Removal characteristics of anionic metals by micellar-enhanced ultrafiltration

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Abstract

Surfactant-based separation of $Fe(CN)_6^{3-}$ and CrO_4^{2-} using regenerated cellulose membrane was studied in order to assess the potential of micellar-enhanced ultrafiltration for the remediation of wastewater or groundwater polluted with ferriccyanide and chromate. In the ferriccyanide/octadecylamine acetate (ODA) and chromate/ODA systems, removal of ferriccyanide increased from 73 to 92% and to 98%, and that of chromate from 64 to 97% and to >99.9% as the molar ratio of ODA to ferriccyanide and to chromate increased from 1 to 2 and to 3, respectively. In the ferriccyanide/chromate/ODA system, while the removal of ferriccyanide increased from 62 to 72% and to 93%, the removal of chromate from 20 to 38% and to 68% as the molar ratio of ferriccyanide:chromate:ODA increased from 1:1:1 to 1:1:2 and to 1:1:4, respectively. With the molar ratio of 1:1:6, the removal was >99.9 and 98% for chromate and ferriccyanide, respectively. Ferriccyanide ions were more easily bound to ODA micelles because the binding power of ferriccyanide was greater than that of chromate.
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1. Introduction

The increasing contamination of urban and industrial wastewater or groundwater by toxic metal ions is a serious environmental problem. These inorganic pollutants are of considerable concerns because they are non-biodegradable, highly toxic and have a probable carcinogenic effect. If directly discharged into the sewage system they may not only

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seriously damage the operation of biological treatment plants but also make the activated sludge unsuitable for application to agricultural land.

Cyanides are used in a number of chemical synthesis and metallurgical processes (as forms of simple salts or cyanide complexes). As a class, cyanides are highly toxic and must be destroyed or removed from wastewaters prior to discharge. Hexavalent chromium is known to be much more toxic than trivalent chromium. It poses a greater threat to human health due to its high solubility and mobility in water. On the other hand, trivalent chromium is an essential element for living beings, playing an important role in carbohydrate metabolism. Lack of appropriate disposal facilities has led to a serious water and soil pollution throughout the world today.

Traditionally, techniques such as sorption and chemical precipitation have been used for the removal of metal ions from aqueous effluents [1–3], however the techniques are incapable of reducing concentration to the levels required by law or are prohibitively expensive. The use of membrane separation process in the treatment of wastewater and groundwater containing toxic metal ions is an attractive and suitable technique, and it has to be easily included in the whole process, which is the reason why membrane separations are being used more and more frequently [4]. In order to separate metallic ions, reverse osmosis or nanofiltration should be used due to the size of the ions in aqueous phase. But the usual permeate fluxes of reverse osmosis membranes are limited and require high transmembrane pressure, which makes the process expensive.

Micellar-enhanced ultrafiltration (MEUF) involves the addition of a surfactant above the critical micellar concentration (CMC) in order to entrap ionic solutes in solution [5–21]. The increased hydrodynamic size of the solutes enables their rejection by polymeric ultrafiltration membranes. Solute rejection and permeate flux depend on the characteristics of solute and membrane. In order to remove metallic chromate and ferriccyanide anions from aqueous solutions, a cationic surfactant is added to the aqueous stream containing the pollutants. The surfactant forms micelles, surfactant aggregates that contain about 50–100 surfactant molecules, above the CMC. Chromate and ferriccyanide ions bind on the surface of the oppositely charged micelles. This solution is then passed through an ultrafiltration membrane with pore sizes small enough to block the passage of micelles. The rejection of micelles brings about the rejection of the chromate and ferriccyanide adsorbed on micelles. The unbounded ions and surfactant monomers pass through the ultrafiltration membrane to the permeate side. A conceptual schematic diagram of MEUF for the removal of chromate and ferriccyanide was shown in Fig. 1.

So far, MEUF has been used to separate the organic pollutants, heavy metals, chromate, nitrate and sulfate using cationic surfactant, anionic surfactants, and polyelectrolytes as additives [5–21]. However, most of researches on MEUF have focused on the single-pollutant system and few researchers reported multi-pollutant system [6,14,15,19]. In a multi-pollutant system, competition due to difference in binding power of pollutants may inhibit the binding of pollutants with weaker binding power.

