

MEUF를 이용한 크롬(VI)과 ferricyanide의 동시제거에 관한 연구

양지원, 김보경, 백기태
한국과학기술원 생명화학공학과 환경복원연구실

Simultaneous removal of chromate and ferricyanide using micellar enhanced ultrafiltration

Ji-Won Yang, Bo-Kyong Kim, Kitae Baek
Environmental Remediation Engineering Lab., Dept. Chem & Biomolecular Eng., KAIST

1. Introduction

Metal ions in wastewater are serious contaminants to be removed because they are highly toxic and non-biodegradable, and they can damage the biological treatment system of wastewater due to their toxicity. Generally, metal ions in wastewater have been treated using their electrical properties such as ion-exchange, electrochemical removal, chemical precipitation. In those operations, anionic metals such as may need additional process because of their opposite electrical properties to cationic metals. Among anionic metals chromate is mainly discharged from refineries, alloy industries and many other processes which use chromium chemicals. Especially hexavalent chromium causes fatal damage to human health than trivalent chromium. Cyanide is used in metallurgy, plating and organic synthesis processes. It can be absorbed fast in the body and have high toxicity.

Micellar-enhanced ultrafiltration(MEUF) has been proposed to remove variety micro-pollutants economically(Sadaoul et al. 1998; Yildiz et al. 1996; Ahmadi et al. 1994). In membrane separation process, ions have to be treated using reverse osmosis due to their small sizes and it needs high operating cost. In MEUF process, enough amount of surfactants are added in metal-bearing wastewater, then the metal ions can adsorb on the micelles. The metal-micelle complexes can be removed by ultrafiltration as seen in Fig.1.

The selection of surfactant is one of key factors for MEUF process. There are several considerations for selection of surfactant such as cost, environmental affinity, biodegradability, binding power with the metal ion. Especially, the counterions of a surfactant need to be considered because they cause secondary contamination in MEUF process. For example, although cetylpyridium chloride(CPC) has been used to remove anionic metals from wastewater effectively, chlorides which are counterions of CPC are concerned to be a secondary pollutant. In this study, the feasibility of MEUF for simultaneous removal of chromate and ferricyanide ions with octadecylamine acetate(ODA) was investigated. ODA has similar removal efficiencies for chromates and ferricyanides compared to CPC, but the counterion of ODA is acetate ion which has less toxicity than chloride. The effects of molar ratio of ODA to anionic metals for MEUF were examined and the competition of two metal ions to adsorb on micelles was discussed by comparison between single- and multi-pollutant systems.

2. Materials and Methods

Octadecylamine acetate(TCI Chemical, Japan) was used as a cationic surfactant, sodium chromate tetrahydrate(Aldrich Chemical, USA) and potassium ferricyanide(Sigma Chemical,

USA) were used in preparing synthetic metal-bearing wastewater. For MEUF, batch-stirred cell (Amicon 8400, USA) with dead-end configuration was used [Fig.1]. The membrane were regenerated cellulose acetate membranes (Milipore YM3, USA), with MWCO 3000. The operating pressure was 2 bar and temperature was room temperature. The stirring speed was about 200 r.p.m. In the permeate the concentrations of surfactant and pollutant were analyzed by UV spectrophotometer (HP8452A, USA). The removal efficiency of chromate and ferricyanide were calculated as following equation [Eqn.1].

$$\text{Removal Efficiency}(\%) = \frac{C_{\text{feed}} - C_{\text{permeate}}}{C_{\text{feed}}} \times 100 \quad [\text{Eqn.1}]$$

