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Abstract: Bromocresol green (BG) was removed from an aqueous solution by solvent sublation of bromocresol green–hexadecyl-pyridiumchlorid (HPC) complex (sublate) into 2-octanol. The effects of many parameters, such as the amount of surfactant, airflow rates, pH, NaCl, and ethanol on the solvent sublation were studied. Different temperatures of the solvent sublation were also investigated. A ratio of surfactant to dye (1.25:1) was the most effective for the removal, with over 99% BG removed from the aqueous solution within 5 min. The removal rate was somewhat enhanced by higher airflow rates and almost independent of the volume of the organic solvent floating on the top of the aqueous column. The effects of electrolytes (e.g. NaCl) and non-hydrophobic organics (e.g. ethanol) reduce the removal efficiency of solvent sublation. This process followed first order kinetics. A characteristic parameter, apparent activation energy of attachment of the sublate to bubbles, was estimated at a value of 1.3 kJ/mol. Furthermore, the simulation of the mathematical and experimental data was made with good results.

Keywords: Solvent sublation, mechanism, kinetics, simulation

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INTRODUCTION

Solvent sublation, originated by Sebba (1) for ionic-surfactant complexes, is one among the several adsorptive bubble separation techniques, wherein a hydrophobic compound is levitated on a bubble surface to the top of an aqueous column where they encounter a solvent layer (e.g. mineral oil and lauryl alcohol) to which the material is transferred as the bubbles move through the solvent layer (2, 3). This method, with its advantages of simultaneous separation and preconcentration, attracts much attention in the fields of environmental analysis and wastewater treatment (4–16). However, these studies are mostly focused on the effects of many parameters on the solvent sublation processes, and studies on mechanisms are limited.

Recently Palagyi and co-workers (17, 18) have proposed an ionic associate formation mechanism and second order kinetics in the separation of iodide from water by solvent sublation with CPC (*N*-cetylpyridinium chloride) into benzene. However, these kind of studies on both kinetics and thermodynamics of the solvent sublation are few (19–21).

Bromocresol green (BG), one of anionic dyes, could induce serious environmental problems. The searches for a method, which can be more or equally efficient, but meanwhile faster and less expensive than traditional methods, have resulted in an interest in the application of solvent sublation. In the present work, the kinetics and thermodynamics of humic acids ion complexes, were carried out. Furthermore, a simulation is made between the experimental and the theoretical results by the mathematical model.

EXPERIMENTAL

Reagents

All chemicals were purchased from Shanghai Chemical Agents Factory (Shanghai, China). Hexadecyl-pyridiumchlorid (HPC) and bromocresol green are reagent grade. All other agents are analytical grade. HPC was dissolved in the distilled water as the stock solution with the concentration of 2×10^{-3} mol/L.

Apparatus and Procedure

The solvent sublation system was similar to that described earlier (22). A glass column with a size of 90 cm $\times$ 7.4 cm i.d. and three access ports were used as a sublation column. The bottom access was applied as the outlet for the aqueous phase, the middle one, for sampling of the aqueous phase for the analysis, and the upper one, for the outlet of the organic layer. A microporous titanium plate was used to introduce air bubbles (the compressed air steel bottom as the source) into the aqueous phase from the bottom of the glass column. For the solvent sublation, HPC was added to the 5.0×10^{-5} mol/L BG solution (300 mL) to form the dye-surfactant complex, followed by a co-solute, such as ethanol and NaCl. The solution containing BG-HPC was then poured into the sublation column, and isopentanol (5 mL) was added immediately. The samples of the aqueous solution were taken out for analysis at a certain time.

The pH of solution was measured with a pHs-3C (Shaihai Rex Industry, China). UV-visible spectra of the sample solution were recorded with a Unico PC2100 UV/Vis spectrophotometer (Unico Com., China) at the maximum peak of 616 nm.

