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The Removal of Chromium, Nickel, and Zinc from Electroplating Wastewater by Adsorbing Colloid Flotation with a Sodium Dodecylsulfate/Dodecanoic Acid Mixture

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Abstract

The removal by adsorbing colloid flotation of Cr(III), Ni(II), and Zn(II) from chromium stream electroplating wastewater was investigated. Adsorbing colloid flotation involves the stripping of contaminants by adsorption or coprecipitation onto added colloidal material and its subsequent flotation by column flotation. The added colloid may be prepared prior to the adsorption step or, as in this case, prepared *in situ* by the hydrolysis of added metal [Fe(III)] ions. Adsorbing colloid flotation using a single surfactant (SDS) in the *batch* mode was shown to result in poor results for "real" industrial samples, presumably due to the chemical complexity of such samples. However, a dual surfactant system [sodium dodecylsulfate (SDS) + dodecanoic acid (DA)] provided encouraging results. By using such a dual surfactant system, chromium stream electroplating wastewater was treated, successfully lowering metal ion contamination levels to below that required for discharge into typical metropolitan drainage systems. Flotation was found to be successful at near neutral pH conditions (7.5) and for several different (electroplating) industrial samples. Adsorbing colloid flotation in the continuous mode was investigated by using the dual surfactant system optimized in *batch* experiments. At flow rates encouraging to full-scale commercial applications, toxic metal ions [Cr(III), Ni(II), Zn(II)] were stripped from contaminated industrial samples to below the 10 ppm typically required for metropolitan discharge. A *two-stage continuous* processing scheme was investigated where once-treated effluent was passed through a second "polishing" column. Use of this two-stage process typically resulted in the stripping of toxic metal ions (from similar samples) to well below the 1 ppm level typically required for environmental discharge.

Key Words: Adsorption; Removal; Coprecipitation; Flotation; Surfactant; Bubble; Heavy metal; Iron hydroxide; Sodium dodecylsulfate, Dodecanoic acid

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INTRODUCTION

Adsorptive bubble separation techniques exploit two physical properties of materials: surface excess charge and surface energy. These properties can be readily controlled by the addition of numerous regulatory agents, thus making flotation an extremely versatile separation technique. Flotation has been used for the concentration of minerals from ore pulps for many years (*1*, *2*). More recently, attention has been turned to the implementation of flotation for the treatment of industrial wastewater (*3*, *4*) as well as for analytical purposes (*5*).

Sodium dodecylsulfate (SDS) is a relatively inexpensive and environmentally safe surfactant—two extremely important characteristics for commercial wastewater treatment. It is, however, less than satisfactory for the practical treatment of many industrial wastewaters due to the ease with which it is displaced from the surface of precipitates by competing anions. Currin et al. (*6*), for example, have shown that the presence of phosphate, EDTA, hexaphosphate, arsenate, oxalate, perchlorate, cyanide, thiocyanate, fluoride, and sulfate all adversely affect the flotation of ferric hydroxide flocs when using SDS. Moreover, the extent of interference varied with the particular anion, making comparative analysis of flotation techniques using real, and thus variable, wastewater samples extremely difficult. It is not surprising then, that the vast majority of literature discussing metal ion flotation using SDS deals with *simulated* wastewater.

Allen et al. (*7*) investigated the use of a surfactant which would bind more strongly to the floc surface than SDS. Sodium dodecyliminodiacetate (DIDA) was evaluated but found to produce insufficient quantities of foam for effective separation. When used in conjunction with a "carrier" surfactant such as SDS or polyoxyethylene sorbitan monolaurate (Tween 20), however, flotation with DIDA was found to be much more successful. With SDS or Tween 20 included, flotation was considerably less prone to interference from both high ionic strengths and the presence of phosphate.

More recently, Gannon (*8*) studied the flotation of Cu(II) with a sodium dodecylphosphate (SDP) and *n*-hexanol mixture using ferric hydroxide as the floc. The presence of interfering anions (sulfate, oxalate, silicate, and phosphate) at concentrations which cause flotation with SDS alone to fail is tolerated when using such SDP/*n*-hexanol mixtures.

