

Removal characteristics of metal cations and their mixtures using micellar-enhanced ultrafiltration

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Abstract—Divalent ions were removed by ultrafiltration of anionic surfactant solution and the removal characteristics in single and mixed systems were investigated. The removal efficiency was >95% when the ratio of sodium dodecyl sulfate (SDS) to metal ions (S/M ratio) was >10. In single metal systems, the removal efficiency of each metal ion was almost the same. In the mixture, however, there was slight difference (ca. 1-2%) of removal efficiency and the order was $\text{Cd}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} \approx \text{Zn}^{2+}$. As S/M ratio increased, the difference in removal efficiency diminished. To explain the difference of removal efficiency in a mixture, complexation of divalent metal ion with counterion was considered. The distribution of complexed form of each metal ion was calculated, but it did not coincide with the experimental results. Further research will be necessary for a clear explanation.

Key words: Heavy Metal, Micelle, Sodium Dodecyl Sulfate (SDS), Ultrafiltration

INTRODUCTION

As environmental concerns increase and the effluent standards are strengthened, it is necessary to remove residual amounts of heavy metals in the effluent from wastewater treatment facilities. Precipitation, ion-exchange, and reverse osmosis are frequently used for heavy metal removal. However, precipitation cannot remove metal ions completely. The cost of ion-exchange resin and the low permeate flux of reverse osmosis are drawbacks [1]. To obtain high removal efficiency and low operating cost, ultrafiltration combined with surfactant micelle (micellar-enhanced ultrafiltration, MEUF) was proposed. When the concentration of surfactants is higher than the critical micelle concentration (CMC), surfactants form micelles—spherical or rod-like aggregates. Anionic surfactants form micelles with negatively charged surfaces, then metal cations can bind or adsorb on the surface of the micelles by electrostatic interaction. A micelle bound with metal ions can be separated from an aqueous stream by a membrane which can retain the colloidal size of the micelle [2]. By hydrophobic interaction, organic pollutants such as *o*-cresol or methyl *tert*-butyl ether (MTBE) can be solubilized in the micelles and can be separated simultaneously [3,4]. In the last 20 years, membrane processes combined with surfactant micelle, polyelectrolyte, or natural humic substances have been studied in the treatment of heavy metals or anionic contaminants [2,5-24]. The removal efficiency of the metal ion mainly depends on the binding strength between the metal ion and the surfactant micelle. So, the removal efficiency of an inorganic ion with high valence is higher than that of an ion with lower valence [5,7,8]. On the other hand, the removal efficiency of each ion is very similar in a mixture of

divalent metal cations. The order of removal efficiencies among divalent metal ions varies according to the experimental conditions [2,13,14,16,25]. And it is not explained clearly why there are such differences in the removal efficiency among divalent metal ions. In this study, the removal efficiency in divalent metal mixtures was compared with that in a single metal system, and the removal characteristics of each metal ion in a mixture were investigated.

MATERIALS AND METHODS

An anionic surfactant, sodium dodecyl sulfate (SDS), was purchased from Sigma Chemical (USA) and used without further purification. Nitrate salts of metal ions, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, were purchased from Aldrich Chemical (USA). To prevent precipitation of metal ions, the solution pH in all experiments was adjusted to 3 by using 1 N HNO_3 . Distribution of various metal complexes in aqueous solution was calculated with commercial software, MINEQL+ (Environmental research software, USA). Regenerated cellulose ultrafiltration membranes (Millipore, USA) with molecular weight cut-off (MWCO) of 3,000 and 10,000 Da were used. Dead-end filtration was carried out by using a solvent-resistant stirred cell (Millipore, USA) and all experiments were duplicated. 100 mL of feed solution was filtered until the volume reduction ratio, $\text{VR} (=V_{\text{feed}}/V_{\text{retentate}})$, reached 1.25 for a system with MWCO of 3,000 Da and 2 for a system with MWCO of 10,000 Da. Filtration was carried out at room temperature and under 2 bar of transmembrane pressure. The concentration of metal ions was measured by atomic absorption spectroscopy (Perkin Elmer 3300, USA), and that of SDS was measured by chemical oxygen demand (COD) kit (Hach, USA). Single, binary, ternary and quaternary systems of Cd^{2+} , Cu^{2+} , Co^{2+} , and Zn^{2+} were investigated. The initial concentration of each metal ion was 1 mM in all systems and

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that of SDS varied from 1 to 30 mM.

