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ORIGINAL ARTICLE

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.

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)
C_o	concentration of solute based on pure solvent (mmol/ml solvent)
C_w	concentration of solute based on pure water (mmol/ml water)
C_{wi}	initial solute concentration based on pure water (mmol/ml water)
d	thickness of water film around bubble (cm)
Es	efficiency process (%)
H_c	Henry's law constant for solute between vapor and aqueous phase (–)
K_a	linear adsorption constant for solute between the air–water interface of bubble and aqueous phase (cm)
K_1	aqueous phase overall mass transfer coefficient (cm/min)
K_{ow}	solute partition constant between organic solvent and aqueous phases (–)
Q	gas flow rate (ml/min)
r_c	radius of column for sublation or laminar liquid–liquid extraction (cm)
t	sublation time (min)
V_b	volume of bubble (ml)
V_o	volume of organic solvent phase (ml)
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

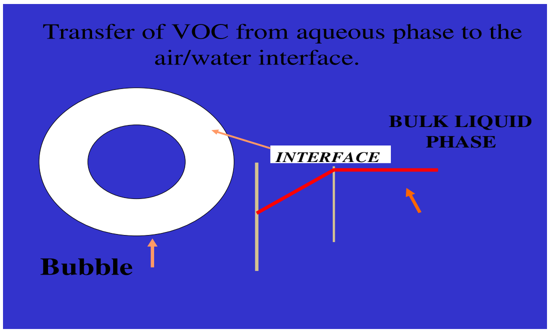

Figure 1 Transfer of VOC from aqueous phase to the air/water interface.