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Removal of 2,4-Dichloro phenoxy acetic acid pesticide by solvent sublation: Experimental and theoretical studies

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Abstract The removal of the pesticide 2, 4 D from water using solvent sublation process was investigated in this paper. A lab scale unit was set up and various experimental runs were carried out to study the efficiency of the removal process. The experimental findings show that the method is very effective (> 90% removal) in removing traces (ppb level) of the pesticide which is not easily removable by simple air stripping. In addition a mathematical model was developed to describe the experimental findings. Some parameters of the model were measured or calculated while others such as the aqueous mass transfer coefficient and the solute partition coefficient were adjusted to fit the experimental data. The calibration of the model was carried out using the experimental results of change in gas flow rate (the easiest parameter to vary). A numerical sensitivity analysis was carried out using the calibrated model to study the effect of various parameters such as the bubble radius, aqueous phase drag-up by air, column radius and ratio of organic to aqueous volume phases.

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1. Introduction

Volatile Organic Compounds (VOC's), e.g. chloro benzenes, chlorinated pesticides etc., are major pollutants of agricultural and industrial wastewaters (Goldfarb, 1985). Even when present in traces, such chemicals are considered contaminants of

ground water resources which are significant to arid countries such as Saudi Arabia. Among other chlorinated phenoxy hydrocarbons, 2, 4 D is known to be a systematic herbicide to control aquatic vegetation. Its active ingredients are strong eye irritants. They have been found to disrupt human hormone systems and may lead to other chronic health effects.

Conventional trace contaminant removal technologies (aeration, biodegradation, and carbon adsorption) are of little use because of either limited efficiency or high cost (Goldfarb, 1985). Solvent sublation process is a technique originally proposed by Sebba (1962). The process was studied extensively in the literature (Clarke and Wilson, 1983; Lu and Zhu, 2001, 2002; Lionel et al., 1981; Huang et al., 1983; Foltz et al., 1986; Smith and Valsaraj, 1997; Thoma et al., 1999; Bryson and Valsaraj, 2001; Lu et al., 2005; Sun et al., 2005; Valsaraj and Thibodeaux, 1991; Karger, 1972; Wilson and Valsaraj, 1982; Caballero et al.,

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Nomenclature

a	bubble radius (cm)	K_I	aqueous phase overall mass transfer coefficient (cm/min)
C_o	concentration of solute based on pure solvent (mmol/ml solvent)	K_{ow}	solute partition constant between organic solvent and aqueous phases (–)
C_w	concentration of solute based on pure water (mmol/ml water)	Q	gas flow rate (ml/min)
C_{wi}	initial solute concentration based on pure water (mmol/ml water)	r_c	radius of column for sublation or laminar liquid–liquid extraction (cm)
d	thickness of water film around bubble (cm)	t	sublation time (min)
Es	efficiency process (%)	V_b	volume of bubble (ml)
H_c	Henry's law constant for solute between vapor and aqueous phase (–)	V_o	volume of organic solvent phase (ml)
K_a	linear adsorption constant for solute between the air–water interface of bubble and aqueous phase (cm)	V_w	volume of pure water (ml)

1990) and was shown to be a potentially efficient and cost effective treatment method for the removal of many hazardous chemical, especially chlorinated hydrocarbons.

In this paper, we present the results of an experimental and theoretical study of the removal of the pesticide 2, 4 D from water using the solvent sublation technique.

Solvent sublation, or adsorbed phase removal in bubble column is non-foaming adsorption bubble separation process in which enriched material on bubble surfaces is collected in immiscible liquids, rather than in foams. The technique consists in the transport of hydrophobic solute from the aqueous phase to an overlying layer of non-volatile solvent on the interface. Volatile or surface-active non-volatile material will be present in a bulk aqueous phase, on top of which is placed an immiscible organic liquid.

Gas bubbles are generated in the aqueous media and are buoyed upward into the organic phase. In this process, bubbles selectively adsorb surface active chemicals to the organic phase. These chemicals are known as the “sublate”. The chemical is either deposited in the top phase after the bubbles burst at the air–liquid interface or is dissolved during the passage of the bubbles through the immiscible organic phase. In either case selective enrichment in the non-aqueous layer occurs. The non-aqueous layer can then be decanted to remove the solute.

