Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Lu, Chung-Shin and Huang, Shang-Da(1992) 'Removal of Organophosphorus Pesticides from Aqueous Solution by Using Adsorptive Bubble Separation Techniques', Separation Science and Technology, 27: 13, 1733 — 1742
To link to this Article: DOI: 10.1080/01496399208019443
URL: http://dx.doi.org/10.1080/01496399208019443

SEPARATION SCIENCE AND TECHNOLOGY, 27(13), pp. 1733–1742, 1992

Removal of Organophosphorus Pesticides from Aqueous Solution by Using Adsorptive Bubble Separation Techniques

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Abstract

Two organophosphorus pesticides, ddvp (phosphoric acid 2,2-dichlorovinyl dimethyl ester) and phorate (phosphorodithioic acid *o*,*o*-diethyl *s*-[(ethylthio)methyl] ester) were removed from aqueous solution by three adsorptive bubble separation techniques: air stripping, solvent sublation, and adsorbing colloid flotation. The effects of pH, flow rate, surfactant, ethanol, ionic strength, and coprecipitant concentration on the efficiency of pesticide removal were studied. Over 97% of phorate was removed in 30 min by solvent sublation, and 90% of phorate was removed in 10 min by adsorbing colloid flotation with $Fe(OH)_3$ floc. The separations of ddvp by these techniques were not effective.

INTRODUCTION

Organophosphorus (o.p.) pesticides have been used for agricultural purposes for at least 30 years (*1*). As many organochlorine (o.c.) pesticides have been withdrawn from registered use because of evidence of toxicity, persistence, and bioaccumulation in the environment, o.p. pesticides have become an important group of pesticides to replace o.c. pesticides in many agricultural applications. Owing to their wide application, highly acute toxicity to aquatic life (*2*, *3*), and possible subtle effects on aquatic life produced by long-term exposure, treatment of wastewater containing these pesticides is necessary, particularly in areas of heavy use, to prevent potential hazard to the aquatic environment that results from misapplication, spills, run-off, or groundwater contamination.

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Organic compounds dissolved in water can be removed by adsorption on activated carbon or macroreticular resin. These methods generally entail large capital and operating expenses. Air stripping and solvent sublation are two other processes capable of removing trace hydrophobic organics from aqueous solutions by using air bubbles. In the solvent sublation procedure, a surface-active (or volatile) solute is transported from the aqueous phase to an overlying layer of a nonvolatile organic liquid on the air–water interface (or in the interior) of bubbles rising through the sublation column, whereas in air stripping no immiscible layer is present over the water column; hence only the material transported in the interior of the bubbles is removed from the aqueous phase (*4*, *5*).

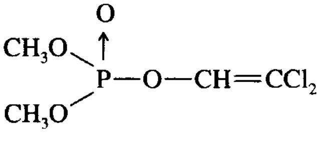
After its introduction by Sebba (*6*) for the removal of inorganic ions, solvent sublation has been studied for the removal of both organic substances and inorganic ions from aqueous solution (*7–13*). The organic compounds studied include heptachlor, hydroxychlordene, aldrin, hexachlorobutadiene, trichlorophenol, toluene, dichlorobenzene, biphenyl, priority pollutants (phenols), and naphthalene. Lionel et al. presented a mathematical model for the removal of volatile organic substances from water by solvent sublation into an organic phase (*14*).

We here describe the removal of the organophosphorus pesticides ddvp (phosphoric acid 2,2-dichlorovinyl dimethyl ester) and phorate (phosphorodithioic acid *o*,*o*-diethyl *s*-[(ethylthio)methyl] ester) from aqueous solution by air stripping, solvent sublation, and adsorbing colloid flotation. Phorate (*15–17*) and ddvp (*18*) are commonly used as vegetable, fruit, seed, and grain protectants. Both are cholinesterase inhibitors. The Food and Agriculture Organization and World Health Organization have recommended residue limits for pesticides used for the protection of grain; the maximum limit for ddvp on grain is 2 mg/kg.

