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The Removal of Mixtures of Metals by an Adsorbing Colloid Foam Flotation Pilot Plant

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Abstract

An adsorbing colloid foam flotation pilot plant was used to remove Cu(II), Zn(II), and Cr (III) from aqueous mixtures of these ions. The simulated wastewater contained 20 mg/L of each of these ions; residual concentrated ions were less than 0.1 mg/L (Cu), 0.5 mg/L (Zn), and 0.2 mg/L (Cr) under optimal conditions. Sodium dodecyl sulfate was used as the collector; and $Fe(OH)_3$, $Al(OH)_3$, and mixtures of the two were used as the carrier floc.

INTRODUCTION

In the United States today there are over 13,000 firms engaged either wholly or partially in electroplating or other metal-finishing operations (*1*). These firms produce more individual wastewater discharges than any other industrial category. Due to the costs of meeting the new strict regulations, combined with the rising costs of energy, raw materials, and chemicals, the Environmental Protection Agency estimates that the metal-plating industry will be one of those industries hardest hit by the new and future regulations. Due to recent changes in economics and regulations, current technologies for the removal of metals should be reevaluated and new technologies explored.

Numerous techniques exist to remove metal ions from aqueous solutions. The most common method is chemical precipitation. Some disadvantages of the precipitation process have been mentioned in our earlier papers (*2, 3*). Other available technologies include ion exchange, reverse osmosis, adsorption on activated carbon, and solvent extraction. These methods are usually extremely expensive, involving either elaborate and costly equipment or high operating costs and energy requirements.

Adsorbing colloid foam flotation as a way to remove metals has been under investigation at Vanderbilt University for some years. The process involves the addition of a coagulant, usually ferric chloride or alum, with sodium hydroxide for pH adjustment, to form a floc. The dissolved metal is then adsorbed onto the floc particle and/or coprecipitated with it. A surfactant, such as sodium lauryl sulfate, is then added, attaches to the floc particle and renders it hydrophobic, and the floc (with adsorbed metal) is removed by air flotation.

When dealing with dilute wastes, foam flotation appears to possess some distinct advantages: low residual metal concentrations, rapid operation, low space requirements, flexibility of application to various metals at various scales, production of small volumes of sludge highly enriched with the contaminant, and a moderately low cost.

Wilson and his co-workers have discussed the theory of adsorbing colloid foam flotation and presented preliminary bench-scale experimental work with a variety of metals and other ions; see the review by Wilson and Clarke (*4*). More recent work involving the removal of copper (*2*) and zinc (*3*) by a large continuous flow pilot has also appeared.

The objective of the present work was to extend the application of this technique to combinations of metals simulating an electroplating waste. The work involving mixtures of metals is of paramount importance because industrial wastes are usually complex mixtures of varying composition rather than a simple solution containing a single contaminant. This work will be helpful in defining the capabilities and limitations of adsorbing colloid foam flotation.

Copper, zinc, and chromium(III) were investigated in this study. These metals can be found in the effluents of a large variety of industrial sources and at a very wide range of concentrations in the raw wastewater. The reported concentrations of copper in industrial wastewaters range between 1 and 7300 mg/L; a typical value is about 25 mg/L. For zinc, the range is between 5 and 3000 mg/L; a typical value is about 50 mg/L (5). Chromium in industrial wastes exists predominantly in the hexavalent form as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$). Removal involves the reduction of hexavalent chromium to its trivalent state and subsequent removal of the trivalent chromium ion. Reported concentrations for hexavalent chromium are in the range between 1 and 50,000 mg/L; a typical value is 50 mg/L (5).

Experiments were conducted with a simulated electroplating waste stream containing 20 mg/L each of copper(II), zinc(II), and chromium(III), and those described herein produced treated effluents which contained concentrations of copper(II) less than 0.1 mg/L, zinc(II) less than 0.5 mg/L, and chromium(III) less than 0.2 mg/L. These low residual metal concentrations are below the standards currently mandated by the regulatory agencies and are below the 1984 BAT-equivalent guidelines.

EQUIPMENT DESCRIPTION

The foam flotation pilot plant used in this work has been described in detail in earlier papers (*2, 6*). Figure 1 shows a schematic diagram of the plant.