In this study, simultaneous removal of chromate and ferriccyanide from the wastewater or groundwater was investigated with MEUF using octadecylamine acetate (ODA) as a cationic surfactant. The removals of chromate, ferriccyanide, and ODA were compared in the chromate/ODA, ferriccyanide/ODA system, and in the chromate/ferriccyanide/ODA system.
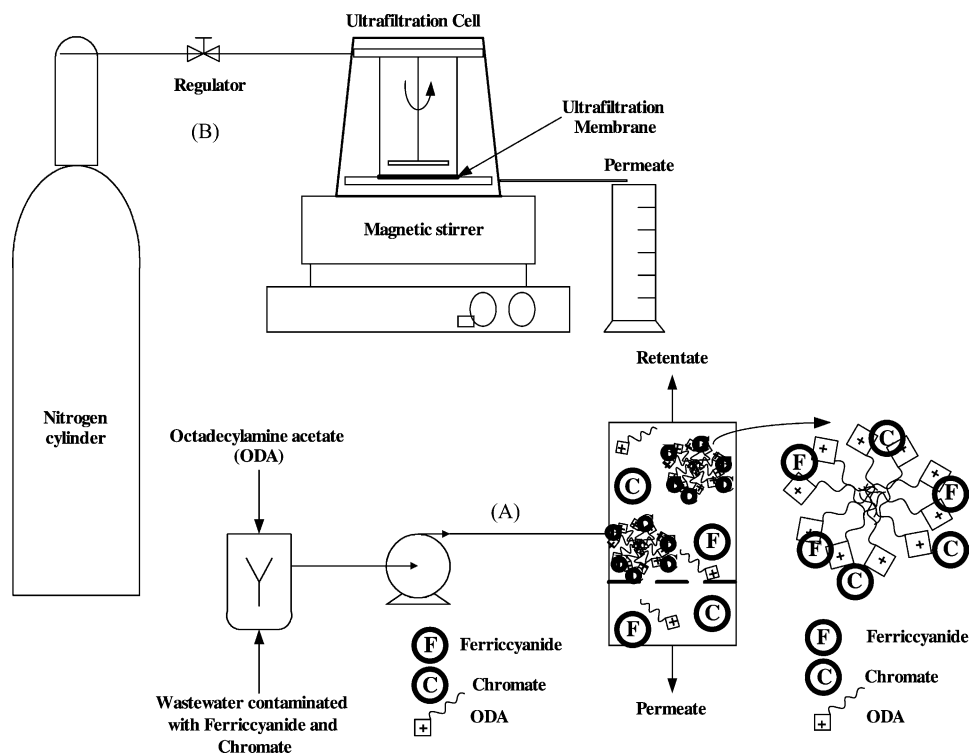
Fig. 1. A conceptual picture of micellar-enhanced ultrafiltration (A) and schematic diagram of experimental apparatus (B).

2. Materials and method

2.1. Chemicals

The octadecylamine acetate (ODA) of 98% purity was obtained from TCI chemicals (Japan). The CMC of ODA was measured by Surface tension meter (Fisher, UK), and the value was 0.9 mM. Ferriccyanide and chromate were purchased from Sigma as a form of sodium salts. Deionized water was used in preparing all solution.

2.2. Procedures

The ultrafiltration experiments were operated in a batch stirred cell (Amicon 8400, Millipore, USA). The ultrafiltration membranes were regenerated cellulose membrane with a diameter of 76 mm and an effective area of 0.045 m^2 (Millipore, USA). Two different sizes of membranes were used: *molecular weight cut-off (MWCO) of 10,000 and 3000*. The pressure was maintained at 2 bar gauge and the temperature was held constant at 25 °C. A schematic configuration of experimental apparatus was shown in Fig. 1.

Feed solution was prepared by mixing stoichiometric amounts of ODA, chromate, and ferriccyanide. The ultrafiltration cell was initially filled with 100 ml of feed solution. The concentrations of chromate, ferriccyanide and ODA of the permeate samples at the desired time intervals were analysed by UV-Vis spectrophotometer (HP 8452 A, USA) at wavelengths of 372, 418, and 600 nm, respectively. The removal of chromate, ferriccyanide, and ODA were calculated from the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_i}\right) \times 100$$

where C_i is the feed concentration of chromate, ferriccyanide, or ODA, and C_p is the concentration of each compound in the permeate.

