

Removal of Organic Pollutants from Waste Streams by Dissolved Air Precipitation/ Solvent Sublation

Fatemeh Bayati^a, Jalal Shayegan^{*a}, Hesamedin Shokrollahi^b, Jalal Basiri Parsa^b

a. Chemical Engineering Department, Sharif University of Technology, Tehran, Iran

b. Department of Chemistry, Bu-Ali Sina University, Hamedan 65178, Iran

*. shayegan@sharif.edu

Organic compounds are major pollutants in many industrial process waste waters. In this work, simulated waste water from two major industrial activities, upstream oil industries and pharmaceutical industries, are subjected to Dissolved Air Precipitation combined with Solvent Sublation (DAP/SS). In this method micro bubbles produced by saturation of air in a pressurized packed column were released in an atmospheric column leading the bubbles to raise resulting trapped contaminants in the Gibbs layer around them to be removed by a layer of immiscible mineral oil at the top of column. The method was conducted to four hydrophobic organics: Methylene Chloride (MCl), Butyl Acetate (BA), Toluene and Chlorobenzene (ClB); and the results obtained for Removal Efficiency (RE) were compared to a mathematical model of separation process. Also Effect of pressure (4, 5, 6, 7 bar) and salinity on RE and bubble size were examined. The results indicated positive effect of pressure and salinity on RE and bubble size reduction. Furthermore the method was applied to a mixture of components to analyze effect of co-existence of components on RE.

1. Introduction

In many industries, process or waste water streams may contain organic compounds which are necessary to be removed from the stream before it is discharged or recycled. Usually high and even low concentrations of these compounds, (e.g. Toluene) may be dangerous for environment. Most of these organic compounds under conditions of high pressure and temperature will be dissolved in the water; thus traditional treatment methods like gas stripping, solvent extraction and activated carbon adsorption may not be efficient or even economical. (Glenn Brayson and Valsaraj 2001)

Solvent sublation, first introduced by Sebba (1962), has shown good results for removal of hydrophobic organic compounds from water. Solvent sublation is one of the adsorptive bubble separation processes in which dissolved hydrophobic organic compounds will be carried on bubble surfaces to the solvent layer at the top of the column. This method has simultaneous advantages of separation and preconcentration and attracts attention of researchers working on waste water treatment fields. (Lu et al. 2005)

One of the advantages of this method compared to bubble aeration is reduction in the probability of redispersion of the components into the aqueous phase upon bubble bursting which usually occurs in conventional bubble aeration columns. Also in solvent sublation, both volatile and non-volatile materials can be removed from water, while in bubble aeration columns, only volatile compounds can be removed. The other advantage of this method over bubble aeration is mitigating release of volatile

compounds to the atmosphere due to presence of the organic solvent layer. Furthermore, the hydrophobic compounds will collect on the surface of the bubble by diffusion through the boundary layer surrounding the air bubble because of their natural tendency to concentrate at the air-water interface. Thus comparing to solvent extraction, solvent sublation has higher efficiency due to increase in concentration of the hydrophobic compounds reaching the solvent layer. (Glenn Brayson and Valsaraj 2001), (Thoma et al. 1999), (Lu et al.2005)

Valsaraj et al. (1991) have presented a mathematical model which can support experimental data for solvent sublation. The mechanisms considered for evaluating this model consist of: 1) transport within and on the surface of the bubbles; 2) diffusive transport between the aqueous and organic phases driven by a concentration gradient. 3) Thin film of water dragged into the solvent phase and then returned as water droplets. (Valsaraj et al. 1991), (Thoma et al. 1999)

The model described by Valsaraj et al. (1991) is presented below:

$$E = 1 - \frac{C_w}{C_{wi}} = (1 - \frac{\beta}{\alpha})(1 - e^{-\alpha t}) \quad (1)$$

$$\beta = \frac{1}{K_{ow}V_o} \left[\pi_c^2 k_1 + Q_a \left(H_c + \frac{3}{a} d_i \right) \right] \quad (2)$$

$$\alpha = \frac{Q_a}{V_w} \left(H_c + \frac{3}{a} K_a + \frac{3}{a} d_i \right) + \frac{\pi_c^2 k_1}{V_w} \left(1 + \frac{V_w}{K_{ow}V_o} \right) + \frac{Q_a}{K_{ow}V_o} \left(H_c + \frac{3}{a} d_i \right) \quad (3)$$

Where E is fractional removal, C_{wi} and C_w are the initial and treated aqueous contaminant concentration (mg l^{-1}), t is treatment time (s), Q_a is the gas flow rate (ml min^{-1}), R and R_c are the bubble and the column radius (m), K_{ow} is the octanol-water partition coefficient (dimensionless), H is Henry's constant (dimensionless), V_o and V_w are the solvent layer volume and the water volume (l), K_a is the interfacial partitioning-coefficient (m), d_i is the thickness of the water layer carried into the solvent layer (m) and k_1 is the solvent layer-water interfacial mass transfer coefficient (m s^{-1}).