Simulated wastewater is pumped from the storage tank through the pilot plant at the desired flow rate. The addition of the coagulant and NaOH (for pH control) occurs upstream of the main pump. The coagulant is fed at the required rate by means of a Masterflex variable feed pump. The NaOH solution flows by gravity through a solenoid valve which is connected to a Horizon 5650 pH controller set to produce the desired pH in the first mixing–flocculating chamber. After passing through the main pump, the wastewater enters a series of three mixing–flocculating chambers, after which NLS is injected at the required rate. The waste is then sent through the top of the flocation column to a spider-shaped spray nozzle. The wastewater then flows downward through the rising foam over an arrangement of 19 baffles which were installed to prevent foam overturning. The air is supplied through a fritted glass disk in the bottom of the column. The treated effluent leaves the column through the bottom and the foam is piped out of the top of the column to a rotating disk foam breaker. The effluent pH is monitored continuously.

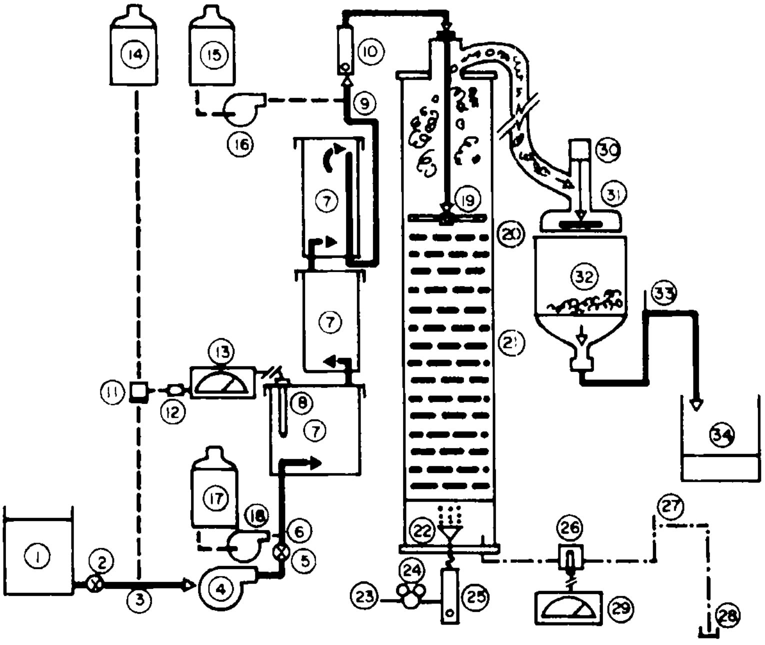
The simulated wastewaters were prepared by dissolving either $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, or $Cr(NO_3)_3 \cdot 9H_2O$, alone or in combinations, in tap water.

The analysis for effluent metal concentrations was done by atomic absorption spectrophotometry. The analysis for NLS in the effluent and in the foamate was done by the methylene blue–chloroform extraction technique as outlined in *Standard Methods* (*7*).

RESULTS AND DISCUSSION

Copper and Zinc

Mixture experiments were first conducted with a simulated wastewater containing 20 mg/L each of copper(II) and zinc(II). In order to determine the optimum operating parameters, the influence of several variables on metal removal efficiency and flotation efficiency was studied. These variables include pH, hydraulic loading rate, coagulant-adsorbent dose, NLS dose, and air flow rate. The optimum operating parameters which were determined



1. Waste Tank
2. Waste Tank Valve
3. NaOH Injection Tee
4. Main Pump
5. Flow Control Valve
6. $FeCl_3$ 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. $FeCl_3$ Tank
18. $FeCl_3$ 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

FIG. 1. Schematic diagram of 30-cm pilot plant.

when working with feeds containing either the metals alone were used to determine the starting point (*2, 3*).