Carboxylic acids and their salts have long been used in the mineral processing industry. They are very powerful collectors which, when used on their own, tend to form gel-like foams (*9*). They are commonly used in conjunction with cosurfactants or froth modifiers to float a wide variety of minerals. Sarker et al. (*10*) investigated the use of carboxylic acids and straight chain alcohols as low cost surfactant extenders for SDS. In their work it was found that these additives reduce quite markedly the quantity of SDS needed in the flotation of ferric hydroxide flocs, including some flocs into which Cu(II) had been coprecipitated/adsorbed. Hiraide et al. (*11*) used a mixture of sodium oleate and SDS to quantitatively recover indium hydroxide precipitated at pH 9–9.5 from seawater. Sonawane et al. (*12*) used the same mixture of surfactants to evaluate the removal of iron, aluminum, and indium hydroxide precipitates in seawater. They found that a 1:3 mixture of sodium oleate and SDS can be successfully applied to the flotation of these hydroxides.

The decreased sensitivity to interference associated with the use of a strongly binding surfactant, as observed by Allen (*7*) and Gannon (*8*), coupled with the increased efficiency of low-cost surfactant extenders [Sarker (*10*)] may be exploited through the use of a carboxylic acid/SDS mixture.

The belief that such mixtures may be tolerant of water conditions encourages their use in the purification of industrial wastewaters using adsorbing colloid flotation. In this paper, several electroplating wastewater samples are treated using a batch mode, as well as a continuous mode, and also a two-stage continuous mode. Typically, a 2:3 mole ratio of dodecanoic acid (DA) to sodium dodecylsulfate (SDS) is used. Ferric hydroxide, formed by *in-situ* hydrolysis of ferric nitrate solution, is used as the carrier, and flotation is carried out as a function of pH. The subsequent flotation behavior is compared to that obtained by the use of SDS alone under similar conditions. The feasibility of the use of such surfactant mixtures to treat industrial wastewater in a continuous mode is also investigated.

EXPERIMENTAL SECTION

Reagents

The following solutions were prepared as follows: 40,000 ppm Fe(III) (0.716 *M*) from AR Grade $Fe(NO_3)_3 \cdot 9H_2O$ (Ajax Chemicals). 5000 ppm SDS (0.017 *M*) from LR Grade sodium dodecylsulfate (BDH Chemicals). Combined surfactant solution (0.012 *M* DA, 0.017 *M* SDS) from LR Grade dodecanoic acid (BDH Chemicals) and LR Grade sodium dodecylsulfate (BDH Chemicals) dissolved in warm alkaline solution.

Industrial Electroplating Wastewater

Chromium stream electroplating wastewater was sampled and stored in 20 L polythene containers. Three samples (A, B, and C) were taken from a small electroplater (wastewater output, 12 kL/d) which carries out predominantly "decorative" chromium plating. One sample (sample D) was collected from a large electroplating establishment (wastewater output 300

TABLE 1
Characterization of Industrial Wastewaters

Sample	Conductivity (Ω^{-1})	pH	Heavy metal concentration (ppm) Cr	Ni	Zn
A	1.39×10^{-3}	2.9	52.0	35.1	0.6
B	1.22×10^{-3}	3.0	79.3	52.9	3.0
C	1.04×10^{-3}	2.9	79.4	24.3	1.0
D		2.8	228.0	69.0	0.9

kL/d) which carries out predominantly engineering-type plating. Likely contaminants in these samples include sulfate, chloride, fluoride, perborate, sulfonate, fluoroborate, phosphates, silicates, sulfide, chromium(III), chromate, nickel(II), zinc(II), and low levels of surface-active agents (e.g., SDS) and organic brightening agents (e.g., sulfonamide). The conductivity, pH, and heavy metal concentrations of these samples are shown in Table 1.

Batch Mode Procedure

The flotation apparatus used to study the foam flotation of electroplating wastewaters in a batch experiment is shown diagrammatically in Fig. 1a.

