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Won Sik Shin[a]; Sang June Choi[b]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, KYUNGPOOK NATIONAL UNIVERSITY, TAEGU, KOREA [b] DEPARTMENT OF ENVIRONMENTAL ENGINEERING, KYUNGPOOK NATIONAL UNIVERSITY, TAEGU, KOREA

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Removal of Cu(II) from Aqueous Solution by Oil–Water Interfacial Emulsion Technique with Adsorbing Colloids

WON SIK SHIN
DEPARTMENT OF CHEMICAL ENGINEERING

SANG JUNE CHOI*
DEPARTMENT OF ENVIRONMENTAL ENGINEERING

KYUNGPOOK NATIONAL UNIVERSITY
TAEGU, 702-701, KOREA

ABSTRACT

Experimental investigations on the removal of Cu(II) from an aqueous solution were carried out by an interfacial emulsion technique with an adsorbing colloid ($Al(OH)_3$, $Fe(OH)_3$). Cu(II) from the aqueous solution was segregated into a compact emulsion between water and a water-immiscible oil phase by an interfacial emulsion technique that uses the adsorptive power of the oil–water interface. Trimethylamine was effective as a surfactant for the removal of Cu(II), and the optimum pH for the removal of Cu(II) was found at 9.0 when using $Fe(OH)_3$ and at 10.0 when using $Al(OH)_3$ as an adsorbing colloid, respectively. The effects of pH, mixing time, initial surfactant concentration, initial Fe(III) concentration, and foreign ions (Na^+, Ca^{2+}, Cl^-, NO_3^-, HPO_4^{2-}) on the removal efficiency were investigated. The adsorption and separation mechanisms for the removal of Cu(II) by the interfacial emulsion technique of adsorbing colloids were observed.

INTRODUCTION

The ability of the oil–water interface to attract and collect dissolved or suspended material is an important property for separation and material conversion or synthesis (1–3). In recent years, increasing attention has

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* To whom correspondence should be addressed.

been paid to the engineering potential of the phenomenon that uses the adsorptive power of oil–water interfaces. It appears that the adsorptive power of the oil–water interface may be just as useful as that of solid–fluid and gas–liquid interfaces. Oil–water interfacial emulsion techniques can be used for the separation or concentration of soluble and/or insoluble materials from aqueous solution.

Material separation by an oil–water interfacial emulsion technique is based on the fact that a surface-active material tends to concentrate at the oil–water interface. If the material to be removed is not surface active, a surface-active agent or collector can be used to draw the material to the interface through union with, or adsorption of, other surface-active materials. The surface-active material can be attached to the oil–water interface and then be separated from the solution through emulsification. Emulsions formed by stirring are well formed with fluidlike features and a large interfacial area. However, the emulsions primarily formed are naturally unstable and easy to break; coalescence of dispersed emulsion droplets thus occurs with a sharp reduction of the interfacial area. A few hours of gravity settling are sufficient to break up the emulsions and result in spontaneous phase splitting. The emulsions are divided into three phases: oil, interfacial emulsion, and water. Most of the materials to be removed are segregated into the compact interfacial emulsion phase that has generally less than 10% of the aqueous-phase volume (1, 2, 4).

In a sense, the interfacial emulsion technique may be viewed as a logical extension of foam separation. If an organic liquid is used in place of a gas (as in flotation), even small particulates (micron and submicron) can be attached to the colliding liquid bubbles due to the increased collision energy between the particulates and the bubbles (5–9). The use of an organic liquid as the flotation medium would extend the applicability of the flotation technique and offer some advantages of a higher separation capacity; a greater flexibility and versatility of the separation process. This makes possible the segregation of metals into a compact emulsion and then into a solid–liquid suspension that can easily be recovered by filtration (1, 2).

Lim's group (1, 2) reported that dissolved or suspended metals in aqueous solution can be removed by the oil–water interfacial emulsion technique. Metal removal efficiency depends on pH and surfactant concentrations. For the removal of suspended metal, an effective collector was a cationic surfactant, and the removal was performed by adsorbed surfactant on metal surfaces that have negative surface charges. For dissolved metals, the effective collectors were complexing agents with a strong amphiphilic character, and the removal was performed by metal–collector colligend formation.

Our recent study (4) has shown that Cu(II) can be removed from aqueous solution by the oil–water interfacial emulsion technique using a Cu(II)–trialkylamine complex formation. Greater than 95% of Cu(II) can be removed from aqueous solution with low molecular trialkylamine as the surfactant at pH 9.0–11.0. In spite of its high removal efficiency, Cu(II) removal by the interfacial emulsion technique of Cu(II)–trialkylamine complex formation has some limitations that may affect its application. Long mixing times were required for complete Cu(II)–trialkylamine complex formation, and long settling times were needed for complete phase separation.

