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Removal of Traces of Pentachlorophenol from Aqueous Acidic Solutions by Solvent Extraction and Solvent Sublation

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Abstract

The removal of pentachlorophenol (a hydrophobic compound of low vapor pressure) from aqueous acidic solutions was studied using solvent sublation (a surface chemical technique) and solvent extraction. Both methods gave appreciable removals in highly acidic solutions (pH = 2.5), but solvent sublation had the added advantage of minimal phase contact of the organic solvent with water and increased removals under certain circumstances. Solvent sublation was also found to be more effective than conventional fine bubble aeration. The removal of pentachlorophenol (PCP) was considerably smaller at pH's near the pK_a of PCP. PCP removal by solvent sublation was enhanced by increasing ionic strength and also by the presence of small amounts of an ionic surfactant in the aqueous phase. The technique of solvent sublation was tried on an actual wastewater sample from a wood preserving industry. pH adjustment, removal of suspended solids, addition of sodium chloride, and subsequent solvent sublation into mineral oil reduced the PCP concentration in the aqueous waste by 99.7%.

INTRODUCTION

Adsorptive bubble separation techniques have been known to be quite useful in the removals of hydrophobic (and therefore surface-active) compounds from aqueous solutions (*5*, *11*). These techniques take advantage of the ability of compounds to adhere (adsorb) at the air–water

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interfaces provided by fine air bubbles rising through aqueous columns. Ions, precipitates, ion-surfactant complexes, and hydrophobic molecules (e.g., chlorinated insecticides, PCBs) are amenable to removal from aqueous solutions using several of these techniques. Foam fractionation involves the removal of ionic species by forming ion-surfactant complexes which are then raised to the foam phase atop the bulk solution on the air-water interface of the rising gas bubbles generated at the bottom of the column. Foam fractionation is used mainly to remove ionic species and requires a large surfactant concentration to maintain a stable foam. Solvent sublation, on the other hand, is useful for the removal of both ionic species and hydrophobic molecular species and requires only a stoichiometric amount of surfactant (for the removal of ionic species) or no surfactant at all (for the removal of naturally hydrophobic molecules) (*5, 14*). In solvent sublation, materials are raised to the top of the aqueous section by attachment to the air-bubble interface where the "sublate" (i.e., the material carried by the bubble) is extracted into an immiscible floating organic solvent. Solvent sublation is also capable of removing materials which are volatile, the sublates being carried almost exclusively in the vapor phase of the air bubbles. Materials which are not appreciably volatile but display high hydrophobic character (thereby aggregating at the air-water interface of the rising bubbles) can be transported simultaneously in the adsorbed phase on the bubbles and in the vapor phase inside the bubbles (*9, 17*). Thus solvent sublation is a considerable improvement over a conventional fine bubble aeration process (*12*). Solvent sublation is also more useful than solvent extraction, where also two liquid phases are in contact. In solvent extraction the extent of removal is limited by an equilibrium condition (a partition coefficient for the solute between the two solvents) whereas in solvent sublation, because of the continuous unidirectional transport of the material across the aqueous-solvent interface by the air bubbles, the removal can sometimes exceed that of solvent extraction. Thus solvent sublation may couple the mechanisms of foam fractionation, solvent extraction, and air stripping to remove not only surface active ionic species but also slightly surface-active and low volatile hydrophobic molecules.

Wilson and coworkers have reported much success in the removal of various hydrophobic compounds (methyl chloroform, dichlorobenzenes, polychlorinated biphenyls, pesticides such as endrin, lindane, aldrin, alkyl phthalate esters, and polynuclear aromatic hydrocarbons) from aqueous solutions using the process of solvent sublation (*4, 9, 11, 15, 17*). We recently reported on the improved efficiency of solvent sublation over conventional fine bubble aeration for the removal of compounds of low vapor pressure and high hydrophobic character (*12*). We also investigated the effects of typical cosolutes (ethanol, inorganic salts, and long chain alkyl ionic surfactants) on the separation of 1,2,4-trichlorobenzene from aqueous solution into mineral oil using solvent sublation (*12*). An extensive investigation into the effects of highly soluble organics (e.g., alkyl alcohols) upon solvent sublation of chlorinated organics has been recently reported by Wilson and coworkers (*4*). Grieves et al. (*7*) reported on the desirability of solvent sublation over solvent extraction and foam fractionation in the removal of phenol from alkaline aqueous solutions.

Models for solvent sublation of volatile compounds, nonvolatile surface-active species, and volatile surface-active compounds are available in the literature (*5, 9, 11, 12, 17, 18, 21*).

Properties of PCP and Available Treatment Alternatives for PCP Removal from Wastewaters

Phenol and its various halogenated derivatives are of significance as water pollutants, some of which are classified as priority pollutants by the U.S. Environmental Protection Agency. The most toxid of these are the chlorophenols. In general, the volatility of chlorophenols decreases and their melting and boiling points increase as the number of chlorine atoms increases. Similarly, their hydrophobic character (as characterized by the octanol–water partition coefficients) and the degree of ionization in aqueous solutions increase as the number of chlorine atoms increase (*2, 20*).

