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Solvent Sublation and Adsorbing Colloid Flotation of Magenta

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Abstract

Magneta was removed from aqueous solution into paraffin oil by solvent sublation of a magenta-lauryl sulfate complex. Over 96% of magenta was removed in 25 min. A stoichiometric amount of surfactant was found to be most effective for magenta removal (1 mol of surfactant to 1 mol of dye). First-order kinetics was not followed. It is proposed that some kinds of aggregate of the dye-surfactant complex may exist in the solution. Magenta was also removed by adsorbing colloid flotation techniques using either ferric hydroxide or aluminum hydroxide as the coagulant. Sodium lauryl sulfate was used as the collector. Over 99.6% of magenta was removed from the solution in as little as 3 min. However, the amount of surfactant needed appears to be high.

INTRODUCTION

Solvent sublation techniques, first used by Sebba (*1*), have shown promise for the removal of certain types of organic compounds from aqueous systems. In this procedure a surface-active solute is transported from the aqueous phase to an overlying layer of a nonvolatile organic liquid on the air-water interfaces of bubbles rising through the solvent sublation column. Volatile solutes of low solubility in water may be removed in the interior of the bubbles in a similar fashion by air stripping into the organic layer. Lemlich's book on adsorptive bubble separation includes a review on solvent sublation by Karger (*2*). Wilson et

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al. included material on this subject in a more general review (*3*) and two recent books (*4*, *5*).

Sebba developed solvent sublation separations mainly for inorganic ions; he also noted that ionizable dyes could be selectively separated by adjustment of conditions and the use of suitable surface-active agents (*1*). Caragay, Karger, and Lee separated methyl orange from rhodamine B with a cationic surfactant at a pH at which the methyl orange was anionic while the rhodamine B was zwitter-ionic (*6*, *7*). Karger, Pinfold, and Palmer carried out a detailed study of the solvent sublation of methyl orange–hexadecyltrimethyl ammonium ion pairs (*8*). Womack, Lichter, and Wilson (*9*) reported on the solvent sublation of two dye–surfactant ion complexes, methylene blue–tetradecyl sulfate and methyl orange–hexadecyltrimethyl ammonium.

Other works of particular interest to our group are the extensive works of Wilson's group on solvent sublation of various organic pollutant from aqueous systems, such as solvent sublation of alkyl phthalates, volatile chlorinated organics, dichlorobenzenes, nitrophenols, polynuclear aromatics, and chlorinated pesticides (*3–5*, *9–14*). Grieves et al. (*15*) studied the removal of phenol by solvent extraction, solvent sublation, and foam fractionation.

The adsorbing colloid flotation technique has been found to be very effective in removing various inorganic constituents from aqueous solutions. A number of excellent reviews are available (*3*, *5*, *16–18*). This technique involves the addition of a coagulant (alum or ferric chloride) to produce a floc. The dissolved inorganic constituents (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 the air through the solution, the floc is adsorbed on the rising bubble and carried out from the solution by the foam.

In this paper we describe some studies we have recently made on the solvent sublation of a cationic dye, magenta (Basic Violet 14), from aqueous solution. Magenta is a cationic dye which bears a single positive charge when dissolved in water. Sodium lauryl sulfate was used as the collector and paraffin oil was used as the top organic layer. It was found that over 96% of magenta was removed from the solution by solvent sublation in 25 min.

It was also attempted to remove magenta by adsorbing colloid flotation techniques. To the author's knowledge, this paper is the first to describe the use of adsorbing colloid flotation techniques for organic dye removal. Both ferric hydroxide and aluminum hydroxide were found to be very effective coprecipitants for magenta removal by adsorbing colloid flotation. Sodium lauryl sulfate was used as the collector and frother. The rate of removal was very fast. Over 99.6% of magenta was removed from solution in just 3 min. However, the amount of collector needed for an effective separation appears to be high.

EXPERIMENTAL

The adsorbing colloid flotation system used was similar to that described earlier (*19*, *20*). A soft glass column 90 cm in length with an inside diameter of 3.5 cm was used for the flotation. There was a side arm with a rubber septum near the bottom to inject the collector. 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.

The solvent sublation system used was similar to that used for the adsorbing colloid flotation system just described above except that the column was somewhat shorter (60 cm in length).