3. Results and discussion

3.1. Chromate/ODA system

Fig. 2 shows the removal of chromate in the chromate/ODA system as a function of molar ratio of ODA to chromate. Chromate removal increased with the molar ratio of ODA to chromate. In the membrane system with MWCO of 10,000, the removal increased from 64 to 97% and to >99.9% as the molar ratio increased from 1 to 2 and to 3, respectively. Even if the molar ratio increased from 3 to 5, the increase in removal efficiency of chromate was not observed, however, the concentration in the permeate decreased (Table 1). As the pore size of membrane decreased from MWCO of 10,000 to 3000, the removal increased from 64 to 76% at the molar ratio of 1, while the removal was not increased at the above molar ratio of 1. As the filtration progressed, removal of chromate decreased slowly because the
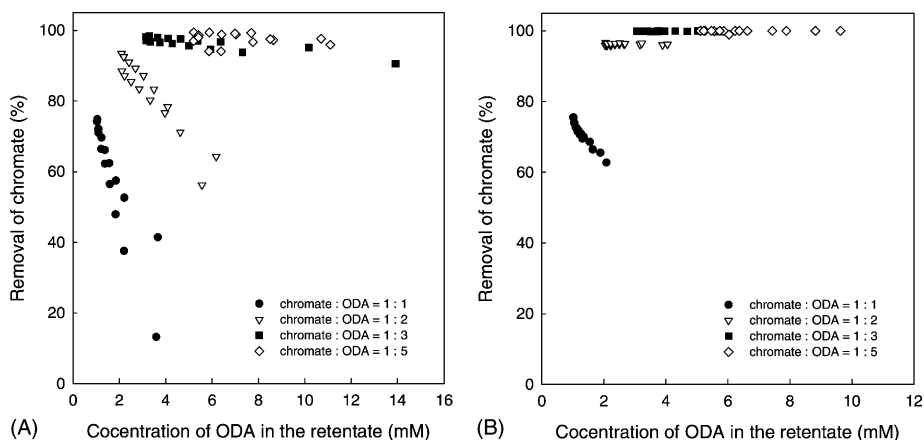

Fig. 2. Effect of membrane MWCO and surfactant concentration on chromate removal from chromate solutions. The initial concentration of chromate was 1 mM and the regenerated cellulose acetate membranes with molecular weight cut-off of 10,000 (A) and molecular weight cut-off of 3000 (B) were used for filtration at 2 bar of transmembrane pressure.

Table 1
The volume reduction and permeate concentration of chromate and ferriccyanide at the end of filtration

System	Molar ratio	$C_{\text{p-chromate}}$ (mM)		$C_{\text{p-ferriccyanide}}$ (mM)		VCR[a]	
		YM10[b]	YM03[c]	YM10[b]	YM03[c]	YM10[b]	YM03[c]
Chromate:CPC system	1:1	5.0E−01	3.6E−01	–	–	4.5	2.2
	1:2	4.8E−02	3.8E−02	–	–	3.4	2.1
	1:3	1.3E−03	1.0E−03	–	–	2.1	1.9
	1:5	2.0E−04	2.0E−04	–	–	1.5	2.0
Ferriccyanide:CPC system	1:1	–	–	7.2E−01	2.6E−01	4.8	2.1
	1:2	–	–	3.9E−01	1.2E−01	3.6	2.2
	1:3	–	–	7.2E−02	2.0E−02	4.5	2.0
	1:5	–	–	3.2E−02	2.6E−03	2.4	2.0
Chromate:ferriccyanide: CPC system	1:1:1	8.2E−01	8.4E−01	6.6E−01	3.7E−01	2.8	2.1
	1:1:2	6.9E−01	6.9E−01	4.8E−01	2.4E−01	2.7	2.0
	1:1:4	3.5E−01	3.3E−01	1.4E−01	5.5E−03	2.6	2.0
	1:1:6	1.0E−03	2.2E−03	2.0E−04	2.0E−04	1.9	1.9
	1:1:10	3.0E−04	1.5E−03	3.0E−03	7.0E−04	1.3	1.9

[a] VCR is the volume concentration factor and defined as follows: VCR = initial feed volume/retentate volume, where the initial feed volume was 100 ml.
[b] YM10 is the regenerated cellulose membrane with MWCO of 10,000.
[c] YM03 is the regenerated cellulose membrane with MWCO of 3000.

retentate in the ultrafiltration cell was concentrated. This phenomenon was severe at the membrane with MWCO of 10,000 and lowest molar ratio of ODA (Fig. 2).

