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INTRODUCTION

There are many small metal-plating firms, and the Environmental Protection Agency estimates that the metal-plating industry will be the industry hardest hit by the new pretreatment standards which require dischargers to limit heavy metal discharges to very low concentrations (1). Existing methods of heavy metal removal, such as lime precipitation, are costly, require large tanks, produce a wet, bulky sludge, and usually require final filters for polishing if very low residual levels of metals are desired. Heavy metal removal methods which are cheaper, require less space (important in old businesses with limited land), and produce less sludge are needed.

In addition, metal-plating and finishing firms are large users of water because plating and rinsing solutions and baths must be discharged periodically when they become contaminated or depleted. If economical methods of removing the contaminants from rinse baths could be developed, recycling and reuse of the water would be more practical and economical. This would reduce demands on scarce water resources in some areas and on treatment and distribution system capacity in all areas. It would also reduce the financial burden on industry and, ultimately, on the public since the waters must be pretreated before discharge anyway and, if they could be reused, the amount of "new water" bought would be reduced.

Adsorbing colloid foam flotation as a means of removing heavy metals has been under investigation at Vanderbilt University for some time. It consists of adding a coagulant (alum or ferric chloride) to produce a floc which

adsorbs the dissolved metal, addition of a surfactant, followed by removal of the floc (and adsorbed metal) by air flotation.

Wilson et al. have published numerous papers in this journal on the theory of adsorbing colloid foam flotation and on preliminary bench scale experimental work with a variety of metals and other ions. Wilson and Clarke (2) also published a lengthy summary review in 1978. Thackston et al. (3) described the removal of lead in a large continuous flow pilot plant. Slapik, Thackston, and Wilson (4, 5) described improvements to the pilot plant which tripled capacity and cut costs of lead removal in half. Lemlich's book reviews the general area of adsorptive bubble separations (6).

EXPERIMENTAL WORK

This project was designed to test the foam flotation process on metal plating wastes. This paper describes the results obtained by the large continuous flow pilot plant treating a simulated copper-bearing waste.

Ferric chloride was added to the wastewater to form a ferric hydroxide precipitate which acts as the adsorbant in the adsorption process. Adjustment of the pH was accomplished using 0.25 *M* NaOH. Sodium lauryl sulfate (NLS) was the surfactant used. The simulated copper-bearing wastewaters were prepared by dissolving copper sulfate in tap water, then adjusting the pH to prevent the precipitation of copper carbonate. All experimental runs were made with an initial copper(II) concentration of 20 mg/L.

The pilot plant apparatus used for this study is shown in Fig. 1. A detailed description of the flotation system appears in earlier papers dealing with lead removal by the same technique (3-5).

Simulated wastewater to be treated is pumped from a 1040-L (275-gal) storage tank. The addition of FeCl_3 and NaOH occurs upstream of the main pump, which simulates a rapid mix unit. FeCl_3 is pumped into the main influent line, and the NaOH flows by gravity feed through a solenoid valve into the influent line. The solenoid valve is operated by a pH-controller set to produce the desired pH in the first mixing chamber. After passing through the main pump, the wastewater enters a series of three mixing chambers of total volume 43.9 L (11.6 gal). Before the wastewater passes through a flowmeter, NLS is injected into the stream and the waste is sent through the top of the flotation column to a spider-shaped dispersion head with eight radial arms located 76.2 cm (2.5 ft) below the top of the column. The column itself consists of two 121.9 cm (4 ft) sections of 29.2 cm (11.5 in.) i.d., 30.5 cm (12 in.) o.d., Lucite column flanged together and O-ring sealed. The column has an arrangement of 19 baffles spaced 7 cm (2.75 in.) apart at the top and 95 cm (3.75 in.) apart at the bottom. The air is supplied through a 12.7 cm (5 in.) diameter fine porosity fritted glass disk at a maximum pressure of 10 psi.

