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Removal of Direct Red from Aqueous Solution by Foam Separation Techniques of Ion and Adsorbing Colloid Flotation

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ABSTRACT

Experimental investigations on the removal of Direct Red from an aqueous solution were carried out through two foam separation techniques: ion flotation and adsorbing colloid flotation with Fe(III). The residual concentration of Direct Red can be lowered to below 0.5 ppm in 3 minutes by ion flotation and below 0.1 ppm in 2 minutes by adsorbing colloid flotation. The optimum pH for the removal of Direct Red was found to be 4 for ion flotation and 3–5 for adsorbing colloid flotation. The effects of surfactant, foreign ions, and Al(III) addition on the removal of Direct Red are discussed.

INTRODUCTION

The removal of dyes has become a problem of current interest in the area of wastewater treatment (1). The concentration of dye may be much less than 1 ppm, but the dye is visible even at such small concentrations; the transparency of streams would also be reduced. Because dyes absorb sunlight, plants in drainage streams may perish; thus, the ecosystem of streams can be seriously affected (2). The potential toxicity of some dyes has long been known, and Disazo dyes based on benzidine are known to be calcinogenic (3). Dyes are not efficiently removed by biological treat-

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ment or by conventional dye wastewater treatment techniques (1). Accordingly, a new method to treat dye wastewater is highly desirable.

Foam separation is generally used in separating or concentrating soluble and/or insoluble materials from aqueous solutions. When one deals with dilute wastes, foam separation has several advantages: rapid operation, low space requirements, high efficiency of removal, flexibility of application to various pollutants at various scales, and low cost. A number of excellent reviews on foam separation are available (4–7), and application of flotation techniques to wastewater treatment has been an important issue in the field of separation science (8–11). Our group also investigated the removal of heavy metals from wastewater by precipitation and adsorbing colloid flotation (12, 13).

Foam separation techniques are based on the fact that a surface-active material tends to concentrate at a gas–liquid interface. By bubbling air through the solution, the surface-active material can be absorbed on the surface of the rising bubbles and then be separated from the solution. The substance to be removed, if not surface active, can be made surface active through union with other surface-active materials. For instance, adsorbing colloid flotation involves the addition of a flocculant (ferric chloride) to produce a floc. The dissolved material is adsorbed onto the floc particle and/or coprecipitated with the floc particle. A surfactant is then added, attaches to the floc particle, renders it hydrophobic, and the floc is removed by flotation.

Although foam separation techniques have been applied in various fields, the application of ion and adsorbing colloid flotation techniques for the removal of dyes has been little investigated. Karger and coworkers (14–16) and other workers (17) have carried out the solvent sublation of several dyes. It was found that solvent sublation depends on the pH of the solution, and that the removal efficiency of dyes by solvent sublation is over 90%. There is almost no benefit from addition of paraffin oil to the separation system; it will be better to remove dyes from solution by ion flotation rather than by solvent sublation. Huang and coworkers (18–20) investigated the adsorbing colloid flotation of Marget, Direct Red, and Acid Red from aqueous solution with $Fe(OH)_3$ and sodium lauryl sulfate. It was found that an optimum pH for good removal exists, and that removal efficiency is inhibited by the presence of foreign salts.

In the present work the performances of two foam separation techniques, ion and adsorbing colloid flotation, were investigated by showing the relative effects of pH, initial surfactant concentration, and concentration of foreign salts on the removal efficiency of Direct Red from aqueous solution. The effect of the addition of Al(III) on adsorbing colloid flotation was also investigated.

EXPERIMENTAL

Chemicals

Aqueous solutions of dye were prepared by dissolving Direct Red in distilled and deionized water. In ion flotation, a laboratory-grade cationic surfactant, hexdecyltrimethylammonium bromide (HTA), was used as the collector. In adsorbing colloid flotation, a laboratory-grade anionic surfactant, sodium lauryl sulfate (NLS), was used as the collector and frother, and $Fe(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were used to generate adsorbing colloids. $NaNO_3$, Na_2SO_4, and $Ca(NO_3)_2$ were used as sources of foreign salts.