3.2. Ferriccyanide/ODA system

Fig. 3 shows the removal of ferriccyanide in the ferriccyanide/ODA systems as a function of molar ratio of ODA to chromate. Ferriccyanide removal increased with the molar ratio of ODA to ferriccyanide. In the system with MWCO of 10,000, the removal of ferriccyanide increased from 73 to 92%, to 98%, and to 99% as the molar ratio increased from 1 to 2, to 3, and to 5, respectively, at the end of the filtration. In the system with MWCO of 3000, however, the removals were 83, 91, 98, and 99%, respectively at the same molar ratios. When the removals at the early stage of filtration were compared to eliminate the effect of retentate concentration, the removal of ferriccyanide was higher than that of chromate at the same molar ratio of ODA because the removal was a monotonic function of valence of ions (i.e. 3 for ferriccyanide and 2 for chromate).

3.3. Chromate/ferriccyanide/ODA system

The removal of chromate in the presence of ferriccyanide/ODA was expressed as a function of molar ratio of chromate to ferriccyanide and to ODA (Fig. 4). The significant increases of chromate removal shown in chromate/ODA system were not observed and the removal was below 40% though the molar ratio increased from 1:1:1 to 1:1:2 (chromate:ferriccyanide:ODA). The removal increased sharply to 65% when the molar ratio
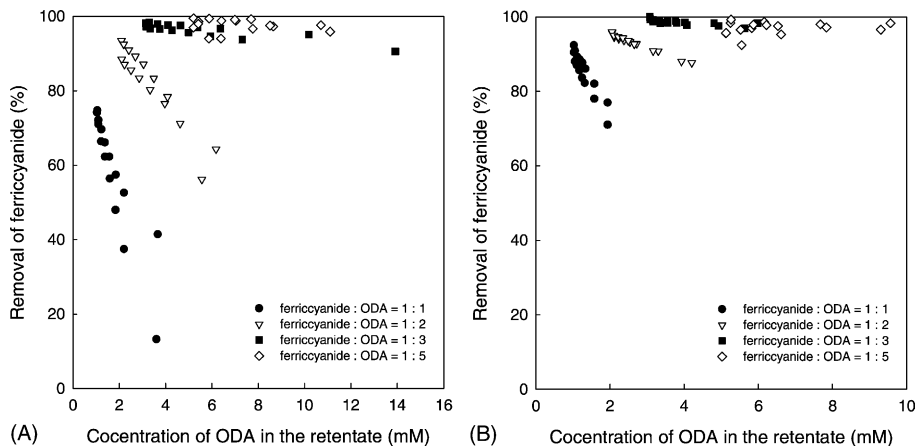
Fig. 3. Effect of membrane MWCO and surfactant concentration on ferriccyanide removal from ferriccyanide solutions. The initial concentration of ferriccyanide was 1 mM and the regenerated cellulose acetate membranes with molecular weight cut-off of 10,000 (A) and molecular weight cut-off of 3000 (B) were used for filtration at 2 bar of transmembrane pressure.