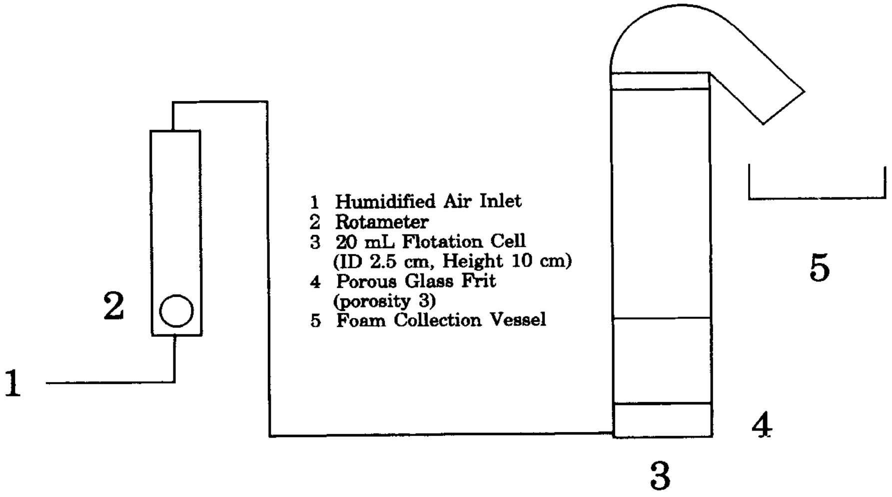

FIG. 1a. Flotation apparatus used for "batch" flotation experiments.

Twenty milliliter aliquots of industrial wastewater were dosed with 0.125 mL of 40,000 ppm Fe(III) solution. The pH was adjusted to within one pH unit of the required value with 0.1 *M* NaOH. NaOH of 0.01 *M* was then used to bring the pH to the required value. A 15-min aging period was allowed before the surfactant was added and flotation attempted. A gas flow rate of 60 mL/min with constant stirring was employed in the flotation cell. The solution remaining in the flotation cell after a 2-min flotation period was sampled, acidified, and analyzed for Cr, Ni, and Zn by atomic absorption spectroscopy.

Continuous Procedure

The cell used to study the continuous adsorbing colloid flotation of these samples is shown in Fig. 1b. Two-liter samples of wastewater were dosed with 1.25 mL of 40,000 ppm Fe(III) solution. The pH was then adjusted to 7.5 ± 0.1 and the sample aged for 30 min prior to pumping to the 100-mL flotation cell (15 cm column). The surfactant was pumped, at the required rate, into the wastewater lines immediately prior to entry into the flotation cell. An air flow rate of 170 mL/min was used.

Sample Characterization

Wastewater samples were analyzed for Cr, Ni, and Zn using atomic absorption spectroscopy. Conductivity measurements were made using a Philips PR 9500 conductivity bridge, and pH measurements were made using a Philips pH meter.

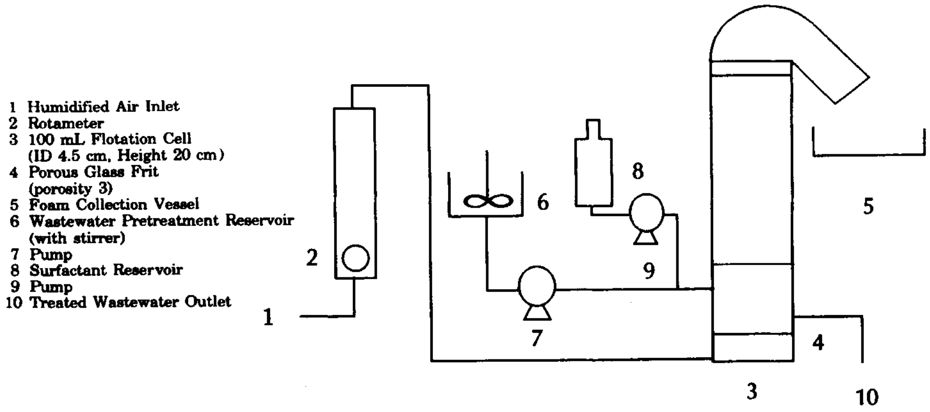

FIG. 1b. Flotation apparatus used for "continuous" flotation experiments.

TABLE 2
Effect of pH on Removal by Adsorbing Colloid Flotation of Heavy Metal Ions (from wastewater sample A, using 50 ppm SDS)

	Residual metal concentration (ppm)		
pH	Cr	Ni	Zn
4.5	8.3	26.5	0.51
5.5	22.8	24.9	0.34
6.5	49.5	21.9	0.60
7.5	52.0	21.6	0.60
8.5	38.2	24.9	0.43