2. Experiments

2.1 Chemicals

The chemicals used in this study consist: Butyl Acetate, Methylene Chloride, Benzene, Toluene, Chlorobenzene, Hexane and methanol (MERK) with purity of 99.8%. Mineral oil was used as the organic solvent layer.

2.2 Apparatus

The DAP/SS system was similar to that prepared earlier by Thoma et al., (1999). An atmospheric column $65 \text{ cm} \times 176.5 \text{ cm}^2$ with one saturated air inlet and one water outlet conjunct to the pump (a chlorinator dosing pump from SALEM AB Co.) and the saturator, $35 \text{ cm} \times 314 \text{ cm}^2$, half of which was filled with packings for providing a large air-water contact area. The schematic of the system is presented in fig.1.

2.3 Preparation of samples

1000 ppm Methylene Chloride solution was prepared by adding 10 gr Methylene

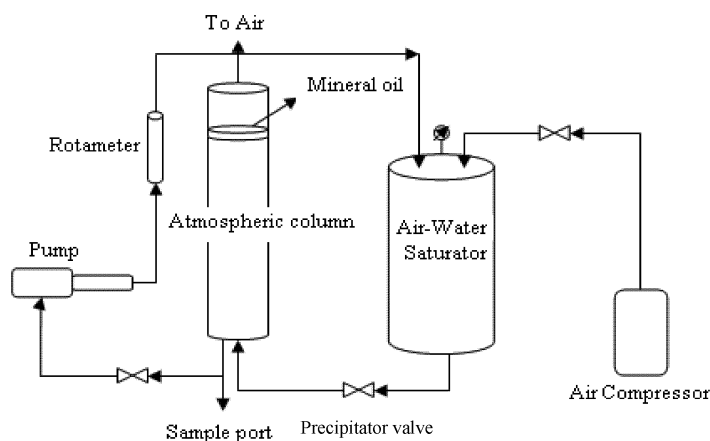


Figure 1. a schematic of the experimental system

Chloride in 10 l tap water, similar solution was prepared for Butyl Acetate. For toluene, Benzene and Chlorobenzene, 1 gr of the component was dissolved in 10 ml methanol, and then the solution was added to 10 l tap water.

2.4 Bubble generation

Experimental runs were performed in which the effect of the saturator pressure and salinity on the size of bubbles precipitated was determined. The pump was turned on and the system valves were opened with air pressure applied to the saturator. After the saturator reached a steady state operation, a cloud of bubbles forms at the valve. The system was operated for 5–7 min, allowing the bubble cloud to fill the column completely. At this time, the column was isolated from the pump and saturator by closing both the depressurization valve and the recycle stream valve and turning off the pump. The bubble swarm rise velocity was found by measuring the time required for 54 cm of the column to clear. For bubbles in the diameter range generated by this system, Stoke's law is adequate for estimation of the bubble diameter.

2.5 Sublation runs

The column was filled with 10 l prepared sample. Then the pump was turned on until the saturator was filled with 5 l sample. 2 cm mineral oil (solvent) was added on the top of the water in the atmospheric column. The compressor was turned on until the pressure would reach the desired pressure. Then the precipitation valve was opened and the bubbles were released in the column. The opening of the valve was adjusted to hold the column water level constant.

2.6 Analysis

Water samples from operational runs (40 ml) were extracted with 1 ml of HPLC-grade hexane and 0.5 μ l of the extract was directly injected on the GC. The GC analysis was done on a 50m*0.201mm*0.5 μ m column (J&W). The conditions were: An initial temperature of 40 °C for 2 min, increasing temperature to 150 °C at 25 °C/min and 1 min in final temperature of 150 °C. An inlet temperature of 200 °C and an FID detector temperature of 220 °C were used through the run.

3. Results and Discussion

The effect of salt concentration and vessel pressure on bubble size is illustrated in Fig.2. As expected results show positive effect of increasing pressure and salt concentration to reduce the size of the bubbles. The effect of salt can be described by increasing surface tension which its direct result is increase in resistance against creation of larger surfaces, resulting smaller bubbles. A sample of oilfield produced water which contains high concentration of salt was also investigated. An interesting point about this produced water is that the bubble size produced in this water (salinity 19%) has decreased significantly because of high concentration of salt but rate of bubble size reduction by increasing pressure has reduced comparing to waters with lower salt concentration.