Pentachlorophenol is used as a bactericide, fungicide, and slimicide primarily for the preservation of wood and wood products. As a chlorinated compound, its biological properties have resulted in its use as an herbicide and insecticide. Its various properties are listed in Table 1. PCP is a slightly soluble, relatively nonvolatile compound of very high hydrophobic character and hence of appreciable surface-active nature. It is a point source contaminant at wood preservation sites and has been noted to be a persistent compound in warm, moist soils [8]. Unlike phenol, which undergoes chemical or biological oxidation, PCP is resistant to such transformations but can undergo photochemical oxidation to release other chlorinated compounds. It may also be noted from Table 1 that the safe concentration of PCP in water is set at 0.021 mg/L as compared to its aqueous solubility of 14–19 mg/L. In some cases PCP solubility has been known to increase to larger values due to a solubilizing effect caused by oils and emulsions present in wastewater. It thus becomes extremely important to treat wastewaters to remove PCP

TABLE 1
Properties of Pentachlorophenol[a]

Property	Value
Molecular weight	266.35
Density (g/mL)	1.978
Melting point (°C)	190–191
Boiling point (°C)	309–310
Aqueous solubility (20–30°C) (mg/L)	14–19
Vapor pressure (20–100°C) (mmHg)	0.00011 to 0.12
Ionization constant, K_a	1×10^{-5}
Aqueous solubility of the sodium salt (mg/L)	79 at pH 5.0 4000 at pH 8.0
Volatility of PCP with steam at 100°C (g PCP/100 g steam at 1 atm)	0.167
No-adverse-effect-level-concentration in drinking water (mg/L)	0.021
Octanol/water partition coefficient	$1 \times 10^{5.01}$

[a] U.S. EPA, *Ambient Water Quality Criteria for PCP,* EPA/440/5-80-065, October 1980. National Research Council, *Drinking Water and Health,* National Academy of Science, Washington, D.C., 1977. A. Bevenue and H. Heckman, *Residue Rev.*, *19,* 83–134 (1967).

before they are discharged into streams and estuaries. PCP has been known to adsorb onto biofloc in activated sludge operations, which creates an added hazardous waste problem. Incineration of the sludge results in the release of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, a thermal degradation product of PCP, and hence is not often recommended as a treatment operation unless very high temperature incinerators are used. Arsenault (*1*) discussed the environmental fate of PCP from wood-preserving industries while Buhler et al. (*3*) discussed its occurrence in sewage and water. A rather comprehensive evaluation of treatment alternatives for PCP removal from wood-preserving industrial wastewater was reported by Wallin et al. (*19*). They evaluated (on a laboratory as well as pilot scale) six treatment technologies (adsorption, bio-oxidation, chemical oxidation, coagulation, extraction, and pH adjustment) and suggested that two combined technologies were most useful:

(1) pH adjustment and subsequent adsorption onto bentonite clay or resins;
(2) pH adjustment and subsequent solvent extraction into a mixture of #2 fuel oil and a cosolvent, amyl alcohol

All experiments were conducted at pH = 4.0, and almost 99% removal efficiencies were reported.

Extraction involves intimate mixing between the two phases (aqueous and organic solvent) and hence involves considerable dissolution of the solvent and/or cosolvent in water, the separation of which is an added problem. Solvent sublation, on the other hand, requires minimal contact between the phases and has the added advantage of achieving a larger removal than simple extraction. This promising technique was therefore evaluated as a modification of solvent extraction, the results of which are reported in subsequent sections of this paper.

EXPERIMENTAL

The solvent sublation studies were carried out in a Pyrex glass column 100 cm high and of 5 cm outer diameter. A porous silica sparger, fitted at the lower end of the column, produced fine air bubbles of average diameter 0.05 cm in distilled water. The overall apparatus is shown in Fig. 1. The air flow rates used were 1.2 and 2.8 mL/s. The lower flow rate was chosen as an ideal value since bubble sizes were more or less uniform at that flow rate, whereas a large number of bubbles of large diameter were observed at 2.8 mL/s. The initial volume of the aqueous solution was 1460 mL in most of the experiments, and the organic liquid volumes were 20 to 80 mL as described in the results section.

The solvent extraction studies were conducted in a 500-mL separatory funnel with 400 mL aqueous solution and 5 to 20 mL organic liquid. Extraction equilibrium was achieved in a matter of a few minutes.

The organic solvents used were paraffin oil, 1-octanol, and hexane (all from Fisher Scientific). The pure pentachlorophenol sample was supplied by Sigma Chemical Company.

Saturated aqueous solutions of PCP were prepared by overnight stirring of PCP in distilled water followed by filtration to remove any suspended solids. The solutions so prepared had a pH of 4.0 ± 0.5 and had concentrations of PCP in the range 5–12 mg/L at 25°C. The pH was adjusted using 1 *N* NaOH or 1 *N* HCl, and the ionic strength was adjusted with HCl and/or NaCl. The pH was measured using a Cole Parmer Digisense pH meter.

A solvent sublation experiment was started by first filling the column with distilled water and adjusting the air flow rate to the desired value. The water was then drained off, the column was quickly filled with the