Table 1 summarizes the results obtained for this set of experiments. The hydraulic loading rate was maintained at 6.9 $m^3/m^2 \cdot h$ (2.8 $gal/min \cdot ft^2$). The

TABLE 1

Foam Flotation of Wastes Containing Cu(II) + Zn(II)[a]

pH	Fe(III) (mg/L)	Al(III) (mg/L)	NLS (mg/L)	Residual copper (mg/L)	Residual zinc (mg/L)
7.0	100	100	70	0.09	2.3
7.2	100	100	70	0.09	1.1
7.2	100	100	50	0.15	1.2
7.4	100	0	35	0.33	9.6
7.4	150	0	45	0.29	6.6
7.4	75	75	50	0.10	1.2
7.4	100	100	70	0.04	0.8
7.5	50	50	50	0.13	1.2
7.5	75	75	50	0.17	0.9
7.5	100	100	70	0.03	0.4
7.7	50	50	40	0.11	0.9
7.7	100	100	70	0.03	0.6
8.0	50	50	40	0.10	0.7

[a] All runs made with initial copper and zinc at 20 mg/L each, influent flow rate at 6.9 $m^3/m^2 \cdot h$, and air flow rate at 14 $Nm^3/m^2 \cdot h$.

previous work on individual metals demonstrated that no substantial decrease in removal efficiency occurs when the hydraulic loading rate is increased, even at levels which are twice the above loading rate. An air flow rate of 14 $Nm^3/m^2 \cdot h$ (0.75 $ft^3/ft^2 \cdot min$) was used in all pilot plant runs.

The tabulated results indicate the necessity of using $Al(OH)_3$ floc in order to obtain high zinc removal efficiencies. When no alum is added to the system, zinc removal percentages below 70% occur, even with 150 mg/L of iron(III) and in the optimum pH range. Effluent zinc levels below 1 mg/L can be obtained at an aluminum(III) dose of 50–100 mg/L.

The optimal pH range for copper and zinc removal has been displaced to a higher value and is substantially wider than that obtained for each metal individually. This can be explained by the fact that there is a higher concentration of positively charged ions in the waste than in our earlier work, which may increase the positive surface charge density of the flocs. This strengthens the attachment of the negatively charged NLS, and subsequent flotation is possible at higher pH values than previously observed. This is of interest from a practical standpoint because the process is not as strongly dependent on the pH, which renders operation and control easier and improves the stability of the process.

Residual copper concentrations of 0.1 mg/L are achieved even at pH values as high as 8. Residual copper concentrations below 0.1 mg/L can be obtained over a pH range of almost one unit when using chemical doses of 100 mg/L iron(III), 100 mg/L aluminum(III), and 70 mg/L NLS. Even when the chemical doses are reduced to 50–75 mg/L of iron(III) and aluminum(III), and 40–50 mg/L of NLS, residual copper concentrations substantially below 0.2 mg/L are consistently achievable in the same pH range. Residual zinc concentrations below 1.0 mg/L are obtainable in a pH range of 7.4 to 8, and values close to 0.5 mg/L are possible even at the lower coagulant-adsorbent and NLS dose concentrations indicated above.

The presence of the $Al(OH)_3$ floc exhibits a beneficial effect on copper removal. In the work discussed earlier (*2*) for a waste containing copper alone and with $Fe(OH)_3$ as the coagulent-adsorbent, the lowest effluent concentration was in the range of 0.1 to 0.2 mg/L. With a mixture of copper and zinc, copper levels below 0.1 and as low as 0.05 mg/L can be achieved with the proper adjustment of iron(III), aluminum(III), and NLS doses. The presence of $Fe(OH)_3$ also improves zinc removal, although its main effect is on copper.

Copper, Zinc, and Chromium

The simulated wastewater to be treated in this set of experiments contained 20 mg/L each of copper(II), zinc(II), and chromium(III).

The results of these experiments appear in Table 2. Again, a hydraulic loading rate of 6.9 $m^3/m^2 \cdot h$ (2.8 $gal/min \cdot ft^2$) and an air flow rate of 14 $Nm^3/m^2 \cdot h$ (0.75 $ft^3/ft^2 \cdot min$) were used. Quite low residual concentrations are achieved over a reasonable wide pH range, with no more than 100 to 115 mg/L of iron(III) and 75 to 100 mg/L of aluminum(III). It is important to adjust the NLS dose according to the total floc concentration in the system. An NLS concentration between 25 and 30% of the total iron(III) and aluminum(III) dose (by weight) was found sufficient to provide proper flotation.

Zinc removal is more effective at pH values higher than 7.3 in the range studied. Copper and chromium are removed more efficiently at pH values between 7.0 and 7.3, although very good results are achievable throughout the experimental pH range. It is interesting to note that the results for zinc are substantially better than those obtained for the experiments with zinc alone or for a mixture of zinc and copper. This is possibly due to some complementary adsorbtion and/or coprecipitation effect produced by the presence of the $Cr(OH)_3$ floc. The $Cr(OH)_3$ floc formation occurs at lower pH values than those needed to form copper and zinc hydroxides.

