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Hui-Ling Chiu[a]; Shang-Da Huang[a]
[a] DEPARTMENT OF CHEMISTRY, NATIONAL TSING HUA UNIVERSITY HSINCHU, TAIWAN, REPUBLIC OF CHINA

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Adsorptive Bubble Separation of Heptachlor and Hydroxychlordene

HUI-LING CHIU and SHANG-DA HUANG*
DEPARTMENT OF CHEMISTRY
NATIONAL TSING HUA UNIVERSITY
HSINCHU, TAIWAN 30034, REPUBLIC OF CHINA

Abstract

Heptachlor (HTC) and its hydrolytic product, 1-hydroxychlordene (HDCD), were removed from aqueous solutions by air stripping, solvent sublation, and foam fractionation. The effects of air flow rate, added salt, ethanol, and surfactants were studied. Foam fractionation was found to be most effective, with 99% of HTC and 97% of HDCD being removed from the aqueous solution in 5 min. This study shows that foam fractionation may find applicability for nonionic organic pollutants removal from aqueous solution. Those nonionic organic pollutants which can be removed by solvent sublation may also be removed by foam fractionation with much better separation efficiency and no organic phase (such as paraffin oil) being required.

INTRODUCTION

Air stripping and solvent sublation are two processes capable of removing trace hydrophobic organics from aqueous solutions by using air bubbles. In the latter process, materials are transported both in the adsorbed phase on the air bubble surface and in the interior of the air bubble and deposited in an overlying immiscible organic solvent like mineral oil, while in the former process no immiscible layer is present over the water column and hence only the material transported in the interior of the bubbles is removed from the aqueous phase (*1*, *2*). The success of conventional air stripping depends solely on the volatility of the hydrophobic material. On the other hand, sublation only requires that either the hydrophobic prefer the air–water interface of the bubbles or the hydrophobic is volatile; partly volatile hydrophobics will be transported in both the adsorbed phase and in the vapor phase of the air bubbles. Lemlich's book on adsorptive bubble separation includes a review of solvent sublation by Karger (*3*). Wilson et al. included material on this subject in a recent book (*4*).

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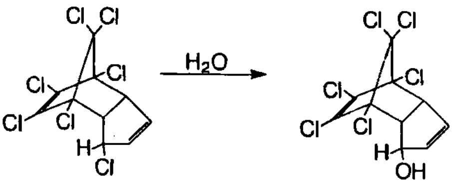
*To whom correspondence should be addressed.

Foam fractionation is another separation technique based on the surface activity of the material to be separated. This technique involves the removal of dissolved material by adsorption on the surface of air bubbles rising through the solution. The adsorbed material is then carried out of the solution by the foam (*5*). The dissolved material separated by foam fractionation may be either in the ion pair or molecular form.

Wilson and coworkers reported much success for solvent sublation in the removal of various hydrophobic pollutants from aqueous solution (*6–11*). Their work involved the removal of alkyl phthalates, volatile chlorinated organics, dichlorobenzenes, polynuclear aromatics, and chlorinated pesticides (such as aldrin, endrin, and lindane) by solvent sublation. Valsaraj and coworkers studied solvent sublation and air stripping of several organic pollutants [such as dichlorobenzene (*1*), pentachlorophenol (*2*), trichloroanisole (*12*), and DDT (*13*)] from aqueous solution. Grieves et al. (*14*) studied the removal of phenol by solvent extraction, solvent sublation, and foam fractionation.

The foam fractionation technique has been studied by many investigators. Most of the work on foam fractionation involves the removal of ionic species through the formation of ion–surfactant ion pairs which are carried out of the solution by adsorption on rising bubbles and the foam phase at the top of the solution. Studies on the foam fractionation of nonionics are rare. A few examples are given in the review by Somasundaran (*5*); these investigations involve the removal of amyl alcohol, isobutyl alcohol, and nonionic surfactant (such as OP-7, OP-10, and Triton X-100).