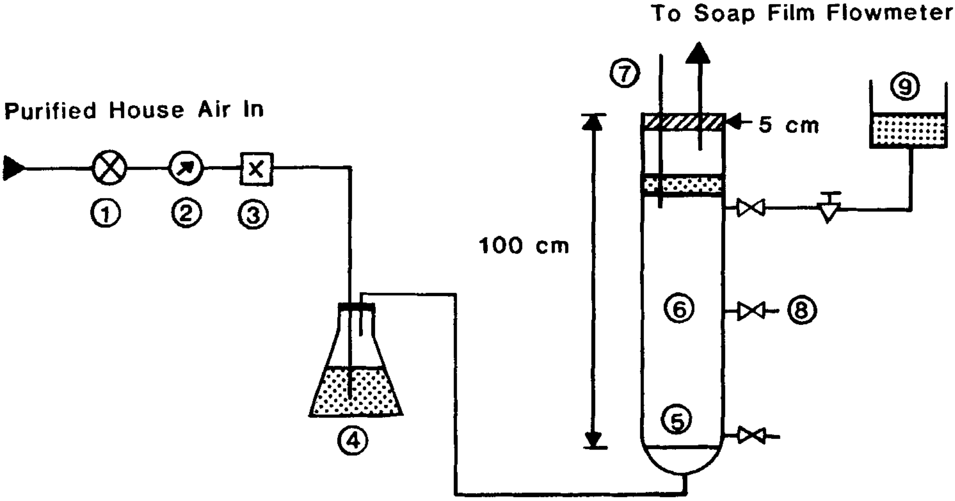


FIG. 1. Diagram of the solvent sublation apparatus: (1) pressure regulator, (2) pressure gauge, (3) micrometer needle valve, (4) saturator, (5) fine fritted disk (30% porosity), (6) sublation column (Pyrex glass), (7) thermometer, (8) sampling port, (9) influent feed tank (for continuous operation).

experimental solution, and the organic liquid poured on top. An initial (time zero) 4 mL of the sample was drawn out of the midport, 1 mL pesticide grade hexane added to it, and the solution stored in a Pierce Septum vial. The solutions were well shaken to ensure complete extraction of PCP into hexane for analysis on the gas chromatograph. Samples were similarly withdrawn from the midport and the PCP hexane extracted at designated intervals. This hexane extraction technique has been used frequently by us (*12*) and by others (*4, 9, 15, 17*) for analysis of chlorinated compounds, and it is known to be fairly sensitive and reliable. All experiments were conducted at room temperature, 25 ± 1°C.

The analysis of PCP in the hexane extract was accomplished on a Hewlett Packard 5890A Gas Chromatograph equipped with a Ni^{63} Electron Capture detector. The oven temperature was 210°C, the injector temperature was 250°C, and the detector temperature was 300°C. A HP Series 530 capillary column was used; it had a length of 12 m, an internal diameter of 0.2 mm, and was coated with crosslinked methyl silicone (OV-1). Prepurified nitrogen of 99.99% purity was used as the carrier gas. A standard calibration curve was obtained using PCP dissolved in pesticide-grade hexane (8 mg/L PCP in hexane was used for the purpose). The detector had a linear range of 4 to 56 ng PCP. Hamilton 701N series

TABLE 2
Some Relevant Properties of the Organic Solvents

Solvent	Molecular weight	Density (g/mL)	Boiling point (°C)	Aqueous solubility (mg/L)	Volatility
Hexane	86.18	0.66	69.0	12.3	Highly volatile
1-Octanol	130.23	0.82	194.4	586	Partly volatile
Mineral oil	200 ± 30	0.80	>225	Insoluble	Nonvolatile

10 μL syringes were used to inject the samples into the GC. The chromographic peaks were recorded and integrated using a HP 3392A Computing Integrator.

RESULTS AND DISCUSSION

The pK_a of PCP is reported to be 5.0. Hence, above pH = 5.0, PCP exists both as the undissociated molecule and as the dissociated phenoxide ion which is not easily extractable into various organic solvents. Most previous experiments dealt with extraction at a pH of 4.0 or near the pK_a. In the experiments reported here the pH was kept well below 5.0 to ensure that all PCP existed as undissociated molecules and also to show the effects of pH on both extraction and sublation.

Solvent Extraction Experiments

A preliminary series of extraction experiments was conducted to determine the most desirable solvent for sublation of PCP. The solvents chosen and their properties are given in Table 2. The choices of solvents were based primarily on the aqueous solubility of the solvent, the volatility of the solvent, and its affinity for PCP. The results of the various experiments are summarized in Table 3. The extent of extraction was good for all the three solvents tested, wih 1-octanol giving the highest extractive efficiency, but as shown in Table 2, it has the largest aqueous solubility. Hexane also gives good extraction and is less soluble in water, but it is highly volatile. From Tables 1 and 2 it is also clear that both 1-octanol and hexane have solubilities in water greater than that of the contaminant of interest (PCP) and would therefore be counterproductive

TABLE 3
Solvent Extraction of PCP into Various Solvents (aqueous volume = 400 mL)[a]

Experiment no.	Organic solvent used	Organic solvent to aqueous volume ratio	$(\text{pH})_i$	$(\text{pH})_f$	% PCP removed from the aqueous phase
1	Mineral oil	1:20	2.35	2.50	95.8
2	Mineral oil	1:40	2.50	2.56	90.6
3 (a)	Mineral oil	1:80	2.54	2.57	86.7
3 (b)[b]	Mineral oil	1:80	2.59	2.60	82.0
4	Mineral oil	1:80	4.83	5.39	44.1
5	Hexane	1:80	2.80	2.90	88.3
6	1-Octanol	1:80	2.55	2.56	95.5

[a] $(\text{pH})_i$ denotes the pH of the initial solution and $(\text{pH})_f$ that after extraction of PCP.
[b] 1.56×10^{-5} *M* HTA-Br surfactant was added to the aqueous solution.

for use on a large scale. If solvent recovery is a consideration, then hexane with its low boiling point would be a good choice. Mineral oil is an economical solvent, and it has properties similar to #2 fuel oil found commonly in wood-preserving operations. It has negligible solubility in water and is also nonvolatile; both these properties are extremely important for its use in solvent sublation. In addition to being cheap, mineral oil is also incinerable in high temperature incinerators (upward of 4000°C to degrade toxic compounds completely), which is an EPA recommended method of disposal of chlorinated organics-containing wastes.