Since the pioneering work of Sebba (1962) the process of solvent sublation has received increasing attention through the years and numerous experimental studies were carried out for the removal of many hazardous chemicals. Clarke and Wilson (1983) provided a review of the applications of the technique. Lu and Zhu (2001) also carried out a survey of the use of the solvent sublation for the removal of inherent hydrophobic.

On the other hand, Wilson and Smith (Lionel et al., 1981; Huang et al., 1983; Foltz et al., 1986) and Valsaraj et al., (Smith and Valsaraj, 1997) reported numerous experimental results on the use of the technique to separate refractory organics from water. Thoma et al. (1999) extended the use of the solvent sublation process for separation of oil-field process water. Bryson and Valsaraj (2001) studied the removal of naphthalene from a process water stream using the solvent sublation process. Lu et al. (2005); Lu and Zhu (2002) studied the solvent sublation for the removal of indigo Carmine and also for the removal of some surfactants.

Recently Sun et al. (2005) described the experimental study on the semi batch sublation for recovering large concentrations of butyl acetate in wastewater from solvent extraction of penicillin. Results show that solvent sublation is a very efficient process for such recovery.

Besides the experimental work on the process, many studies on the theoretical modeling of solvent sublation were also carried out to provide design equations for the process to help predict the effect of different parameters on the process efficiency and to help the optimization of the operation of the process. The mathematical modeling of the process depends evidently on the assumed transport mechanisms for the process.

Although various mechanisms were proposed and improved on in the literature, the basic mechanisms of the process is shown in Fig. 1. The rising bubbles cause three kinds of mass transfer to take place in the aqueous phase: (1) transfer of air to the aqueous solution; (2) transfer of hydrophobic solutes (low solubility organics, both volatile and non-volatile) to the boundary layer of the bubbles (boundary layer transport) and (3) transfer of volatile components from water to the vapor phase of the bubbles. It is the second process that is characteristic of adsorbed phase transport. Both first and last transport are characteristic of any processes of air sparging in water. The concentration profile that develops adjacent to the bubble is shown in Fig. 1. The importance of the concentration of hydrophobic components in the bubble boundary

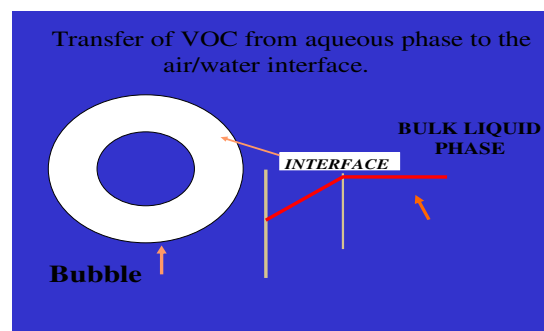


Figure 1 Transfer of VOC from aqueous phase to the air/water interface.

layer (step 2) is that this boundary layer concentration is higher than in the bulk liquid. This means that vapor concentration within the bubble can be greater than that which is in equilibrium with the bulk liquid.

Since this boundary layer has a high concentration of the hydrophobic solute, it will concentrate the organic phase layer when it comes in contact with it. When the bubble are small enough that they rise in laminar flow, the boundary layer transport becomes important. Layer bubble, rising in turbulent flow, will show very little boundary layer transport since the concentration is nearly equal to the bulk mean value (Valsaraj and Thibodeaux, 1991). The behavior of hydrophobic organic materials (non-polar, low solubility) in the presence of the bubble boundary layer is very much like a typical surface active chemical.

In the modeling area, Sebba (Goldfarb, 1985) provided the first mathematical description of the solvent sublation process. The author assumed that the sublute moved across the water-solvent interface in one direction only. Later Karger (1972) described qualitatively the possible transport pathways in solvent sublation, where there existed two predominated transport processes: (1) transport within and on the surface of the bubbles and (2) a diffusive transport between the phases driven by a concentration gradient.

