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Solvent Sublation and Adsorptive Flotation/Sublation of Diphenyl

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Abstract

Diphenyl is readily removed from aqueous systems by solvent sublation into mineral oil. The process is slightly enhanced by increasing aeration rate, added salts, and surfactants, and slightly retarded by organic solvent. A new technique, adsorptive flotation/sublation, was found to be more effective in removing diphenyl from aqueous solution than either adsorbing colloid flotation or solvent sublation. Over 99% of diphenyl can be removed from the solution in 30 min by a three-step batch process of adsorptive flotation/sublation.

INTRODUCTION

Solvent sublation, a surface chemical separation method originated by Sebba (*1*), has shown promise for the removal of some classes of organic compounds from wastewater. In the method, a surface-active solute is transported from an aqueous phase to an overlying immiscible layer of a nonvolatile 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 similar fashion by air stripping into the organic layer. Valsaraj investigated the solvent sublation of dichlorobenzene, a commercial polychlorinated biphenyl mixture, lindane, endrin, and two nitrophenols (*2*). Huang et al. investigated the solvent sublation of naphthalene and phenanthrene (*3*). Womack et al. studied the solvent sublation of methylene blue and methyl orange (*4*). Lionel et al. presented a mathematic model for the removal of volatile organics from water by solvent sublation into an organic phase (5).

We present here experimental results on the solvent sublation of diphenyl from water. It was found that the separation efficiency was enhanced by increasing the aeration rate, added salts, and added surfactant, and slightly retarded by organic solvent.

We also present here a new technique which will be called adsorptive flotation/sublation. Diphenyl was coprecipitate with either ferric hydroxide or aluminum hydroxide, sodium lauryl sulfate was added to render the floc hydrophobic, and a layer of paraffin oil was put on the top of the solution. The floc with coprecipitated diphenyl was carried out from the solution, passing through the layer of paraffin oil, by the foam; some of the diphneyl was carried out from the solution to the layer of paraffin oil by the mechanism of solvent sublation. It was found that adsorptive flotation/sublation was more effective in removing diphenyl from aqueous solution than either solvent sublation or adsorbing colloid flotation. Over 99% of diphenyl can be removed from the solution in 30 min by a three-step batch process of adsorptive flotation/sublation.

EXPERIMENTAL

The apparatus for solvent sublation and foam flotation consisted of a 3.2 cm diameter × 100 cm high Pyrex column fitted with a rubber stopper at the bottom through which passed a fine fritted glass gas dispersion tube and a sampling stopcock. House air was passed through a glass wool filter, 1.0 *M* sodium hydroxide solution, and a water saturator before going to the gas dispersion tube. Air flow rates were adjusted with a needle valve and measured with a soap film flowmeter. The air flow rate was kept at 100 mL/min unless otherwise specified.

Wako Laboratory Grade diphenyl was dissolved in distilled water by stirring with a magnetic stirrer for over one day. The solutions were filtered to remove suspended solids. The concentrations of diphenyl in the solutions were 2.2 to 2.9 mg/L.

The volume of the sample solution used for a run was 200 mL. The solution was poured into the column, 10 mL paraffin oil was added immediately, and the timer started. Five milliliters of diphenyl solution was taken each time for analysis. The diphenyl concentrations of the samples were measured with a Shimadzu UV 200S spectrophotometer at 248.5 nm.

In the adsorptive flotation/sublation experiments, aluminum chloride or ferric chloride solution was added to the diphenyl solutions, the pH was adjusted to the desired value, and then sodium lauryl sulfate was added. The solution with the floc was poured into the column, 10 mL paraffin oil was added immediately, and the timer started.

All runs were made at room temperature. Data were plotted as the percentage of diphenyl remaining in solution versus the time in minutes on a semilog scale to test the existence of first-order kinetics.

RESULTS AND DISCUSSION

The rates of separation of diphenyl from aqueous solutions by spontaneous volatilization (test by putting diphenyl solution in an UV cell without a cover), simple aeration (without an organic layer on the top of the separation column), and solvent sublation are shown in Fig. 1. The runs follow first-order kinetics approximately. The first-order rate constants for the separation are listed in Table 1. The rate constant for simple aeration is larger than that for spontaneous volatilization. The improvement is presumably due to the increased liquid–air interface associated with the rising bubbles. The rate constant for solvent sublation is more than three times as large as that for simple aeration. The improvement in separation is presumably due to the surface adsorption