We have reported on the solvent sublation of two organic dye [magenta (*15*) and direct red (*16*)], diphenyl (*17*), hexachlorobutadiene and 2,4,6-trichlorophenol (*18*), and polynuclear aromatic hydrocarbon (*10*). In this paper we describe some studies we have made on the removal of the chlorinated pesticide heptachlor (1,4,5,6,7,8,8-heptachloro-3*a*,4,7,7*a*-tetrahydro-4,7-methanoindene; HTC) and its hydrolytic product 1-hydroxychlordene (HDCD) from aqueous solution by air stripping, solvent sublation, and foam fractionation. HTC is classified as a priority pollutant by the U.S. Environmental Protection Agency. It can be hydrolyzed into HDCD at room temperature (*19, 20*). HTC is volatile, with a vapor pressure of 3 × 10^{-4} mmHg at 25°C (*21*). The structural formulas of HTC and HDCD are



HTC **HDCD**

EXPERIMENTAL

The separation system used was similar to that described earlier (*15*, *16*). A soft glass column 60 cm in length with an inside diameter of 3.5 cm was used for the separation. 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.

Compressed air in a gas tank was used. The air flow rate was adjusted and measured with a flow controller and readout system. The air flow rate was double checked with a soap film flowmeter.

Reagent-grade sodium lauryl sulfate (NLS, Wako Pure Chemical Industry, Japan) and hexadecyltrimethylammonium bromide (HTA, Aldrich, 95%) were used without further purification. Merck reagent-grade heptachlor (HTC) and *n*-hexane were used for sample preparation.

Saturated (or nearly saturated) aqueous solutions of HTC were prepared by overnight stirring of HTC in deionized water (purified by the Mili-Q Water Purification System; Millipore) followed by filtration to remove suspended solids. The solutions so prepared had HTC concentrations in the 35 to 45 mg/L range at room temperature (approximately 25°C). Some HTC hydrolyzed into its hydrolytic product (HDCD) during sample preparation. The exact concentration of HDCD in the sample solution was not measured. Its peak area in a gas–liquid chromatogram (with an electron capture detector) was approximately 75% of the peak area of HTC. The percent removal of HTC and HDCD from solution at different time intervals was measured by comparing its peak area in the gas–liquid chromatogram with that of the sample taken at time zero.

The 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 sample solution, 30 mL of paraffin oil was added immediately, and the timer was started. The volume of sample solution used for a run was 200 mL. Five milliliters of sample solution was taken each time for analysis.

The procedures of air stripping and foam fractionation were similar to that of solvent sublation except that no paraffin oil was added. The substance to be separated was carried from the solution by air bubbles and foam for the foam fractionation runs, and it was carried from the solution only by air bubbles for the air stripping runs. Analysis of HTC and HDCD in the aqueous sample was accomplished by extracting 5 mL sample solution with 5 mL of *n*-hexane. Sodium sulfate was added to enhance the extracting efficiency and to shorten the time needed for phase separation. The hexane sample (4 μL) was injected into the gas–liquid chromatography column for analysis.

A Shimadzu GC-9AM gas–liquid chromatography with a ^{63}Ni electron capture detector was used. A Shimadzu CR-3A data processor was used for data analysis. A glass column, 1.8 × 4 mm i.d., packed with SE-30 was used. The injection temperature, column temperature, and detector temperature were 250°, 200°, and 280°C, respectively. Nitrogen of 99.99% purity was used as the carrier gas. The nitrogen gas was further purified by passing it through an Alltech gas purifier (with Molecular Sieve 5A and indicating Drierite) and an Oxiclear gas purifier (oxygen absorbing gas purifier). The carrier gas flow rate was maintained at 50 mL/min.

Some of the data of solvent sublation and air stripping were plotted as $C(t)/C_0 \times 100$ vs time in minutes on a semilog scale to display any deviations from first-order kinetics which would yield linear plots. All runs were performed at room temperature (approximately 25°C).

The pH of the solution was measured with a Radiometer pHM83 Autocal pH meter.

RESULTS AND DISCUSSION

The rates of removal of HTC (heptachlor) and HDCD (1-hydroxychlordene) by air stripping and by solvent sublation are compared in Fig. 1.