Wilson et al. (Lu and Zhu, 2001; Sun et al., 2005; Valsaraj and Thibodeaux, 1991), on the other hand, proposed different models of batch or continuous sublation including the effect of the rate of solute mass transfer from the aqueous phase to the air-water interface. Valsaraj and Thibodeaux (1991) built a model for the process based on an analogy with the conventional liquid-liquid extraction. They considered two additional processes in the solvent sublation process: a thin film of water is dragged into the solvent phase and is then returned as water droplets. Smith et al. improved the latter model by including the effect of gas holdup on the diffusive mass transport at the water-solvent interface.

Valsaraj and Thibodeaux disregarded the amount of solute lost to the atmosphere in an overall solute mass balance across the organic solvent and aqueous phases in order to simplify the calculation (Karger, 1972). Recently Sun et al. (2005) relaxed the assumption of constant volume of solvent layer during the sublation. The authors built a model and used it for the simulation of the semi-batch sublation for recovering large concentrations of butyl acetate in the wastewater from solvent extraction of penicillin.

2. Apparatus and procedure

A 100-cm high, 15 cm I.D. Plexiglas column was used as the sublation column. The column had 10 sampling ports placed at different heights in order to determine the concentration of 2, 4 D at 10 locations on the column (Fig. 2). These ports were located at equal spacing of 10 cm from the bottom of the column. The sublation column was equipped with a fritted silica disk at its bottom to generate fine air bubbles (diameter less than 0.5 mm) when air was forced through the bottom. Pre-saturated house air was introduced at the bottom of the column. The air flow rate was controlled using a pressure regulator and a needle valve. A solvent layer of mineral oil (paraffin oil) was placed on the top of the 2, 4 D/water solution in the sublation column. The depth of mineral oil was always constant at 20 mm.

Chemicals used included Fisher HPLC grade diethyl ether (solvent extraction) and paraffin oil (mineral oil) and Aldrich GC pest anal (pesticide analytical) grade 2, 4 D. Known concentrations of 2, 4 D in water (10 mg/l, 5 mg/l) were prepared with the aid of a magnetic stirrer and left in ultrasonic bath for 1 h. This definite solution used for all experiments.

Experiments were performed to determine the mass removal rate for adsorbed phase transport of (2, 4 D) from water. Water containing dissolved 2, 4 D was treated by the sublation process and the concentration of 2, 4 D was then determined as a function of time. Samples were collected in 10-ml septum vials from three different sampling ports at the same time, and time was recorded accordingly. Sample size ranged from 2 to 4 ml, so that fluid balance would not be upset. Before samples were taken from the sampling ports, a small amount of liquid was discarded to purge the sampling port itself. This discarded amount of liquid was estimated at 1–2 ml.

Samples were collected in the labeled septum bottles and saved under refrigeration for later analysis. These samples were analyzed by gas chromatography (Hewlett-Packard) connected to an Electron Capture Detector (ECD). The gas chromatograph was calibrated with standard 2, 4 D/diethyl ether solutions at least once, then recalibrated every day on which analyses were made (a typical run lasted from 6 to 7 h).

All experiments were conducted at temperatures of 21 ± 1 °C. One useful characteristic of the 2, 4 D is its low volatility. Low volatility is an advantage because it avoids the prospect that mass transfer will occur significantly by vapor phase transfer to the air phase bubbles. It also provides for low concentrations of the chemical in the laboratory environment, thus contributing to increased laboratory safety.

2.1. Mathematical model of the process

The model used in this paper is similar to the ones used for the study of solvent sublation of a number of chemicals (Smith et al., 1996; Thoma et al., 1999; Valsaraj et al., 1986). First, it is assumed that air bubbles reaching the solvent-water interface are in equilibrium with the aqueous phase. Second, we assume that axial dispersion in both phases is sufficiently large to make both phases completely mixed.