RESULTS AND DISCUSSION

1. Single Metal System

In all single metal systems, the removal efficiency of metal ions increased as the concentration of SDS increased (Fig. 1(a)). When the retentate concentration of SDS is greater than the critical micelle concentration (CMC, 8.27 mM at 25 °C [16]), the SDS monomers form micelles. The molecular weight of an SDS micelle is from 17,000 to 23,000 Da [26,27]. The 3,000 and 10,000 MWCO membranes in this study are small enough to separate the micelles bound with metal ions from aqueous solution. The removal efficiency of each metal ion increased significantly up to 90% with 10 mM of SDS. Even though the concentration of SDS was lower than the CMC (S/M ratio=5, $[SDS]_{initial}=5$ mM), approximately 60% of metal was removed. As filtration proceeds, retained solutes can accumulate at the membrane surface and the solute concentration at the membrane surface can be higher than the bulk concentration [28]. Although the bulk concentration of SDS in retentate was 5 mM, the concentration at the membrane surface reached the CMC by concentration polarization and certain amount of metal ions could be separated. Since the valence of metal ion determines the removal efficiency of MEUF, divalent metal cations show similar removal

efficiencies [25]. As the initial concentration of copper increased from 1 mM to 3 mM, the removal efficiency increased from 91.5 to 96.2% at the same S/M ratio of 10. The relative flux, the ratio of flux of solution to that of pure water, decreased as the concentration of SDS increased (Fig. 1(b), (c)). Because concentration polarization is greater in a membrane with higher pore size, the flux decline in a membrane with MWCO of 10,000 was greater than that of 3,000. However, the actual flux in a membrane with MWCO of 10,000 (30–45 L/m²h) was still greater than that in a membrane with MWCO of 3,000 (12–13 L/m²h). A membrane with MWCO of 10,000 will be beneficial in terms of operation capacity. The permeate concentrations of SDS were similar to the CMC of SDS (~8 mM, data not shown). At a high concentration of SDS, the permeate concentration above CMC resulted from the formation of n-mers. N-mers (for example, dimer and trimers) are small aggregates of monomers of surfactant and they can also bind metal cations in their negatively charged heads. Because the molecular weight of n-mer is much smaller than that of micelle, n-mers could pass through a membrane [29].

2. Binary Metal Mixtures

The removal characteristics of metals in binary mixtures, Cd/Cu, Cu/Cd/Co and Cu/Co, were investigated. In the Cd/Cu system, the removal efficiency of cadmium and copper was 89.9% (± 0.64) and 89.1% (± 0.83), respectively, at 10 mM of SDS in a 3,000 MWCO