In a set of experiments for Methylene Chloride, Butyl Acetate, Chlorobenzene and Toluene, effect of DAP/SS on RE has been investigated (Fig. 3) and the results are compared to the mathematical model presented by Valsaraj, 1991. It is clear that the experimental data follow the model trend. Analysis of solvent layer composition after treatment shows that in the case of toluene less amount of solute are entrapped in the solvent layer and most of it has escaped to air. This can be related to higher volatility of Toluene which helps most of its molecules to enter gas phase of bubbles and finally escape to atmosphere without being entrapped in the organic solvent layer.

Fig. 4 presents results of experiments conducted on studying effect of pressure on RE in case of Toluene and CIB. As discussed before, by increasing saturator pressure the size of the bubbles decreases which will result in improving RE of solute due to increase in the Gibbs layer area (liquid around the bubbles containing active sites which can take contaminant molecules) around the bubbles. The larger the Gibbs area available, the larger amount of solute entrapped and finally more solute sublated to the organic solvent phase, which is mineral oil here. Furthermore increasing pressure while the liquid recycle rate is constant causes more air dissolved in the water and thus more bubbles released in the atmospheric column. Hence the contact area available for solute will be enhanced by increasing number of bubbles (Fig.2) as well as reducing their size. In another experiment a Simulated Produced Water (SPW) containing similar concentrations of Benzene, Toluene and Chlorobenzene (as part of BTEX present in

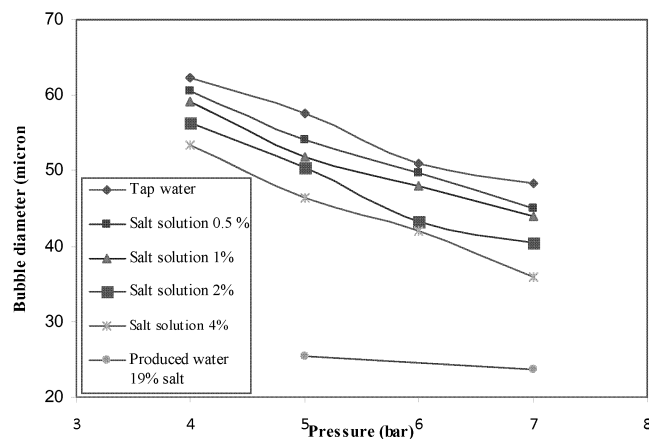


Figure 2. Effect of the saturator pressure and salt concentration on the bubble size

Most of produced waters) have been treated. Fig. 5 shows the results of applying DAP/SS operation to this mixture. Comparing the results, multi-component solution shows less RE for each component in the same time respecting to the case of single component solution (Fig.3), although by the time the RE of the multi-component solution reaches those values of single cases. The reason can be described by occupation of bubbles surface with co-existing contaminant and lower chance of adsorption for each component.

Furthermore, in the initial stages of the operation, higher volatility of Toluene causes faster removal of Toluene compared to CIB and Benzene. Also, comparing Benzene and CIB RE indicates that at initial stages of operation, higher Henry Constant of Benzene will result in faster removal by gas stripping while gradually by increasing the concentration of solution greater interfacial partitioning coefficient of CIB overcomes this feature and CIB RE reaches that of Benzene.

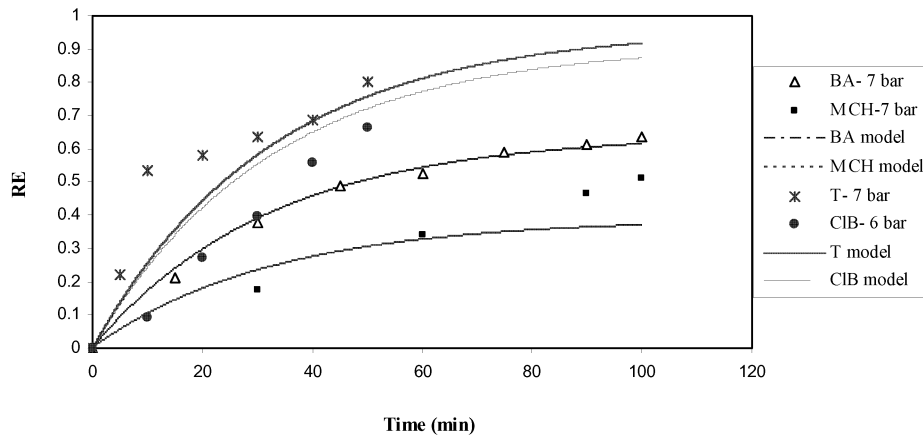


Figure 3. Removal Efficiency of organics by DAP/SS and comparing the results with model