Table 3 compares the results obtained with a waste bearing a mixture of copper(II), zinc(II), and chromium(III) with the BPT- and BAT-equivalent

TABLE 2

Foam Flotation of Wastes Containing Cu(II) + Zn(II) + Cr(III)[a]

pH	Fe(III) (mg/L)	Al(III) (mg/L)	NLS (mg/L)	Residual copper (mg/L)	Residual zinc (mg/L)	Residual chromium (mg/L)
7.0	100	100	70	0.10	2.00	0.12
7.2	100	100	70	0.07	0.90	0.13
7.2	115	75	50	0.12	1.10	0.31
7.2	150	100	85	0.07	0.60	0.12
7.3	75	75	50	0.42	2.40	0.60
7.3	100	100	70	0.11	0.60	0.17
7.3	115	75	70	0.08	0.56	0.20
7.3	115	75	50	0.14	0.75	0.33
7.3	150	100	85	0.06	0.40	0.12
7.4	115	75	70	0.07	0.16	0.20
7.4	150	100	85	0.11	0.30	0.21
7.6	100	100	70	0.22	0.20	0.26

[a] All runs made with initial copper, zinc, and chromium at 20 mg/L each, influent flow rate at 6.9 $m^3/m^2 \cdot h$, and air flow rate at 14 $Nm^3/m^2 \cdot h$.

guidelines. These are mass discharge guidelines converted to concentrations to provide a common basis for comparison (5).

Economic Analysis

The intent of this economic analysis is to determine whether or not adsorbing colloid foam flotation is cost competitive with the conventional

TABLE 3

Results for Simulated Electroplating Waste
Compared to BPT- and BAT-Equivalent Guidelines

	Concentration (mg/L)		
Pollutant	Effluent[a]	BPT	BAT
Copper	<0.1	0.5	0.40
Zinc	<0.5	1.0	0.50
Chromium (total)	<0.2[b]	1.0	0.50

[a] Influent = 20 mg/L Cu^{2+} + 20 mg/L Zn^{2+} + 20 mg/L Cr^{3+}.
[b] For Cr(III).

lime precipitation process. The costs generated in this comparison should only be regarded as rough estimates. The only costs used in this comparison are initial capital costs amortized at 15% over a 10-year period and chemical costs. Other operation and maintenance costs are not included. The cost of pretreatment for cyanide removal and chromium reduction would be the same for both processes, as would the power requirements. Foam flotation would most likely have a higher maintenance cost, but would also have a much less costly sludge handling operation. Therefore, the operation and maintenance costs should trade off somewhat evenly.

The hypothetical plant to be used in this comparision will have a flow of 190,000 L/d (50,000 gal/d) containing 20 mg/L each of Cu(II), Zn(II), and Cr(III). A two-shift per day, 50-week operation at 6 d per week will be assumed.

Adsorbing Colloid Flotation Plant

Design Parameters

Hydraulic loading rate	15 $m^3/m^2 \cdot h$
Column diameter	1 m
Allowable loading per column	11.8 m^3h
Two shifts	15 h actual operation
Flow to column	190 $m^3/15\ h = 12.7\ m^3/h$
Number of columns	$(12.7\ m^3/h)/(11.8\ m^3/h) = 1.1$

Therefore use two column. NLS recycling included

Chemical Consumption

NLS	28mg/L	5.3 kg/d
$FeCl_3$	290 mg/L [100 mg/l Fe(III)]	54.9 kg/d
Alum	926 mg/L [75 mg/l Al(III)]	173.3 kg/d
NaOH (0.25 *M*)	40 mg/L wastewater (for pH control and NLS recovery)	76.0 kg/d

Chemical Costs*

NLS at $1.65/kg	4.6¢/1000 L
$FeCl_3$ at $275/metric ton	7.9¢/1000 L
Alum at $218/metric ton	20.1¢/1000 L
NaOH at $286/metric ton	11.4¢/1000 L
Total	0.44/1000 L ($1.67/1000 gal)

Capital Costs

The pilot plant used in this study was built in 1976 for a cost of $5000. A larger capacity industrial plant built today would cost approximately $10,000. Therefore, for two units, a total capital cost of $20,000 amortized at 15% over a 10-year period would be $3985/year. For a 50-week operation at 6 d per week and 190,000 L/d, this amortized cost equals 7.1¢/1000 L.