We report here on the removal of Cu(II) by the oil–water interfacial emulsion technique with adsorbing colloids. It was suggested that the limitations of Cu(II) removal by Cu(II)–trialkylamine complex formation may be overcome by adding flocculating agents such as $Fe(OH)_3$ and $Al(OH)_3$. The effects of pH, mixing time, initial surfactant (collector) concentration, initial Fe(III) concentration, and foreign ions on the removal efficiency were investigated. The adsorption and separation mechanisms for the removal of Cu(II) by the interfacial emulsion technique of adsorbing colloids were also studied.

EXPERIMENTAL

Chemicals

Laboratory-grade trimethylamine was used as the cationic surfactant for the removal of Cu(II). Stock solutions of Cu(II) were prepared by dissolving copper(II) chloride ($CuCl_2 \cdot 2H_2O$) in distilled water. Ferric chloride ($FeCl_3 \cdot 2H_2O$) and aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) were used to generate adsorbing colloids. Sodium nitrate ($NaNO_3$), sodium sulfate (Na_2SO_4), and sodium phosphate (Na_2HPO_4) were used as sources for foreign anion, and sodium chloride (NaCl) and calcium chloride ($CaCl_2$) were used as sources for foreign cations. Laboratory-grade kerosene was used as the oil phase.

Procedure

The removal of Cu(II) by the oil–water interfacial emulsion technique was studied in a Nalgene 125 mL separatory funnel. Aqueous liquid mixtures were prepared by adding surfactant and Fe(III) or Al(III) to the Cu(II) solutions. All experimental runs were made with an initial Cu(II) concentration of 0.0025 M (158.75 ppm). Foreign ions, if needed, were also introduced. Each mixture was mixed thoroughly by a magnetic stirrer. The precipitates were generated at a given pH by adding small amounts of NaOH. The aqueous mixture and oil were added by funnel, mixed by a separatory funnel shaker (300 rpm maximum) for 30 seconds, and then settled for 30 minutes. Samples were taken from the aqueous phase, and then the residual concentrations of Cu(II), Fe(III), and Al(III) were analyzed by an atomic absorption spectrophotometer (Varian, Model Video 12). The residual Cu(II) concentration was determined after the precipitates had been removed by filtering through 0.45 μm Millipore filter paper. The typical volumes of the oil and water phases were 40 and 50 mL, respectively. All experiments with trimethylamine were performed under a nitrogen atmosphere to prevent oxidation to trimethylamine oxides.

RESULTS AND DISCUSSION

Effect of Adsorbing Colloids

The effect of adsorbing colloids on the removal of Cu(II) by the interfacial emulsion technique is shown in Tables 1A and 1B. We have previously reported on the removal of Cu(II) by Cu(II)–trialkylamine complex formation at the oil–water interface (4). However, Cu(II) removal by Cu(II)–trialkylamine complex formation requires at least 10 hours for mixing and settling. This limitation was overcome by adding flocculating agents such as $Fe(OH)_3$ and $Al(OH)_3$. It took 30 minutes for mixing and settling when Fe(III) or Al(III) was added. The reasons for the time improvement are the increases in the particle size and zeta potential of the floc, which presumably creates a stronger electrical attraction energy between the interface and the floc. It is believed that larger particles can be collected more rapidly than smaller ones (11–14). The improvement in separation

TABLE 1A
Effect of Adsorbing Colloids on the Removal of Cu(II) by the Oil–Water Interfacial Emulsion Technique. Cu(II) Removal by Cu(II)–Trialkylamine Complex Formation[a]

Surfactant	Oil	pH	I.S. (%)
Trimethylamine	Kerosene	9.0	96.8
	CCl_4	9.0	96.6
	Hexane	9.0	96.4
Triethylamine	Kerosene	9.0	95.1
	CCl_4	9.0	94.5
Tripropylamine	Kerosene	9.0	81.0
	CCl_4	9.0	84.3
Tributylamine	Kerosene	9.0	81.0
	CCl_4	9.0	71.6

[a] Cu(II) = 0.005 M, surfactant = 0.005 M, T = 25°C, I.S. (%) = interfacial segregation percentage, mixing and settling time = 10 hours.