A solute mass balance in the aqueous phase is described by the following equation:

$$V_w \frac{dC_w}{dt} = -Q \left(H + \frac{3}{a} K_a + \frac{3}{a} d \right) C_w - \pi r_c^2 (1 - \varepsilon) K_1 \left(C_w - \frac{C_o}{K_{ow}} \right) + Q \left(H + \frac{3}{a} d \right) \frac{C_o}{K_{ow}} \quad (1)$$

where V_w is the volume of the aqueous phase, C_w is the concentration of the solute in the aqueous phase, Q is the air flow rate, a the bubble radius, K_a the adsorption constant for the solute in the air-water interface, d the thickness of the aqueous phase layer around the bubbles, r_c the column radius, K_1 the aqueous phase mass transfer coefficient, C_o the concentration of the solute in the organic phase, K_{ow} the solute partition constant between the organic and the aqueous phase and ε is the void fraction.

In the derivation of the mass balance of Eq. (1) it can be seen that the negative term is composed of three physically relevant processes: $(Q(3/a)K_a)C_w$ represents the amount of solute

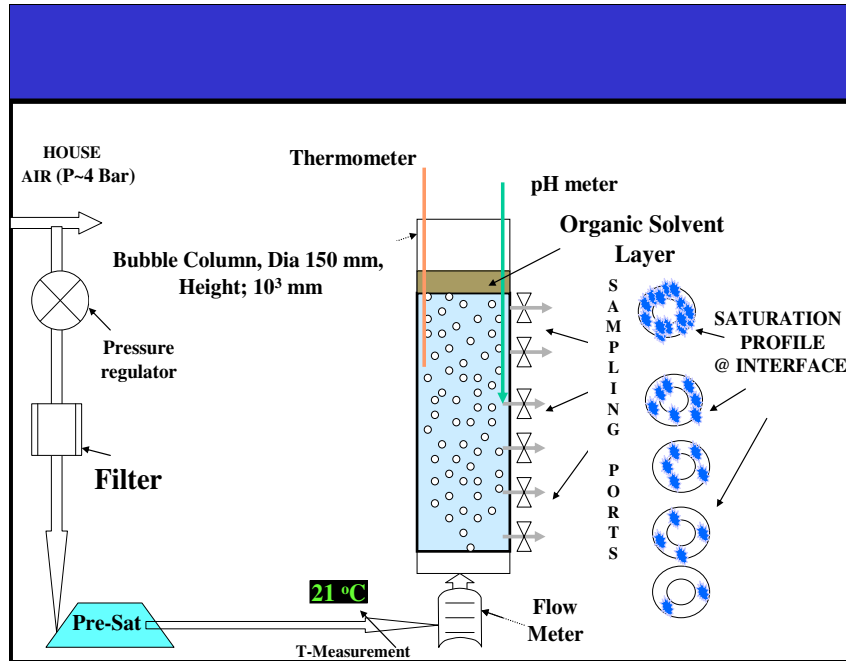


Figure 2 Schematic diagram of the adsorbed phase transport apparatus.

adsorbed on the surface of the bubbles. $(Q((3/a)d)C_w)$ is the amount of solute carried out up with the water layer thickness d around the bubbles, and the term $\pi r_c^2 K_1 (C_w - (C_o/K_{ow}))$ represents the amount of solute transported by molecular diffusive transport across the cross-sectional area of the column.

The positive term $(Q(3/a)d)C_o/K_{ow}$, on the other hand, represents the amount of returning with the water droplets from the solvent phase to the atmosphere. The term $V_w(dC_w/dt)$ represents the transported solute from the aqueous phase to the organic phase. To Eq. (1), we should add the overall solute mass balance between aqueous and organic phases

$$V_w C_{wi} = V_w C_w + V_o C_o \quad (2)$$

where C_{wi} is the aqueous initial solute concentration and V_o is the volume of the organic phase.

Substituting Eq. (2) into Eq. (1) yields the following simple differential equations as following:

$$\frac{dC_w}{dt} = \alpha C_w + \beta C_{wi} \quad (3)$$

With initial conditions $C_w = C_{wi}$ at $t = 0$.