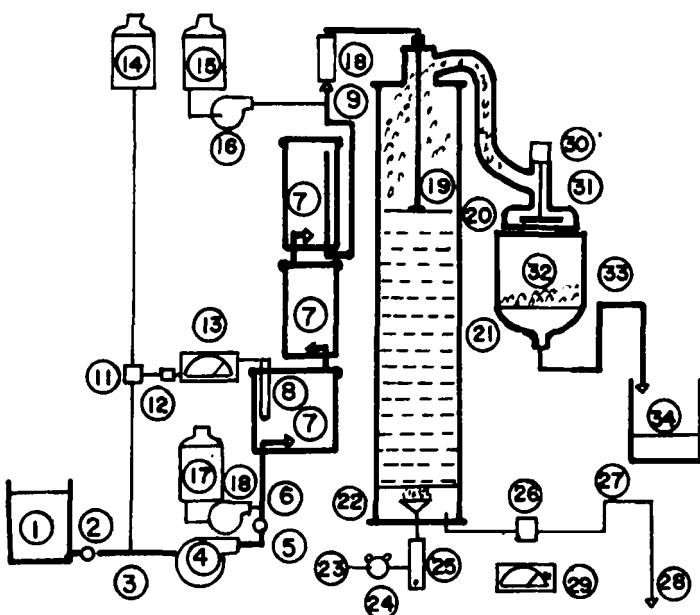


FIG. 1. Schematic diagram of 30-cm pilot plant. 1: Waste tank. 2: Waste tank valve. 3: NaOH injection tee. 4: Main pump. 5: Flow control valve. 6: FeCl₃ injection tee. 7: Mixing chamber. 8: Control pH electrode. 9: NLS injection tee. 10: Waste flow rotometer. 11: NaOH solenoid valve. 12: Electrical junction box. 13: Control pH meter. 14: NaOH tank. 15: NLS tank. 16: NLS feed pump. 17: FeCl₃ tank. 18: FeCl₃ feed pump. 19: Flow dispersion head. 20: Column. 21: Baffles. 22: Air diffuser. 23: Air supply line. 24: Air pressure regulator. 25: Air flow rotometer. 26: Monitoring pH electrode. 27: Column liquid level control. 28: Effluent line. 29: Monitoring pH meter. 30: Foam breaker motor. 31: Foam breaker. 32: Clarifier. 33: Clarifier liquid level control. 34: Broken foam container.

The treated effluent leaves the column from the bottom and foam is piped out of the top of the column to a rotating disk foam breaker. The liquid from the broken foam is collected in 49.2 L (13 gal.) plastic clarifier mounted under the foam breaker. A pH electrode is located in the effluent line to determine the effluent pH. The effluent pH is generally 0.5 to 1.0 units higher than the pH in the mixing chamber. This difference is due to the alkalinity of the NLS. After every run the collected samples were again checked for pH and no significant difference was observed from that shown by the effluent pH meter.

The analysis for final copper(II) concentrations in the effluent was accomplished by atomic absorption spectrophotometry. The analysis was made on a Model 305 B Perkin Elmer instrument at a wavelength of 325 nm. The analysis for NLS in the effluent and in the foamate was accomplished by the chloroform extraction technique as outlined in *Standard Methods* (7).

RESULTS AND DISCUSSION

The variables having an influence on the efficiency of the system which were studied are pH, Fe(III) and NLS concentrations, wastewater hydraulic loading rate, ionic strength, and air flow rate.

Table 1 shows the influence of pH on copper removal. Tabulated pH values correspond to those of the effluent. As indicated before, there is a difference of 0.5 to 1.0 pH units between the effluent pH and the pH in the mixing tank. There is a reasonably wide pH range in which copper levels below 0.5 mg/L are obtained and a range of 0.3 to 0.4 units around neutral pH where excellent results are achieved. At pH values higher than 7.4, the decrease in flotation efficiency leads to the presence of some Fe(OH)_3 in the effluent.

