

Ion and Adsorbing Colloid Flotation of Auramine

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Auramine, a cationic dye, was removed from synthetic wastewater by ion flotation of auramine-sodium lauryl sulfate complex. Over 98% of auramine was removed from the solution in 15 min. A stoichiometric amount of surfactant (1 mol of surfactant to 1 mol of dye) was found to be most effective for auramine removal. The rate of separation and ultimate removal of auramine increased with increasing the rate of air flow and decreased with increasing concentration of NaNO₃. Auramine was also removed by adsorbing colloid flotation technique using ferric hydroxide as the coagulant. Sodium lauryl sulfate was used as the collector, and over 95% of auramine was removed in 10 min. The separation efficiency decreased with increasing ionic strength of the solution. The deleterious effect of neutral salt was compensated somewhat with the aid of aluminum ions as the activator. Both ion flotation and adsorbing colloid flotation are promising approaches for the removal of cationic dye from wastewater.

Keywords: Auramine; Ion flotation; Adsorbing colloid flotation.

INTRODUCTION

Auramine is used as a cationic dye (C.I. Solvent Yellow 34) for paper, textiles, and leather.¹ It has also been used as an antiseptic or a fungicide. It may enter the environment from industrial discharges or spills. Auramine may be a carcinogen in humans since it has been shown to cause liver and lymphatic cancers in animals.² Chemicals similar to auramine can destroy or disturb the ability of the blood to carry oxygen. Continuous exposures to auramine-like chemicals have caused liver and kidney damage. Therefore, a method to treat dye wastewater containing auramine is highly desirable now and in the near future.

Ion flotation technique³⁻⁶ is a process in which an ionic solute, called the colligend, is removed from aqueous solution by adding surface-active collector ions of a charge opposite to that on the colligend, and then bubbling the air through the solution. If the concentrations of the collector and colligend are sufficiently high, a precipitate is formed and when bubbles are passed into the solution, the particles are carried and floated out. At lower concentrations, no precipitate forms prior to the advent of air, but instead collector ions adsorb on the bubbles and attract colligend ions to them. When the bubbles reach the surface of the aqueous solution, a foam is formed in which a solid phase is deposited.

Applications of ion flotation technique for treatment of dye wastewater are rare. Huang et al.⁷ reported that Direct Blue 1 (an anionic dye) can be effectively removed from aqueous solutions by ion flotation. This technique has never been applied for cationic dye removal. In this paper we describe some studies we have recently made on the ion flotation of auramine (a cationic dye) from aqueous solution. Sodium lauryl sulfate (NLS) was used as the collector. It was found that 98% auramine is removed from the solution by ion flotation in 15 min.

The adsorbing colloid flotation technique has been applied in removing various inorganic species from aqueous solutions.⁸⁻¹² This technique involves the addition of a coagulant (ferric or aluminum) to produce a floc. The dissolved inorganic species (metal ions or anion) are adsorbed onto the floc particle and/or coprecipitated with it. A surfactant is then added, adsorbs onto the floc particle, and renders it hydrophobic. On bubbling air through the solution, the floc is adsorbed on the rising bubbles and carried out from the solution by the foam.

The applicability of adsorbing colloid flotation as a technique to treat dyes in wastewater has been investigated for dyes of only four kinds- Magenta,¹³ Direct Red,¹⁴ Acid Red,¹⁵ and Direct Blue.⁷ Previous work on the adsorbing colloid flotation of Magenta (a cationic dye) with ferric hy-

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droxide and NLS showed that even though the rate of separation of the floc (with adsorbed dye) was fast, particulates, which settled in a small amount at the bottom of the separation column, were not removed by the foam. Furthermore, a relatively large amount of surfactant (200 ppm) was required to remove the floc from the solution. These drawbacks were not found in the adsorbing colloid flotation of anionic dyes: Direct Blue,⁷ Direct Red,¹⁴ and Acid Red;¹⁵ all the flocs were removed from the aqueous solution by the foam, and the concentration of surfactant needed for an effective separation was much smaller (40 ppm). It is thus worthwhile to test adsorbing colloid flotation on wastewater containing other cationic dyes to assess whether this technique is generally useful to treat such wastewater or not. In this paper the data revealed that NLS concentration at 60 ppm was sufficient for an effective separation, and over 95% of auramine was removed in 10 min.