Compressed air was generated from an air pump. The air-flow rate was adjusted with a Hoke needle valve with micrometer control and measured with a soap-film flowmeter. The air was purified by passing it through glass wool to remove particulates, through Ascarite to remove carbon dioxide, and through distilled water for controlled rehumidification.

Laboratory-grade sodium lauryl sulfate (NLS) was used as the collector without further purification. Merck reagent-grade magenta, ferric nitrate, and aluminum nitrate were used for sample preparation.

For the runs of solvent sublation, NLS was added to the sample solution to form the dye–surfactant complexes, the pH of the solution was adjusted, the solution was poured into the separation column, 5 mL of paraffin oil was added immediately, and the timer started. A 5-mL portion of the sample solution was used to prepare a standard calibration curve with a Jasco 505 UV/Vis Spectrophotometer. The absorbance was measured at the absorption peak (5481 Å). It was found that the absorption peak did not shift after NLS was added to the dye solution. However, the absorbance decreased somewhat (about 15%) due to dye–surfactant complex formation.

Data were plotted at $\log_{10} C(t)/C_0$ versus time in minutes to display any deviations from first-order kinetics, which would yield linear plots.

For the runs of adsorbing colloid flotation, ferric nitrate or aluminum nitrate was added to the sample solution, the pH was adjusted to produce the floc, magenta 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 Radiometer pHM83 Autocal pH Meter.

All runs were made with 250 mL of test solution which contained 25 ppm magenta. The experiments were performed under room temperature.

RESULTS AND DISCUSSIONS

The effect of pH on solvent sublation of magenta-sodium lauryl sulfate is shown in Table 1 and Fig. 1. Over 96% of the magenta was removed from the solution by solvent sublation in 25 min at pH 4.5 to 6.5. The rate of separation decreased somewhat if the pH of the solution was adjusted either too high or too low, probably due to the interference of the magenta-sodium lauryl sulfate complex formation by the added acid or base. First-order kinetics are obvious not being followed; the removal rate of magenta drops much too sharply after the first 10 min or so of the run. This was earlier noted by Karger et al. (*8*) with solvent sublation of methyl orange-hexadecyltrimethyl ammonium into 2-octanol. They ascribed it to the gradually increasing concentration of 2-octanol in the water layer. Wilson et al. (*9*) studied the solvent sublation of methylene blue-tetradecylsulfate and methyl orange-hexadecyltrimethyl ammonium into 2-octanol. The curvatures of their plots exhibit a fast initial

TABLE 1
The Effect of pH on Solvent Sublation of Magenta[a]

	Residual magenta level (ppm) at time (min) of				
pH	10	15	20	25	30
3.0	3.4	3.0	2.6	2.1	1.6
4.0	2.6	2.4	1.6	1.5	1.0
5.0	2.5	2.0	1.3	0.7	0.5
5.5	3.2	2.4	1.5	0.9	0.6
6.0	4.0	2.4	1.5	1.0	0.7
6.5	4.9	2.6	1.6	1.0	0.8
7.5	5.2	3.0	2.4	1.8	1.4
8.0	5.6	3.5	2.6	1.9	1.5

[a] Air flow rate = 120 mL/min, mole ratio NLS/dye = 1.0.