The adsorbing colloid flotation technique has been found to be effective for removal of various inorganic substances from aqueous solutions. This technique involves the addition of a coagulant [alum or iron(III) nitrate] to produce a floc. The dissolved inorganic substances (metal ions or anion) are adsorbed onto the floc particle and coprecipitated with it. A surfactant is then added, adsorbs onto the floc particle, and renders it hydrophobic. When air is bubbled through the solution, the floc is adsorbed onto the rising bubbles and carried from the solution by the foam.

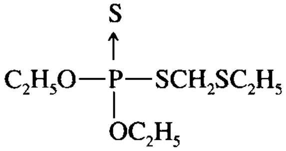
Applications of adsorbing colloid flotation for removal of organic substances are rare. Several dyes can be effectively removed from aqueous solutions by adsorbing colloid flotation (*19–21*). In the present work we also attempted to remove pesticides by adsorbing colloid flotation.

The structural formulas of ddvp and phorate are



$$(CH_3O)_2\overset{O}{\overset{\uparrow}{P}}-O-CH=CCl_2$$

ddvp



$$C_2H_5O-\underset{OC_2H_5}{\underset{|}{\overset{S}{\overset{\uparrow}{P}}}}-SCH_2SC_2H_5$$

phorate

EXPERIMENTAL

The apparatus for solvent sublation and air stripping consisted of a Pyrex column of 3.5 cm diameter × 45 cm high fitted with a rubber stopper at the bottom through which passed a fine fritted-glass gas dispersion tube and a sampling stopcock. A lipped side arm near the top of the column served as a foam outlet. Compressed air in a gas tank was used. The rate of airflow was adjusted and measured with a flow controller and readout system; the flow rate was checked with a soap-film flowmeter.

The adsorbing colloid flotation system was similar to that used for air stripping as described above except that the column was longer (60 cm in length).

Reagent-grade sodium lauryl sulfate (NLS, Wako Pure Chemical Industry, Japan) was used without further purification. Hexane (Merck reagent grade), ddvp, and phorate (Polyscience Co.) were used for sample preparation.

For the solvent sublation runs, NLS was added to the sample solution, the pH of the solution was adjusted, the solution was poured into the separation column, paraffin oil (30 mL) was added immediately, and the timer was started. The rate of airflow was maintained at 150 mL/min.

The procedure of air stripping was similar to that of solvent sublation except that no paraffin oil was added.

For the adsorbing colloid flotation runs, iron(III) nitrate was added to the sample solution, the pH was adjusted to produce the floc, phorate and ddvp were 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 rate of airflow was maintained at 120 mL/min.

All runs were made with 500 mL of test solution which contained 5 ppm ddvp and 5 ppm phorate. Analysis of ddvp and phorate in the aqueous sample was accomplished by extracting a sample solution (5 mL) with hexane (5 mL). Sodium sulfate was added to enhance the extracting efficiency and to decrease the period needed for phase separation. The hexane sample (4 μL) was injected into the gas–liquid chromatography column for analysis.

A gas–liquid chromatograph (Shimadzu GC-9AM) with a flame photometric detector (P filter 526 nm) was used. A data processor (Shimadzu C-R3A) was used for data analysis. A glass column, 2 m × 4 mm i.d., packed with 3% silicone OV-17 was used. The injection temperature, detector temperature, column temperature, and auxiliary temperature were 300, 300, 180, and 300°C, respectively; nitrogen (99.99% purity) was used as the carrier gas. The N_2 was further purified by passing it through a gas purifier (Alltech with Molecular Sieve 5 Å and indicating Drierite) and another gas purifier (Oxiclear oxygen-adsorbing gas purifier). The rates of flow of carrier gas, hydrogen, and air were maintained at 50, 60, and 60 mL/min, respectively.

Some solvent sublation and air stripping data were plotted as $\log_{10} C(t)/C_0$ versus time in minutes (linear plots) to display any deviations from first-order kinetics. All runs were performed at room temperture (approximately 25°C).

The pH of the solution was measured with a pH meter (Radiometer pH M83 Autocal).