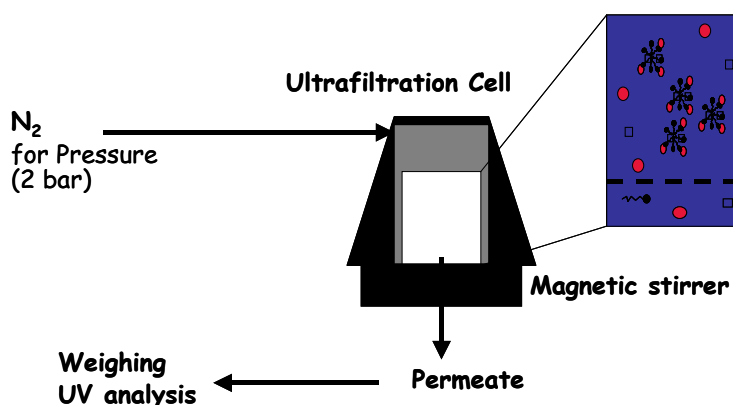


Figure 1. Schematic diagram of MEUF

3. Results and Discussions

Removal of chromate and ferricyanide in single-pollutant system

In the chromate/ODA and ferricyanide/ODA system, the removal efficiencies of each pollutant as the molar ratio of surfactant to metal ion were shown in Fig.2. The concentrations of metal ions were fixed as 1mM, that of ODA was increased from 1 to 2, 3, 5mM. As the molar ratio of surfactant to metal ion was increased, the removal efficiencies of metal ions are increased. When the molar ratio of metal ion to ODA was 1:1, the removal efficiency of ferricyanide is larger than chromate, but chromate and ferricyanide were removed over 95% at the ratio greater than 2. The removal efficiencies of metal ion were little decreased as operation progressed because of the concentration of retentate.

Removal of chromate and ferricyanide in multi-pollutant system

In the multi-pollutant system, the concentration of surfactant increased from 1 to 2, 4, 6, and 10mM with the fixed concentration of metal ions as 1mM [Fig.3]. The removal efficiency of chromate increased from 25% to 35%, to 68%, to 99%, and to 99.7% that for ferricyanide

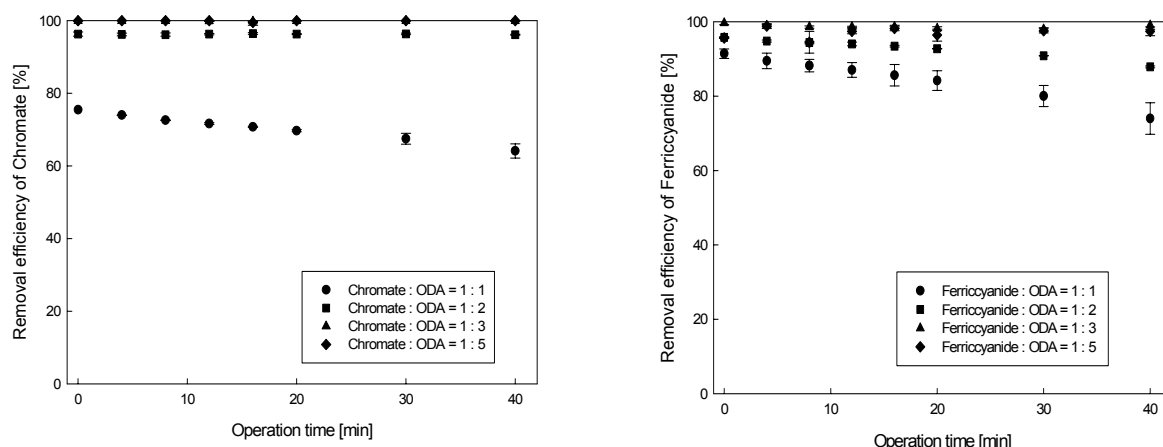


Figure 2. Removal efficiencies of Chromate and Ferricyanide in single-pollutant system