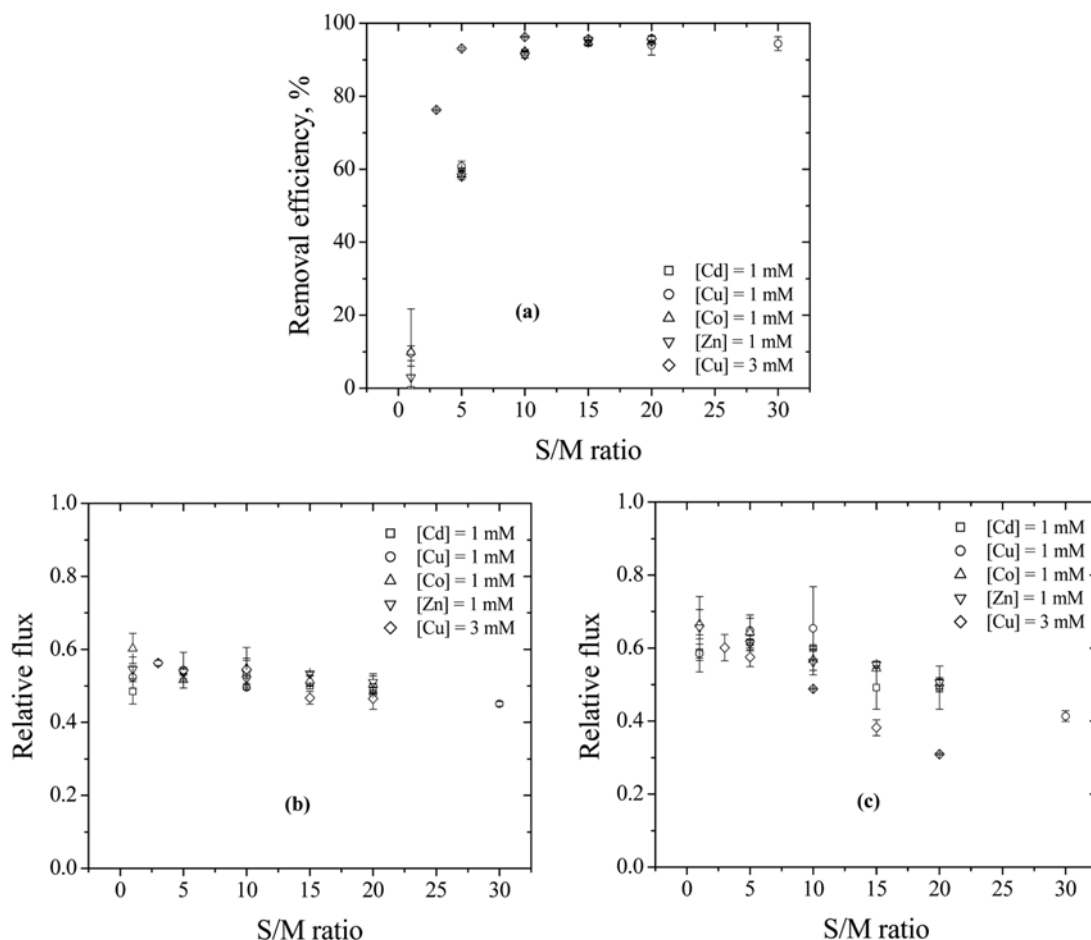


Fig. 1. Removal efficiency of metal ions (a), relative flux in a membrane with MWCO of 3,000 (b) and 10,000 (c) in single metal systems.