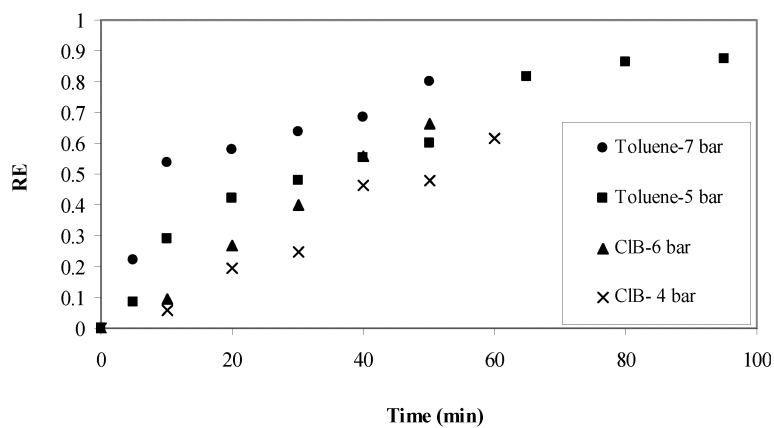


Figure 4. Effect of Pressure on Removal of Toluene and Chlorobenzene.

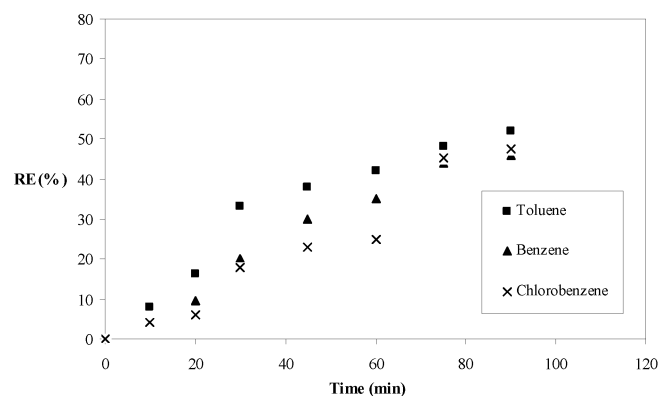


Figure 5. Removal of dissolved aromatics from a simulated mixture of Toluene, Benzene and Chlorobenzene.

4. Conclusions

It has been found that the effect of pressure on bubble size is significant. Noting to this fact and considering the major role of bubble size in the solvent sublation process (as can be seen in the Valsaraj model), in this research, DAP method with different pressures has been coupled with solvent sublation to investigate the effect of pressure on RE. Also experimental data indicate that salt concentration is another major factor affecting the size of bubbles. Comparing the results from experiment with those of mathematical model, an acceptable agreement achieved with a non-significant difference in final value of RE. Experimental data showed that the RE for a mixture of contaminants can differ from case of single contaminants due to difference in their physical properties like Henry's constant and interfacial partitioning coefficient.

References

- Glenn Brayson, B., and K.T Valsaraj. "Solvent sublation for waste minimization in a process water stream— a pilot-scale study." *Journal of Hazardous Materials*, 2001: 65-75.
- Lu, Y.J., and X.H. Zhu. "A mathematical model of solvent sublation of some surfactants." *Talanta* 57 (2002): 891–898.
- Lu, Yujuan; Li, Jizhen; Zhang, Xueli; Tan, Jie. "Studies on the mechanism of Indigo Carmine removal by solvent sublation." *Journal of Colloid and Interface Science* 292 (2005): 210-218.
- Sebba, F. "Ion Flotation." *American Elsevier*, 1962: 112.
- Smith, Jeffrey S., Kalliat T. Valsaraj, and Louis J. Thibodeaux. "Bubble Column Reactors for Wastewater Treatment. 1. Theory and Modeling of Continuous Countercurrent Solvent Sublation." *Ind. Eng. Chem. Res.* 35 (1996): 1688-1699.
- Thoma, G.J., M.L. Bowen, and D. Hollensworth. "Dissolved air precipitation/solvent sublation for oil-field produced water treatment." *Separation and Purification Technology* 16 (1999): 101-107.
- Valsaraj, K. T., G. J. Thoma, and L. J. Thibodeaux. "Nonfoaming adsorptive bubble Separation Processes." *Separations Technology* 1 (1991): 234-244.