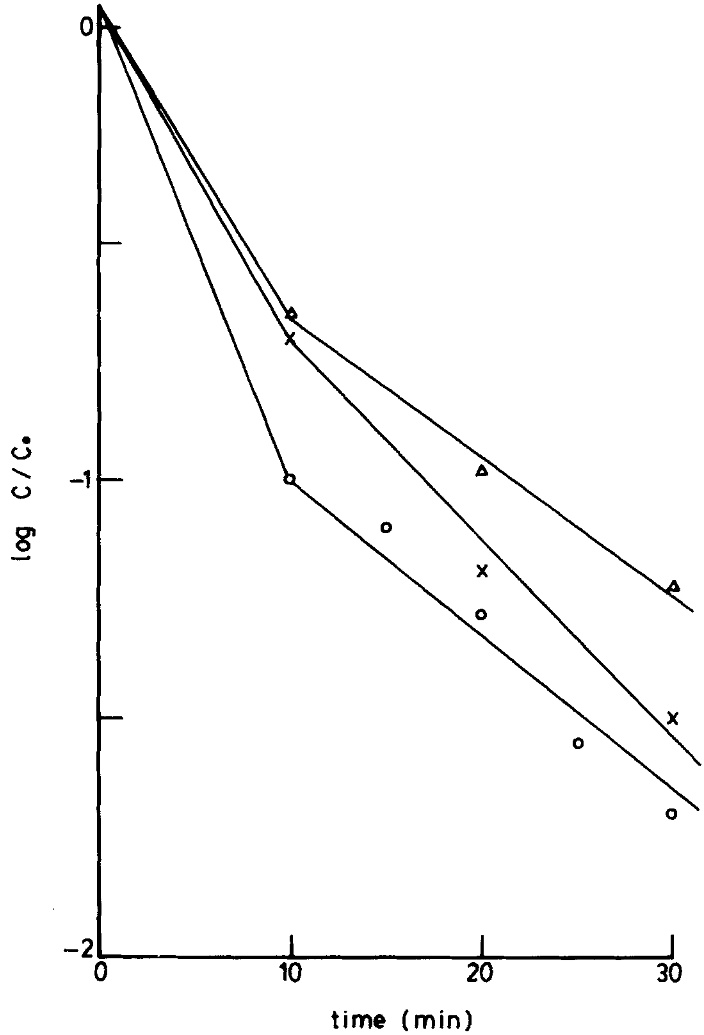

FIG. 1. Effect of pH on the rate of removal of magenta by solvent sublation: (△) pH = 8.0, (×) pH = 6.5, (○) pH = 5.0.

removal rate which subsequently decreases markedly, and are consistent with Karger's results (*8*) and ours. Since their runs were made with water saturated with 2-octanol, they tentatively concluded that the accumulation of octanol in the water layer during the course of a run is not responsible for the curvature. They suggested that the systems they were dealing with might be some sort of mobile equilibrium between dye, surfactant, and complex, and additional work on this is needed. They also examined theoretically (*9*) three possible mechanisms and compared them with the experimental results. They found that the initial very rapid rise of the experimental plots followed by a slower rise at later times is quite a bit more abrupt than predicted by the one-to-one ion pair model. Another proposed mechanism, which assumes a dye–surfactant complex, is formed which contains 2 mol of surfactant per mol of dye, produces plots which are qualitatively in agreement with the experimental results. We use paraffin oil instead of 2-octanol for the top organic layer. Since paraffin oil is less soluble in water than is 2-octanol, it is not likely that the dissolution of paraffin oil during the course of a run is responsible for the curvature. The effect of dosage of surfactant on separation (see Table 2, which will be discussed later) shows that the complex formed by magenta and sodium lauryl sulfate appears to be a one-to-one mole ratio. Therefore, the mechanism proposed for the system of methylene blue–tetradecyl sulfate by Wilson et al. (*9*) cannot be used to describe the system we studied. We propose that some aggregates of magenta–sodium lauryl sulfate complexes might exist in the solution. The aggregates were removed during the initial stage of the run, which resulted in a faster rate of separation. Subsequent removal of the dye–surfactant ion pair resulted in a slower rate of separation.

The effect of surfactant concentration on separation is shown in Table 2. It was found that a 1:1 mole ratio of surfactant to dye gave the fastest rate of separation and the lowest residual dye concentration. At lower surfactant concentration, the rate of separation is slower and the residual dye level is higher, presumably due to the incomplete dye–surfactant complex formation. At higher concentration the rate of separation is lower, presumably due to the competition of the bubble surface by the excess surfactant ion with the dye–surfactant complex. Note that this finding is quite different from the results of solvent sublation of methylene blue and methyl orange studied by Wilson (*9*) and Karger (*8*), who found that the rate of removal of methylene blue and methyl orange increased with increasing surfactant concentration which 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

TABLE 2
The Effect of Surfactant Dosage on Solvent Sublation[a]

Mole ratio NLS/dye	NLS dosage (ppm)	Residual magenta level (ppm) at time (min) of				
		20	25	30	40	50
0.9	19.2	3.3	2.5	1.8		
1.0	21.3	1.3	0.7	0.5		
1.1	23.4	2.2	1.7	1.1		
1.2	25.6			3.4	2.2	1.6

[a] Air flow rate = 120 mL/min, pH = 5.0.

complexes and also due to the difference in the mole ratio of the dye and surfactant of the complexes.