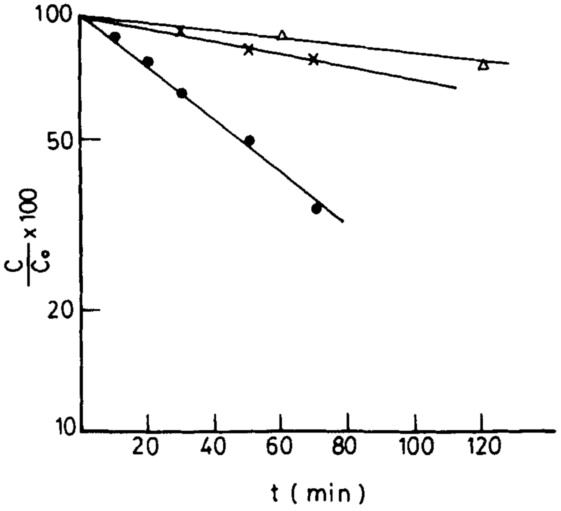

FIG. 1. Removal of diphenyl from aqueous solution: (●) solvent sublation, (×) simple aeration, (△) spontaneous volatization.

TABLE 1
Separation Rate Constants for Spontaneous Volatization, Simple Aeration, and Solvent Sublation of Diphenyl[a]

Method	Rate constant $K \times 10^3$ (min^{-1})
Volatization	1.0
Aeration	1.7
Sublation	6.3

[a] Air flow rate = 34 mL/min.

of surface-active diphenyl on the surface of the bubbles. The surface-adsorbed diphenyl and the diphenyl in the vapor phase inside the bubble are carried into the organic layer on the top of the separation column during solvent sublation. Only the diphenyl vapor inside the air bubble is removed by simple aeration.

The effect of air flow rate is shown in Fig. 2 and Table 2. The rate of separation increases with increasing air flow rate, as expected.

The influence of organic solvents, such as ethanol and acetone, is exhibited in Table 3. The rate of separation decreases somewhat with increasing ethanol concentration. This is probably due to the attractive

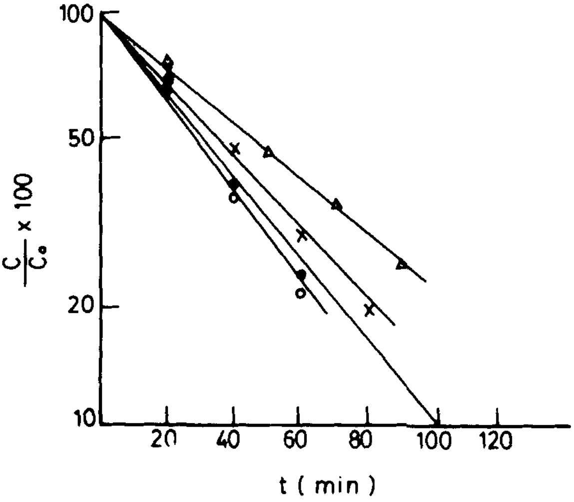

FIG. 2. Effect of air flow rate on solvent sublation: (△) water, 34 mL/min; (○) water, 100 mL/min; (×) 0.01% ethanol, 73 mL/min; (●) 0.01% ethanol, 100 mL/min.

TABLE 2
Effect of Air Flow Rate on Solvent Sublation

Composition of aqueous phase	Air flow rate (mL/min)	Rate constant $K \times 10^3$ (min^{-1})
H_2O	34	6.3
H_2O	100	10.2
0.01% Ethanol	73	8.8
0.01% Ethanol	100	9.8

forces between diphenyl and ethanol molecules, which would increase the solubility of diphenyl in the aqueous solution. We found 83% removal of diphenyl in 110 min from the solution containing 10% by weight ethanol. Acetone produced a smaller effect on the rate of separation to ethanol at the same concentration. The rate constant for the solution containing 1% acetone is 93% of its value for diphenyl removed in the absence of acetone. The corresponding value for the removal of diphenyl from 1% ethanol solution is 84%. The difference between ethanol and acetone may be due in part to the increased volatilization of low-boiling acetone.

The effects of added salts on the solvent sublation of diphenyl are shown in Table 4. We see that the presence of salts somewhat increases the rate of separation. Presumably this is due to the same mechanism that causes the widely used "salting out" effect in which organics are made less soluble in aqueous phases by the addition of salts. These tie up water molecules in ion hydration shells, thereby decreasing the amount of water available for solubilizing the organic. Similar effects were observed on the solvent sublation of naphthalene (*3*).

