The European Journal of Mineral Processing and Environmental Protection
Vol. 4, No. 1, 1303-0868, 2004, pp. 43-48

Removal of iron-cyanide complexes using micellar-enhanced ultrafiltration

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Received 30 September 2002; accepted 15 April 2004

ABSTRACT

Micellar-enhanced ultrafiltration (MEUF)-based separation of iron-cyanide complexes, ferriccyanide and ferrocyanide, was investigated in order to assess the potential of MEUF for the removal of ferriccyanide and ferrocyanide with a cationic surfactant, cetylpyridinium chloride (CPC). The removals of ferriccyanide and ferrocyanide were >99% and 99%, respectively, with the molar ratio of CPC to ferriccyanide/ferrocyanide of 3 and 4, respectively. Both the rejection and the concentration of CPC in the permeate were low enough to meet effluent standard. The MEUF process can be a good alternative to reverse osmosis or ion exchange for removal of iron-cyanide complexes.

Keywords: Cyanide; Micellar-enhanced ultrafiltration; Cetylpyridnium chloride

1. INTRODUCTION

Various pollutants such as heavy metals, cyanide, surfactants are contained in the wastewater generated from electroplating process. Currently, hydroxide precipitation is one of the most widely used techniques to treat heavy metals (Lee *et al.*, 1995). However, the chemical precipitation method becomes ineffective to treat the wastewater containing cyanide due to the formation of complexes between metals and cyanide. Abother well known method to treat cyanide is the alkaline chlorination technique which oxidizes cyanide under alkaline conditions. Recently, electrooxidation and ozone oxidation have been reported as an alternative method to treat wastewater containing metallic cyanides (Carrillo-Pedroza and Soria-Aguilar, 2001; Szpyrkowicz *et al.*, 2002).

Micellar-enhanced ultrafiltration (MEUF) is a new method to treat wastewater containing heavy metals and toxic organic compounds (Ahmadi *et al.*, 1994; Lee *et al.*, 1995; Yildiz *et al.*, 1996; Park *et al.*, 1997; Gzara and Dhahbi, 2001; Tangvijitsri *et al.*, 2002; Danis and Keskinler, 2002; Baek *et al.*, 2003a,b,c,; 2004; Baek and Yang, 2004). It combines the high rejection of reverse osmosis and the higher flow rate of ultrafiltration. In order to remove metallic cyanides from aqueous solution, a cationic surfactant is added to the aqueous stream containing iron-cyanides. Surfactant forms surfactant aggregates (i.e. micelles) which contain about 50 to 100 surfactant molecules, above the critical micelle concentration (CMC). Iron-cyanides bind on the surface of the oppositely charged micelles. The feed 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 removal of the ferriccyanide and ferrocyanide bound on micelles. Unbounded iron-cyanides and surfactant monomers pass through the ultrafiltration membrane to the permeate side. A conceptual schematic diagram of MEUF for the removal of ferriccyanide and ferrocyanide is shown in Figure 1.

In this study, two different forms of iron-cyanides, ferriccyanide and ferrocyanide, were removed by MEUF process with a cationic surfactant, cetylpyridinium chloride (CPC), using ceramic ultrafiltration membrane. The removal characteristics of cyanide complexes were investigated as a function of molar ratio of CPC to ferriccyanide/ferrocyanide.