The parameters α and β in Eq. (2) are defined as follow:

$$\alpha = -\frac{Q}{V_w} \left(H + \frac{3}{a} K_a + \frac{3}{a} d \right) - \frac{Q}{V_o} \frac{3}{a} \frac{d}{K_{ow}} - \pi r_c^2 (1 - \varepsilon) \frac{K_1}{V_w} \left(1 + \frac{V_w}{V_o K_{ow}} \right) \quad (4)$$

$$\beta = \frac{1}{V_o K_{ow}} \left(\pi r_c^2 (1 - \varepsilon) K_1 + Q \frac{3}{a} d \right) \quad (5)$$

This equation can be readily integrated to yield the profile of versus time.

$$\ln \left(\frac{C_w}{C_{wi}} \right) = \ln(\alpha) + \alpha t - \ln((\alpha - \beta) + \beta e^{\alpha t}) \quad (6)$$

The sublation efficiency is defined as

$$E(\%) = \left(1 - \frac{C_w}{C_{wi}} \right) * 100 \quad (7)$$

where the ratio (C_w/C_{wi}) is obtained from Eq. (6).

2.2. Estimation of model parameters

The model parameters include the following mass transfer coefficients: partition coefficient K_{ow} , the adsorption constant K_a , the Henry law constant H_c . The value of the Henry constant was obtained from the literature while both the partition coefficient and the linear adsorption constant were taken as adjustable parameters to calibrate the model. The other parameters of the model consist in hydrodynamic parameters consisting of the mean bubble diameter a and the thin water film thickness d around bubble. The latter can be linked to the volume of the bubble and the volume of the wake by the following relations

$$V_{wk} = 4\pi a^2 d \quad (8)$$

$$\frac{V_{wk}}{V_b} = 1.5 \times 10^{-4} V_b^{-0.741} \quad (9)$$

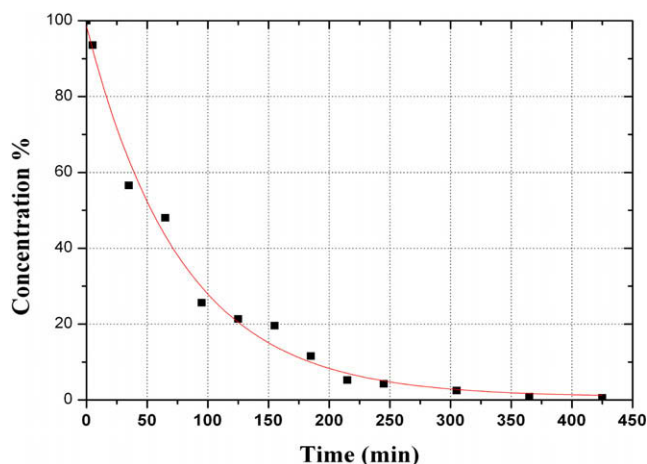
where V_{wk} is the volume of the wake and V_b is the volume of the bubble.

The void fraction ε was taken to be constant. Table 1 summarizes the nominal values of model parameters used in the simulations.

Fig. 3 shows the concentration versus time curves resulting from the experimental data and the calibrated model. The fitting seems to be reasonable. It is obvious that a steady state is reached at approximately time $t = 425$ min as shown in Fig. 3, after which the concentration is very low. The figure also shows that the relation of $\ln(C_w/C_{wi})$ is linear suggesting a first order kinetics.