The effect of gas flow rate is shown in Table 3. The rate of separation increases with increasing gas flow rate, as expected.

A series of experiments was performed using adsorbing colloid flotation techniques to remove magenta from aqueous solution. The effect of pH on adsorbing colloid flotation of magenta with ferric hydroxide floc is shown in Table 4. Sodium lauryl sulfate was used as the collector. It was found that the rate of removal was extraordinarily fast under the pH range studied (pH 4–6). Over 99.6% of magenta was removed in just 3 min. The residual magenta level was as low as 0.1 ppm. However, a large amount of surfactant (200 ppm) was required to remove the floc and dye from the solution. Furthermore, a small amount of particulates, which settled readily at the bottom of the column, was not removed by the foam. Further studies will be required to reduce the amount of surfactant dosage in order to make this technique more practical. The effect of iron dosage is shown in Table 5. Less than 100 ppm of iron was required for an effective separation.

TABLE 3
The Effect of Air Flow Rate on Solvent Sublation[a]

Air flow rate (mL/min)	Residual magenta level (ppm)
85	2.2
120	1.3
150	0.8

[a] pH = 5.0, duration of treatment = 20 min, mole ratio NLS/dye = 1.0.

TABLE 4
The Effect of pH on Adsorbing Colloid Flotation of Magenta with $Fe(OH)_3$[a]

pH	Residual magenta level (ppm)
4.0	0.2
4.5	0.1
5.0	0.2
5.5	0.2
6.0	0.2

[a] [Fe(III)] = 150 ppm, NLS = 200 ppm, air flow rate = 150 mL/min, time of flotation = 3 min.

Aluminum hydroxide was also tried as the coprecipitant for magenta removal by adsorbing colloid flotation. The effect of pH is shown in Table 6. It was found that the pH variation (from 5.5 to 7.0) did not have a significant effect on separation, with a somewhat lower residual magenta level at pH 5.5 to 6.0. The rate of separation was also very fast; the floc was removed in 3 min with the residual magenta level at 0.1 ppm. The amount of surfactant needed was also high. A small amount of particulates was found to precipitate at the bottom of the column. A brief settling tank or filtration tank may be required to remove the particulates in the effluent after foam flotation treatment. The effect of aluminum dosage is shown in Table 7. Less than 100 ppm of aluminum was required for an effective separation.

TABLE 5
The Effect of Iron Dosage on Adsorbing Colloid Flotation[a]

Fe(III) (ppm)	Residual magenta level (ppm)
300	<0.1
250	<0.1
200	<0.1
150	<0.1
100	0.1
50	0.6

[a] pH = 5.0, air flow rate = 150 mL/min, NLS = 250 ppm, time of flotation = 3 min.

TABLE 6
The Effect of pH on Adsorbing Colloid Flotation of Magenta with $Al(OH)_3$[a]

pH	Residual magenta level (ppm)
5.5	0.1[b]
6.0	0.1
6.5	0.2
7.0	0.3
8.0	0.6

[a] Al(III) = 100 ppm, NLS = 250 ppm, air flow rate = 150 mL/min, time of flotation = 3 min.

[b] NLS = 400 ppm.

CONCLUSION

Magenta can be removed effectively from an aqueous solution into paraffin oil by solvent sublation of magenta-sodium lauryl sulfate complex. Over 96% of magenta was removed in 25 min. A stoichiometric amount of surfactant was found to be most effective for magenta removal (1 mol of surfactant to 1 mol of dye). First-order kinetics was not followed. It was proposed that some kinds of aggregates of the dye-surfactant complex may exist in the solution.

Magenta can also be removed by adsorbing colloid flotation techniques using either ferric hydroxide or aluminum hydroxide as the coagulant. Sodium lauryl sulfate was used as the collector. Over 99.6% of magenta was removed from the solution in 3 min. However, the amount of surfactant needed appeared to be high.

TABLE 7
The Effect of Aluminum Dosage on Absorbing Colloid Flotation[a]

Al(III) (ppm)	Residual magenta level (ppm)
50	0.2
100	0.1
125	0.1
150	0.2

[a] pH = 6.0, NLS = 250 ppm, air flow rate = 150 mL/min, time of flotation = 3 min.

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