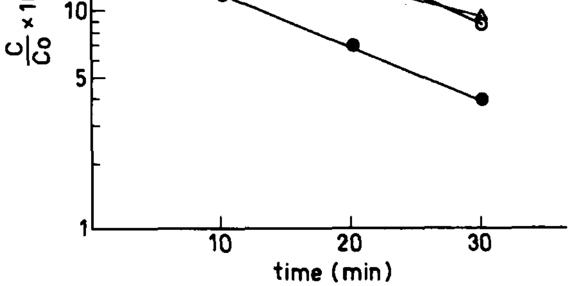


FIG. 1. Rate of removal of HTA and HDCD by air stripping and solvent sublation: (×) air stripping of HDCD, (△) air stripping of HTC, (○) solvent sublation of HDCD, (●) solvent sublation of HTC.

The removal of HTC by air stripping was quite effective, with 91% removal in 30 min. The rate of removal of HDCD by air stripping (21% removal in 30 min) was much slower than that of HTC, presumably due to the much lower volatility of HDCD. Both HTC and HDCD were effectively removed by solvent sublation; 96% of HTC and 91% of HDCD were removed in 30 min. The improved performance of the solvent sublation process as compared to air stripping (without any mineral oil on top of the aqueous phase) is apparent. This is presumably due to HDCD and HTC adsorbing on the surface of air bubbles which are extract into the paraffin oil as they transit the solvent phase during the solvent sublation process. On the other hand, in conventional air stripping, where there is no floating organic phase, the adsorbed phase mixes with the aqueous phase as the bubbles break the surface of the aqueous phase, and only the material carried in the interior of the air bubbles is removed. This phenomenon has also been observed for solvent sublation and air stripping of other organic pollutants from aqueous solutions (*1*, *10*, *12*, *18*).

Both solvent sublation and air stripping of HTC and HDCD do not follow first-order kinetics. Similar phenomena were also observed on the solvent sublation of alkyl phthalates (*7*), polychlorinated biphenyls (*11*), and pentachlorophenol (*2*). 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.

It was found that varying the solution pH has almost no effect on the removal of HTC and HDCD by solvent sublation or air stripping except that air stripping of HDCD is somewhat slower in basic solution. Therefore, all runs were performed at the original solution pH (6.7 to 6.8).

The effect of air flow rate on solvent sublation of HTC and HDCD is shown in Table 1. The rate of removal increases somewhat with increasing air flow rate, as expected. Increases in removal rates were not proportional to increases in air flow rates. Similar effects were observed in the solvent sublation of alkyl phthalate esters (*7*), pentachlorophenol (*2*), and trichlorobenzene (*13*). The reason for such an effect is the increase in mean bubble radius as the air flow rates increase. Smaller bubbles are more efficient for solvent sublation than are larger bubbles; they rise more slowly, which results in a longer contact time with the solvent, and they have a larger surface-to-volume ratio than do larger bubbles. The larger the surface area generated, the greater in the number of sites available for adsorption, and consequently the faster the rate of separation.

The effect of an inorganic salt, such as $NaNO_3$, on the solvent sublation of HTC and HDCD is shown in Table 2. We see that the presence of salt increases the rate of removal of HTC significantly (with 97% removal of HTC in 5 min) from a solution containing 0.3 *M* $NaNO_3$ as compared to

TABLE 1
Effect of Air Flow Rate on Solvent Sublation (percent removal)

Flow rate (mL/min)	Compound	Time (min) 5	10	30	60
100	HTC	40.3	56.7	87.3	96.2
120	HTC	54.8	76.6	90.5	95.3
150	HTC	78.7	86.6	94.6	>99
180	HTC	80.6	85.8	96.7	>99
200	HTC	80.7	86.3	96.9	>99
100	HDCD	38.7	50.9	71.5	>99
120	HDCD	50.5	58.0	88.4	>99
150	HDCD	53.5	60.2	92.5	>99
180	HDCD	57.1	63.3	93.5	>99
200	HDCD	58.1	68.3	94.2	>99

79% removal without any $NaNO_3$ present in the solution. The rate of separation of HDCD also increases somewhat with the addition of salt. Similar effects were observed on the solvent sublation of other organic substances (*1*, *2*, *10*, *17*).