RESULTS AND DISCUSSION

A. Batch Mode

The results for the removal of Cr(III), Ni(II), and Zn(II) from wastewater sample A by adsorbing colloid flotation using a single surfactant, SDS, at 50 ppm and a carrier floc formed *in situ* from 250 ppm Fe(III) are given in Table 2 and shown graphically in Fig. 2. Adsorbing colloid flotation (under these conditions) appears unable to adequately strip electroplating wastewater of its contaminant metals. Such an observation is in contrast to the results obtained by Huang et al. (*13*) for the removal of Cr(III), Ni(II), Cu(II), and Zn(II) from simulated wastewater (20 ppm with respect to each metal), also using a single surfactant [50 ppm SDS, 160 ppm Fe(III)]. For the *simulated* wastewater, near complete removal of all metal ions was observed in the pH 7.5 to 9.5 range. In our study the generally poor flotation behavior over the entire pH range may be attributed to the complex composition of industrial samples. At lower pH values, unfavorable pH conditions prevent adequate adsorption and/or coprecipitation of ions such as Ni(II) in both simulated and real wastewaters. At higher pH values (7.5 to 9.5), where flotation of simulated samples was efficient, the adsorption of surfactant onto the carrier floc is most susceptible to interferences from other anions. In the higher pH range, the surface of the carrier floc is negatively charged or at best only weakly positively charged. Adsorption of the anionic surfactant is thus weaker than at lower pH values and much more likely to be influenced by interfering ions.

The removal of Cr(III), Ni(II), and Zn(II) from wastewater sample A by adsorbing colloid flotation using a mixed surfactant system (100 ppm

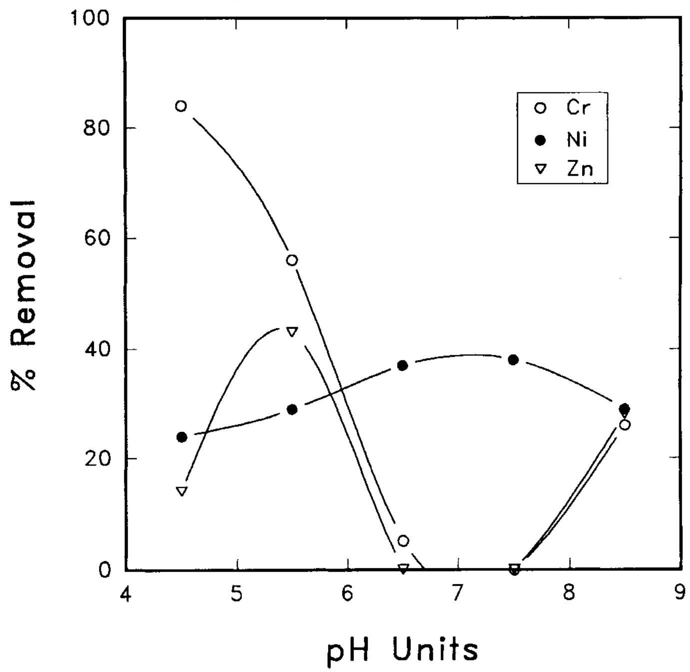

FIG. 2. Effect of pH on removal by adsorbing colloid flotation of heavy metal ions (from wastewater sample A, using 50 ppm SDS).

DA, 200 ppm SDS) is much more effective. This is illustrated by the results given in Table 3 and shown graphically in Fig. 3. As can be seen from these results, a pH of 8.5 was found to result in excellent removal of heavy metals Cr(III), Ni(II), and Zn(II).

Removal at these relatively high pH values may be attributed to a two-stage adsorption mechanism for the surfactants, similar to that first outlined by Held and Samachwaler (*14*) for the adsorption of alkali carboxylates on barium sulfate or cinnabar. The carboxylate ion adsorbs onto the surface first by chemically reacting with metal ions at the surface according to

$$Fe(OH)_3 + C_{11}H_{23}COO^- \rightarrow C_{11}H_{23}COOFe(OH)_2 + OH^-$$

Once adsorption in this mode has taken place, the adsorption of surface-active molecules remaining in solution is then enhanced by hydrophobic interactions. In this way, adsorption (and packing) at the floc surface of one surfactant is enhanced by the other.