RESULTS AND DISCUSSION

The effect of pH on solvent sublation of ddvp and phorate is shown in Table 1. Variation of the solution pH had almost no effect on the removal of ddvp and phorate by solvent sublation, presumably due to the molecular

TABLE 1
Effect of pH on Solvent Sublation[a]

		% Removal[b]		
pH	Compound	10 min	20 min	30 min
5.33	phorate	74.81 ± 2.38	91.61 ± 1.02	97.28 ± 0.59
7.00	phorate	75.71 ± 2.86	94.19 ± 1.27	98.52 ± 0.29
9.00	phorate	75.86 ± 0.86	92.25 ± 0.58	97.06 ± 0.28
5.33[c]	phorate	41.61 ± 2.09	50.77 ± 0.57	55.44 ± 1.51
5.33	ddvp	12.59 ± 0.28	18.81 ± 2.62	21.61 ± 0.75
7.00	ddvp	13.37 ± 2.31	20.88 ± 2.18	22.83 ± 1.30
9.00	ddvp	12.34 ± 2.84	21.46 ± 4.83	23.84 ± 2.67
5.33[c]	ddvp	6.38 ± 0.25	9.44 ± 0.15	10.57 ± 0.45

[a] Rate of flow of air = 150 mL/min.

[b] Average value and standard deviation of duplicate runs.

[c] Percent removal of air stripping.

structures, and hence the surface activity and volatility of the molecules are not affected by any pH variation. Therefore, all runs were performed at the original pH of the solution (5.33). The removal of phorate by solvent sublation was effective, with 97% removal in 30 min. The rate of removal of ddvp by solvent sublation (21% removal in 30 min) was much smaller than that of phorate, presumably due to the smaller volatility and the greater solubility of ddvp [solubility in water (*22*) for ddvp, 1.0%, and for phorate, 50 ppm].

The rates of removal of ddvp and phorate by solvent sublation and by air stripping are compared in Fig. 1. Neither air stripping nor solvent sublation of ddvp and phorate follow first-order kinetics. Similar phenomena were also observed on the solvent sublation of pentachlorophenol (*5*), alkyl phthalates (*23*), and polychlorinated biphenyls (*24*). The reason for such an observation was explained as due to a reverse mass transfer from the organic phase (paraffin oil) to the aqueous phase.

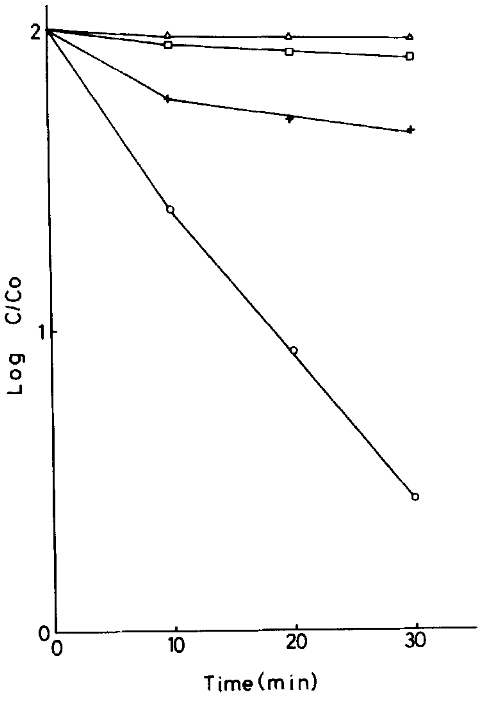


FIG. 1. Rate of removal of phorate and ddvp by air stripping and solvent sublation: (+) air stripping of phorate, (△) air stripping of ddvp, (○) solvent sublation of phorate, (□) solvent sublation of ddvp.

The rate of removal of ddvp and phorate by solvent sublation exceeds that by air stripping. The improvement in separation by solvent sublation is presumably due to the adsorption of surface-active pesticide on the surface of the bubbles. The surface-adsorbed pesticide and the pesticide in the vapor phase inside the bubble are carried into the organic layer on the top of the separation column during the solvent sublation process. Only the pesticide vapor inside the air bubble is removed by air stripping. This phenomenon has also been observed for solvent sublation and air stripping of other organic pollutants from aqueous solutions (*4*, *9*, *13*).