The effect of the phase volume ratio is apparent; the percent removal increases from 86.7 at 1:80 ratio to 95.8 at 1:20 ratio. The effect of the initial pH of the aqueous solution upon the extraction of PCP is more remarkable; with a phase ratio of 1:80 at pH 2.54 the percent removal is 86.7 as compared to only 44.1 at pH 4.83. This may be due to the low extractability of the pentachlorophenolate ion and the high extractability of the undissociated pentachlorophenol. This argument is strengthened by the observation that at a strongly acidic pH (2.5 ± 0.2) the initial and final pH do not show a large difference whereas at pH 4.83 (which is near the $\text{p}K_a$ of PCP) the initial and final pH do show a considerable difference.

Experiment 3(b) shows the effect of the presence of a cationic surfactant, hexadecyltrimethylammonium bromide, upon the extraction of PCP into mineral oil. This was done to enable comparison with solvent sublation and foam fractionation. The effect is rather negligible; a 3% decrease in extraction was observed.

Solvent Sublation

Due to the reasons mentioned earlier and the results on extraction, mineral oil was chosen as the organic solvent for solvent sublation.

The effects of pH were rather similar to those obtained with extraction, except that the degree of PCP removal was generally smaller than that obtained by extraction. Of course, the sublations were carried out for only 2 h in most cases, representative of a reasonable air-to-water ratio of 6:1 at an air flow rate of 1.2 mL/s. If sublations were carried out for longer periods of time, a greater degree of removal might be obtained. It may also be noticed from the results in Table 4 that the initial rate of sublation increases with a decrease in pH (Experiments 7, 8, and 9). The results indicate that solvent sublation is indeed capable of giving PCP removals of the order of or sometimes exceeding that of solvent extraction. The reason for such a statement also seems justified in light of earlier observations by us and others (*5, 7, 12*) that solvent sublation is a rate-controlled process whereas solvent extraction is an equilibrium-controlled process.

The only difference between solvent sublation and conventional fine bubble aeration is the presence of a solvent layer atop the aqueous section in the former process. The solvent layer in sublation helps to capture any material adsorbed on the air-water interface of the rising air bubbles in addition to the material that is carried within the vapor phase of the bubbles. In conventional fine bubble aeration the adsorbed material continuously remixes and redistributes within the aqueous section as the bubbles burst at the top of the aqueous section, and hence one gets removal of the material carried within the vapor phase. This effect is more pronounced for compounds of very low volatility and high hydrophobic character (e.g., chlorinated pesticides, polychlorinated biphenyls, chlorobenzenes, and polynuclear aromatic hydrocarbons) and has been explored in greater detail by Valsaraj et al. (*12*) and by Huang, Valsaraj, and Wilson (*9*). The same effect is also evident for PCP removal when Experiments 9 and 10 are compared (see Table 4). The extent of removal increases from 30.7% in 2 h for simple aeration to 82.4% by solvent sublation (see also Fig. 2).

Unlike earlier observations for chlorinated benzenes (*12*), we observed a slight effect on the sublation efficiency by changing the organic to aqueous volume ratios from 1:70 to 1:18; the extent of removal in 2 h increases from 77.3 to 82.4% (see Table 2, Experiments 9 and 12). The effect is smaller than that for solvent extraction. Grieves et al. (*7*) also noticed a similar effect in the solvent sublation of phenol in alkaline aqueous solutions. These observations indicate that an extraction

TABLE 4
Solvent Sublation of Pentachlorophenol from Aqueous Solutions into Mineral Oil (aqueous volume = 1460 mL)

Experiment no.	Process	Mineral oil to aqueous volume ratio	Air flow rate (mL/s)	$(pH)_i$	$(pH)_f$	Percent PCP removed	
						In 1 h	In 2 h
7	Solvent sublation	1:18	1.2	4.68	5.20	36.7	47.0
8	Solvent sublation	1:18	1.2	3.00	3.25	57.4	82.0
9	Solvent sublation	1:18	1.2	2.00	2.20	75.7	82.4
10	Simple aeration[a]	—	1.2	2.67	2.70	12.8	30.7
11	Solvent sublation[b]	1:18	2.8	2.61	2.64	77.0	85.0
12	Solvent sublation	1:73	1.2	2.58	2.59	67.4	77.3
13	Solvent sublation[c]	1:70	1.2	2.60	2.58	94.4	95.0
14	Solvent sublation[d]	1:70	1.2	2.38	2.40	91.5	93.9

[a] A run made without any mineral oil on top. At the end of the experiment a thin film of PCP was found floating on top of the aqueous solution.

[b] 50 mL mineral oil was replaced with fresh mineral oil after 2 h, and removal was 87.7% in 2½ h and 91% in 3 h.