TABLE 3
Influence of Organic Solvent on the Separation Rate Constants for Solvent Sublation[a]

Composition of aqueous phase	Rate constant $K \times 10^3$ (min^{-1})
0.01% Ethanol	9.9
0.1% Ethanol	9.8
1% Ethanol	8.6
5% Ethanol	7.5
10% Ethanol	7.1
1% Acetone	9.5

[a] Air flow rate = 100 mL/min.

TABLE 4
Influence of Inorganic Salts on the Separation Rate Constants for Solvent Sublation[a]

Composition of aqueous phase	Rate constant $K \times 10^3$ (min^{-1})
0.01 M $NaNO_3$	8.1
0.01 M Na_2SO_4	8.8
0.02 M Na_2SO_4	9.3
0.03 M Na_2SO_4	9.8
0.01 M $AlCl_3$	10.2

[a] Air flow rate = 34 mL/min.

The influence of various surfactants on the solvent sublation of diphenyl is shown in Table 5. It is evident that these surfactant enhance the removal of diphenyl. This effect may be due in part to the reduced bubble size and thus increased surface area for diphenyl adsorption. The rate constants are larger for the solutions containing higher concentrations of surfactant. It was found that polyoxyethylene sorbitan monostearate (Tween 60) is more effective in enhancing the rate of separation than polyoxyethylene sorbitan monolaurate (Tween 20). There might be a weak attractive force between the diphenyl molecule and the surfactant such that the surface activity of diphenyl is increased by associated with the surfactant, and therefore, the rate of separation of diphenyl by solvent sublation is enhanced by the addition of surfactant. The longer the chain length of the hydrophobic part of the surfactant molecule, the more effective is the surfactant in enhancing the rate of separation.

A series of experiments was performed to study the efficiency of ferric hydroxide or aluminum hydroxide as an adsorbing floc for diphenyl.

TABLE 5
Influence of Surfactants on Separation Rate Constants for Solvent Sublation[a]

Composition of aqueous phase	Rate constant $K \times 10^3$ (min^{-1})
0.1% Tween 20	11.9
0.01% Tween 20	10.6
0.01% Tween 60	17.8
0.001% Tween 60	11.9
0.01% Sodium lauryl sulfate	12.0

[a] Air flow rate = 100 mL/min.

Various amounts of Fe(III) or Al(III) salts were added to the diphenyl solution. The pH of the solution was adjusted to 5.5 (for Fe) or 8.0 (for Al). Sodium lauryl sulfate was thten added to coagulate the floc. The floc was removed from the solution by filtration. The concentration of diphenyl in the filtrate was measured. The results are shown in Tables 6 and 7. It was found that the residual diphenyl levels decrease with increasing dosage of floc at low concentration; the residual diphenyl levels reach a plateau with further addition of the floc.

The effects of pH on adsorptive flotation/sublation of diphenyl using $Al(OH)_3$ or $Fe(OH)_3$ as the coprecipitants are shown in Tables 8 and 9. A layer of paraffin oil was put on the top of the solution. The floc was carried out from the solution, through the layer of paraffin oil, by foam. The diphenyl adsorbed on the surface of the rising bubbles was carried from the solution to the paraffin oil. This technique, taking advantage of both adsorbing colloid flotation and solvent sublation, may be called adsorptive flotation/sublation. The optimum pH for separation was 8.0 when aluminum hydroxide was used as the adsorbing floc. The separation efficiency decreased significantly at pH below 6.5 or at pH higher than 8.5. At pH below 6.5, the precipitation of aluminum hydroxide was incomplete. At pH higher than 8.5, the aluminum hydroxide floc redissolved.

More diphenyl was removed (with ferric hydroxide as the coprecipitant) from the solutions at pH 6.0 to 7.5 than from that at pH 5.5. However, some of the floc remained after foaming in the solutions at pH 6.0 to 7.5. The floc can be removed effectively from the solution at pH 5.5. Therefore the value 5.5 was chosen as the optimum pH when ferric hydroxide was used as the coprecipitant. The effect of floc dosage is shown in Tables 10 and 11. It was found that excess floc could not improve the separation. These results are consistent with the results of the coprecipitation experiments shown in Tables 6 and 7.

Adsorptive flotation/sublation was more effective in removing di-

TABLE 6

Effect of Disage of Al (III) on Diphenyl Removal by Coprecipitation[a]

Al(III) (ppm)	% Removal
15	18
17.5	29
20	34
50	35

[a] pH = 8.0, NLS = 100 ppm, floc removed by filtration.