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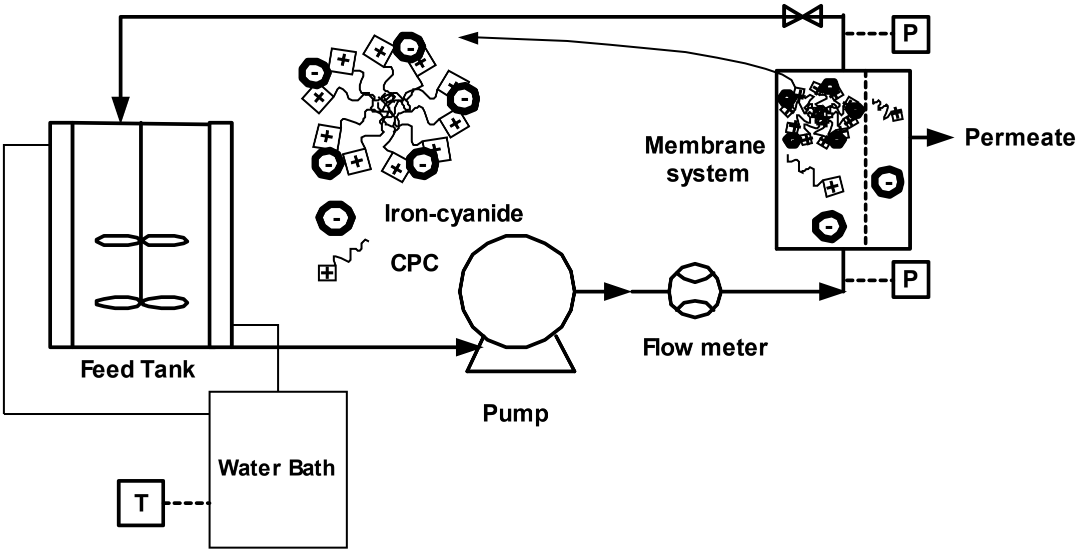

Figure 1. Schematic diagram of MEUF for removal of iron-cyanide

2. MATERIALS AND METHODS

Ferricyanide and ferrocyanide were purchased from Sigma chemicals as a form of potassium salt. CPC, a cationic surfactant, was also obtained from Sigma chemicals (USA). Deionized water was used to prepare all solutions. A cross-flow ultrafiltration system was made by Ceracomb (Asan, Korea) as shown in Figure 1. A ceramic membrane purchased from Ceracomb (Asan, Korea) with pore size of 0.02μm was used for ultrafiltration. The feed tank was initially filled with 2L of the feed solution. Filtration was carried out under 2bar of transmembrane pressure at 25℃. The concentrations of ferricyanide, ferrocyanide, and CPC were determined by UV/VIS-spectrophotometer (HP 8452 A, USA) at wavelength of 418nm, 278nm, and 258nm, respectively. The removal of ferricyanide, ferrocyanide and CPC were calculated from the following equation:

$R = (1 - \frac{C_p}{C_i}) \times 100$ where R is removal efficiency for ferricyanide, ferrocyanide, or CPC, and C_p and C_i are permeate and initial concentration for each compounds.

3. RESULTS AND DISCUSSION

In the ferricyanide/CPC system, the removal of ferricyanide is shown in Figure 2 as a function of the molar ratio of CPC to ferricyanide. The removal of ferricyanide reached the steady state within 4min in the case of the molar ratio of 1, while steady state was obtained immediately with the higher molar ratio of CPC. As the molar ratio increased from 1 to 2 and to 3, the removal of ferricyanide increased from 64% to 80% and to >99%, respectively. In the ferricyanide/CPC system, ferricyanide binds to the cationic CPC micelle spontaneously because ferricyanide has chelating power agent for cations. At the 3 molar ratio of CPC, most of ferricyanides can bind to the micelles assuming a 1:3 (ferricyanide:CPC) complex stoichiometry because the ionic balance of CPC and ferricyanide are +1 and -3, respectively.