EXPERIMENTAL SECTION

Materials

Reagent-grade sodium lauryl sulfate (NLS, Mallinckrodt Baker, Inc.) was used as the collector without further purification. Reagent-grade auramine (Sigma-Aldrich Corporation), sodium nitrate, ferric nitrate, and aluminum nitrate (RdH Laborchemikalien GmbH & Co. KG.) were used for sample preparation.

The apparatus for ion flotation and adsorbing colloid flotation was similar to that described earlier.¹⁶ A soft glass column 60 cm in length with an inside diameter of 3.5 cm was used. The bottom of the column was closed with a rubber stopper with holes for a gas sparger and a stopcock to take samples and to drain the column. The gas sparger was a commercially available gas dispersion tube. A lipped side arm near the top of the column served as a foam outlet.

Compressed air was generated from a Hiblow SPP-6EBS air pump. The rate of air flow was adjusted with a Hokeneedle valve with micrometer control and measured with a soap film flowmeter. The air was purified by passage through glass wool to remove particulates, through Ascarite to remove carbon dioxide, and through distilled water for controlled humidification.

Flotation Procedure of Auramine

For the ion flotation runs, NLS was added to the sample solution to form the dye-surfactant complex, the pH of the solution was adjusted, the solution was poured into the separation

column, and the timer was started. The rate of air flow was adjusted before the sample solution was poured into the column.

For the adsorbing colloid flotation runs, ferric nitrate was added to the sample solution, and the pH was adjusted to produce the floc. Auramine was adsorbed on or coprecipitated with the floc. NLS was added to render the floc hydrophobic, and the solution was then poured into the column for separation.

The pH of the solution was measured with a pH meter (Suntex pH 537 Microprocessor pH meter). All runs were made with 250 mL of test solution that contained 25 ppm auramine. The experiments were performed under room temperature. Duplicate runs were performed for each set of conditions.

Instrumental Analysis

The concentrations of dye in the sample solutions were determined using a UV/Vis spectrophotometer (Varian Cary 300). The absorbance of the sample solution was measured at the absorption peak (430 nm) and compared with the calibration curve obtained by measurement of the absorbance of the standard aqueous solution. It was found that the addition of NLS to the solution had no effect on the absorption at 430 nm. For the adsorbing colloid flotation runs, a sample (5 mL) was withdrawn and the pH of the solution was adjusted to 3. Auramine was desorbed almost completely from the Fe(OH)₃ floc which was removed by centrifugation (Hettich, 2500 rpm, 3 min). The absorbance of the supernatant was measured at 430 nm and compared with the calibration curve.

RESULTS AND DISCUSSION

The effect of pH on the ion flotation of the auramine-NLS is shown in Table 1. The mole ratio of NLS to dye was

Table 1. The Effect of pH on Ion Flotation^a

pH	% Removal ^b		
	5 min	10 min	15 min
3	45.8 ± 4.2%	77.4 ± 2.5%	92.4 ± 2.3%
4	46.0 ± 1.7%	77.4 ± 1.4%	93.0 ± 0.3%
6	47.6 ± 2.3%	77.0 ± 3.7%	93.2 ± 0.0%
7	59.8 ± 3.7%	89.8 ± 3.1%	97.4 ± 0.3%
8	54.8 ± 0.0%	87.6 ± 1.1%	97.2 ± 2.8%
9	62.8 ± 7.4%	88.6 ± 4.8%	97.2 ± 0.0%

^a Air flow rate = 120 mL/min, mole ratio NLS/dye = 2.0.

^b Average value and standard deviation of duplicate runs.

2.0 for these runs. Over 97% of the auramine was removed from the solution by ion flotation in 15 min at pH 7-9. The rate of separation and separation efficiency decreased somewhat if the pH of the solution was adjusted too low, probably due to the interference of the auramine-NLS complex formation by the added acid.