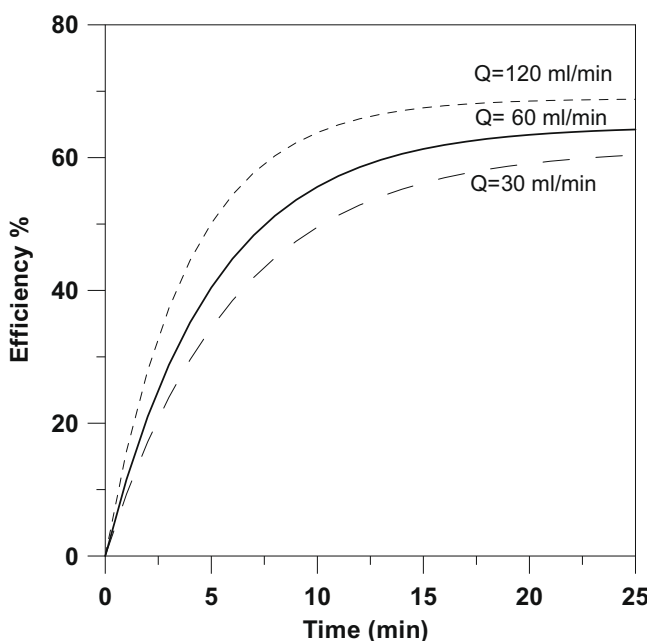
Table 1 Nominal values of model parameters.

Parameter	H	K_a (cm)	K_{ow}	K_1 (cm/min)	A (cm)	D (cm)	r_c (cm)	Q (ml/min)	V_w (ml)	V_o (ml)	ε
Value	8.3×10^{-3}	3×10^{-3}	65	5.4×10^{-2}	0.03	1.26×10^{-3}	15	60	100	10	0.02

**Figure 3** Concentration profiles: airflow rate = 60 ml/min and the rest of values as shown in Table 1.

2.2.1. Effect of gas flow rate

The adsorbed phase transport of 2, 4 D from water was investigated at three different airflow rates (0.5, 1, 2 ml/s). The experimental results agree well with the results of model simulations (Fig. 4). Increasing the flux of air through the column should normally increase the rate of removal from the aqueous phase, since more solute is brought into the solvent phase.

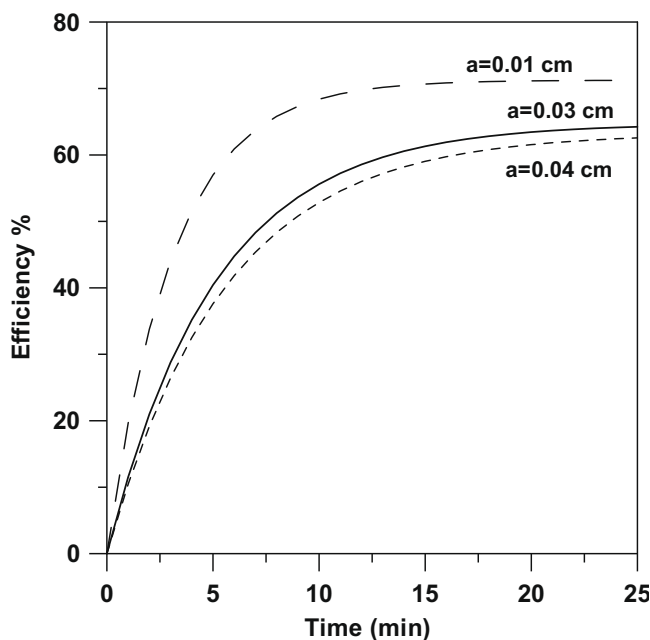
**Figure 4** Concentration profiles: effect of change in air flow rate.

However, the increase in removal rate was out of proportional to the increase of airflow rates. This was probably explained by the finding that with increasing airflow rates the mean bubble radius increased, thus the interfacial area per unit volume of air (which is given by $3/a$) decreased, and the bubble residence time is also reduced since larger bubbles had higher rise velocities.

High air flow rates would be useful only if the bubble sizes are kept small. Furthermore, the axial dispersion certainly increased with the increase of the airflow rates, which would impair the performance of the sublation process. It was observed that at higher flow rates the oil–water interface was drastically disrupted and some drops of the top layer could return to the solution.