TABLE 7
Effect of Dosage of Fe(III) on Diphenyl Removal by Coprecipitation[a]

Fe(III) (ppm)	% Removal
15	13
17.5	24
20	25
25	25

[a] pH = 5.5, NLS = 50 ppm, floc removed by filtration.

phenyl from the aqueous solution than was adsorbing colloid flotation under the same conditions. (The only difference between the two techniques was a layer of paraffin oil.) The results are shown in Tables 12 and 13. The improvement in separation by adsorptive flotation/sublation is presumably due to the additional amount of diphenyl removed from the solution by the mechanism of solvent sublation.

Successive batch processes of adsorptive flotation/sublation were performed as shown in Tables 14 and 15. Over 99% of diphenyl was removed by the three-step batch process using either ferric hydroxide or aluminum hydroxide. The duration of the run for each step was 10 min.

CONCLUSION

The efficiency of solvent sublation of diphenyl can be enhanced by increasing air flow rate, and by adding inorganic salts or surfactant, but is slightly reduced by organic solvents. Adsorptive flotation/sublation, a new technique which combines adsorbing colloid flotation and solvent sublation, is found to be more effective in removing diphenyl from aqueous solution than either adsorbing colloid flotation or solvent

TABLE 8
Effect of pH on Adsorptive Flotation Sublation Using $Al(OH)_3$ as the Coprecipitant[a]

pH	6.5	7.0	7.5	8.0	8.5
% Removal	45	66.2	67.8	68.3	41

[a] NLS = 100 ppm, Al(III) = 50 ppm, duration of runs = 10 min, air flow rate = 100 mL/min.

TABLE 9

Effect of ph on Adsorptive Flotation Sublation Using $Fe(OH)_3$ as the Coprecipitant[a]

pH	4.5	5.0	5.5	6.0	6.5	7.5
% Removal	43	49	49	54	56	56

[a] NLS = 50 ppm, Fe(III) = 50 ppm, duration of runs = 10 min, air flow rate = 100 mL/min.

TABLE 10

Effect of Dosage of Al(III) on Adsorptive Flotation/Sublation[a]

Al(III) (ppm)	% Removal
50	52.3
100	52.2

[a] NLS = 50 ppm, pH = 8.0, duration of runs = 10 min, air flow rate = 100 mL/min.

TABLE 11

Effect of Dosage of Fe(III) on Adsorptive Flotation Sublation*

Fe(III) (ppm)	% Removal
50	49.4
100	50.3
150	48.8

*NLS = 50 ppm, pH = 5.5, duration of runs = 10 min., air flow rate = 100 mL/min.

TABLE 12
Comparison between Adsorbing Colloid Flotation and Adsorptive Flotation Sublation with $Al(OH)_3$[a]

Method	% Removal[b]
Adsorbing colloid flotation	57.8 ± 0.7
Adsorptive flotation sublation	68.6 ± 0.5

[a] Al(III) = 50 ppm, NLS = 100 ppm, pH = 8.0, duration of runs = 10 min, air flow rate = 100 mL/min.

[b] The average and standard deviation of duplicated runs.

TABLE 13
Comparison between Adsorbing Colloid Flotation and Adsorptive Flotation Sublation with $Fe(OH)_3$[a]

Method	% Removal[b]
Adsorbing colloid flotation	38.2 ± 1.7
Adsorptive flotation sublation	53.3 ± 1.6

[a] NLS = 50 ppm, Fe(III) = 100 ppm, pH = 5.5, duration of runs = 10 min, air flow rate = 100 mL/min.

[b] The average and standard deviation of triplicate runs.

TABLE 14
Removal of Diphenyl by Stepwise Batch Adsorptive Flotation Sublation with $Al(OH)_3$[a]

Step no.	% Removal[b]
1	50.2 ± 3.4
2	82.8 ± 1.0
3	>99

[a] 50 ppm NLS and 50 ppm Al(III) were added for each step, pH = 8.0, duration of runs for each step was 10 min, air flow rate = 100 mL/min.

[b] The average and standard deviation of duplicate runs.

TABLE 15

Removal of Diphenyl by Stepwise Batch Adsorptive Flotation Sublation with $Fe(OH)_3$[a]

Step no.	% Removal[b]
1	54.1 ± 4.0
2	76.7 ± 3.8
3	>99

[a] 50 ppm NLS and 50 ppm Fe(III) were added for each step, pH = 5.5, duration of runs for each step was 10 min, air flow rate = 100 mL/min.

[b] The average and standard deviation of duplicate runs.

sublation. Over 99% of diphenyl can be removed from the solution in 30 min by a three-step batch process of adsorptive flotation/sublation.

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