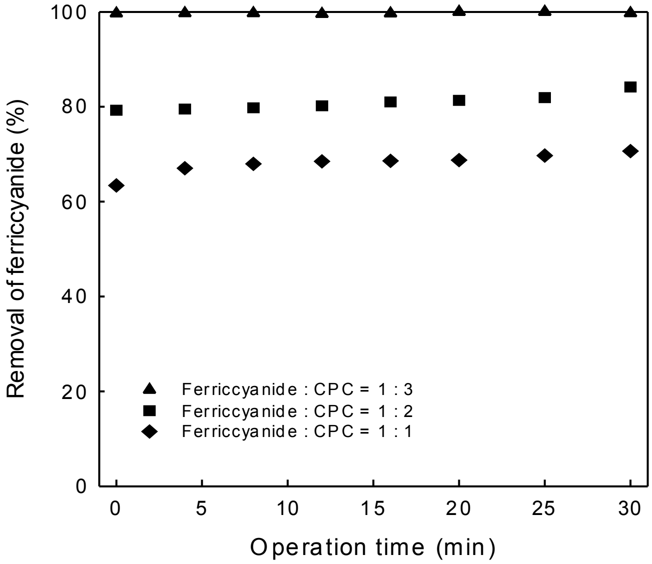

Figure 2. Removal of ferriccyanide in the ferriccyanide/CPC system. Initial ferriccyanide concentration: 1mM; membrane pore size: 0.02µm; transmembrane pressure: 2bar

The rejection of CPC shown in Figure 3 was high enough because of the high binding power of ferriccyanide with cationic micelles. Concerning of CPC rejection, the values increased from 90% to 97% and to 99%, respectively, as the molar ratio of CPC to ferriccyanide increased from 1 to 2 and to 3. The concentration of surfactant in the permeate as well as the rejection of surfactant should be considered in MEUF process because the surfactant (i.e., treated water) may bring secondary pollution in the permeate stream.

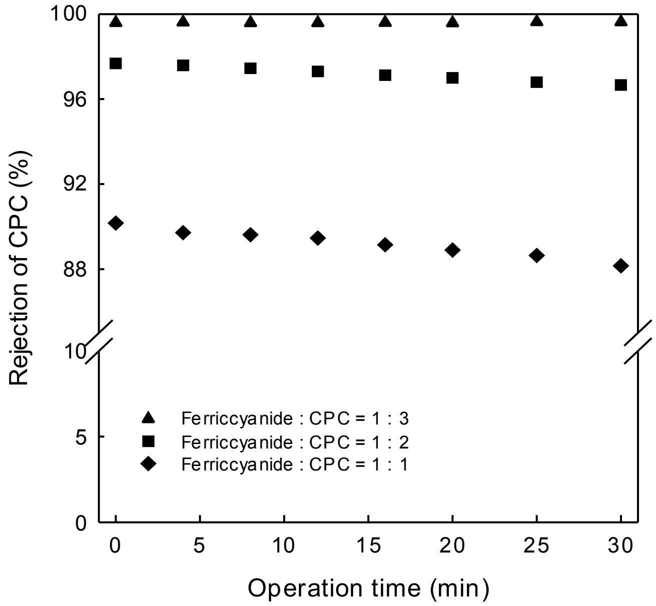

Figure 3. Rejection of CPC in the ferriccyanide/CPC system. Initial ferriccyanide concentration: 1mM; membrane pore size: 0.02µm; transmembrane pressure: 2bar

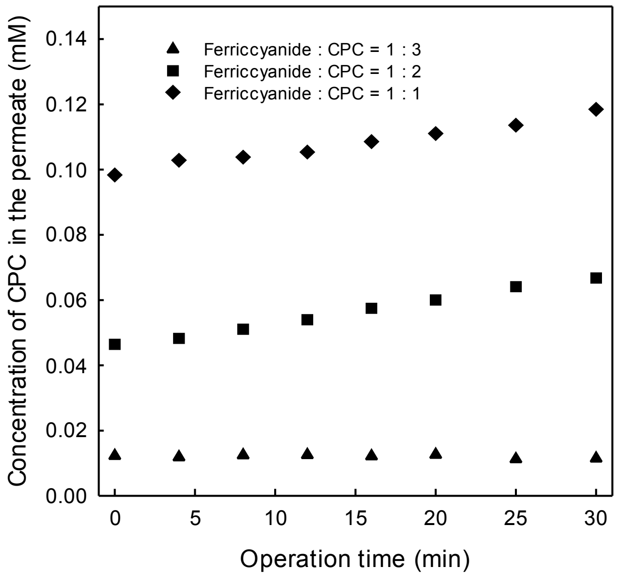

Figure 4. Concentration of CPC in the permeate in the ferriccyanide/CPC system. Initial ferriccyanide concentration: 1mM; membrane pore size: 0.02µm; transmembrane pressure: 2bar