increased to 1:1:4. With the molar ratio of 1:1:6, the removal of >99.9% was obtained. The presence of ferriccyanide decreased the removal of chromate significantly compared to chromate/ODA system because of the competition for binding on the micelles (Table 1). In the membrane with MWCO of 3000, small increase in the removal of chromate was observed, but overall trends were similar to those in the membrane with MWCO of 10,000 (Fig. 4).
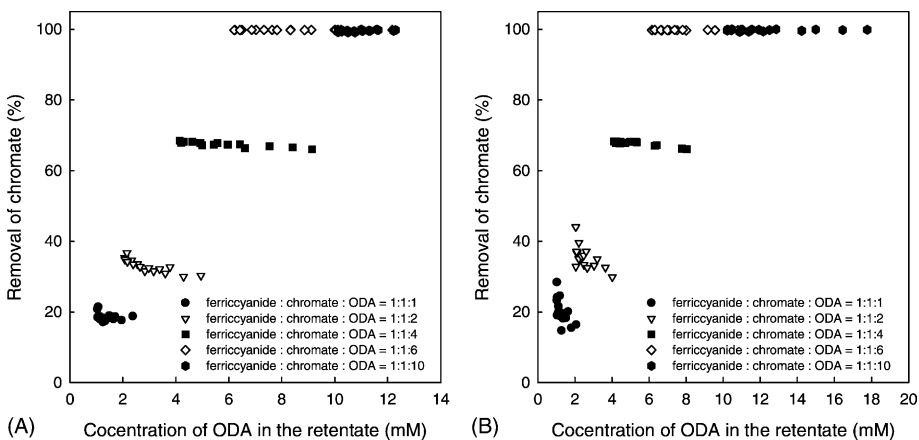

Fig. 4. Effect of membrane MWCO and surfactant concentration on chromate removal from equimolar chromate/ferriccyanide solutions. The initial concentration of chromate and ferriccyanide were 1 mM and the regenerated cellulose acetate membranes with molecular weight cut-off of 10,000 (A) and molecular weight cut-off of 3000 (B) were used for filtration at 2 bar of transmembrane pressure.
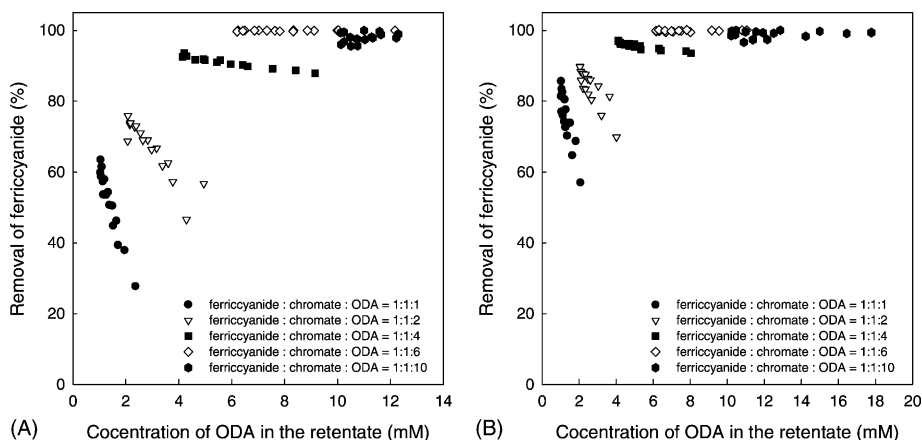
Fig. 5. Effect of membrane MWCO and surfactant concentration on ferriccyanide removal from equimolar chromate/ferriccyanide solutions. The initial concentration of chromate was 1 mM and the regenerated cellulose acetate membranes with molecular weight cut-off of 10,000 (A) and molecular weight cut-off of 3000 (B) were used for filtration at 2 bar of transmembrane pressure.

The removal of ferriccyanide in the presence of chromate/ODA was expressed as a function of molar ratio of chromate to ferriccyanide and to ODA (Fig. 5). The removal of ferriccyanide increased with the molar ratio of ODA added in the feed as shown in ferriccyanide/ODA system. The removal increased to >98% with the molar ratio of 1:1:6 (chromate:ferriccyanide:ODA). It means that the presence of chromate in the system does not significantly affect the removal of ferriccyanide though the removal decreased about by 10% compared to ferriccyanide/ODA system at the low molar ratio of ODA.