TABLE 3
Effect of pH on Removal by Adsorbing Colloid Flotation of Heavy Metal Ions (from wastewater sample A, using 100 ppm and 200 ppm SDS)

	Residual metal concentration (ppm)		
pH	Cr	Ni	Zn
4.5	0.7	22.9	0.34
5.5	0.0	18.1	0.08
6.5	0.1	5.4	0.00
7.5	0.1	1.0	0.00
8.5	0.2	0.0	0.00

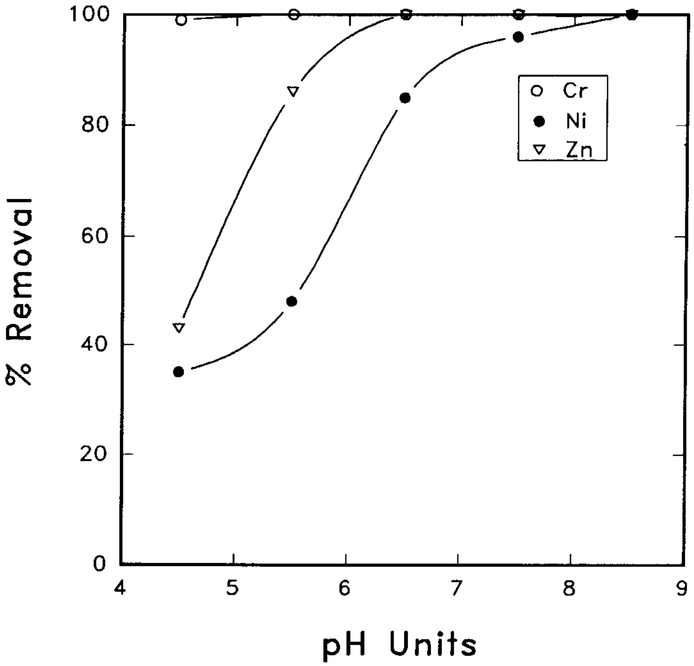

FIG. 3. Effect of pH on removal by adsorbing colloid flotation of heavy metal ions (from wastewater sample A, using 100 ppm DA and 200 ppm SDS).

TABLE 4

Effect of Surfactant Concentration on Removal by Adsorbing Colloid Flotation of Heavy Metal Ions (from wastewater sample B at pH 8.5)

DA concentration (ppm)	SDS concentration (ppm)	Residual metal concentration (ppm)		
		Cr	Ni	Zn
0	25	77.7	51.9	2.9
0	50	61.8	41.2	2.3
0	100	43.2	27.8	1.5
0	150	34.1	18.5	1.1
0	200	28.4	17.8	0.9
0	300	15.8	8.4	0.4
3	6	29.4	21.6	1.1
8	16	7.5	5.3	0.29
16	32	1.0	1.4	0.05
32	64	0.5	0.9	0.03
50	100	1.6	0.5	0.09
66	135	1.5	0.6	0.10
100	200	0.6	0.9	0.03

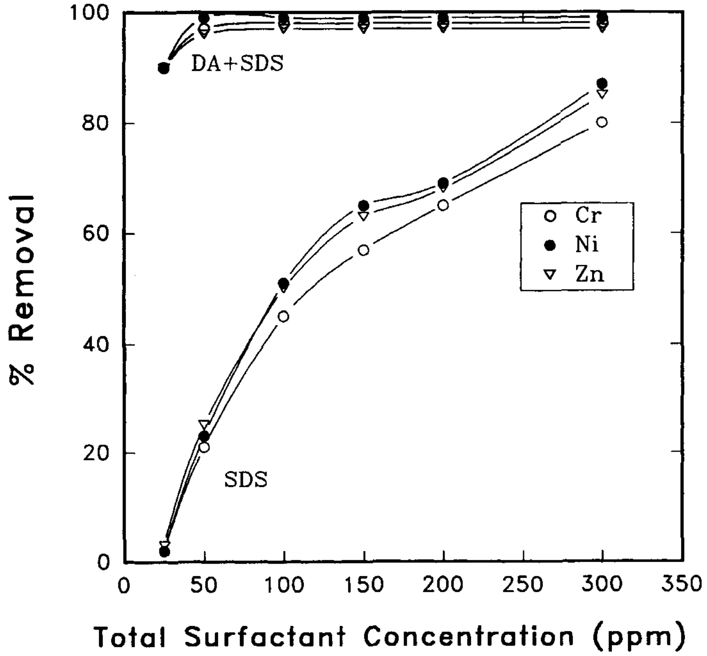

FIG. 4. Effect of surfactant concentration on removal by adsorbing colloid flotation of heavy metal ions (from wastewater sample B, at pH 8.5).