Tables 2 and 3 show the influence of Fe(III) and NLS dose, respectively. The optimum Fe(III) concentration seems to be between 90 and 100 mg/L. Concentrations above 100 mg/L do not improve copper removal. At Fe(III) concentrations of 150 mg/L, a decrease in flotation efficiency was noticed and Fe(OH)_3 started to appear in the effluent.

For NLS, a concentration of 15 mg/L was found to be sufficient to maintain a good stable foam pattern in the column. Higher concentrations of surfactant do not improve the performance of the flotation system and lead to higher NLS concentrations in the effluent. For the data tabulated, the experimental run was conducted at $6.8 \text{ m}^3/\text{m}^2 \cdot \text{h}$ ($2.8 \text{ gal/min} \cdot \text{ft}^2$)

TABLE I
Influence of pH on Copper Removal^a

| pH effluent | Cu^{2+} (mg/L) |
|----------------|----------------------------|
| 5.6 | 1.99 |
| 6.0 | 1.04 |
| 6.6 | 0.57 |
| 6.8 | 0.36 |
| 6.9 | 0.11 |
| 7.0 | 0.12 |
| 7.2 | 0.12 |
| 7.4 | 0.50 |
| 7.6 | 1.00 |
| 7.7 | 1.54 |

^aInitial $\text{Cu}^{2+} = 20 \text{ mg/L}$. Operating conditions: $\text{Fe(III)} = 100 \text{ mg/L}$, $\text{NLS} = 35 \text{ mg/L}$, hydraulic loading (H.L.) = $0.45 \text{ m}^3/\text{h}$ (2 gal/min), hydraulic loading rate (H.L.R.) = $6.8 \text{ m}^3/\text{m}^2 \cdot \text{h}$ ($2.8 \text{ gal/min} \cdot \text{ft}^2$), air flow (A.F.) = $12.9 \text{ Nm}^3/\text{m}^2 \cdot \text{h}$ (30 SCFH). Conclusion: Optimum pH range = 6.9 to 7.3.

TABLE 2
Influence of Fe(III) Dose on Copper Removal^a

| Fe(III) (mg/L) | Cu ²⁺ (mg/L) |
|-------------------|----------------------------|
| 50 | 0.56 |
| 75 | 0.41 |
| 90 | 0.19 |
| 100 | 0.12 |
| 120 | 0.12 |
| 150 | 0.21 |

^aOperating conditions: Initial Cu²⁺ = 20 mg/L, NLS = 35 mg/L, pH = 7.0 (6.9-7.2), H.L. = 0.45 m³/h (2 gal/min), H.L.R. = 6.8 m³/m² · h (2.8 gal/min · ft²), A.F. = 12.9 Nm³/m² · h (30 SCFH). Conclusions: Optimum Fe(III) = 100 mg/L, Optimum range Fe(III) = 90 to 120 mg/L.

TABLE 3
Influence of NLS Dose^a

| NLS (mg/L) | Cu ²⁺ (mg/L) |
|---------------|----------------------------|
| 35 | 0.12 |
| 30 | 0.12 |
| 25 | 0.15 |
| 20 | 0.17 |
| 15 | 0.23 |

^aOperating conditions: Initial Cu²⁺ = 20 mg/L, pH = 6.9-7.2, Fe(III) = 100 mg/L, H.L. = 0.45 m³/h (2 gal/min), H.L.R. = 6.8 m³/m² · h (2.8 gal/min · ft²), A.F. = 12.9 Nm³/m² · h (30 SCFH). Conclusion: Optimum range (NLS) = 15 to 35 mg/L. With the modification of independent feed pumps, once the foam has stabilized the NLS concentration can be reduced to 15 mg/L and one can still have good flotation. This greatly reduces NLS in the effluent.

hydraulic loading rate, but good performance of the flotation column was observed at hydraulic loading rates as high as 13.6 m³/m² · h (5.6 gal/min · ft²) without increasing the NLS dose.