The effect of surfactant concentration on the ion flotation of auramine is shown in Table 2. At a smaller concentration of surfactant, the rate of separation is slower, presumably due to the incomplete dye-surfactant complex formation. It was found that a 1:1 mole ratio of surfactant to dye is enough for an effective separation with approximately 94% removal in 15 min. Increases in surfactant dosage had little effect on the separation efficiency. This finding is quite different from the results of solvent sublation of Magenta-NLS,¹³ Direct Red-HTA,¹⁴ Acid Red-HTA¹⁵ and ion flotation of Direct Blue⁷ studied by Huang et al., who found that the rate of removal of dyes decreased with increasing concentration of surfactant, when it was much in excess of the stoichiometric amount. This contradiction is probably due to the difference in the formation constant of the different surfactant-dye complexes and also due to the difference in the mole ratio of the dye and surfactant of the complexes.

Solvent sublation of the auramine-NLS complex operates in a way similar to that occurring in ion flotation except that the surface-active material is transferred to the paraffin oil on the top of the aqueous solution. The mole ratio of NLS to dye was 1.0 for solvent sublation runs. The separation efficiency of auramine removed by solvent sublation is similar to that by ion flotation; 94.4% of auramine was removed by solvent sublation in 15 min. There is almost no benefit resulting from the addition of paraffin oil to the separation system; it is advisable to remove auramine-NLS complex from solution by ion flotation rather than by solvent sublation. The effect of

Table 2. The Effect of NLS Concentration on Ion Flotation^a

NLS/dye (mole ratio)	% Removal ^b		
	5 min	10 min	15 min
0.5	38.4 ± 1.7%	57.6 ± 0.6%	68.2 ± 1.4%
1.0	52.4 ± 0.0%	81.6 ± 0.6%	94.0 ± 0.6%
1.5	56.6 ± 2.0%	85.0 ± 2.5%	95.4 ± 0.8%
2.0	59.8 ± 3.7%	89.8 ± 3.1%	97.4 ± 0.3%
2.5	59.4 ± 1.4%	88.8 ± 2.3%	97.8 ± 0.8%
1.0 ^c	51.2 ± 2.3%	80.4 ± 1.1%	94.4 ± 0.6%

^a Air flow rate = 120 mL/min, pH = 7.0.

^b Average value and standard deviation of duplicate runs.

^c Percent removal of solvent sublation.

Table 3. The Effect of Air Flow Rate on Ion Flotation^a

Air flow rate (mL/min)	% Removal ^b		
	5 min	10 min	15 min
120	52.4 ± 0.0%	81.6 ± 0.6%	94.0 ± 0.6%
150	70.6 ± 2.0%	92.4 ± 0.6%	98.0 ± 1.1%
180	75.8 ± 0.3%	92.8 ± 0.6%	98.0 ± 0.6%
200	74.0 ± 2.3%	92.8 ± 0.0%	97.6 ± 1.7%

^a pH = 7.0, mole ratio NLS/dye = 1.0.

^b Average value and standard deviation of duplicate runs.

gas flow rate on the ion flotation of auramine is shown in Table 3. The rate of separation increased somewhat with increasing rate of gas flow as expected.

The effect of NaNO₃ on the rate of removal of auramine-NLS complex by ion flotation is shown in Table 4. The separation efficiency decreased significantly with the addition of neutral salt, presumably due to the competition for collector between the colligend and the ions of salt.^{5,8,12} Wilson et al.¹⁷ also observed the inhibiting effect of neutral salts (NaNO₃, KCl and NaH₂PO₄) on the solvent sublation of both methylene blue-tetradecyl sulfate and methyl orange-HTA dye-surfactant complexes.

Another series of experiments were performed using the adsorbing colloid flotation technique to remove auramine from aqueous solution. The effect of pH on the adsorbing colloid flotation of auramine with ferric hydroxide floc is shown in Table 5. Sodium lauryl sulfate was used as the collector and frother. It was found that the rate of removal was rapid at a pH range of 5-8; over 93% of auramine was removed in 10 min. The rate of separation and separation efficiency decreased somewhat if the pH of the solution was adjusted too low, probably due to incomplete formation of ferric hydroxide floc at lower pH.