EXPERIMENTAL RESULTS

The Effect of the Molar Ratio of HPC to BG

The effect of HPC concentration on the solvent sublation of BG was shown in Fig. 1. It was found that 1.25:1 or 1.5:1 of the surfactant-to-dye mole fraction gave the fastest rate of separation and the lowest residual dye concentration, with over 98% of BG being removed in 5 min. At a smaller concentration of the surfactant, the rate of removal was slower and the level of the residual dye greater, presumably due to incomplete formation of a dye-surfactant complex. However, when the ratio was greater than 1.5:1, the rate of solvent sublation was smaller and the removal efficiency slower, presumably due to the competition of the bubble surface by the excess surfactant ion with the dye-surfactant complex. It was observed that the excess surfactant could also

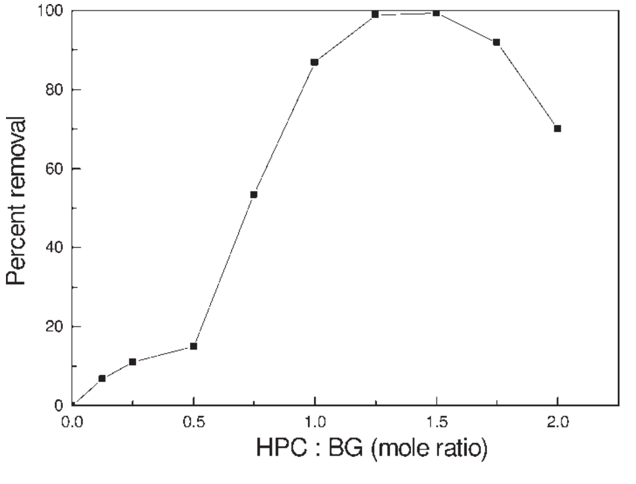

Figure 1. Effect of HPC: BG mole ratio on solvent sublation, $C = 5.0 \times 10^{-5}$ mol/L, $V_w = 300$ mL, $V_o = 5$ mL, rate of airflow = 75 mL/min, duration of airflow = 5 min.

cause the emulsification of the isopentanol (which was observed during the solvent sublation process with a larger excess of surfactant), and the dye-surfactant complex in the isopentanol was constantly dispersed back into the solution to decrease the separation significantly. This observation was the same as the results of the solvent sublation of methylene blue and methyl orange studied by Wilson et al. (14) and Karger and Pinfold (15), who argued that the rate of removal of dyes increased with larger surfactant concentration when it was much in excess of the stoichiometric amount. The optimal separation efficiency with surfactant dosage at the stoichiometric amount was also observed for the solvent sublation of HTA-Acid Red (9). This contradiction was probably due to different formation constants of the varied complexes of surfactant-dye or the altered molar ratio of the surfactant and dye in the complexes (9).

The Effect of Different Airflow Rates

The solvent sublation of BG into isopentanol was investigated at three different airflow rates (38, 75, and 185 mL/min). It was observed that the removal rates increased with the increase of airflow rates, as shown in Fig. 2. However, the increase in removal rate was out of proportion to that of airflow rates, similar to the results by Valsaraj et al. (11). This was probably explained by the observation that with increasing airflow rates the mean bubble radius went up, thus the interfacial area per unit volume of air (which is given by 3/r) decreased, and the bubble residence time also

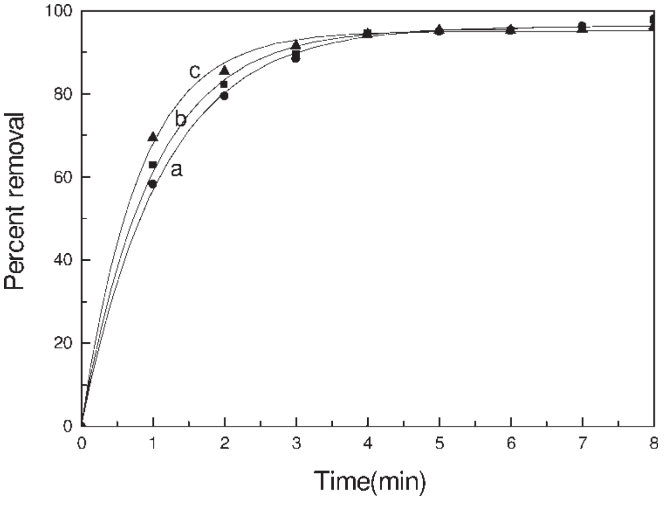

Figure 2. Effect of rate of airflow on solvent sublation, $C = 5.0 \times 10^{-5}$ mol/L, ratio of HPC to BG = 1.25:1, $V_w = 300$ mL, $V_o = 5$ mL, a: 38, b: 75, c: 185 mL/min.

reduced as a result of higher rise velocities of larger bubbles. Furthermore, the axial dispersion certainly enhanced 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. Although the increased airflow rate can improve the removal rate of solvent sublation, the removal efficiency decreases if the airflow rate is quite high, for the air currents arise from the quite high airflow rates would disrupt the oil-aqueous interface.