As reported in Table 4, increasing the hydraulic loading rate leads to a decrease in copper removal efficiency, but copper levels below 0.5 mg/L are consistently achievable even at 13.6 m³/m² · h (5.6 gal/min · ft²). Working at high hydraulic loading rates did not show any detrimental effects on the flotation system performance and a clear effluent free of Fe(OH)₃ was always obtained at pH values below 7.4. The decrease in copper removal

TABLE 4
Influence of Hydraulic Loading Rate on System Performance^a

| Hydraulic loading rate $\text{m}^3/\text{m}^2 \cdot \text{h}$ | (gal/min \cdot ft ²) | Cu^{2+} (mg/L) |
|--|------------------------------------|----------------------------|
| 6.8 | 2.8 | 0.11 |
| 8.5 | 3.5 | 0.12 |
| 10.2 | 4.2 | 0.26 |
| 12.6 | 5.2 | 0.34 |
| 13.6 | 5.6 | 0.48 |
| 14.8 | 6.1 | 0.57 ^b |

^aOperating conditions: $\text{Fe(III)} = 100 \text{ mg/L}$, $\text{NLS} = 35 \text{ mg/L}$, $\text{pH} = 7.0$, $\text{Air} = 12.9 \text{ Nm}^3/\text{m}^2 \cdot \text{h}$ (30 SCFH), Initial $\text{Cu}^{2+} = 20 \text{ mg/L}$. Conclusion: The copper concentration in the effluent increases as the hydraulic loading rate increases, but reasonable results have been obtained at all loading rates tested.

^bMaximum of column. This result occurred at a pH of 6.60, which might have caused the higher Cu^{2+} concentration in the effluent.

efficiency is apparently due to the reduction in contact time between the Fe(OH)_3 floc and the copper-bearing wastewater in the mixing chambers. From the hydraulic loading data and volume of the mixing chambers (43.9 L or 11.6 gal), a nominal retention time of 4.0 to 4.5 min seems to be necessary to achieve adsorption equilibrium.

Air flow rates of 11 to 13 $\text{Nm}^3/\text{m}^2 \cdot \text{h}$ (0.6 to 0.7 $\text{ft}^3/\text{min} \cdot \text{ft}^2$) are enough to provide a good performance of the flotation column, even at the lowest NLS concentration and the highest hydraulic loading rate $14.8 \text{ m}^3/\text{m}^2 \cdot \text{h}$ (6.1 $\text{gal}/\text{min} \cdot \text{ft}^2$).

Table 5 indicates that increasing the ionic strength has a negative influence on the treatment efficiency. Very good results are achievable up to 0.5 M NaCl concentration. Higher concentrations drastically reduce the efficiency of the system, leading to the presence of Fe(OH)_3 in the effluent. The most reasonable explanation for the poor efficiency at high ionic strengths is that chloride ions displace the NLS attached to the flocs, thereby causing the flocs to lose their hydrophobic character.

NLS RECOVERY

Table 6 shows the results obtained in the NLS recovery experiments. Approximately 60% of the total surfactant is utilized for foam production, the remainder coming out in the effluent. An NLS dose of 15 mg/L leads to a

TABLE 5
Influence of Ionic Strength, Cu^{2+} (mg/L)^a

| pH | I.S. = 0 | I.S. = 0.01 M | I.S. = 0.05 M | I.S. = 0.10 M | I.S. = 0.15 M |
|-----|----------|---------------|---------------|---------------|---------------|
| 6 | 1.04 | 1.72 | 3.0 | 6.1 | 7.70 |
| 7 | 0.11 | 0.14 | 0.35 | 3.6 | 6.80 |
| 7.2 | 0.12 | 0.16 | 0.34 | 3.6 | 6.30 |
| 7.3 | 0.12 | 0.18 | 0.30 | 3.7 | — |

^aOperating conditions: Initial Cu^{2+} = 20 mg/L, Fe(III) = 100 mg/L, NLS = 35 mg/L, H.L. = 0.45 m^3/h (2 gal/min), H.L.R. = 6.8 $\text{m}^3/\text{m}^2 \cdot \text{h}$ (2.8 gal/min · ft²), A.F. = 12.9 $\text{Nm}^3/\text{m}^2 \cdot \text{h}$ (30 SCFH). Ionic strength was adjusted with NaCl.

final concentration in the effluent which represents no more than 8 mg/L BOD_5 . At such a low NLS concentration in the system, no further surfactant stripping was achieved by increasing the height of the liquid pool level above the air diffuser. Increasing the height of the pool also causes a decrease in copper removal efficiency.