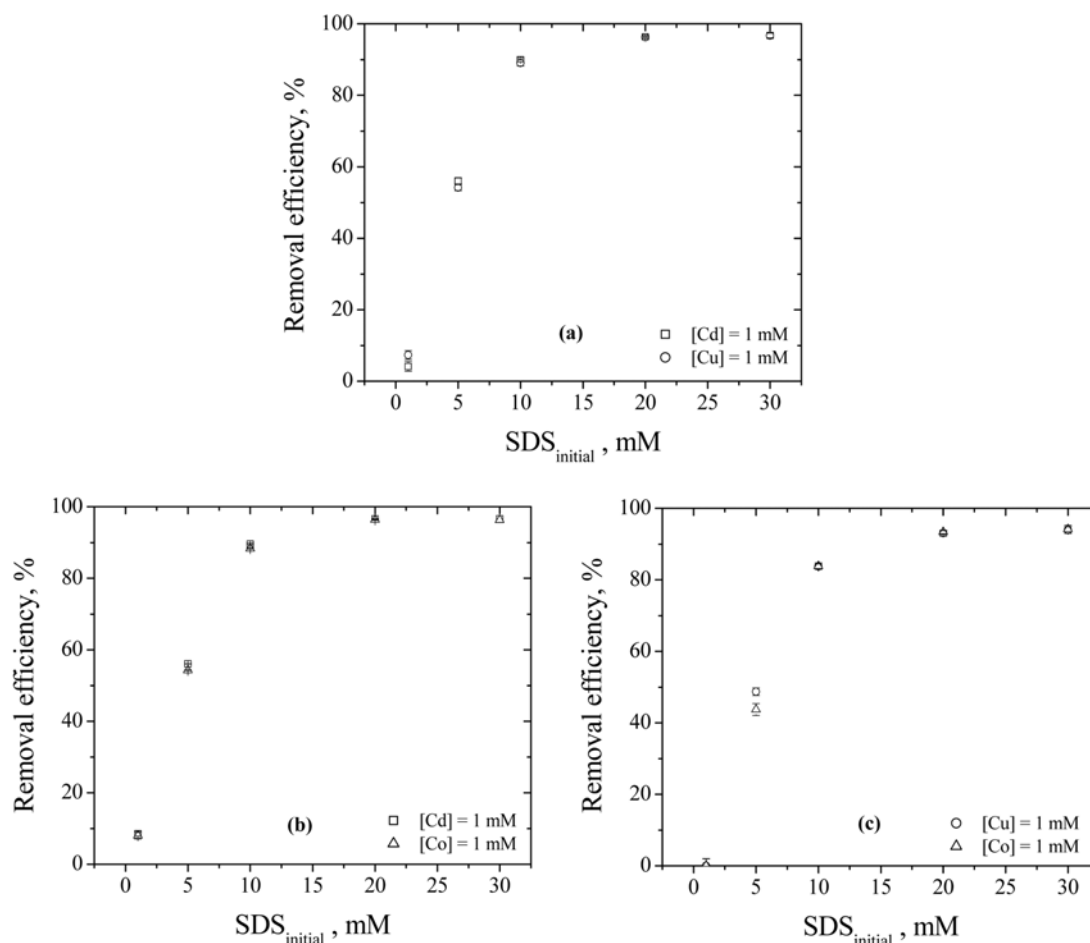


Fig. 2. Removal efficiency of metal ions in (a) Cd/Cu, (b) Cd/Co, and (c) Cu/Co systems.

membrane (Fig. 2(a)). Those values were slightly lower than 91.9% (± 0.54) removal of cadmium and 91.5% (± 1.07) removal of copper at the same SDS concentration in the single metal systems. At a fixed SDS concentration, the S/M ratio in the Cd/Cu mixture is reduced to half compared with that in the single metal system. Therefore, the removal efficiency in the binary mixture is lower than that in the single system at the same SDS concentration. When the binding site (surfactant micelle) was limited, there was slight difference in the removal efficiency. At 5 mM of SDS, removal efficiency of cadmium ($56.1\% \pm 0.85$) was higher than that of copper ($54.1\% \pm 0.86$). In the Cd/Co system (Fig. 2(b)), the removal efficiency of cadmium was obviously higher than that of cobalt at a low SDS concentration. Cadmium removal at 5 mM of SDS was $56.0\% (\pm 0.04)$, whereas cobalt removal was $54.3\% (\pm 0.08)$. As the SDS concentration increased, the removal efficiency of cadmium and cobalt became similar. At 30 mM of SDS, the removal efficiency of cadmium and cobalt in a 3,000 MWCO membrane was 96.6% and 96.3%, respectively. In the Cu/Co mixture (Fig. 2(c)), copper ($48.7\% \pm 1.03$) was removed more than cobalt ($43.7\% \pm 1.67$) at 5 mM of SDS. As the SDS concentration increased, the removal efficiency of both metals was almost the same. When the concentration of surfactant is low, the available sites for binding with metals are limited. In that case, the metal ion with greater affinity to surfactant micelle will bind first and strongly. According to the experimental results, it seems

that the binding affinity of copper to an SDS micelle is stronger than that of cobalt. The orders of removal efficiency in binary mixtures were $\text{Cd} > \text{Cu}$, $\text{Cd} > \text{Co}$, and $\text{Cu} > \text{Co}$.

3. Ternary Metal Mixture

At 10 mM of SDS and in a 3,000 MWCO membrane, the removal efficiency of cadmium, copper, and cobalt was 83.4%, 81.3%, and 79.4%, respectively (Fig. 3(a)). As the concentration of SDS increased, the removal efficiency of the three metals was almost the same. The removal efficiency in a ternary mixture was similar to that in a single metal system with 3 mM of initial copper concentration. It means that the overall removal efficiency can be approximated from the S/M ratio regardless of the initial concentration of divalent metal cations. In a ternary mixture, there was a slight difference in removal efficiency of metal ions, especially at low SDS concentration. When SDS concentration was 5 mM, the removal efficiencies of cadmium, copper, and cobalt were $45.8\% \pm 0.10$, $45.0\% \pm 0.07$, and $39.7\% \pm 0.11$, respectively. Therefore, the removal efficiency was in the order of $\text{Cd} > \text{Cu} > \text{Co}$ in a ternary mixture.