2.2.2. Effect of bubble radius

Besides the gas flow rate, bubble radius is another important operating parameter in solvent sublation. Smaller bubble size lead to an increased in the interfacial area of bubbles and to the increased contact time of the bubbles. From the model equations (Eq. (2)) it can be seen that the size of bubble radius affects the following three processes: The decrease in the size of bubble increase the amount $((Qa(3/a)di)C_w)$ of the solute carried up with the water layer of thickness d . It also increase of the amount $((Qa((3/a)di)C_o/K_{ow}))$ of solute returning with the water droplets from the solvent phase to the aqueous phases. And finally it increases the amount $(Qa((3/a)K_a)C_w)$ of solute absorbed on the surface of the bubbles. Fig. 5 shows

**Figure 5** Concentration profiles: effect of change in bubble radius.

the simulation results for three values of bubble radius. The simulation results confirm that the apparent rate constant increases with the decrease of the bubbles radius.

2.2.3. Effect of thickness of aqueous layer around bubbles

The thickness of aqueous phase layer around the bubbles d is characterized as the effect of the dragged-up liquid. Fig. 6 shows the simulation results for three values of d . The increase of the layer thickness also increases the apparent rate constant of the process. This is due to the fact that the increase in the layer thickness increases the amount of the solute carried up with the water layer of thickness, and also increase of the amount of solute returning with the water droplets from the solvent phase to the aqueous phases.

A note, however, should be made about the state of equilibrium between the aqueous and organic phases in the column. As it was mentioned in other works, the amount of the water dragged up by bubbles represents only a fraction of the aqueous phase and it is this small amount which is in equilibrium with the organic phase, while the whole system (aqueous and organic) is in a non-equilibrium state. This is in contrast to the classical solvent extraction process where an equilibrium persists between the two phases.

2.2.4. Effect of organic phase volume

Fig. 7 shows the model simulations for the effect of ratio of organic to aqueous phase volumes. Generally in solvent sublation process the solute mass transfer occurs from air bubbles while the molecular diffusive transport across the interface is not important. In this case the ratio of the volume of the two phases should not be important.

However, when the aqueous phase mass transfer coefficient is large, then the process approaches the solvent extraction where the organic volume becomes important. Moreover, if the ratio of organic to aqueous phase volume used in the process is too low then the interface will be drastically disrupted at a high gas flow rate resulting in a decrease in the process efficiency. Consequently, the ratio of the two phases and the air

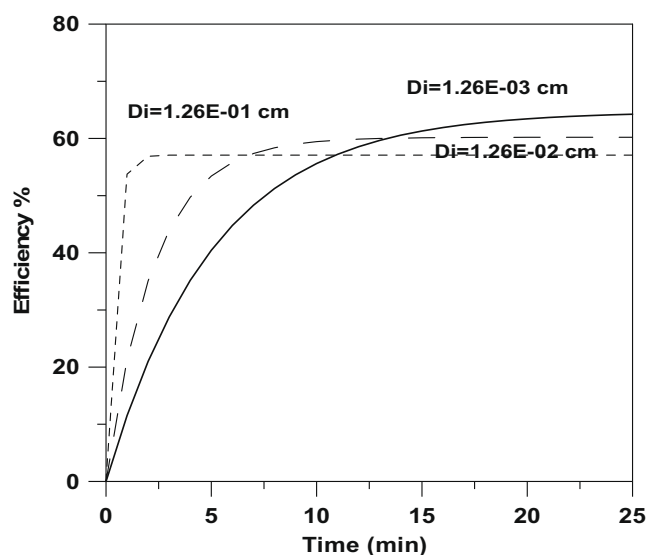


Figure 6 Concentration profiles: effect of change in bubble layer thickness.