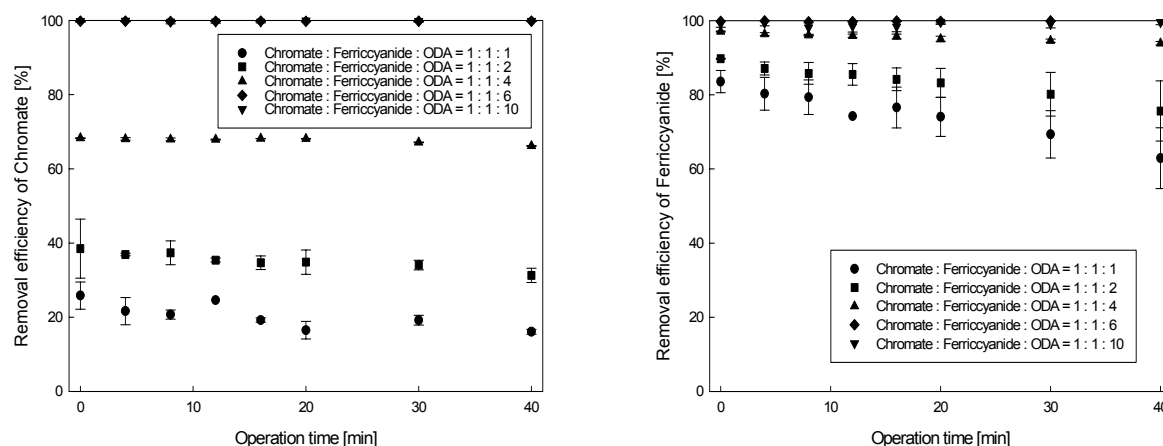


Figure 3. Removal efficiencies of Chromate and Ferricyanide in multi-pollutant system

from 80%, 85%, 95%, 99%, 99% as the molar ratio of chromate : ferricyanide : ODA increased from 1:1:1 to 1:1:2, 1:1:4, 1:1:6, and to 1:1:10. The competition between chromate and ferricyanide could reduce the extent of adsorption of themselves on ODA micelles, so the removal efficiencies of both metals were reduced compared to single-pollutant system. The reductions of removal efficiencies of chromate were greater than those of ferricyanide at the same conditions. That is because the binding power of ferricyanides with ODA was stronger than that of chromates and all of ferricyanides bound to micelles, after then chromates bound to the rest sites of them. So over 4mM of ODA, most of ferricyanide ions bind to ODA micelles and the removal efficiencies of chromate could be similar to the values in single-pollutant systems.

The rejections of ODA in MEUF system were greater than 98% at the concentration of ODA greater than 1mM[Fig.4]. It seems that the size of ODA micelle is big enough not to pass through membrane pore.

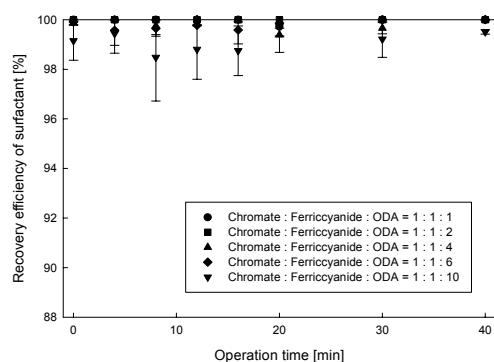


Figure 4. Recovery efficiency of ODA

4. Conclusion

Wastewater containing chromate and ferricyanide can be treated by micellar-enhanced ultrafiltration with octadecylamine acetate as a surfactant. In the ODA/chromate and ODA/ferricyanide system from over 2 of the molar ratio of ODA to chromate/ferricyanide the removal efficiency of the pollutants was >95%. In the ODA/chromate/ferricyanide system, the removal efficiencies of each pollutants were smaller than single-system because of the competition between chromate and ferricyanide for the site to adsorb on micelles. The ferricyanide could be removed more than chromate due to its binding power with ODA was greater than that of chromate. The chromate and ferricyanide could be removed 99% at the ratio of chromate : ferricyanide : ODA as 1:1:6. So ODA can be used an alternative surfactant for removal of chromate and ferricyanide in MEUF process, which has safer counterions and higher rejection.

5. Acknowledgements

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6. References

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