The effect of surfactant dosage on the separation efficiency of adsorbing colloid flotation of auramine is shown in

Table 4. The Effect of NaNO₃ Concentration on Ion Flotation^a

NaNO ₃ (N)	% Removal ^b		
	5 min	10 min	15 min
0.00	75.8 ± 0.3%	92.8 ± 0.6%	98.0 ± 0.6%
0.05	54.0 ± 0.0%	89.2 ± 1.7%	98.4 ± 0.6%
0.10	45.2 ± 4.0%	79.4 ± 2.5%	96.6 ± 0.8%
0.20	33.4 ± 0.8%	62.4 ± 5.1%	89.0 ± 4.8%
0.40	28.6 ± 0.8%	50.6 ± 0.8%	77.6 ± 2.8%

^a Air flow rate = 180 mL/min, pH = 7, mole ratio NLS/dye = 1.0.

^b Average value and standard deviation of duplicate runs.

Table 5. The Effect of pH on Adsorbing Colloid Flotation with $\text{Fe}(\text{OH})_3^a$

pH	% Removal ^b		
	3 min	5 min	10 min
3	44.4 ± 5.7%	53.0 ± 0.3%	74.8 ± 0.0%
4	52.2 ± 1.4%	58.6 ± 0.3%	69.6 ± 1.1%
5	60.6 ± 0.3%	75.2 ± 2.3%	93.0 ± 0.8%
6	58.0 ± 2.3%	74.2 ± 3.7%	93.2 ± 0.6%
7	58.6 ± 2.0%	74.6 ± 3.1%	92.4 ± 0.0%
8	59.2 ± 1.1%	74.2 ± 0.8%	93.0 ± 2.0%

^a $\text{Fe}(\text{OH})_3 = 100$ ppm, NLS = 80 ppm, air flow rate = 120 mL/min.

^b Average value and standard deviation of duplicate runs.

Table 6. The Effect of NLS Concentration on Adsorbing Colloid Flotation^a

NLS (ppm)	% Removal ^b		
	3 min	5 min	10 min
20	29.6 ± 0.6%	33.8 ± 2.0%	42.0 ± 0.6%
40	37.2 ± 1.1%	48.0 ± 4.0%	68.2 ± 0.8%
60	63.2 ± 0.0%	75.4 ± 1.4%	91.8 ± 0.8%
80	60.6 ± 0.3%	75.2 ± 2.3%	93.0 ± 0.8%
100	65.8 ± 3.1%	78.8 ± 4.0%	92.4 ± 1.7%

^a $\text{Fe}(\text{OH})_3 = 100$ ppm, pH = 5.0, air flow rate = 120 mL/min.

^b Average value and standard deviation of duplicate runs.

Table 6. NLS concentration at 60 ppm was sufficient for an effective separation. Increases in the surfactant dosage had little effect on the separation efficiency.

The effect of rate of air flow on the separation efficiency of adsorbing colloid flotation of auramine is shown in Table 7. The rate of separation increased somewhat with increasing rate of air flow, as expected. A total of 95.4% of auramine was removed in 10 min with an air flow rate of 180

Table 7. The Effect of Air Flow Rate on Adsorbing Colloid Flotation^a

Air flow rate (mL/min)	% Removal ^b		
	3 min	5 min	10 min
90	50.4 ± 1.7%	53.6 ± 4.5%	66.6 ± 3.7%
120	63.2 ± 0.0%	75.4 ± 1.4%	91.8 ± 0.8%
150	71.4 ± 2.5%	85.4 ± 0.8%	93.4 ± 0.8%
180	82.2 ± 0.8%	90.2 ± 0.3%	95.4 ± 0.3%
200	77.4 ± 3.7%	91.2 ± 2.3%	94.0 ± 1.7%

^a $\text{Fe}(\text{OH})_3 = 100$ ppm, NLS = 60 ppm, pH = 5.0.

^b Average value and standard deviation of duplicate runs.