Increasing the ionic strength of the aqueous solution helps in two ways (*2*). 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 small. Second, the presence of inorganic salts gives rise to a so-called "salting out" effect which decreases

TABLE 2
Effect of $NaNO_3$ on Solvent Sublation (percent removal)

$NaNO_3$ (*M*)	Compound	Time (min) 5	10	20	30
0.00	HTC	78.6	87.1	94.9	97.1
0.05	HTC	82.5	94.3	>99	>99
0.10	HTC	88.4	95.6	>99	>99
0.20	HTC	91.4	98.5	>99	>99
0.30	HTC	96.9	99	>99	>99
0.00	HDCD	57.4	66.2	81.3	88.0
0.05	HDCD	58.3	67.8	87.5	94.5
0.10	HDCD	60.5	69.7	89.1	96.4
0.20	HDCD	62.0	73.9	90.0	98.9
0.30	HDCD	68.4	81.8	91.9	>99

the number of water molecules available for solubilizing the hydrophobic organic. The two effects together give rise to an increased separation rate by sublation.

The effects of added ethanol (representative of a polar organic solute) on the rate of solvent sublation of HTC and HDCD are shown in Table 3. The rate of separation increases with increasing ethanol concentration. This is presumably due to a decrease of air bubble size caused by the added ethanol, which reduces the surface tension of the solution. The decrease in bubble size with decreasing surface tension of the solution may be explained by using the Yound–Laplace equation (*22*); assuming the same pressure inside the air bubbles which are freshly generated from the surface of the gas sparger, the radius of the air bubble decreases with decreasing surface tension of the solution. The rate of removal of HDCD was not significantly affected by the added ethanol. This is probably because the increased rate of separation of HDCD due to decreased air bubble size with added ethanol is compensated for by the deleterious effect on the rate of removal of HDCD due to the increased solubility of HDCD in ethanol solution.

The effects of the anionic sufactant on solvent sublation of HTC and HDCD are shown in Table 4. The rates of separation of HTC and HDCD increase significantly with an increased dose of NLS; over 97% of HTC and over 99% of HDCD were removed in as little as 5 min with a 20-ppm dose of NLS. The improvement in the rate of removal is presumably due to the decrease of air bubble size by the added surfactant, which reduces the surface tension of the solution very effectively.

TABLE 3
Effect of Ethanol on Solvent Sublation (percent removal)

Ethanol		Time (min)			
(%, v/v)	Compound	5	10	20	30
0.00	HTC	80.0	86.9	92.8	96.8
0.05	HTC	83.9	92.1	97.0	98.8
0.13	HTC	85.0	96.9	98.2	99.2
0.25	HTC	90.0	95.7	99.0	99.7
0.50	HTC	89.4	96.8	99.2	99.8
0.00	HDCD	57.0	63.9	80.4	90.5
0.05	HDCD	51.9	55.5	75.0	89.0
0.13	HDCD	52.1	71.4	79.2	86.9
0.25	HDCD	56.7	70.8	82.2	85.0
0.50	HDCD	58.9	65.6	81.6	88.7

TABLE 4
Effect of NLS on Solvent Sublation (percent removal)

NLS (ppm)	Compound	Time (min) 5	10	20	30
0	HTC	80.4	87.1	95.0	98.3
10	HTC	84.9	91.3	93.5	93.7
15	HTC	86.6	92.5	95.6	97.5
20	HTC	97.2	98.4	>99	>99
0	HDCD	57.0	65.1	83.4	88.0
10	HDCD	68.6	77.2	95.5	97.6
15	HDCD	75.3	96.7	96.7	96.6
20	HDCD	>99	>99	>99	>99

The rate of separation of HTC and HDCD can also be improved by adding the cationic surfactant HTA. The results are shown in Table 5. Over 93% of HTC and HDCD can be removed in 5 min with a 15-ppm dose of HTA. The removal of HTC and HDCD was over 99% for a 20-min run with only a 10-ppm dose of HTA. The reason for improved separation by HTA addition is also due to a decrease in bubble size. HTA is somewhat more efficient than NLS (i.e., a smaller amount of HTA is required for effective separation compared to NLS). This is presumably because HTA is more surface active than NLS (the hydrophobic chain length of HTA is longer).