The Effect of the Volume Ratio of Organic Solvent to Aqueous Solution

Sebba (1) has showed that in the case of the solvent sublation of ion-surfactant complexes from aqueous solution into 2-octanol, the removal efficiency is independent on the amount of the volume of 2-octanol. Caballero (23) has made a conclusion that the sublation efficiency is independent on the organic solvent volume only until the saturation of the phase by the sublate. We achieved the same result with these experiments. It was observed that the removal efficiency was about 97% without the organic solvent, which suggests that the organic solvent was not a key factor. No significant changes in removal efficiency was observed when the volume of 2-isopentanol was from 0 mL to 10 mL in the 300 mL solution. Generally, mass-transfer occurs from gas bubbles crossing the aqueous-solvent interface and not from the diffusion of the solute across this interface, the amount of material transferred should depend only on the amount of air crossing the interface and not on the organic volume. While in liquid-liquid extraction the volume ratio of the two immiscible phases is a very important parameter, which is much different between the liquid-liquid extraction and solvent sublation. But if the organic volume used in solvent sublation is too low, the oil-water interface will be drastically disrupted at a high airflow rate and the process will lose its efficiency. Hence the airflow rates and solvent volume have to be chosen to keep the minimal disruption of the interface.

The Effects of the Co-Solute

The influence of various mole fractions of ethanol used as the co-solute ranging from 0.005 to 0.05 upon the removal rates of BG was shown in Fig. 3. The ethanol used as co-solute impaired the process of the solvent sublation for the solubility of the sublate.

The effect of NaCl used as co-solute on the sublation of BG-HPC complex is shown in Fig. 4. The increasing of NaCl concentration tended to decrease the removal rate and the removal efficiency. This was attributed to

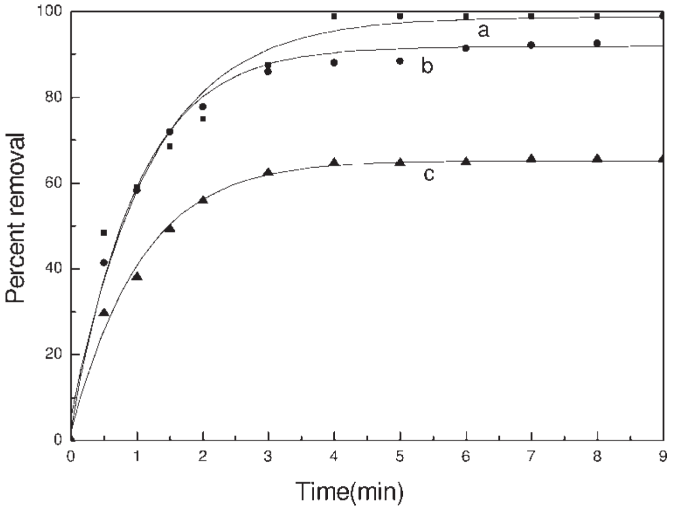

Figure 3. Effect of mole fraction of ethanol on solvent sublation, C = 5.0×10^{-5} mol/L, ratio of HPC to BG = 1.25:1, V_w = 300 mL, V_o = 5 mL, rate of airflow = 75 mL/min, a: 0; b: 0.005; c: 0.05.

an ion-pair equilibrium existed in the aqueous solution between the dye and surfactant molecules. In aqueous solution, there existed the equilibrium:

$$A^+BG^- + Na^+Cl^- \overset{K_e}{\longleftrightarrow} A^+Cl^- + Na^+BG^- \quad (1)$$