The effect of the rate of airflow on solvent sublation of ddvp and phorate was studied. The rate of removal increases somewhat with increasing flow rate from 120 to 150 mL/min, as expected. Any further increase of the airflow rate does not improve the rate of separation. The reason for such an effect is the increase in mean bubble radius as the flow rate increases. Smaller bubbles are more efficient for solvent sublation than are larger bubbles; they rise more slowly, which results in a greater period of contact with the solvent, and they have a larger ratio of surface to volume than do larger bubbles. The larger the surface area generated, the greater the number of sites available for adsorption, and consequently the more rapid is the rate of separation.

The effects of added salts, such as $NaNO_3$, on the solvent sublation of ddvp and phorate were studied; the presence of salts somewhat increases the rate of separation. The amounts of phorate and ddvp removed by solvent sublation were 80 and 20%, respectively, for a run of 10 min from a solution containing 0.3 *M* $NaNO_3$. Presumably the mechanism is the same as that which causes the widely used "salting out" effect in which organics are made less soluble in aqueous phases by the addition of salts, such that water molecules are bounded in shells of ion hydration, thus decreasing the amount of water available for solubilizing the organic. Similar effects were observed on the solvent sublation of naphthalene (*13*)

The effect of added ethanol (representative of a polar organic solute) on the rate of solvent sublation of ddvp and phorate is shown in Table 2. The rate of removal of ddvp increases with increasing concentration of ethanol, presumably due to a decrease in the size of the air bubble caused by the added ethanol; this means that the surface tension of the solution is decreased. The decrease in bubble size with decreasing surface tension of the solution may be explained by using the Young–Laplace equation (*25*); if the pressure inside the air bubbles which are freshly generated from the surface of the gas sparger is the same, the radius of the air bubble decreases with decreasing surface tension of the solution. The separation efficiency of phorate decreased significantly with increasing concentration of ethanol, as the solubility of the phorate was increased by the alcohol in solution.

TABLE 2
Effect of Ethanol on Solvent Sublation[a]

Ethanol (% by volume)	Compound	% Removal[b] 10 min	20 min	30 min
0.00	phorate	74.81 ± 2.38	91.61 ± 1.02	97.28 ± 0.59
0.10	phorate	58.20 ± 0.60	86.15 ± 0.58	96.37 ± 0.32
0.25	phorate	60.11 ± 1.28	82.81 ± 2.43	94.51 ± 1.42
0.50	phorate	50.70 ± 0.15	77.11 ± 3.50	90.36 ± 1.73
0.00	ddvp	12.59 ± 0.28	18.81 ± 2.62	21.61 ± 0.75
0.10	ddvp	17.88 ± 1.30	25.26 ± 0.78	41.53 ± 1.38
0.25	ddvp	26.89 ± 0.15	42.86 ± 4.16	48.61 ± 3.89
0.50	ddvp	31.53 ± 2.19	42.35 ± 1.88	50.26 ± 0.89

[a] Rate of flow of air = 150 mL/min, pH 5.33.

[b] Average value and standard deviation of duplicate runs.

The effect of NLS addition on the solvent sublation of ddvp and phorate was also studied. The separation efficiency increases with increasing NLS dose (from 0 to 30 ppm), presumably due to the decrease of the size of the air bubbles by the added surfactant, by which the surface tension of the solution is decreased. Over 82% of phorate and over 20% of ddvp were removed in 10 min when NLS (30 ppm) was also added to the solution before solvent sublation runs.

A series of experiments was performed to study the efficiency of iron(III) hydroxide as an adsorbing floc for ddvp. Various amounts of $Fe(OH)_3$ were added to the ddvp solution. The pH of the solution was adjusted to 6.5. Sodium lauryl sulfate was then added to coagulate the floc. The floc was removed from the solution by filtration. The concentration of ddvp in the filtrate was measured. The residual ddvp levels decreased with increasing dosage of floc at small concentrations; the residual ddvp levels reach a plateau [at a 100 ppm dose of iron(III)] with further addition of the floc.