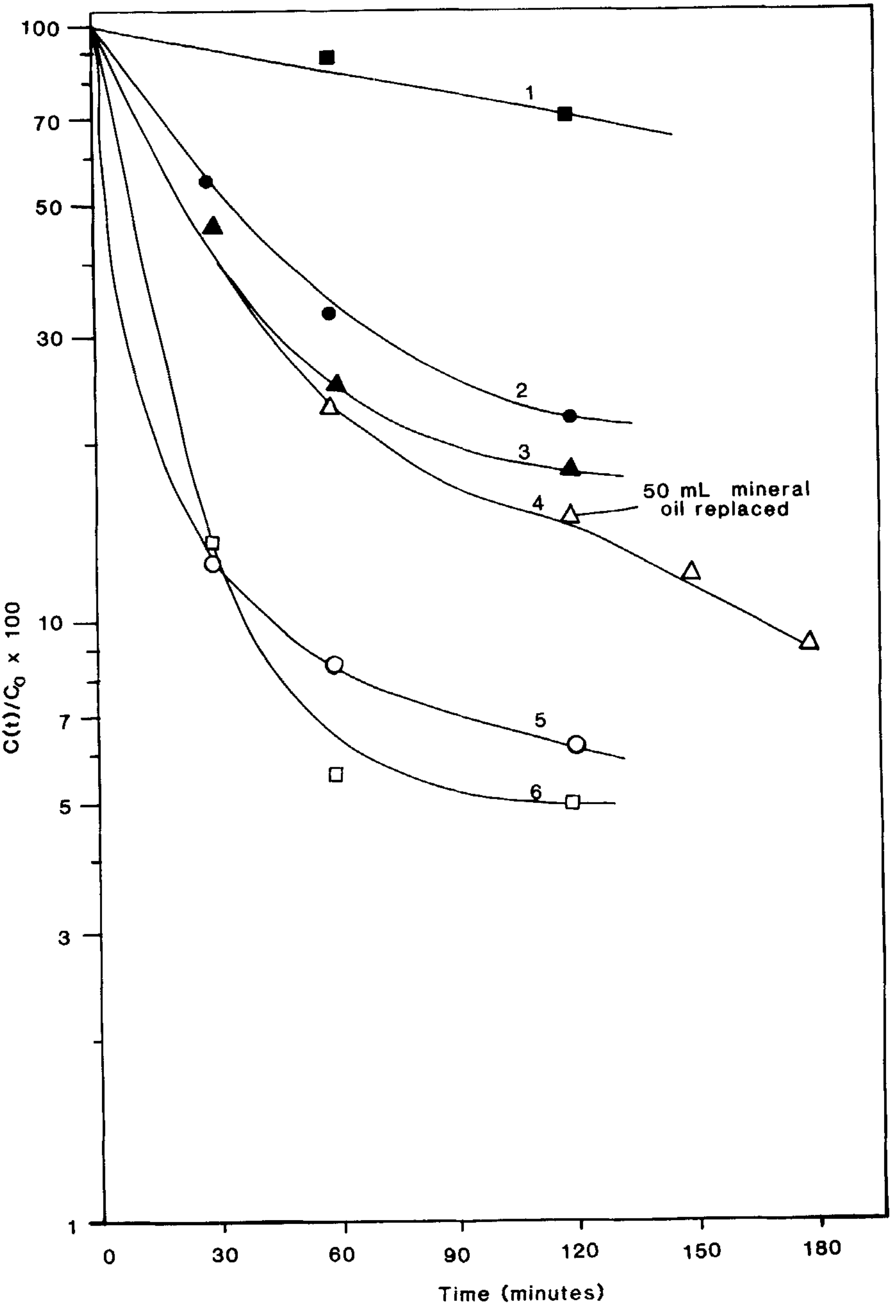
[c] Solvent sublation with 1.56×10^{-5} *M* HTA^+-Br^- surfactant. The first 30 min produced a large volume of stable foam, and the foaming subsided gradually after 40 min. A 3-cm height of foam was present above the solvent layer throughout the rest of the experiment. Bubble sizes were uniformly small.

[d] Solvent sublation with 10% w/v of NaCl in the aqueous solution. Bubble sizes were uniformly small.

mechanism coupled with simple bubble transport across the solvent/aqueous interface seems to be responsible for the removal of phenolic compounds from aqueous solution. Unlike solvent extraction where the solvent effect cannot be negated (without changing the solvent volume), in solvent sublation (being a rate-controlled process) such effects may be overridden to some extent by simply increasing the air flow rate and still maintaining a low volume of organic solvent.

Experiments 9 and 11 compare the effect of increasing the air flow rate upon the extent of removal of PCP by solvent sublation. The results show that the increase in removal is quite small. Similar effects were observed by Tamamushi and Wilson (*15*) in the removal of alkyl phthalate esters by solvent sublation. The reason for such an effect is the increase in mean bubble radius as the air flow rate increases. In our column the mean bubble diameter was 0.05 cm at 1.2 mL/s as compared to 0.15 cm at 2.8 mL/s. Large bubble sizes are detrimental to the sublation process for three important reasons. First, large bubbles mean a smaller air–water interfacial area per unit volume of air through the column (the area to volume ratio is $3/r$, where r is the average bubble radius). Second, larger bubbles have higher rise velocities and hence have shorter residence times in the column (for example, a 0.05-cm diameter bubble has approximately a 10 times lower rise velocity than a 0.15-cm diameter bubble in aqueous solution). The two effects combined reduce the extent of mass transfer to rising bubbles in the column; to some extent this may be offset by the higher flux of air through the column. Third, the large air flow rates give rise to a high degree of axial dispersion which has also been found to impair the performance of the sublation process (*5*). The overall conclusion is that the advantages gained by increasing air flow rates through the column will be minimal unless the bubble sizes are kept as small as possible. One way of accomplishing this has been described recently by Wilson and Pearson (*20*) and involves recirculation of water over the sparger so as to shear the bubbles off the sparger as soon as they are formed. They reported a considerable improvement in the efficiency of the process. This is worth considering on a large-scale process.