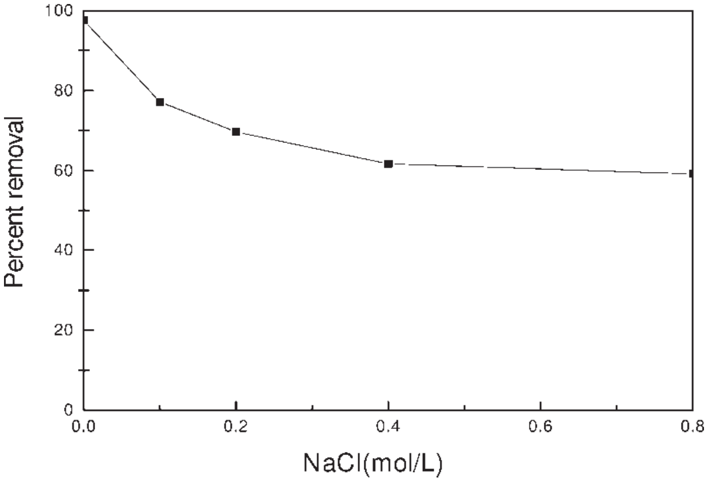

Figure 4. Effect of NaCl concentration on solvent sublation, C = 5.0×10^{-5} mol/L, ratio of HPC to BG = 1.25:1, V_w = 300 mL, V_o = 5 mL, rate of airflow = 75 mL/min, duration of airflow = 5 min.

where A represents the surfactant ion. Dye-surfactant complex A^+BG^- and surfactant A^+Cl^- act as the active surface. It was apparent that the increase of the salt concentration (e.g. NaCl) drove the equilibrium toward a larger concentration of Na^+BG^-which was hydrophilic, and less HPC-BG complex molecules (i.e., A^+BG^-) existed in the aqueous phase. As a result, the rate of removal decreased.

The Effect of pH

The effect of pH on the removal of BG-HPC in the process of solvent sublation is shown in Fig. 5. The removal efficiency of BG reached the highest removal efficiency at pH 3 to pH 4, and 99% of BG was removed from the solution by solvent sublation in 5 min. Then the removal efficiency of BG decreased greatly at pH 5.8 with 48% of BG removed. At higher pH, the removal efficiency increased to 60%.

The Kinetics and Thermodynamics of the Solvent Sublation

In the solvent sublation process, the BG-HPC molecules and the bubbles were first attracted. Then, the repulsive forces increased, which would cause the compressed thinner layer and eclipsing finally. The change of energy of this

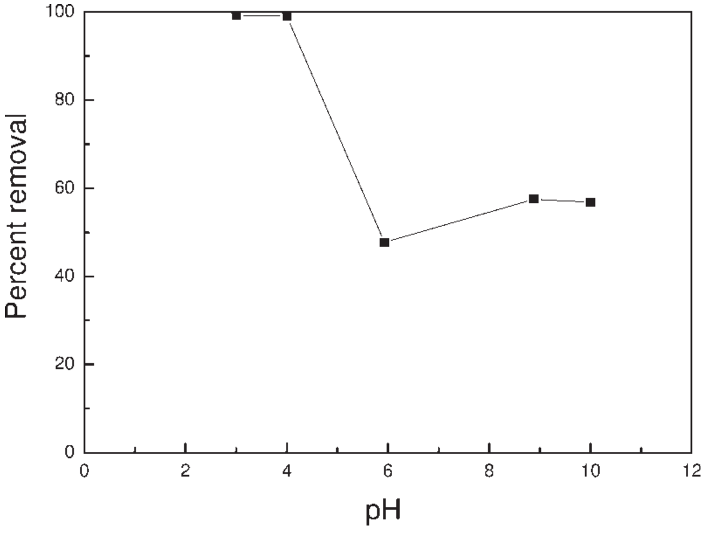

Figure 5. Effect of pH on solvent sublation, C = 5.0×10^{-5} mol/L, ratio of HPC to BG = 1.25:1, V_w = 300 mL, V_o = 5 mL, rate of airflow = 75 mL/min, duration of airflow = 5 min.