4. Quaternary Metal Mixture

At 5 mM of SDS and in a 3,000 MWCO membrane, the removal efficiency of cadmium, copper, cobalt and zinc was $34.4\% (\pm 1.93)$, $34.0\% (\pm 1.63)$, $31.0\% (\pm 1.37)$, and $30.9\% (\pm 0.19)$, respectively (Fig. 3(b)). As the concentration of SDS increased, the difference in removal efficiencies of four metal ions decreased. In the quater-

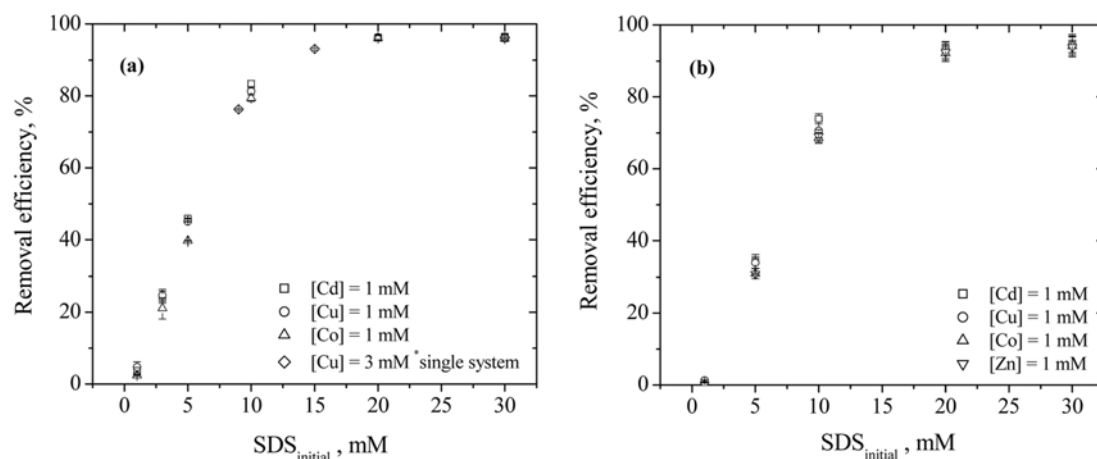


Fig. 3. Removal efficiency of metal ions (a) in the Cd/Cu/Co mixture and (b) in the Cd/Cu/Co/Zn mixture.

nary mixture, the order of removal efficiency was $\text{Cd} > \text{Cu} > \text{Co} \approx \text{Zn}$. At higher concentration of SDS, the removal efficiency of four metal ions in mixture was similar to that in the single metal system.

5. Discussions

It has been explained that the degree of complexation between divalent cations and counter-anions caused a slight difference in the removal efficiency [2,16,17]. For example, the cadmium ion complexes with chloride ion in solution and forms CdCl^+ or CdCl_2 . The binding affinity of CdCl^+ or CdCl_2 is not as strong as Cd^{2+} due to their lower valence. Then the removal efficiency of cadmium

will decrease. In this study, possible complexes of metal ion and their distributions were calculated by MINEQL+ software. At pH 3, all metal cations, cadmium, copper, cobalt and zinc, exist mostly as a divalent metal ion, Me^{2+} , and only small amounts of metal ions exist as the complexed form, MeNO_3^+ (Table 1). In both a single and multi-metal system, most of the cobalt exists as Co^{2+} . Cadmium and copper form the complex, MeNO_3^+ , more than other metals. According to the conventional explanation, the removal efficiency of cobalt should be higher than that of cadmium or copper. However, the experimental results of the present study were opposite to

Table 1. The percentage of equilibrium concentrations of metal ion and its nitrate complexes calculated by MINEQL+

System		Cd		Cu		Co		Zn	
		Me^{2+}	MeNO_3^+	Me^{2+}	MeNO_3^+	Me^{2+}	MeNO_3^+	Me^{2+}	MeNO_3^+
Single		99.4	0.6	99.4	0.6	99.7	0.3	99.5	0.5
Binary	Cd/Cu	98.8	1.2	98.8	1.2				
	Cd/Co	98.8	1.2			99.4	0.6		
	Cu/Co			98.8	1.2	99.4	0.6		
Ternary	Cd/Cu/Co	98.1	1.9	98.1	1.9	99.1	0.0		
Quaternary	Cd/Cu/Co/Zn	97.5	2.4	97.6	2.4	98.7	1.2	98.0	2.0

Table 2. The percentage of metal ion and complexed form in other researches calculated by MINEQL+