Apparatus and Procedure

A schematic diagram of the foam separation apparatus is shown in Fig. 1. The flotation column was made of Pyrex tubing of 4.5 cm diameter and 70 cm length. The foams were generated by bubbling an air stream into an aqueous solution through a coarse fritted glass sparger. Compressed air was generated from an air tank. The air flow rate was adjusted with a needle valve and measured with an air flowmeter. The air was purified by passage through glass wool to remove particulates and through distilled water for controlled rehumidification.

For the ion flotation runs, HTA 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

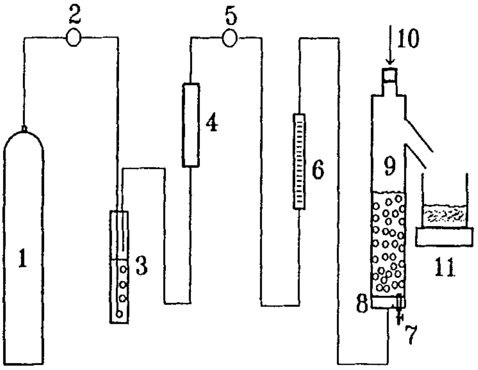

FIG. 1 Schematic diagram of the experimental system. 1) Air tank; 2) valve; 3) humidifier; 4) glass wool column; 5) needle valve; 6) air flowmeter; 7) sample outlet; 8) sparger; 9) flotation column; 10) inlet; 11) discharge foam.

started. The air flow rate was adjusted before the sample solution was poured into the column. The dye–surfactant complex was carried by the foam through the foam outlet.

For the adsorbing colloid flotation runs, the pH was adjusted to produce the floc. Direct Red was absorbed on and/or coprecipitated with the floc. NLS was added and absorbed on the surface of the floc to render the floc hydrophobic, and the sample solution was then poured into the column for separation.

All runs were made with a test solution (250 mL) that contained Direct Red (25 ppm). The experiments were performed at room temperature. The concentrations of dye in the sample solutions were determined using a UV/Vis spectrophotometer (HP 8452A). Spectrophotometric experiments revealed a peak shift and change in the absorbance for Direct Red in the aqueous phase when HTA was added. The change in absorbance depended on the molar ratio of HTA to Direct Red. For the ion flotation runs, a portion (4 mL) of the sample solution was mixed with acetone (2 mL) to dissolve the dye–surfactant complex. The absorbance was measured and compared with a calibration curve that was obtained by treating the standard solutions (with the same HTA to Direct Red mole ratio as the sample solution) by the same procedure as was used for sample solutions (assuming the molar ratio of HTA to Direct Red does not vary greatly during ion flotation). For the adsorbing colloid flotation runs, a sample (5 mL) was withdrawn and the pH of the solution was adjusted to 11. Direct Red was desorbed almost completely from the $Fe(OH)_3$ floc which was removed by centrifugation. The absorbance of the supernatant was measured and compared with the calibration curve obtained by measurement of the absorbance of the standard aqueous solution at pH 11. The addition of NLS to the solution had no effect on the adsorption at 504 nm.

RESULTS AND DISCUSSION

Effect of Flotation Time

The effects of flotation time on the removal of Direct Red by ion flotation and adsorbing colloid flotation from aqueous solution are plotted in Fig. 2. The removal efficiency is represented by the lowness of the residual Direct Red concentration. The residual concentration of Direct Red can be lowered to below 0.5 ppm after 3 minutes treatment by ion flotation and below 0.1 ppm after 2 minutes treatment by adsorbing colloid flotation.

The flotation time was taken as 3 minutes for ion flotation and as 2 minutes for adsorbing colloid flotation in the remaining parts of this work.

