for porous membrane characterization: pore characterization. *Journal of Membrane Science* **87** (1–2), 35–46.

Kumar, B., Tikariha, D., Ghosh, K. K., Barbero, N. & Quagliotto, P. 2013 Effect of polymers and temperature on critical micelle concentration of some gemini and monomeric surfactants. *The Journal of Chemical Thermodynamics* **62**, 178–185.

Landaburu-Aguirre, J., Pongrácz, E. & Keiski, R. L. 2011 Separation of cadmium and copper from phosphorous rich synthetic waters by micellar-enhanced ultrafiltration. *Separation and Purification Technology* **81** (1), 41–48.

Lee, S. H. & Shrestha, S. 2014 Application of micellar enhanced ultrafiltration (MEUF) process for zinc (II) removal in synthetic wastewater: Kinetics and two-parameter isotherm models. *International Biodeterioration & Biodegradation* **95**, Part A, 241–250.

Lei, X., Zhao, G., Liu, Y. & Turro, N. J. 1992 Influence of binding strength of added electrolytes on the properties of micelles and of micellized radical pairs. *Langmuir* **8** (2), 475–480.

Li, C.-W., Liu, C.-K. & Yen, W.-S. 2006 Micellar-enhanced ultrafiltration (MEUF) with mixed surfactants for removing Cu(II) ions. *Chemosphere* **63** (2), 353–358.

Lisiecki, I. & Pileni, M. P. 1993 Synthesis of copper metallic clusters using reverse micelles as microreactors. *Journal of the American Chemical Society* **115** (10), 3887–3896.

Liu, C.-K. & Li, C.-W. 2005 Combined electrolysis and micellar enhanced ultrafiltration (MEUF) process for metal removal. *Separation and Purification Technology* **43** (1), 25–31.

Liu, C.-K., Li, C.-W. & Lin, C.-Y. 2004 Micellar-enhanced ultrafiltration process (MEUF) for removing copper from synthetic wastewater containing ligands. *Chemosphere* **57** (7), 629–634.

Missel, P. J., Mazer, N. A., Benedek, G. B. & Carey, M. C. 1983 Influence of chain length on the sphere-to-rod transition in alkyl sulfate micelles. *The Journal of Physical Chemistry* **87** (7), 1264–1277.

Oda, R., Panizza, P., Schmutz, M. & Lequeux, F. 1997 Direct evidence of the shear-induced structure of wormlike micelles: gemini surfactant 12–2–12. *Langmuir* **13** (24), 6407–6412.

Pileni, M.-P. 2003 The role of soft colloidal templates in controlling the size and shape of inorganic nanocrystals. *Nat Mater* **2** (3), 145–150.

Rupp, C., Steckel, H. & Müller, B. W. 2010 Mixed micelle formation with phosphatidylcholines: The influence of surfactants with different molecule structures. *International Journal of Pharmaceutics* **387** (1–2), 120–128.

Singh, K., Dharaiya, N., Marangoni, D. G. & Bahadur, P. 2013 Dissimilar effects of solubilized p-toluidine on the shape of micelles of differently charged surfactants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **436**, 521–529.

Srinivasan, V. & Blankschtein, D. 2003 Effect of counterion binding on micellar solution behavior: 1. Molecular-thermodynamic theory of micellization of ionic surfactants. *Langmuir* **19** (23), 9932–9945.

Vinder, A. & Simoni, D. M. 2012 Removal of AOX from waste water with mixed surfactants by MEUF. *Desalination* **289**, 51–57.

Witek, A., Kołtuniewicz, A., Kurczewski, B., Radziejowska, M. & Hatalski, M. 2006 Simultaneous removal of phenols and Cr^{3+} using micellar-enhanced ultrafiltration process. *Desalination* **191** (1–3), 111–116.

Zeng, G.-M., Li, X., Huang, J.-H., Zhang, C., Zhou, C.-F., Niu, J., Shi, L.-J., He, S.-B. & Li, F. 2011 Micellar-enhanced ultrafiltration of cadmium and methylene blue in synthetic wastewater using SDS. *Journal of Hazardous Materials* **185** (2–3), 1304–1310.

Zhao, Y., Cheung, P. & Shen, A. Q. 2014 Microfluidic flows of wormlike micellar solutions. *Advances in Colloid and Interface Science* **211**, 34–46.

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