System	Metal	Species (%)			Removal order in the paper	Reference
		Me^{2+}	MeCl^+	$\text{MeCl}_{2(aq)}$		
Single	Cd	47.87	49.87	2.27	$\text{Ca} > \text{Cu} \approx \text{Zn} > \text{Cd}$	Scamehorn et al., 1989
	Zn	96.4	3.6	0		
	Cu	97.6	2.3	0		
	Ca	100	0	0		
Single	Cr	100	0	0	$\text{Cr} > \text{Co} > \text{Ni} > \text{Mg}$	Yang et al., 1996
	Co	99.30	0.67	0		
	Ni	99.50	0.51	0		
	Mg	100	0	0		
Mixture	Cd	57.89	41.28	1.26	$\text{Cu} > \text{Zn} > \text{Cd}$	Scamehorn et al., 1994
	Zn	98.49	1.82	0.02		
	Cu	98.49	1.16	0		

the prediction. It seems that the complexation of metal ions with counterions cannot explain the result clearly. To test the explanation of the removal efficiency by complexation, the distribution of metal complexes was also calculated for other researches where SDS was used as a surfactant (Table 2). The carbon dioxide in the atmosphere and the Na^+ ion of SDS were considered, but the dodecyl sulfate (DS^-) ion of SDS was not. When the pH of the experiment was not shown in the text, the pH was set as 4 to prevent precipitation. The order of removal efficiency among divalent metals was reported as $\text{Ca} > \text{Cu} \approx \text{Zn} > \text{Cd}$ [2]. According to the experimental conditions of the report, calcium exists as only Ca^{2+} and most of the zinc and copper exist as Me^{2+} . On the other hand, more than 50% of cadmium exists as MeCl^- and $\text{MeCl}_{2(aq)}^-$. Although more than half of the cadmium exists as complexes whose charge is less than +2, the removal efficiency of cadmium (98.9%) was slightly lower than that of calcium (99.5%). Another paper reported that the order of removal efficiency was $\text{Cr} > \text{Co} > \text{Ni} > \text{Mg}$ [16]. Although magnesium exists only as Mg^{2+} , the removal efficiency was the lowest. In Scamehorn's research [25], the order was $\text{Cu} > \text{Zn} > \text{Cd}$ in the Cd/Zn/Cu mixture. 98.5% of zinc and copper exist as Me^{2+} and only 60% of cadmium exists as Cd^{2+} . However, the removal efficiency of cadmium, zinc, and copper was nearly close (the difference in removal efficiency of three metal ions was only 0.03%). As a result, it seems that the complexation of metal cations with counterions cannot explain clearly the difference in removal efficiency among divalent metal ions in MEUF. If the radius of each metal ion is considered, the radii of Cd^{2+} , Cu^{2+} , Co^{2+} , and Zn^{2+} are 0.103, 0.072, 0.082, and 0.083 nm, respectively [30,31]. The larger radius of cadmium ion might be one reason for the higher removal efficiency. To explain this phenomenon clearly, additional research will be necessary.

CONCLUSIONS

In the present study, the removal characteristics of divalent metal cations, cadmium, copper, cobalt and zinc were investigated in MEUF by using sodium dodecyl sulfate (SDS) as an anionic surfactant.

1. With S/M ratio greater than 10, Cd^{2+} , Cu^{2+} , Co^{2+} , and Zn^{2+} were removed more than 95% in membranes with MWCO of 3,000 and 10,000. Even if the bulk concentration of SDS was lower than CMC of SDS, significant amounts of metal ions were removed due to the buildup of a concentration of SDS near a membrane by concentration polarization.

2. In single metal systems, Cd^{2+} , Cu^{2+} , Co^{2+} , and Zn^{2+} showed similar removal efficiency. In a multi-metal system, a slight difference in removal efficiency was observed at low concentration of SDS. As the concentration of SDS increased, the removal efficiency of each metal ion became similar to each other. In the mixtures of metal ions, the order of the removal efficiency, that is, the order of binding affinity of metal ion to micelle of SDS, was $\text{Cd} > \text{Cu} > \text{Co} \approx \text{Zn}$.

3. Researchers have attempted to explain the difference in removal efficiency in mixtures by the complexation of metal cations with counterions in solution. However, the complexation cannot explain clearly the difference in removal efficiency of metals. Additional study will be required for a clear explanation of this difference of

removal efficiencies.

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