TABLE 1B
Effect of Adsorbing Colloids on the Removal of Cu(II) by the Oil–Water Interfacial Emulsion Technique. Cu(II) Removal Using $Fe(OH)_3$ or $Al(OH)_3$ as the Adsorbing Colloid[a]

Adsorbing colloid	pH	Residual Cu(II) (ppm)
Fe(III)	8.0	3.87
	9.0	0.34
	10.0	0.36
	11.0	2.92
Al(III)	10.0	3.18
	11.0	3.48

[a] Cu(II) = 0.0025 M, Fe(III) = 0.0025 M, Al(III) = 0.0025 M, trimethylamine = 0.005 M, T = 25°C, mixing and settling time = 30 minutes.

rate is also due to the sharp reduction of the oil–water interface, such that the coalescence of dispersed emulsion droplets occurs very rapidly. The increase of floc density may accelerate the coalescence rate of emulsion droplets, and thus the interfacial segregation of Cu(II) into the interfacial emulsion phase occurs spontaneously.

Effect of pH

The effect of pH on the removal of Cu(II) from aqueous solution using Fe(III) and Al(III) as adsorbing colloids is plotted in Fig. 1. The removal efficiency is represented by the low residual Cu(II) concentration. The optimum pH for the removal of Cu(II) was found at 9.0 when using Fe(III) and at 10.0 when using Al(III) as the adsorbing colloids. The residual concentration of Cu(II) can be lowered to below 0.4 ppm by using Fe(III) and below 3.2 ppm by using Al(III) as the adsorbing colloids for the treatment of an aqueous solution containing 0.0025 M (about 159 ppm) of Cu(II). For the removal of Cu(II), $Fe(OH)_3$ was more efficient as an adsorbing colloid than was $Al(OH)_3$.

The dissolved Cu(II) is adsorbed onto the floc particle and/or coprecipitated with it. A surfactant adsorbs onto the floc particle, renders it hydrophobic, and then the floc (with adsorbed metal) is removed by attachment to the oil–water interface. By stirring the liquid mixtures, an emulsion is formed and the metal precipitates are adsorbed at the oil–water interface. By settling, the coalescence of emulsion droplets occurs with a sharp reduction of the oil–water interface, and the interfacial emulsion phase is produced between water and a water-immiscible oil phase. The metal precipitates are segregated into the interfacial emulsion phase as a solid–liquid suspension that can easily be recovered by filtration.

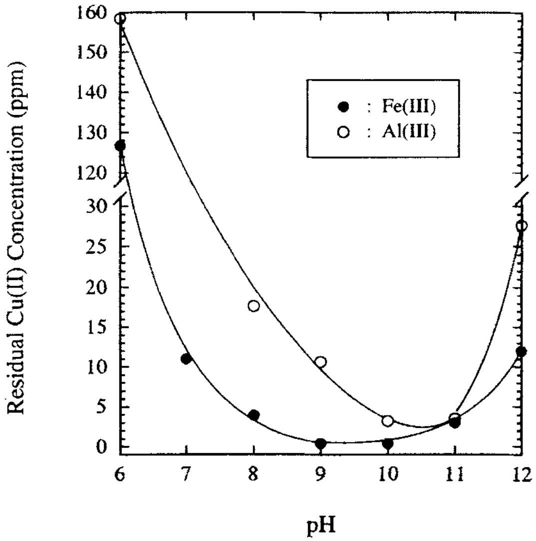

FIG. 1 Effect of pH on the removal of Cu(II) using $Fe(OH)_3$ or $Al(OH)_3$ as the adsorbing colloid [Cu(II) = 0.0025 M, Fe(III) = 0.0025 M, Al(III) = 0.0025 M, trimethylamine = 0.005 M, T = 25°C].

The adsorption is facilitated by the nature of the surfactant. Since trimethylamine is a cationic surfactant, it is desirable that the metal precipitates have some negative surface charges (i.e., they should be above the isoelectric points) to be removed. It was reported that the isoelectric point of $Fe(OH)_3$ in water is about 7.1 (10). Figure 1 shows that the optimum pH for the removal of Cu(II) was at a pH value above its isoelectric point. The optimum pH for the removal of Cu(II) using Al(III) as an adsorbing colloid was higher than that of Fe(III); this may be because the isoelectric point of $Al(OH)_3$ is about 9.0 (10).

Metal precipitates tend to have more negative surface charges with increasing pH above their isoelectric points. Figure 1 also shows that the removal efficiency was very poor above the optimum pH, presumably due to the effect of excess OH^- ions at high pH. These OH^- ions compete with negatively charged metal precipitates for the cationic surfactant trimethylamine, the thus adsorption of surfactant on the metal precipitates becomes weaker.