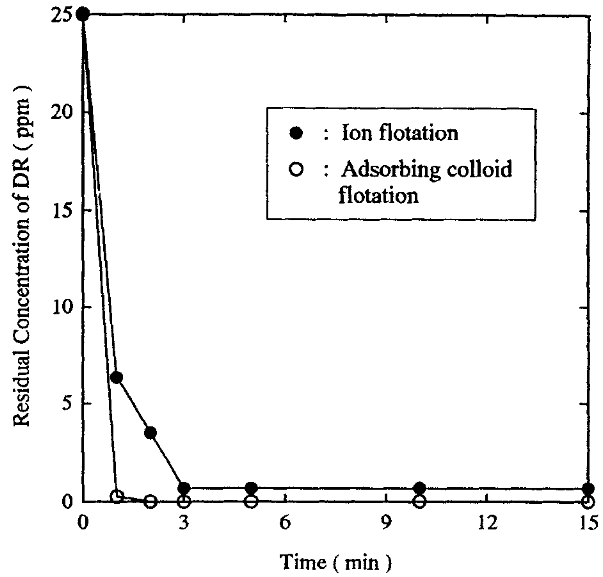

FIG. 2 Effect of flotation time on Direct Red removal. For ion flotation, the initial Direct Red concentration was 25 ppm, the air flow rate 100 mL/min, [HTA]/[DR2] 2.0, pH 4.0. For adsorbing colloid flotation, the initial Direct Red concentration was 25 ppm, the air flow rate 100 mL/min, NLS concentration 60 ppm, Fe(III) concentration 100 ppm, pH 5.0.

Effect of pH on the Removal

The effect of pH on ion flotation and adsorbing colloid flotation of Direct Red are plotted in Fig. 3. For the foam separations there exists an optimum pH value which is about 4 for ion flotation and 3–5 for adsorbing colloid flotation in the present study. Adsorbing colloid flotation shows better removal efficiency than ion flotation over the pH 3–5 range. The residual concentration of Direct Red was reduced below 0.5 ppm by ion flotation at pH 4. The residual concentration of Direct Red increased with increasing pH at a pH above 5, probably due to interference with Direct Red–HTA complex formation by the added base.

For adsorbing colloid flotation, the residual concentration of Direct Red was lowered to below 0.1 ppm in a pH 3–5 range. The residual concentration of Direct Red increased very sharply above pH 6.

During flotation, the coprecipitate of $Fe(OH)_3$ with Direct Red adsorbed on the surfaces of foam bubbles. The adsorption is facilitated by the nature of the surfactant. Since NLS is an anionic surfactant, it is desirable that

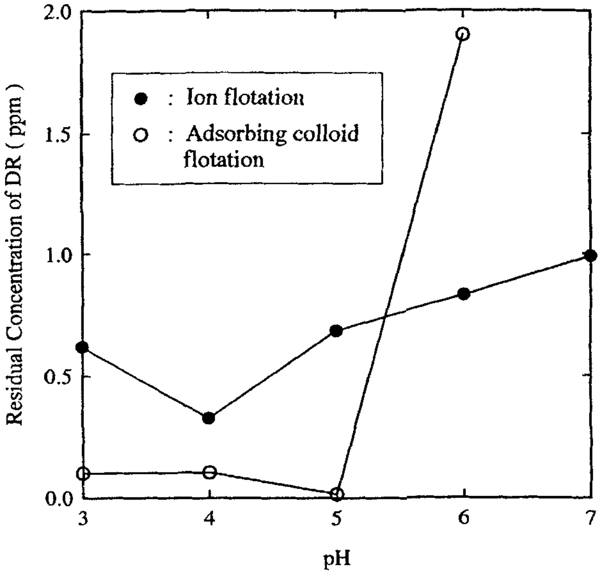

FIG. 3 Effect of pH on Direct Red removal. For ion flotation, the initial Direct Red concentration was 25 ppm, the air flow rate 100 mL/min, [HTA]/[DR2] 2.0, pH 4.0. For adsorbing colloid flotation, the initial Direct Red concentration was 25 ppm, the NLS concentration 60 ppm, Fe(III) concentration 100 ppm, air flow rate 100 mL/min.

the coprecipitate has some positive charges (i.e., that they be below the isoelectric point). It was reported that in water the isoelectric point of $Fe(OH)_3$ is about 7.1 (20). Above the isoelectric point, the charges of the coprecipitate tend to become less positive. Therefore, adsorption of the anionic surfactant (NLS) becomes weaker and the residual concentration of Direct Red increases with pH.