Figure 4 shows the concentration of CPC in the permeate in the ferriccyanide/CPC system as a function of the molar ratio. In the ferriccyanide/CPC system, the concentration of CPC in the permeate stream decreased from 0.1mM to 0.05mM and to 0.01mM as the molar ratio increased from 1 to 2 and to 3, respectively. With 3 molar ratio of CPC, >99% of ferriccyanide and >99% of CPC were removed by MEUF process and the concentration of CPC in the permeate was lower to <0.1mM.

The removal of ferrocyanide is shown in Figure 5 in the ferrocyanide/CPC system. The removal increased from 35% to 58%, to 79%, and to 99% as the molar ratio of CPC to ferrocyanide increased from 1 to 2, to 3, and to 4, respectively. The removal of ferrocyanide was lower than those of ferriccyanide at the same molar ratio of CPC. At the low molar ratio of CPC, a ferrocyanide molecule with -4 as a valence can bind to multi-CPC molecules (i.e. one CPC molecules to four CPC molecules with one ferrocyanide molecule).

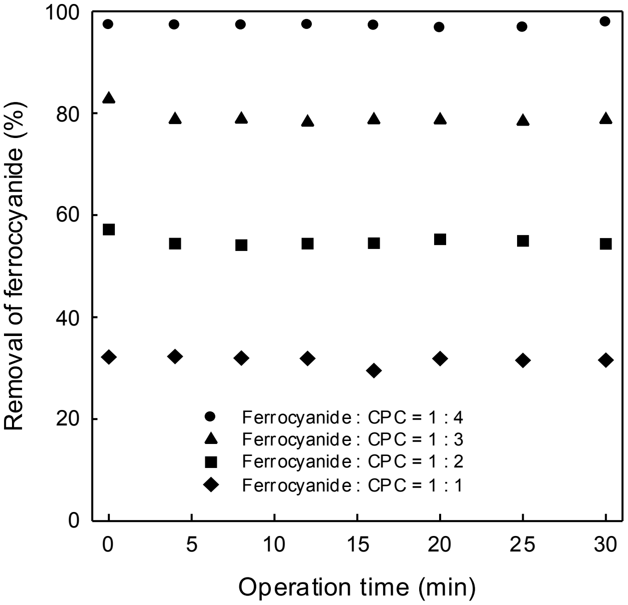

Figure 5. Removal of ferrocyanide in the ferrocyanide/CPC system. Initial ferrocyanide concentration: 1mM; membrane pore size: 0.02µm; transmembrane pressure: 2bar

The rejection of CPC shown in Figure 6 proved this assumption. Generally, in MEUF process, the rejection of surfactant increased with the increasing molar ratio of surfactant (Yildiz *et al.*, 1996; Baek *et al.*, 2003a,b,c; 2004; Baek and Yang, 2004). However, the rejection of CPC decreased from >99.9 to 99.9, to 99.8, and to 99.7 though the molar ratio of CPC to ferrocyanide increased from 1 to 2, to 3, and to 4. The rejection of CPC was much higher in the ferrocynaide/CPC system than in the ferriccyanide/CPC system.

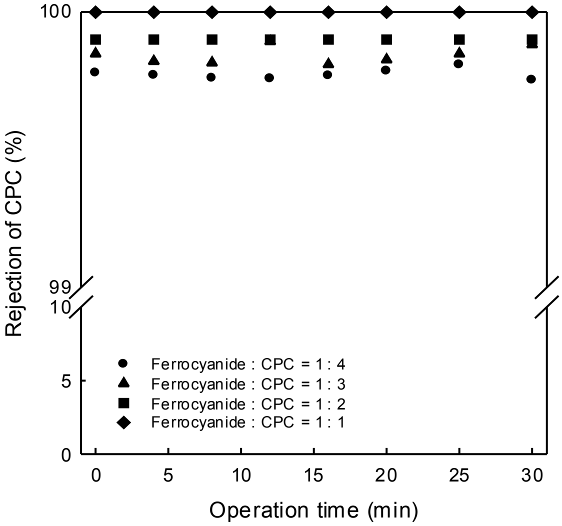

Figure 6. Rejection of CPC in the ferrocyanide/CPC system. Initial ferrocyanide concentration: 1mM; membrane pore size: 0.02μm; transmembrane pressure: 2bar