Table 8. The Effect of $\text{Fe}(\text{III})$ Concentration on Adsorbing Colloid Flotation^a

$\text{Fe}(\text{III})$ (ppm)	% Removal ^b		
	3 min	5 min	10 min
20	64.2 ± 3.1%	81.6 ± 5.7%	92.2 ± 3.1%
40	71.6 ± 0.6%	84.8 ± 0.6%	91.6 ± 2.3%
60	77.4 ± 3.1%	88.6 ± 3.1%	95.2 ± 1.7%
80	81.8 ± 1.7%	90.6 ± 0.6%	95.8 ± 0.6%
100	82.2 ± 0.8%	90.2 ± 0.3%	95.4 ± 0.3%

^a NLS = 60 ppm, pH = 5.0, air flow rate = 180 mL/min.

^b Average value and standard deviation of duplicate runs.

mL/min.

The effect of iron(III) dosage on the separation efficiency of auramine is shown in Table 8. Iron(III) concentration at 80 ppm was sufficient for an effective separation. Increases in the iron(III) dosage had little effect on the separation efficiency. The rate of separation decreased somewhat if the iron(III) dosage was lower (20 or 40 ppm), presumably due to incomplete coprecipitation of auramine with an insufficient amount of ferric hydroxide floc.

The effect of neutral salt (NaNO_3) on the separation efficiency of adsorbing colloid flotation of auramine is shown in Table 9. The separation efficiency decreased with increasing ionic strength of the solution, presumably due to a decrease of the surface potential of the floc by the adsorption of the anion (nitrate ion) in the solution, such that the surface potential of the floc was no longer positive enough for a sufficient amount of an ionic surfactant to be adsorbed. It was found that only 50% of auramine was removed in 10 min from a solution containing 0.4 equiv/L of NaNO_3 .

The inhibition effect of neutral salts on adsorbing colloid flotation of various heavy metal ions¹⁸⁻²² and dyes^{7,13-15} with

Table 9. The Effect of NaNO_3 Concentration on Adsorbing Colloid Flotation^a

NaNO_3 (N)	% Removal ^b		
	3 min	5 min	10 min
0.00	81.8 ± 1.7%	90.6 ± 0.6%	95.8 ± 0.6%
0.05	44.2 ± 1.4%	55.6 ± 0.0%	85.0 ± 2.0%
0.10	38.0 ± 0.6%	47.4 ± 0.3%	74.0 ± 1.1%
0.20	32.6 ± 1.4%	39.0 ± 1.4%	56.8 ± 5.1%
0.40	28.6 ± 2.0%	31.6 ± 4.0%	50.4 ± 0.0%

^a $\text{Fe}(\text{OH})_3 = 80$ ppm, NLS = 60 ppm, pH = 5.0, air flow rate = 180 mL/min.

^b Average value and standard deviation of duplicate runs.

Table 10. The Effect of Al(III) Concentration on Adsorbing Colloid Flo tation of Auramine from Solution Containing 0.4 N of NaNO₃^a

Al(III) (ppm)	% Removal ^b		
	3 min	5 min	10 min
0	28.6 ± 2.0%	31.6 ± 4.0%	50.4 ± 0.0%
10	34.4 ± 1.7%	42.8 ± 3.4%	60.6 ± 0.3%
20	41.6 ± 0.6%	54.6 ± 0.3%	78.6 ± 4.8%
40	51.8 ± 3.1%	63.6 ± 2.8%	85.8 ± 0.3%
80	56.5 ± 1.1%	69.3 ± 2.8%	93.6 ± 0.3%

^a Fe(OH)₃ = 80 ppm, NLS = 60 ppm, pH = 5.0, air flow rate = 180 mL/min.

^b Average value and standard deviation of duplicate runs.

Fe(OH)₃ floc and NLS can be compensated for with the aid of aluminum ion as the activators. We attempted to use the same technique for the removal of auramine from solution containing 0.4 equiv/L of NaNO₃ by adsorbing colloid flo tation. The results are shown in Table 10. Aluminum ion was a very effective activator for this system. Effective separation with 93.6% removal of auramine was achieved in 10 min when 80 ppm of aluminum(III) was added. The effect of aluminum ion as the activator is presumably due to the increase of the surface potential of the floc by the adsorption of aluminum(III) species on the Fe(OH)₃ floc (or by forming a mixed precipitate), such that a sufficient negatively charged surfactant (NLS) can be adsorbed onto the surface of the floc, thus rendering the surface of the floc hydrophobic. This results in an effective separation.