The effects of pH on the adsorbing colloid flotation of ddvp and phorate with iron(III) hydroxide floc are shown in Table 3. Sodium lauryl sulfate was used as the collector and frother. The iron dosage was 100 ppm. The optimum pH for separation was 6.0, with 90% of phorate removal in 10 min. The removal efficiency decreased significantly at a pH less than 5.5 or greater than 7.0. At a pH less than 5.5, the precipitation of iron(III) hydroxide was incomplete. At a pH greater than 7.0, the adsorption of hydroxide anion on $Fe(OH)_3$ floc decreases the surface potential of the floc. This effect may cause the surface potential of the floc to be insufficiently positive for efficient anionic surfactant adsorption.

TABLE 3
Effect of pH on Adsorbing Colloid Flotation with $Fe(OH)_3$[a]

pH	Compound	% Removal 3 min	5 min	10 min
5.0	phorate	54.29	69.27	77.51
5.5	phorate	56.77	68.29	81.91
6.0	phorate	61.32	73.32	90.38
6.5	phorate	59.27	71.28	89.66
7.0	phorate	59.63	69.78	83.13
7.5	phorate	47.99	60.05	78.13
5.0	ddvp	14.06	16.13	18.82
5.5	ddvp	17.99	19.13	22.39
6.0	ddvp	19.08	20.26	24.32
6.5	ddvp	22.54	24.50	28.72
7.0	ddvp	8.20	12.85	15.56
7.5	ddvp	9.27	10.46	10.45

[a] $Fe(OH)_3$ = 100 ppm, NLS = 200 ppm.

The removal of ddvp by adsorbing colloid flotation with $Fe(OH)_3$ was poor. The floc was removed effectively from the aqueous solution by flotation at pH 6.0 and 6.5; however, over 70% of ddvp remained in solution. The poor separation of ddvp was presumably due to the incomplete coprecipitation (or adsorption) of ddvp with the $Fe(OH)_3$ floc, as indicated

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

NLS (ppm)	Compound	% Removal 3 min	5 min	10 min
100	phorate		58.45	73.83
150	phorate		61.60	80.59
180	phorate	58.54	72.66	87.14
200	phorate	59.27	71.28	89.66
220	phorate	60.35	72.51	89.38
100	ddvp		11.33	16.17
150	ddvp		13.25	16.38
180	ddvp	17.69	22.00	28.90
200	ddvp	22.54	24.50	28.72
220	ddvp	18.53	22.79	26.65

[a] $Fe(OH)_3$ = 100 ppm, pH 6.5.

by the results of the coprecipitation experiments. The incomplete coprecipitation of ddvp with the floc was presumably due to the high solubility of ddvp in water.

The effect of the NLS dosage is shown in Table 4. The removal efficiency increased with increasing NLS dosage. However, the separation of ddvp was poor, even by flotation with 220 ppm of NLS.

CONCLUSION

Phorate, a hydrophobic organophosphorus pesticide, can be effectively removed from aqueous solution by solvent sublation. Effective separation with over 97% phorate removal in 30 min was achieved by this technique. The rate of removal of phorate by air stripping is less rapid than that by solvent sublation. The rate of separation of phorate by solvent sublation increases with an increasing airflow rate, ionic strength of solution, and added surfactant. Adsorbing colloid flotation with $Fe(OH)_3$ floc and NLS is also effective; 90% of phorate can be removed in 10 min.

The removal of a hydrophobic organic solute from an aqueous solution by adsorbing colloid flotation has been little investigated. Based on our present work, we suggest that adsorbing colloid flotation may be applicable for removal of hydrophobic organic pollutants from aqueous solutions. Such pollutants, which can be removed by solvent sublation, may also be removed by adsorbing colloid flotation at a greater rate of separation and with no organic phase required.

The removal of ddvp by solvent sublation is poor. Adsorbing colloid flotation with $Fe(OH)_3$ floc and NLS is also ineffective in removing ddvp from aqueous solution. Presumably the much greater solubility of ddvp than phorate makes ddvp more difficult to remove by adsorptive bubble separation techniques.

Acknowledgment

We thank the National Science Council of the Republic of China for support.

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Received by editor September 17, 1991
Revised March 16, 1992