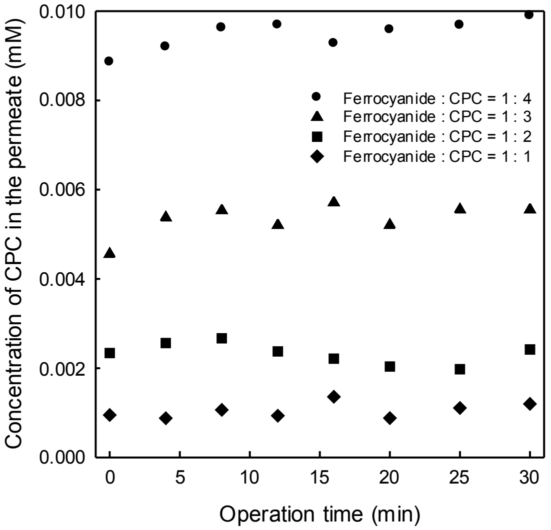

Figure 7. Concentration of CPC in the permeate in the ferrocyanide/CPC system. Initial ferrocyanide concentration: 1mM; membrane pore size: 0.02μm; transmembrane pressure: 2bar

As shown in Figure 7, the concentration of CPC in the permeate stream was much lower in the ferrocyanide/CPC system than that of ferriccyanide/CPC system. In the ferrocyanide/CPC system, the concentration of CPC in the permeate increased with increase of CPC molar ratio, while the concentration in the ferriccyanide/CPC system decreased. Recently, Tangvijitsri *et al.* (2002) reported that the removal of ions in the polyelectrolyte-enhanced ultrafiltration was proportioned to the valence of ions. However, this study shows that the removal of ferrocyanide with higher valence (-4) is lower than that of ferriccyanide with lower valence (-3). It may be due to the physicochemical properties of iron-cyanides such as chelating. At 4 molar ratio of CPC, >99% of ferrocyanide and >99% of CPC were removed by MEUF process and the concentration of CPC in the permeate was <0.01mM.

In the MEUF system, the flux of permeate was about 260l/m^2/hr, and decrease in the flux was not observed as the filtration was progressed. This value was half of the flux of deionized water because the addition of surfactant decreased the flux sharply. The size of CPC micelle was about the molecular weight cut-off (MWCO) of 50,000 – 100,000, however, the size of membrane pore was 0.02μm (roughly MWCO of 150,000). Regardless of slightly larger pore size of membrane compared to CPC micelle, the removals of ferriccyanide, ferrocyanide, and CPC were high enough. This seems that the size of micelle-ferriccyanide/ferrocyanide becomes bigger than pore size due to the formation of complex.

4. CONCLUSIONS

The two different forms of iron-cyanide complex, ferriccyanide and ferrocyanide, were efficiently removed by using MEUF process with CPC. The removals of ferriccyanide and ferrocyanide were >99% and 99%, respectively, with 3 molar ratio of CPC and 4 molar ratio of CPC, respectively. The rejection of CPC was low enough, as a result, the concentration of CPC in the permeate was very low. The removal of ferriccyanide was higher than that of ferrocyanide with the exactly same conditions due to multi-binding of a ferrocyanide molecules with CPC. The MEUF process can be an alternative to remove iron-cyanide complex from aqueous phase.

ACKNOWLEDGEMENTS

This work was partially supported by a grant (M1-0203-000-001) from Korea Ministry of Science and Technology through National Research Laboratory program and by KOSEF through the Advanced Environmental Monitoring Research Center at Kwangju Institute of Science and Technology.

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