CONCLUSION

Auramine was removed effectively from synthetic waste water by ion flo tation with an anionic surfactant, sodium lauryl sulfate; over 98% of auramine was removed from the solution in 15 min. A stoichiometric amount of surfactant (1 mol of surfactant to 1 mol of dye) was found to be most effective for removal of auramine. The separation efficiency increased with increasing rate of air flow and decreased with increasing concentration of NaNO₃.

Adsorbing colloid flo tation of auramine with Fe(OH)₃ floc and NLS is effective with 95% removal of auramine in 10 min. The efficiency of separation decreased with increasing concentration of neutral salt (NaNO₃), presumably due to decreased surface potential of the positively charged floc by the adsorption of an ion (nitrate ion) in the solution; the surface

potential of the floc was no longer positive enough for adsorption of a sufficient anionic surfactant. The deleterious effect of neutral salt on the adsorbing colloid flo tation of auramine is compensated for by the use of aluminum ion as activator, which increases the surface potential of the floc as a result of the adsorption of Al(III) species.

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REFERENCES

- Zollinger, H. In *Color Chemistry*; 1st ed. VCH: New York, 1987.
- Sax, N. I. *Cancer Causing Chemicals*; 1st ed.; DC 9625000, VNR: New York, 1981.
- Sebba, F. *Nature* **1959**, *184*, 1062.
- Sebba, F. *Ibid.* **1960**, *188*, 736.
- Sebba, F. *Ion Flo tation*; Elsevier: Amsterdam, 1962.
- Karger, B. L.; Pinfeld, T. A.; Palmer, S. E. *Sep. Sci.* **1970**, *5*, 603.
- Horng, J.-Y.; Huang, S.-D. *Environ. Sci. Technol.* **1993**, *27*, 1169.
- Clarke, A. N.; Wilson, D. J. *Sep. Purif. Methods* **1978**, *7*, 55.
- Wilson, D. J.; Clarke, A. N. *Developments in Foam Flo tation*; Dekker: New York, 1983.
- Grieves, R. B. *Chem. Eng. J.* **1975**, *9*, 93.
- Somasundaran, P. *Sep. Sci.* **1975**, *10*, 93.
- Lemlich, R. *Adsorptive Bubble Separation Techniques*; Academic: New York, 1972.
- Sheu, G.-L.; Huang, S.-D. *Sep. Sci. Technol.* **1987**, *22*, 2253.
- Cheng, M.-H.; Huang, S.-D. *J. Colloid Interface Sci.* **1988**, *126*, 346.
- Huang, J.-Y.; Huang, S.-D. *Sep. Sci. Technol.* **1991**, *26*, 59.
- Lu, C.-S.; Huang, S.-D. *Sep. Sci. Technol.* **1992**, *27*, 1733.
- Womack, J. L.; Lichter, J. C.; Wilson, D. J. *Sep. Sci. Technol.* **1982**, *17*, 897.
- Huang, S.-D.; Fann, C.-F.; Hsieh, H.-S. *J. Colloid Interface Sci.* **1982**, *89*, 504.
- Huang, S.-D.; Tzuoo, J.-J.; Gau, J.-Y.; Hsieh, H.-S.; Fann, C.-F. *Sep. Sci. Technol.* **1985**, *19*, 1061.

20. Ferng, T.-F.; Tzuoo, J.-J.; Huang, S.-D. *Appl. Surf. Chem.* **1982**, 5, 2.
21. Huang, S.-D.; Huang, M.-K.; Gau, J.-Y.; Wu, T.-P.; Huang, J.-Y. Paper Presented at the 6th International Symposium on Surfactants in Solution, New Delhi, India, 1986 August 18-22.
22. Huang, S.-D.; Wang, T.-F. Paper Presented at the Sixth International Conference, Chemistry for Protection of the Environment, Torino, Italy, 1987 September 15-18.