Effect of Initial Surfactant Concentration

The effect of initial surfactant concentration on the removal of Cu(II) using Fe(III) as the adsorbing colloid is shown in Table 2. When the surfac-

TABLE 2
Effect of the Initial Surfactant Concentration on the Removal of Cu(II) Using $Fe(OH)_3$ as the Adsorbing Colloid[a]

Initial surfactant (M)	Residual Cu(II) (ppm)
0.001	11.42
0.002	7.82
0.002	7.93
0.003	5.40
0.004	3.40
0.005	0.34
0.006	1.49
0.006	1.97
0.007	3.21
0.008	3.55
0.009	4.00
0.010	4.59

[a] Cu(II) = 0.0025 M, Fe(III) = 0.0025 M, surfactant = trimethylamine, pH 9.0, T = 25°C.

tant is less than 0.005 M, the removal efficiency is very low, presumably due to insufficient adsorption of surfactant on the floc to create floatability. Table 2 shows that Cu(II) can be effectively removed provided that the concentration of surfactant is 0.005 M. Concentrations above 0.005 M result in poor separation.

The most effective removal of Cu(II) can be obtained when there is just sufficient cationic surfactant (trimethylamine) adsorption on the surface of negatively charged metal precipitates to make the surface hydrophobic. If there is an excess surfactant concentration, it may cause a second surfactant adsorption on top of the primary adsorption layer, presumably forming a hydrophilic surface that inhibits the attachment of metal precipitates to the interface. The presence of a surfactant overdose thus makes the floc less floatable (14–17).

Effect of Initial Fe(III) Concentration

The effect of initial Fe(III) and Al(III) concentration on the removal of Cu(II) using Fe(III) as an adsorbing colloid is shown in Tables 3 and 4. Table 3 shows that Cu(II) can be effectively removed from a solution provided that the initial concentration of Fe(III) is 0.0025 M. When the concentration of Fe(III) is less than 0.0025 M, the removal efficiency is poor, presumably due to incomplete coprecipitation of Cu(II) with $Fe(OH)_3$ floc. Complete coprecipitation was performed with 0.0025 M

TABLE 3
Effect of the Initial Fe(III) Concentration on the Removal of Cu(II) Using $Fe(OH)_3$ as the Adsorbing Colloid[a]

Initial Fe(III) (M)	Residual Cu(II) (ppm)
0.0005	4.72
0.001	4.71
0.002	1.02
0.0025	0.34
0.003	2.78
0.004	9.59
0.005	11.87

[a] Cu(II) = 0.0025 M, trimethylamine = 0.005 M, pH 9.0, T = 25°C.

TABLE 4
Effect of the Initial Al(III) Concentration on the Removal of Cu(II) Using $Fe(OH)_3$ as the Adsorbing Colloid[a]

Initial Al(III) (M)	Residual Cu(II) (ppm)
0.001	3.86
0.002	3.48
0.0025	3.18
0.003	3.68
0.004	4.37
0.005	4.74

[a] Cu(II) = 0.0025 M, trimethylamine = 0.005 M, pH 9.0, T = 25°C.

Fe(III). An excess of Fe(III) may result in poor separation, possibly because the excess Fe(III) increases the quantity of floc so much that the floc particles cannot be fully contained in the interfacial emulsion phase. Then, floc begins to fall out of the emulsion into the aqueous phase. The coagulation of the floc by the addition of Fe(III) may result in poor separation if the floc is too heavy (12). It was found that Fe(III) is more efficient than Al(III) as an adsorbing colloid.

Effect of Foreign Anions

The effect of foreign anions on the removal of Cu(II) using Fe(III) as the adsorbing colloid is shown in Fig. 2. Anions (HPO_4^{2-}, SO_4^{2-}, NO_3^-) were introduced as sodium salts (Na_2HPO_4, Na_2SO_4, $NaNO_3$). The figure

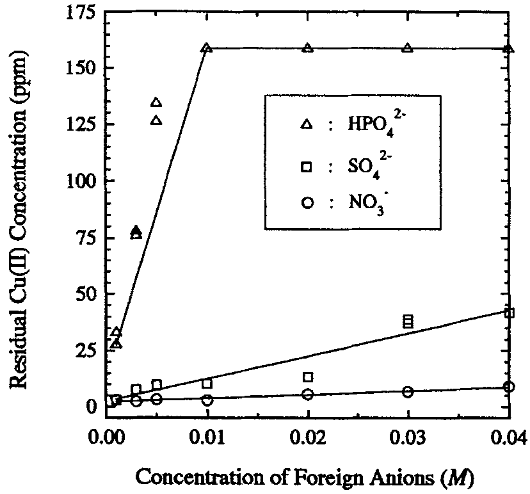

FIG. 2 Effect of foreign anions on the removal of Cu(II) ion using $Fe(OH)_3$ as an adsorbing colloid [Cu(II) = 0.0025 M, Fe(III) = 0.0025 M, trimethylamine = 0.005 M, pH 9.0, T = 25°C].