In order to study the possibility of NLS recovery, samples of foamate were collected in beakers. The foamate consisted of a liquid subnatant and a dark brown layer of floating scum. To break down this floating layer, various amounts of 0.25 N NaOH were added, followed by flocculating and settling. A dose of 10% NaOH by volume was found sufficient to obtain a readily-

TABLE 6
NLS Experiments^a

| Sample | Height of pool above head | | % Foamate | NLS (mg/L) in effluent | Cu (mg/L) in effluent |
|--------|------------------------------|-----|-----------|---------------------------|--------------------------|
| | cm | in. | | | |
| 1 | 5 | 2 | 7.0 | 5.5 | 0.15 |
| 2 | 25 | 10 | 7.2 | 6.0 | 0.30 |
| 3 | 80 | 32 | 8.4 | 6.0 | 0.60 |

^aOperating conditions: Cu_0 = 20 mg/L, Fe = 100 mg/L, NLS = 15 mg/L, H.L. = 0.45 m^3/h (2 gal/min), H.L.R. = 6.8 $\text{m}^3/\text{m}^2 \cdot \text{h}$ (2.8 gal/min · ft²), A.F. = 12.9 $\text{Nm}^3/\text{m}^2 \cdot \text{h}$ (30 SCFH), pH = 6.9–7.2. Conclusions: NLS in the effluent \cong 40% of total NLS, NLS in the supernatant = 60% of total NLS, NLS in the settled sludge = 0% of total NLS. Foamates were treated with 10, 20, and 35 mL of 0.25 NaOH per 100 mL of foamate. 10 mL of NaOH was found to be sufficient to give a readily-settleable sludge and clarified supernatant. The supernatant from foamate Sample 3 was analyzed for copper and NLS: Cu^{2+} = 0.70 mg/L, NLS = 112.5 mg/L.

TABLE 7
Optimum Operating Parameters for 30-cm Pilot Plant

| Parameter | Optimum value |
|------------------------|---|
| Effluent pH | 6.9-7.3 |
| Fe(III) concentration | 90-100 mg/L |
| NLS concentration | 15-20 mg/L |
| Hydraulic loading rate | 7-12 m ³ /m ² · h (3-5 gal/min · ft ²) |
| Air flow | 12-13 Nm ³ /m ² · h (0.7 ft ³ /min · ft ²) |

settleable sludge and clear liquid supernatant. Copper analysis carried out on the supernatant yielded Cu(II) values lower than 0.7 mg/L, which indicated that the vast majority of the copper removed ends up in the sludge.

A mass balance can be performed to calculate the theoretical NLS concentration in the foamate:

$$C_I = f C_F + (1 - f) C_E$$

where C_I = operating NLS concentration

f = foamate volume fraction

C_F = theoretical NLS concentration in the foamate

C_E = effluent NLS concentration

To confirm the validity of analysis and the release of NLS from the collapsed foamate, a portion of the clarified liquid (from Sample 3, Table 6) after NaOH addition was analyzed for NLS. The NLS concentration was found to be 112.5 mg/L. The concentration calculated by the mass balance was 113.1 mg/L, in good agreement.

CONCLUSION

High removals of copper by adsorbing colloid foam flotation were demonstrated in a continuous-flow pilot plant. Effluent copper(II) concentrations in the range of 0.1 to 0.3 mg/L can be routinely obtained by means of this technique.

The results here indicate that NLS recovery from the foamate and recycle of NLS back to the system are possible after treatment with NaOH.

Table 7 lists the recommended optimum operating conditions as determined by the work done with the 30-cm continuous flow pilot plant.

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