The removal of HTC and HDCD by solvent sublation was improved greatly with the addition of a surfactant. It is very interesting to know

TABLE 5
Effect of HTA on Solvent Sublation (percent removal)

HTA (ppm)	Compound	Time (min) 5	10	20	30
0	HTC	80.4	87.1	95.0	98.3
10	HTC	94.3	97.7	>99	>99
15	HTC	93.8	97.7	>99	>99
20	HTC	95.0	97.2	>99	>99
0	HDCD	57.0	65.1	83.4	88.0
10	HDCD	85.2	96.2	>99	>99
15	HDCD	93.4	97.5	>99	>99
20	HDCD	95.1	96.1	>99	>99

TABLE 6
Effect of NLS on Foam Fractionation (percent removal)

NLS		Time (min)			
(ppm)	Compound	5	10	20	30
10	HTC	88.6	96.0	98.8	>99
15	HTC	86.1	93.5	97.5	97.9
20	HTC	98.9	98.9	>99	>99
10	HDCD	71.3	85.1	94.1	96.7
15	HDCD	71.9	86.1	94.5	97.8
20	HDCD	97.2	97.3	>99	>99

whether or not the separation is effective if no paraffin oil is added. The surface-adsorbed HTC and HDCD may be carried out of solution by the foam, i.e., by the foam fractionation mechanism. The results of foam fractionation of HTC and HDCD with NLS and HTA are shown in Tables 6 and 7, respectively. Separation was very effective, with 99% of HTC and 97% of HDCD removed in 5 min (with a 20-ppm dose of NLS). Similar results were obtained by using HTA as the frother. The separation efficiency of foam fractionation is similar to that of solvent sublation (with the same dose of surfactant), and it is much better than that of solvent sublation and air stripping without any added surfactant. Surfactants used in foam fractionation 1) reduce the bubble size so that the surface area of the bubble is substantially increased, and 2) act as a frother so that a stable foam is produced on the top of the solution and therefore the surface-adsorbed HTA and HDCD are constantly carried out of the solution by the foam rather than being dispersed back into the aqueous solution as the air bubbles transit the aqueous phase.

TABLE 7
Effect of HTA on Foam Fractionation (percent removal)

HTA		Time (min)			
(ppm)	Compound	5	10	20	30
10	HTC	94.1	97.7	>99	>99
15	HTC	98.0	>99	>99	>99
20	HTC	95.8	>99	>99	>99
10	HDCD	84.6	96.7	>99	>99
15	HDCD	89.6	95.9	97.9	>99
20	HDCD	92.3	97.7	>99	>99

CONCLUSION

Both HTC and HDCD were effectively removed by solvent sublation (with 96% removal in 30 min for HTC and 91% removal in 30 min for HDCD). Removal of HTC by air stripping was also effective (with 91% removal in 30 min), but removal of HDCD by air stripping was very poor (21% removal in 30 min). The rate of separation of HTC and HDCD by solvent sublation increases with increasing air flow rate, the ionic strength of solution, and with the addition of surfactant.

Foam fractionation of HTC and HDCD was very effective with 99% of HTC and 97% of HDCD being removed in 5 min. Either an anionic or a cationic surfactant can be used as the frother. The separation efficiency of foam fractionation is similar to that of solvent sublation (with the same dose of surfactant), and it is much better than that of solvent sublation without any surfactant added.

Studies on the removal of a nonionic organic solute from an aqueous solution by foam fractionation are rare. Based on our present study, it is suggested that foam fractionation may be applicable for nonionic organic pollutant removal from aqueous solutions. Those nonionic organic pollutants which can be removed by solvent sublation may also be removed by foam fractionation with much better separation efficiency and no organic phase (such as paraffin oil) being required.

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