shows that the presence of anions in aqueous solution results in a serious obstacle for the removal of Cu(II). Significant reduction in Cu(II) removal efficiency by phosphate and sulfate anions may be due to the stronger union of divalent anions than of monovalent nitrate anions with the cationic surfactant trimethylamine. The anions compete with negatively charged metal precipitates for interaction with the cationic surfactant; thus, the surfactant adsorption on metal precipitates is inhibited at high concentration of anions. The electrostatic attraction between the cationic surfactant and negatively charged coprecipitates will be weaker in the presence of anion, and the removal efficiency decreases sharply at high concentration of anions (18). Figure 2 also shows that Cu(II) removal efficiency is extremely poor when the concentration of phosphate anion is over 0.01 M; this may be due to a stronger interaction of surfactant with the phosphate anion which has a strong complexing ability (19).

Effect of Foreign Cations

The effect of foreign cations on the removal of Cu(II) using Fe(III) as the adsorbing colloid is shown in Fig. 3. Cations (Na^+, Ca^{2+}) were introduced as chlorides (NaCl, $CaCl_2$). Figure 3 shows that a divalent cation inhibits the removal efficiency more significantly than does a monovalent cation. It is believed that the presence of Ca^{2+} may lessen the

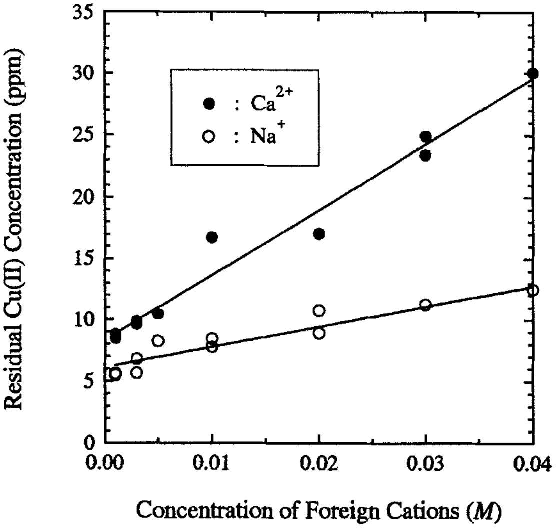

FIG. 3 Effect of foreign cations on the removal of Cu(II) ion using $Fe(OH)_3$ as an adsorbing colloid [Cu(II) = 0.0025 M, Fe(III) = 0.0025 M, trimethylamine = 0.005 M, pH 9.0, T = 25°C].

flocculating ability of $Fe(OH)_3$. The particle size of the coprecipitates decreases, presumably due to reduced floc formation.

CONCLUSION

Cu(II) can be removed from aqueous solution and segregated into a compact emulsion between water and a water-immiscible oil phase by the oil–water interfacial emulsion technique with adsorbing colloids. It is suggested that a more rapid separation can be achieved by adding flocculating materials such as $Fe(OH)_3$ and $Al(OH)_3$. The reason for the improvement is the larger particle size and higher zeta potential of the floc, which presumably has a strong electrical attraction to the interface. The improvement in the separation rate is also due to an increase of the floc density which can accelerate the coalescence rate of emulsion droplets. Then the interfacial segregation of Cu(II) into the interfacial emulsion phase occurs spontaneously. $Fe(OH)_3$ was more efficient than $Al(OH)_3$ as an adsorbing colloid for the removal of Cu(II). The residual concentration of Cu(II) can be lowered to below 0.4 ppm using Fe(III) as an adsorbing colloid at pH 9.0 from an aqueous solution containing 0.0025 M (about 159 ppm) of Cu(II). As a collector, trimethylamine has an optimum concentration to give sufficient adsorption of surfactant on metal precipitates to have floatability. An excess dose of surfactant may result in poor separation due to secondary adsorption of surfactant on top of the primary adsorption layer, presumably yielding hydrophilic surfaces. An excess dose of Fe(III) may also result in poor separation if the floc becomes too heavy. The presence of foreign ions inhibits separation efficiency. Divalent ions (Ca^{2+}, HPO_4^{2-}) inhibit the separation efficiency more seriously than do monovalent ions (Na^+, NO_3^-, and Cl^-). Cu(II) removal efficiency was extremely poor with 0.001 M phosphate anion due to its strong chelating ability.

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