This phenomenon can be explained by the binding power between ions and ionic surfactants. Recently, Tangvijitsri et al. [10] reported that differences in the rejection of nitrate, sulfate, and chromate were resulted due to the valence of ions in the polyelectrolyte-enhanced ultrafiltration. Rejection of sulfate and chromate with valences of 2 was similar, but greater than that of nitrate. In the chromate/ferriccyanide/ODA system, ferriccyanide has 3 as valence values, but 2 for chromate. Based on the valences of ions, the binding power of ferriccyanide is greater than that of chromate to bind on the ODA micelles. In this system, ferriccyanide bound on the ODA micelles first because of greater binding power. Theoretically, ferriccyanide of 1 mol needs ODA of 3 mol to bind completely because ferriccyanide has −3 valences and +1 for ODA. The ferriccyanide bound on the micelles in the system to the molar ratio of 1:1:3 (chromate:ferriccyanide:ODA), after then chromate started to bind on the micelles. This assumption is accordance with the removal of chromate/ferriccyanide in the presence of ferriccyanide/ODA or chromate/ODA. The removal of chromate did not increase at the molar ratio of 1:1:1 and 1:1:2, while the removal of ferriccyanide increases with the molar ratio of ODA added in the system. With the greater than molar ratio of 1:1:4, the removal of chromate was similar to those in the chromate/ODA system, while the removal of ferriccyanide was saturated (Table 1). At the molar ratio of 1:1:4, ODA of 3 mol bound to ferriccyanide and ODA of 1 mol bound to chromate.
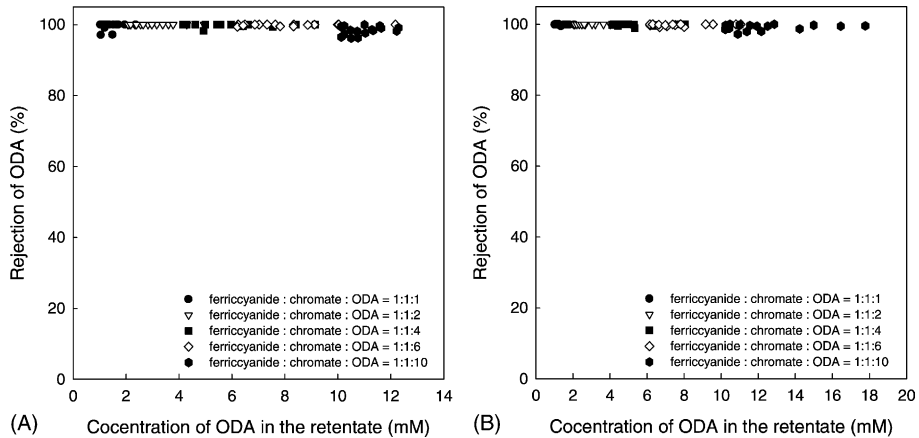
Fig. 6. Effect of membrane MWCO and surfactant concentration on octadecylamine acetate removal from equimolar chromate/ferriccyanide solutions. The initial concentration of chromate was 1 mM and the regenerated cellulose acetate membranes with molecular weight cut-off of 10,000 (A) and molecular weight cut-off of 3000 (B) were used for filtration at 2 bar of transmembrane pressure.

In the MEUF process, the rejection of surfactant as well as the removal of pollutants should be considered. Fig. 6 shows the rejection of ODA as a function of molar ratio. The rejection of ODA was high compared to chromate and ferriccyanide because the concentration of ODA in the feed was greater than the CMC of ODA and the size of ODA micelle is big enough not to pass through the pore of membrane. High rejection of ODA means that secondary contamination due to surfactant leakage through membrane is not severe in MEUF process.

4. Conclusions

Simultaneous removal of ferriccyanide and chromate by MEUF with octadecylamine acetate as a cationic surfactant was investigated. The removal of ferriccyanide and chromate in the ferriccyanide/ODA and chromate/ODA systems were 98 and >99.9%, respectively with the 5 molar ratio of ODA. In the ferriccyanide/chromate/ODA system, the removal of ferriccyanide was similar to that in the ferriccyanide/ODA system, while the removal of chromate was reduced significantly due to the presence of ferriccyanide. It can be explained that the binding power of ferriccyanide is greater than that of chromate because the binding power is in proportion to the valence of ions. The rejection of ODA was high because the size of micelle was big enough compared to the pore size of membrane. Although the removal of chromate was inhibited by the presence of ferriccyanide, MEUF could be an alternative process to treat wastewater simultaneously contaminated by chromate and ferriccyanide.

Acknowledgements

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