The effect of surfactant concentration on removal efficiency using the surfactant mixture (1:2 weight ratio; 2:3 mole ratio, dodecanoic acid/SDS) is shown in Table 4 and Fig. 4, where it is compared with the use of SDS alone. In both cases the carrier floc was generated by the addition, *in situ*, of 250 ppm Fe(III) at a pH of 8.5. By interpolation, a total surfactant concentration as low as approximately 50 ppm (16.5 ppm DA + 33 ppm SDS) is sufficient to obtain removal of all heavy metal ions in the 95–100% range. By contrast, the use of 50 ppm SDS alone results in removals in the 20–25% range. To achieve equivalent results (removals in the 95–100% range), more than 300 ppm of SDS alone would have to be used. Such high surfactant concentrations would be prohibitively expensive and lead to large quantities of wet foamate which would in turn require treatment before disposal.

TABLE 5

Effect of Surfactant Concentration on Removal by Adsorbing Colloid Flotation of Heavy Metal Ions (from wastewater sample C)(at pH 7.5, 170 mL/min air flow rate, 10 mL wastewater throughput)

DA concentration (ppm)	SDS concentration (ppm)	Sampling time after start of run (min)	Residual metal concentration (ppm)		
			Cr	Ni	Zn
8	16	5	26.1	7.9	0.38
		15	23.7	7.7	0.38
		20	24.5	—	0.38
		25	25.3	7.8	0.36
		30	23.6	7.7	0.34
20	40	5	12.6	3.8	0.2
		10	15.6	4.1	0.2
		15	14.2	4.2	0.2
		20	10.3	3.1	0.2
		25	11.1	3.0	0.1
30	60	5	3.9	1.9	0.07
		10	7.1	2.2	0.10
		15	7.9	3.1	0.14
		20	6.3	2.2	0.08
		25	3.2	3.4	0.04
50	100	5	3.1	2.2	0.04
		10	2.4	1.9	0.05
		15	4.7	2.1	0.05
		20	4.6	1.4	0.05
		25	3.9	0.7	0.06
		30	4.7	1.9	0.05

B. Continuous Mode

The effect of surfactant concentration on the removal efficiency at pH 7.5, 10 mL/min wastewater throughput, 25 ppm Fe(III), and an air flow rate of 170 mL/min is shown in Table 5 and Fig. 5. At this flow rate (one-tenth of liquid volume in cell per minute, i.e., a 10-min retention time) a surfactant concentration of 30 ppm DA plus 60 ppm SDS is required to achieve heavy metal concentrations consistently below 10 ppm, which is the usual limit for metropolitan discharge. The effect of wastewater throughput on removal efficiency at pH 7.5, 30 ppm DA + 60 ppm SDS, and 170 mL/min air flow rate is shown in Table 6 and Fig. 6. Retention times as low as 2.6 min were sufficient to give metal concentrations below the 10 ppm discharge limit.

More stringent requirements for heavy metal removal need to be met for direct discharge to the environment (for example, typical EPA limits of 1 ppm for each metal). The addition of a second flotation (polishing)

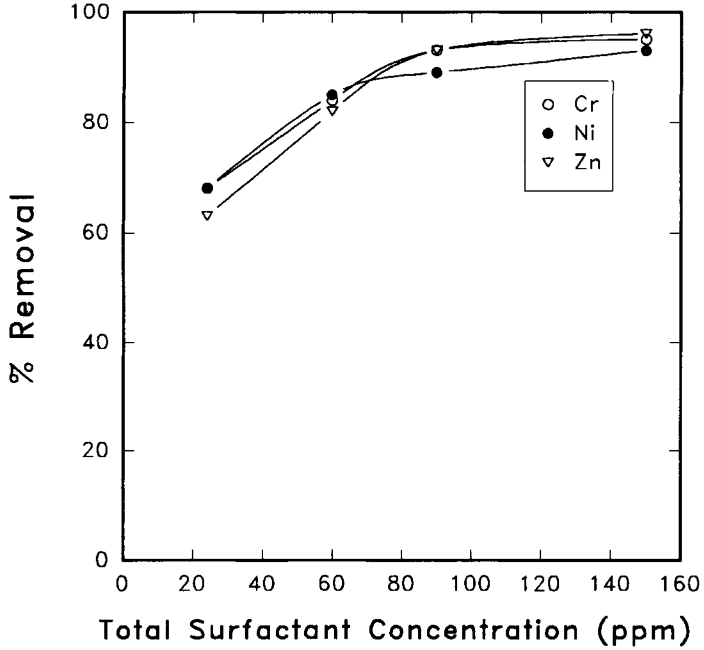

FIG. 5. Effect of surfactant concentration on removal by adsorbing colloid flotation of heavy metal ions (from wastewater sample C, at pH 7.5, 170 mL/min air throughput, 10 mL/min wastewater throughput).