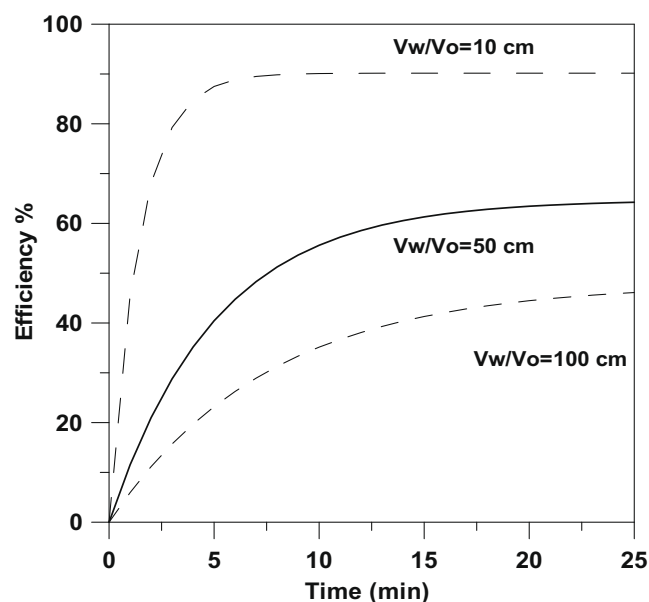


Figure 7 Concentration profiles: effect of change in the ratio of the volume of the two phases.

flow rates are two parameters that need to be carefully adjusted.

2.2.5. Effect of column radius r_c

The results of model simulations for the effect of column radius are shown in Fig. 8. An increase in the diameter also increases the apparent rate constant. This is due to the fact that the molecular diffusive transport increases with the increase in column radius. This results show that the columns radius has some effect on the solvent sublation process which makes the recovery in large scale possible.

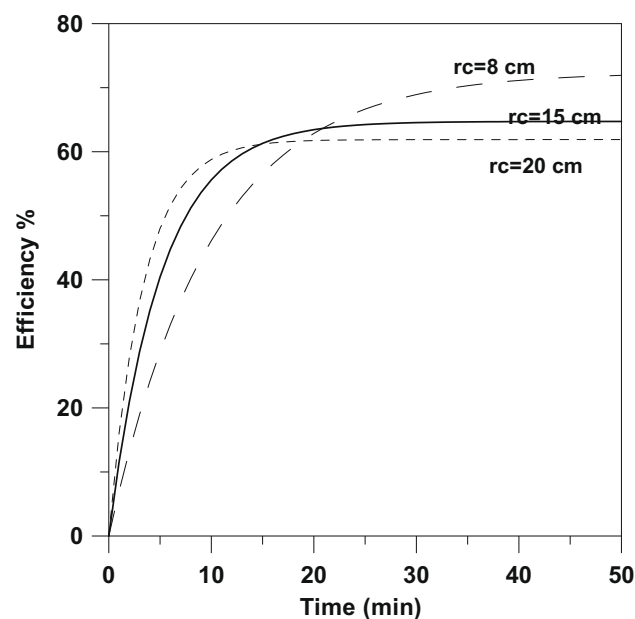


Figure 8 Concentration profiles: effect of change in the diameter of the column.

3. Conclusions

The paper has addressed the technical feasibility of the removal of the harmful pesticide 2, 4 D from water using the solvent sublation process. Experimental studies were carried out that show the effectiveness of the removal process. A simple mathematical model was also proposed on the basis of the mechanisms of transport assumed in the separation process. The model parameters were either measured or used as fitting parameters. The variations of sublation efficiency, and solute concentration with sublation time were calculated and discussed. The results suggest a simple first-order kinetics of the process, at least for not very large values of model operating parameters. Simulations showed that increasing the gas flow rate and decreasing the bubble size, could improve the process efficiency and increase the rate of the sublation, respectively. The ratio of volume of organic to aqueous phase plays a smaller role in the efficiency of the process. Numerical simulations also show that larger column diameter increases the efficiency of the process making large scale removal of the solute a potentially feasible option.

Two areas of research could be continued for a better optimization of the operation of the lab scale column. The study of using a different gas system than air. Water-insoluble gases such as natural gas (methane) or hydrogen might have a potential advantage over air, since 2, 4 D and other chlorinated hydrocarbons have higher affinity to methane than they have to air. This can suggest methane as a potential alternate gas provided that it is readily available (not expensive) and dealt with safely. A technical as well as an economical evaluation of the previously proposed gas systems can be investigated. The study of different sparger. Smaller bubble sizes have the advantage of possessing higher mass transfer area, which makes almost all of the gas bubbled involved in the removal process. Various bubble producing equipment can be investigated. Smaller bubble sizes should prove to be very useful in the case of existing industrial wastewater ponds.

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