The primary aim of solvent sublation is to maximize the efficiency of the removal of PCP with as small an amount of organic solvent as possible. As explained earlier, we observed that at an air flow rate of 1.2 mL/s at pH 2.5 for a phase volume ratio of 1:73, the efficiency of removal for 2 h of sublation is only 77.3% as compared to 86.7% for a phase volume ratio of 1:80 by extraction. This is a general observation that at



100
70
50
30
10
7
5
3
1
C(t)/C$_0$ x 100
0
30
60
90
120
150
180
Time (minutes)
1
2
3
4
5
6
50 mL mineral oil replaced

low air flow rates the sublation efficiency is generally smaller than for extraction unless sublation is carried out for longer periods of time. Recently several authors (*4, 9, 12, 15*) have reported that there are other ways of increasing the separation efficiency of sublation processes at low air flow rates.

The first method is to increase the ionic strength of the solution by the addition of inert electrolytes like NaCl or KCl (*9, 12*). Increasing the ionic strength of the aqueous solution helps in two ways. First, the presence of salts at the air–water interface introduces an energy barrier for bubble coalescence and hence coalescence will be reduced. The bubble sizes therefore remain uniformly small. Second, the presence of inorganic salts gives rise to a so-called "salting out" effect which decreases the number of water molecules available for solubilizing the hydrophobic organic. The two effects together give rise to an increased separation rate by sublation. This is demonstrated by Experiment 14 where 94% removal of PCP was obtained by the addition of 10% w/v NaCl as compared to 77.3% removal without any NaCl present in the aqueous solution.

The second method is to add a small amount of an ionic surfactant to the aqueous solution (*12*). Here also the effect is mainly to decrease the bubble size and prevent the bubbles from coalescing. The bubbles which have ionic surfactants adsorbed on their surface provide an electrical barrier to coalescence. This "skin" around the bubble may reduce the extent of diffusion of the hydrophobic across the boundary layer (*22*), but the increased surface area made available by decreased bubble size apparently more than compensates for such effects (*6*). Hence the overall effect is to increase the removal rate. Experiment 13 proves the point. 1.56×10^{-5} *M* cationic surfactant (hexadecyltrimethylammonium bromide) was added to the solution and the removal increased to 95% in 2 h. The only problem was that a large amount of foam was formed for the first 30 min of the run; this had to be removed periodically at the top of the column. This may be a nuisance for a large-scale process. This

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FIG. 2. Removal of pentachlorophenol from aqueous solutions at pH = 2.5. 1:70 ratio of volumes of mineral oil to aqueous solutions used in all the sublation experiments unless otherwise noted. Air flow rate = 1.2 mL/s. (1) Fine bubble aeration (no mineral oil used). (2) Solvent sublation with 1:70 mineral oil to aqueous volume ratio. (3) Solvent sublation with 1:18 mineral oil to aqueous volume ratio. (4) Solvent sublation with 1:18 mineral oil to aqueous volume ratio, air flow rate = 2.8 mL/s, 50 mL mineral oil replaced after 2 h to show effects of backmixing from the mineral oil layer. (5) Solvent sublation with 10% w/v NaCl in aqueous phase. (6) Solvent sublation with 1.5×10^{-5} *M* hexadecyltrimethylammonium bromide in the aqueous phase.

situation may be avoided by using an antifoaming agent (e.g., 1-octanol) as the organic solvent instead of mineral oil. However, the presence of surfactant in the aqueous solution may also help in removing any phenolate ion as an ion-surfactant complex (HTA-phenolate complex) and thus would provide a way of extending the viable pH range even to alkaline regions. This type of ion flotation of alkaline solutions of phenolic compounds was demonstrated by Grieves et al. (*7*) and by Valsaraj and Wilson (*17*). The effect of surfactant as far as extraction was concerned was quite minimal (Experiment 3b, Table 2).

An actual wastewater sample is likely to have a high ionic strength and also some surfactant associated with the waste, both of which would act favorably to increase the separation of PCP by solvent sublation.

Inspection of Fig. 2 shows that the removal of PCP from aqueous solution by solvent sublation does not seem to follow first-order kinetics, especially as the rate of removal increases. The reason for such an observation may be explained as due to a reverse mass transfer from the organic to the aqueous phase; the rate at which this happens is initially very small and then becomes very important as the extent of removal increases. Slow, continuous removal and replacement of the organic solvent may help to reduce the effect. This argument is strengthened by Experiment 11 (Curve 4 in Fig. 2) which shows the effect of replacing 50 mL of mineral oil after 2 h sublation; evidently the reverse mass transfer is responsible for the leveling out of the curves. The above explanation is based on earlier observations of an identical nature in the solvent sublation of polychlorinated biphenyls and alkyl phthalate esters from aqueous solutions into mineral oil (*15, 17*).

Removal of PCP from an Actual Wastewater Sample

Since sublation was successful in reducing PCP concentrations in simulated wastewater, some trial runs were attempted on an actual wastewater sample obtained from a woodpreserving industry in northeastern Oklahoma. The wastewater obtained was first separated from the oil layer which was found floating on top. The pH of the solution was 2.9. The first experiment was conducted with the raw wastewater sample without any adjustment of pH or pretreatmnet. The solution contained a large amount of suspended solids (nonsettleable), had a dark color, and had an oily odor. The experimental sublation was done with 500 mL of the solution and 20 mL of mineral oil, thus giving a phase ratio of 1:25. The pH was 2.9 and the air flow rate was 1.5 mL/s. 4 mL of the sample was withdrawn at designated intervals and the PCP was extracted into 1