Effect of Initial Surfactant Concentration

Figures 4 and 5 show the effects of the initial surfactant concentration on Direct Red removal by ion and adsorbing colloid flotation, respectively.

For ion flotation it was found that a 2:1 molar ratio of HTA to dye gave the fastest rate of separation and the lowest residual dye concentration. At a smaller concentration of surfactant, the rate of separation is smaller and the level of residual dye is greater, presumably because of the incomplete formation of a dye–surfactant complex. At a greater concentration of surfactant, the rate of separation of Direct Red is smaller and the level of

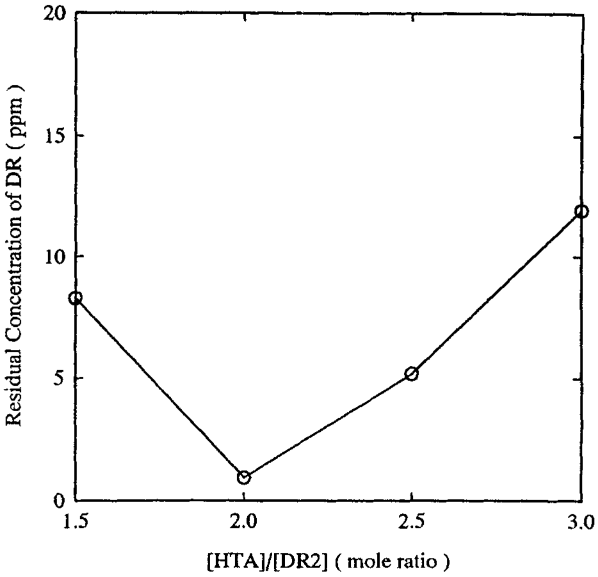

FIG. 4 Effect of HTA concentration on Direct Red removal by ion flotation. The initial Direct Red concentration was 25 ppm, the air flow rate 100 mL/min, [HTA]/[DR2] 2.0, pH 4.0.

residual dye is greater, presumably due to the competition for the bubble surface by the excess surfactant ion with the dye–surfactant complex.

In contrast to ion flotation, adsorbing colloid flotation requires less surfactant for the favorable removal of Direct Red, and a certain optimum surfactant concentration exists. When the surfactant is less than 60 ppm, the removal efficiency is low, presumably due to insufficient adsorption of surfactant on the floc to create floatability. On the other hand, concentrations above 70 ppm result in poor separation, which seems to be due to the creation of a second surfactant adsorption on top of the primary adsorption layer, presumably forming a hydrophilic surface that inhibits the attachment of precipitates to the interface. The presence of a surfactant overdose thus makes the floc less floatable.

Effect of Initial Fe(III) Concentration on the Adsorbing Colloid Flotation

The effect of initial Fe(III) concentration on the removal of Direct Red is shown in Fig. 6. Direct Red can be effectively removed from a solution

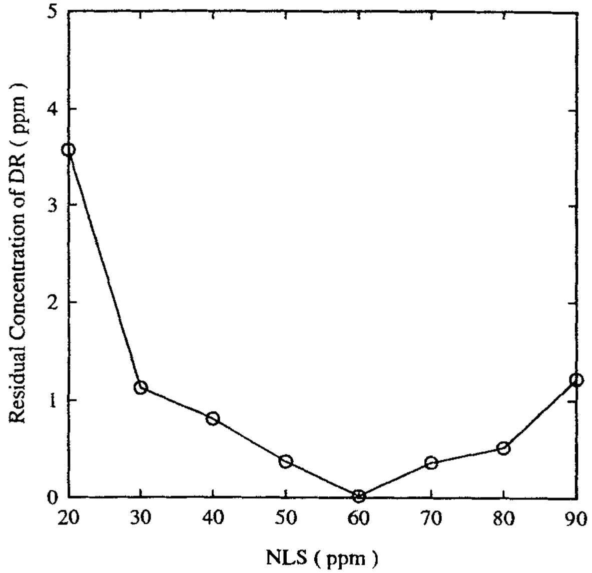

FIG. 5 Effect of NLS concentration on Direct Red removal by adsorbing colloid flotation. The initial Direct Red concentration was 25 ppm, the air flow rate 100 mL/min, NLS concentration 60 ppm, Fe(III) concentration 100 ppm, pH 5.0.