Cost Summary

Capital	$0.071/1000 L
Chemical	0.44/1000 L
Total	$0.51/1000 L ($1.93/1000 gal)

Lime Precipitation Plant

The unit processes in the lime precipitation plant would include lime slurrying and chemical feed, a neutralization/precipitation system, and a flocculation/clarification system. Whether or not lime precipitation can achive effluent metal concentrations below the 1984 BAT-equivalent guidelines has not been well documented in the literature. It has been reported that,

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*Costs obtained from local supplier and are subject to variation due to local market conditions.

in some instances, clarification alone can yield an effluent quality equal to that of final effluent filtration (5). However, these are rare instances, and filtration would most likely be required to meet the BAT-equivlaent guidelines. For the purpose of simplicity, this cost comparison will *not* include filtration.

Cost curves for the unit processes mentioned above were not utilized because a cost for a comparable system, believed to be more realistic, was found in the literature. The installation cost for the precipitation plant to treat a mixed metal plating wastewater was $293/1000 L ($1108/1000 gal) treated per day (1968 cost) (*9*, *10*). The cost for 1981 would be at least $886/1000 L ($3355/1000 gal) treated per day, or $167,750. This cost amortized over 10 years at 15% would be $33,425/year or, for the 190,000 L/day plant, $0.59/1000 L.

To justify the above capital cost of $0.59/1000 L, the capital cost of several recently constructed lime precipitation plants was obtained from a local consultant (*8*). These are capital costs only, amortized at 15% over a 10-year period and adjusted to 1981 dollars. The 1978 capital cost for a lime precipitation plant used to treat a maximum flow of 190,000 L/d (50,000 gal/d) was $750,000. This corresponds to a 1981 cost of $3.32/1000 L ($12.70/1000 gal). Another plant used to treat a maximum flow of 816,500 L/d (216,000 gal/d) cost $1,000,000 in 1980. This corresponds to a 1981 cost of $0.89/1000 L ($3.38/1000 gal). Therefore, a capital cost of $0.59/1000 L seems to be reasonable, or even low.

The pH range for minimum solubilities of the metals being discussed here are: Cu(II), pH 9.0 to 10.3; Zn(II), pH 10.0 to 10.5 (values in the literature vary considerably, with pH's as low as 9.0 and as high as 11.0); Cr(III), pH 8.5 to 9.5 (*5*, *9*). The lime requirement determined in the lab for the synthetic wastewater to raise the pH from 4.0 to 9.0 was 135 mg/L. With lime costing $86/metric ton, the lime cost would be 1.2¢/1000 L. This yields a total cost of $0.60/1000 L ($2.27/1000 gal).

As can be seen, the comparative cost of absorbing colloid foam flotation is competitive with lime precipitation: $0.51/1000 L versus $0.60/1000 L. It should be pointed out that the cost of a filtration step in the lime precipitation plant was not included. Since filtration would probably be a necessity in order to meet the BAT-equivalent guidelines (filtration having a high capital and operating cost), this would increase the cost of lime precipitation considerably. This definitely results in adsorbing colloid foam flotation being the cheaper alternative.

If space requirements and the possible acquisition of a piece of land were to be included, the economics would again favor the foam flotation plant. The pilot plant used for this study required less than 25 ft^2 of floor space. Two larger flotation columns could fit into a 100-ft^2 area.

On the other hand, the lime precipitation plant would require somewhere in the area of 800 ft^2. Therefore, the possibility of a real estate purchase enhances the economic margin even more.

CONCLUSION

The results presented in this study indicate that the actual application of adsorbing colloid foam flotation for treating metal-bearing wastewaters on an industrial scale is quite feasible. The low residual metal concentratins consistently achieved are below the standards currently mandated by the regulatory agencies and are below the 1984 BAT-equivalent guidelines. It now becomes obvious that one of the best applications of this process would be as a polishing treatment in order to achieve the future stringent regulations. The excellent results produced by this research most definitely indicate that the process of adsorbing colloid foam flotation deserves further study.

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