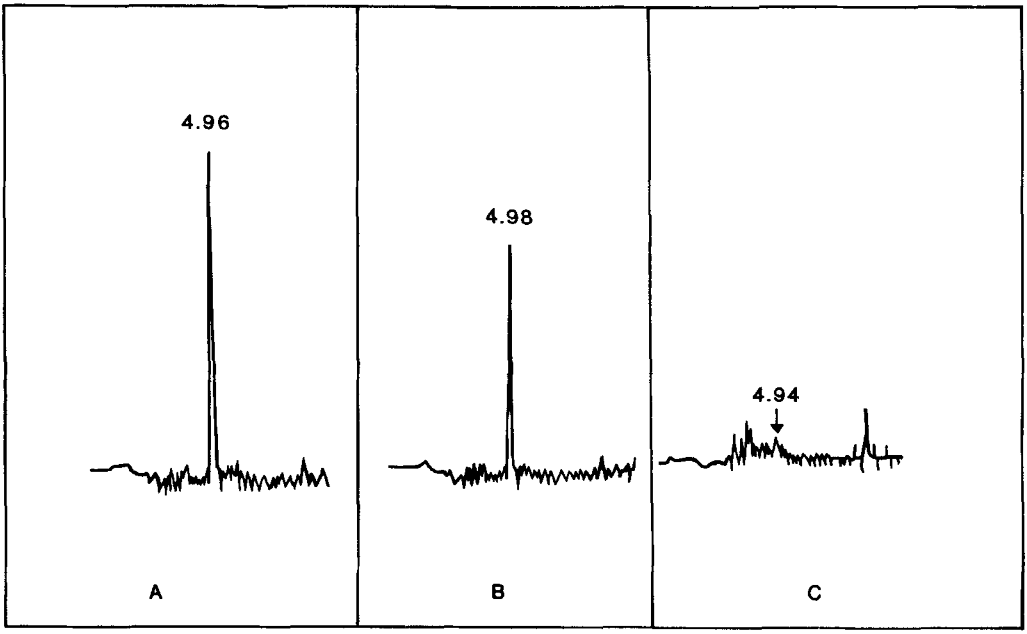
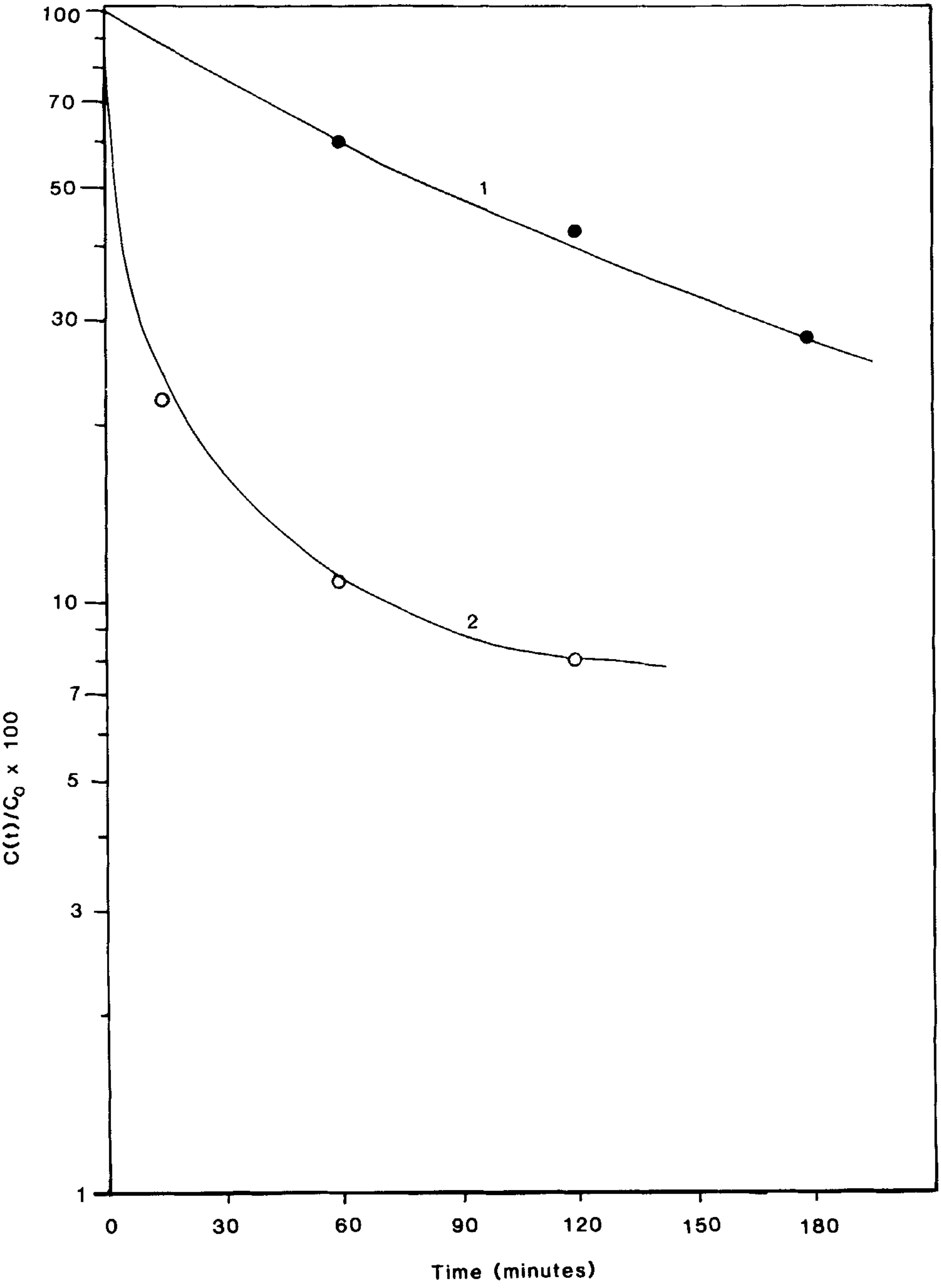