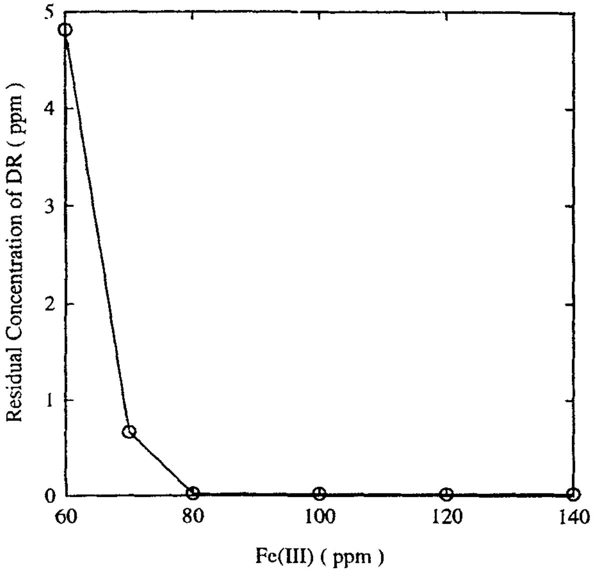

FIG. 6 Effect of Fe(III) concentration on Direct Red removal by adsorbing colloid flotation. All other conditions as in Fig. 5.

provided that the initial concentration of Fe(III) is above 80 ppm. When the concentration of Fe(III) is less than 70 ppm, the removal efficiency is poor, presumably due to incomplete coprecipitation of Direct Red with $Fe(OH)_3$ floc.

Effect of Foreign Salt

The effect of foreign neutral salts [$NaNO_3$, Na_2SO_4, $Ca(NO_3)_2$] on the ion flotation of Direct Red appears in Table 1. The presence of neutral salts increases the residual concentration of Direct Red because of competition for HTA between the Direct Red and the ions of salts.

The effect of Na_2SO_4, which contains the divalent sulfate anion SO_4^{2-}, was stronger than that of $NaNO_3$, which contains the monovalent nitrate anion NO_3^-, because of the stronger adsorption of divalent sulfate anion than of monovalent nitrate anion on the positively charged HTA.

Also, the effect of $Ca(NO_3)_2$, which contains the divalent calcium cation Ca^{2+}, was stronger than that of $NaNO_3$, which contains the monovalent natrium cation Na^+, due to the stronger adsorption of divalent calcium

TABLE 1
Effect of Foreign Salts on Direct Red Removal by Ion Flotation[a]

$NaNO_3$ (M)	Na_2SO_4 (M)	$Ca(NO_3)_2$ (M)	Residual concentration (ppm)
0.0	0	0	0.33
0.1	0	0	4.88
0.2	0	0	7.59
0.3	0	0	8.27
0.4	0	0	8.88
0.5	0	0	9.32
0	0.0	0	0.33
0	0.1	0	8.61
0	0.2	0	9.82
0	0.3	0	11.20
0	0.4	0	12.33
0	0.5	0	13.49
0	0	0.0	0.33
0	0	0.1	6.50
0	0	0.2	8.71
0	0	0.3	10.10
0	0	0.4	11.22
0	0	0.5	12.38

[a] Direct Red = 25 ppm, [HTA]/[DR] = 2.0, pH 4.0, air flow rate = 100 mL/min, flotation time = 3 minutes.

cation than of monovalent natrium cation on the negatively charged Direct Red.

The effect of foreign salts [$NaNO_3$, Na_2SO_4, $Ca(NO_3)_2$] on the adsorbing colloid floatation of Direct Red appears in Table 2.