TABLE 6
Effect of Wastewater Throughout on Removal by Adsorbing Colloid Flotation of Heavy Metal Ions (from wastewater sample C) [at pH 7.5, 30 ppm DA + 60 ppm SDS, 170 mL/min air flow rate, 25 ppm Fe(III)]

Flow rate (mL/min)	Residual metal concentration (ppm)		
	Cr	Ni	Zn
11	7.1	3.4	0.07
16	9.5	4.1	0.14
22	11.8	4.6	0.14
24	7.9	3.1	0.07
28	5.5	4.1	0.10
34	6.3	4.1	0.10
38	8.7	4.3	0.10
42	10.3	4.8	0.10
45	12.6	5.0	0.20
50	10.3	4.1	0.10
54	13.4	4.1	0.20

stage to the adsorbing colloid flotation process results in heavy metal concentrations below the limit for environmental discharge (Table 7). Such a polishing stage, which required a second column as part of the continuous processing, involved the addition of a further 25 ppm Fe(III) and pH readjustment to 8.0, but no further addition of surfactant.

CONCLUSIONS

Adsorbing colloid flotation using a mixed surfactant system (DA and SDS) has been shown to be a promising technique for the removal of aqueous heavy metal contaminants from industrial electroplating wastewater. The use of a surfactant mixture has been shown to result in far superior removals over a single surfactant system. It is postulated that this increased efficiency is due to strong binding of dodecanoic acid (DA) to the floc surface and its subsequent enhancement of the SDS adsorption. Since both these surfactants are relatively inexpensive and environmentally safe, their use in industrial wastewater treatment is warranted.

The present results suggest that the removal of heavy metals by flotation with this surfactant mixture is also sufficiently rapid to warrant experi-

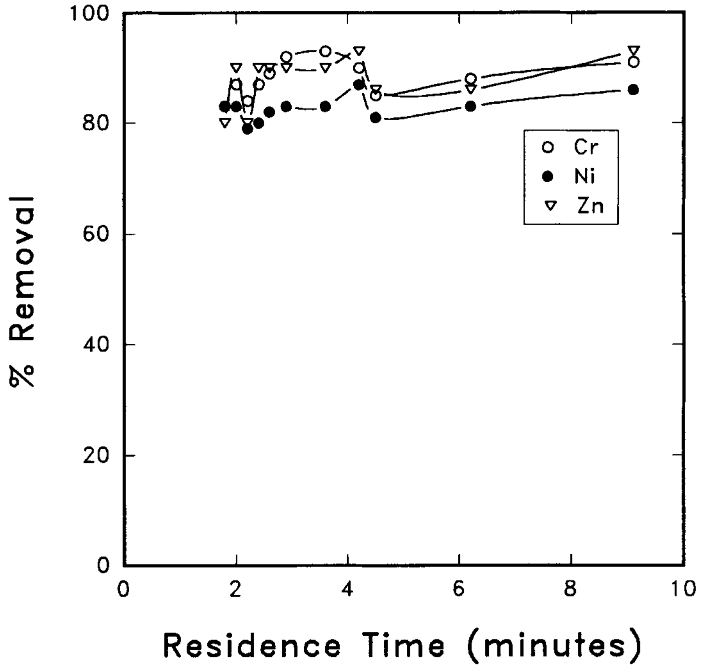

FIG. 6. Effect of effluent throughput on removal by adsorbing colloid flotation of heavy metal ions [from wastewater sample C, at pH 7.5, 30 ppm DA + 60 ppm SDS, 170 mL/min air throughput, 25 ppm Fe(III)].

TABLE 7

Effect of a Second (polishing) Stage on Removal by Adsorbing Colloid Flotation of Heavy Metal Ions (from wastewater sample D, at pH 7.5 and 170 mL/min) (100 mL/min wastewater throughput, 1000 mL/min air throughput, first stage) (50 mL/min wastewater throughput, 600 mL/min air throughput, second stage)

Metal	Heavy metal concentration before flotation (ppm)	Heavy metal concentration after first flotation (ppm)	Heavy metal concentration after second flotation (ppm)
Cr	228	3.7	0.85
Ni	69	1.7	0.48
Zn	0.92	0.11	0.12

mentation on a large continuous scale. Such work will be reported subsequently.

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