FIG. 3. Gas chromatographic tracings of hexane extracts at various stages of sublation of the raw wastewater. HP 5890A Gas Chromatograph with ^{63}Ni ECD used. Oven temperature = 210°C, injector temperature = 250°C, detector temperature = 300°C. A 12-m capillary column of i.d. 0.2 mm and coated with crosslinked methyl silicone was used. Prepurified nitrogen flow rate (total) = 76 mL/min, with a split ratio of 200:1. (A) Solvent sublation of raw wastewater, t = 0 (1 μL extract). (B) Solvent sublation of raw wastewater, t = 180 min (1 μL extract). (C) 5 μL extract of the treated wastewater after pH adjustment and subsequent solvent sublation for 120 min.

mL of hexane for analysis on the gas chromatograph. The initial PCP concentration was 13.6 mg/L in the aqueous solution, which was reduced to 3.8 mg/L in 3 h. Gas chromatographic tracings of 1 μL hexane extracts at the start and 3 h into the experiment are shown in Fig. 3. A 10-cm height of foam persisted above the solvent layer, presumably the result from some surfactants being associated with the wastewater. The extent of removal was only 72% for an air:water ratio of 1:32 at an air flow rate of 1.5 mL/s and a phase ratio of 1:25. This disappointing removal (as shown in Fig. 4) was probably due to the fact that most of the air introduced into the column was used for the flotation of suspended solids, grease, and oily materials from the aqueous solution which formed a scum at the top of the column in the foam. We also noticed that the aqueous solution was still dark in color at the end of the experiment and was not completely


100
70
50
30
10
7
5
3
1
0
30
60
90
120
150
180
1
2
C(t)/C$_0$ x 100
Time (minutes)

cleared of the nonsettleable materials. In spite of all these interferences a 72% removal of PCP from the aqueous sample is, we feel, a satisfactory one, even though the air-to-water ratio is quite large.

In order to enhance the removal, the raw wastewater was first subjected to a pH adjustment to 2.3 by adding 1 *N* HCl. The ionic strength of the solution was also adjusted by the addition of 5% w/v NaCl. This resulted in the settling of most of the suspended impurities as a dark material which was filtered. The resulting solution had its PCP concentration reduced by 95%; presumably most of the PCP was removed by being adsorbed onto the separated floc. A reduction of 80% PCP on pH adjustment to 4.0 was reported by Wallin et al. (*19*). The treated solution had a PCP concentration of 0.45 mg/L. 500 mL of this solution was subjected to solvent sublation using mineral oil (a phase ratio of 1:20) at an air flow rate of 1.5 mL/s. The rate of removal was considerably faster than that for the raw wastewater as shown in Fig. 4. A further reduction of 92% was observed in 2 h sublation which corresponds to a concentration of 0.04 mg/L for an air-to-water ratio of 21.1 at a phase volume ratio of 1:20. The solution had also changed remarkably in color and odor. The final PCP concentration was thus 0.3% of its initial value in the raw wastewater. A gas chromatographic tracing of 5 μL hexane extract of the final solution is shown in Fig. 3. The increased rate of removal by sublation in the second experiment can be due to several factors, viz., the removal of interferences from suspended solids, increased ionic strength, reduced pH, and also reduced PCP concentration at the start of the sublation. Nevertheless, the experiment does indicate that solvent sublation may be used as a tertiary treatment operation to remove very low concentrations of a hydrophobic-like PCP. The capital costs involved may be considerably smaller since a conventional submerged aeration unit can easily be retrofitted to use sublation as a treatment operation by adding a floating immiscible organic solvent on top of the aqueous waste. Since #2 fuel oil is used often in wood-preserving operations, it is conceivable that a facility using fuel oil for sublation could prove to be an economical method for removal of PCP. A pilot scale experiment is therefore warranted.

FIG. 4. Results on the solvent submation of a wastewater sample containing pentachlorophenol into mineral oil. (1) Raw wastewater without any pH adjustment, pH = 2.9, phase volume ratio = 1:25, air flow rate = 1.5 mL/s, initial PCP concentration = 13.4 mg/L. (2) Treated wastewater with an initial PCP concentration of 0.45 mg/L subjected to solvent sublation, pH = 2.3, phase volume ratio = 1:20, 5% w/v NaCl added, air flow rate = 1.5 mL/s.

CONCLUSIONS

From the results reported here we conclude the following:

(a) Both solvent sublation and solvent extraction are effective in removing pentachlorophenol from aqueous solutions. Solvent sublation has the added advantage of minimal contact of the solvent phase with the aqueous section (and therefore minimal dissolution of the organic solvent in the aqueous phase), and, being a rate-controlled process, may sometimes give removals exceeding that of solvent extraction.

(b) Both solvent sublation and solvent extraction of PCP are more effective at low pH values.

(c) Solvent sublation is more effective at high ionic strength. The presence of added surfactants in the aqueous solution shows a similar degree of enhancement in sublation of PCP.

(d) High air flow rates in solvent sublation did not give a corresponding degree of enhancement in removal because large bubbles at high air flow rates are inefficient for transporting PCP from the aqueous phase to the organic phase. Higher air flow rates would be useful only if the bubble sizes are kept small.

(e) Solvent sublation of an actual raw wastewater sample gave disappointingly low removal, presumably due to interferences from the suspended solids present with the aqueous waste.

(f) A combined treatment consisting of pH adjustment to more acidic values, removal of suspended materials, and sublation at increased ionic strength into a mineral oil phase gave 99.7% removal of PCP from the aqueous phase.

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