Anions from neutral salts are adsorbed on the positively charged precipitates, resulting in the reduction of the zeta potential of the particles. The attraction between the positively charged precipitates of Direct Red and the anionic surfactant will then weaken, and the removal efficiency decreases sharply.

Cations from neutral salts are believed to deprive $Fe(OH)_3$ of its flocculation role. The particle size of the coprecipitates will then become small due to reduced floc formation. With a fixed amount of surfactant, precipitate particles smaller than an optimum size are entrained with air flotation less easily than the large ones (12).

In the same ion flotation manner, the effect of Na_2SO_4 was stronger than that of $NaNO_3$. Also, the effect of $Ca(NO_3)_2$ was stronger than that of $NaNO_3$.

TABLE 2

Effect of Foreign Salts on Direct Red Removal by Adsorbing Colloid Flotation[a]

$NaNO_3$ (M)	Na_2SO_4 (M)	$Ca(NO_3)_2$ (M)	Residual concentration (ppm)
0.0	0	0	0.02
0.1	0	0	0.89
0.2	0	0	3.54
0.3	0	0	6.65
0.4	0	0	8.71
0.5	0	0	11.33
0	0.0	0	0.02
0	0.1	0	1.05
0	0.2	0	4.13
0	0.3	0	7.59
0	0.4	0	11.03
0	0.5	0	13.84
0	0	0.0	0.02
0	0	0.1	1.10
0	0	0.2	3.64
0	0	0.3	7.01
0	0	0.4	10.54
0	0	0.5	13.38

[a] Direct Red = 25 ppm, NLS = 60 ppm, Fe(III) = 80 ppm, pH 5.0, air flow rate = 100 mL/min, flotation time = 2 minutes.

TABLE 3
Effect of Al(III) on Direct Red Removal by Adsorbing Colloid Flotation[a]

Na_2SO_4 (M)	$Ca(NO_3)_2$ (M)	Fe(III) (ppm)	Al(III) (ppm)	Residual concentration (ppm)
0.5	0	80	0	13.84
0.5	0	80	5	2.15
0.5	0	80	10	1.18
0.5	0	80	20	0.81
0.5	0	80	30	0.80
0	0.5	80	0	13.38
0	0.5	80	5	1.20
0	0.5	80	10	0.93
0	0.5	80	20	0.86
0	0.5	80	30	0.90

[a] Direct Red = 25 ppm, NLS = 60 ppm, pH 5.0, air flow rate = 100 mL/min, flotation time = 2 minutes.

Effect of Al(III) on the Adsorbing Colloid Flotation

The results of Table 2 show that removal of Direct Red by adsorbing colloid flotation was poor in the presence of foreign salts. Improvement of the removal of Direct Red from an aqueous solution with a high salt concentration was attempted by adding Al(III) as an activator, and the results are shown in Table 3. By adding small amounts of Al(III), Direct Red could be removed from the solution more effectively. Al(III) has been known to increase the zeta potential of the coprecipitates (21), which presumably increases the affinity between the coprecipitates and the anionic surfactant. The removal efficiency seems to increase significantly, in agreement with this.

CONCLUSIONS

Experimental investigations on the removal of Direct Red from aqueous solutions were carried out through two foam separation techniques: ion flotation and adsorbing colloid flotation.

Adsorbing colloid flotation shows better removal efficiency than ion flotation. The residual concentration of Direct Red can be lowered to below 0.5 ppm after 3 minutes treatment by ion flotation and below 0.1 ppm after 2 minutes treatment by adsorbing colloid flotation.

The optimum pH for the removal of Direct Red was found to be 4 for ion flotation and 3–5 for adsorbing colloid flotation.

HTA and NLS as collectors had optimum concentrations for the formation of stable foams which can transport Direct Red effectively.

Foreign ions inhibit the separation efficiency. The extent of inhibition by divalent ions was found to be larger than that by monovalent ions.

Al(III) added as an activator improved removal efficiency, especially when divalent ions inhibited the performance of adsorbing colloid flotation with $Fe(OH)_3$.

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