process was similar to that of the chemical reaction process. So we could use the Arrhenius equation to describe the process:

$$\ln k = -E_s/RT + B \qquad (2)$$

where k is the apparent rate constant, R is the common gas constant, B is the integration constant, and E_s is the solvent sublation apparent activation energy. The effect of temperature on the removal rate and efficiency of BG–HPC in the process of solvent sublation is shown in Fig. 6. The removal rate and efficiency increased with the increase of the temperature. As depicted in Fig. 7, a linear relationship was found between ln k and $1/T$ and from the slope of the resulting straight line, the activation energy can be calculated using the same concentration of BG-HPC solution, at three different temperatures: 279, 298, 333 K. The value of the apparent activation energy was calculated as 1.3 kJ/mol by the slope of Fig. 8, which was so small that the solvent sublation process was very rapid.

COMPARISON OF THEORETICAL AND EXPERIMENTAL DATA

The mathematical model of the dye-surfactant for the solvent sublation has been described in our earlier reports (21). In the experimental condition, the

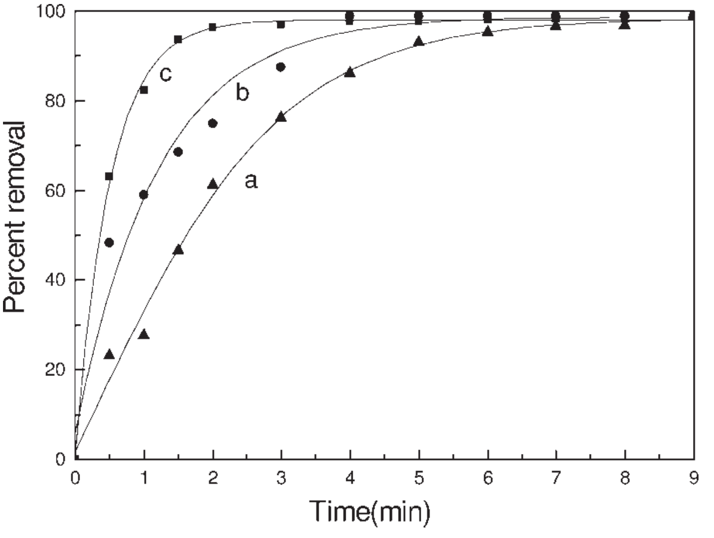

Figure 6. Effect of temperature on solvent sublation, C = 5.0×10^{-5} mol/L, ratio of HPC to BG = 1.25:1, V_w = 300 mL, V_o = 5 mL, rate of airflow = 75 mL/min, a: 279K; b: 288K; c: 333K.

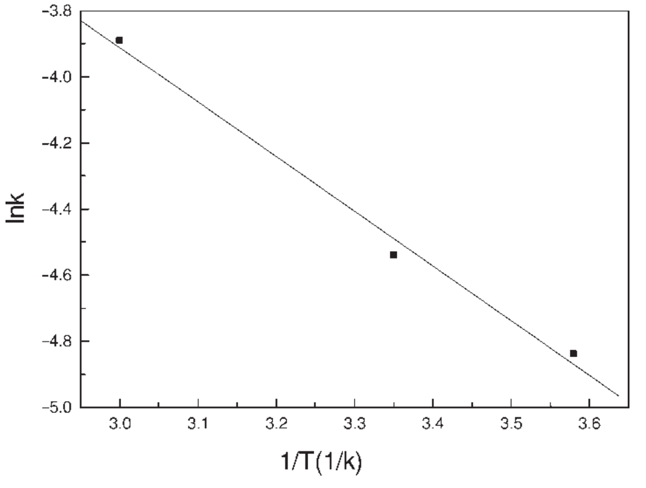

Figure 7. Curve of ln k vs. $1/T$, the data from Fig. 7, $C = 2.5 \times 10^{-5}$ mol/L, ratio of HPC to BG = 1.25:1, $V_w = 300$ mL, $V_o = 5$ mL, rate of airflow = 75 mL/min, duration of airflow = 5 min.

BG was anionic species in the solution. So the mathematical model can be applied to the BG-HPC complex system. The experimental parameters such as the column radius, airflow rate, concentration of BG and HPC, organic volume, and aqueous phase volume etc. are the real experimental data in

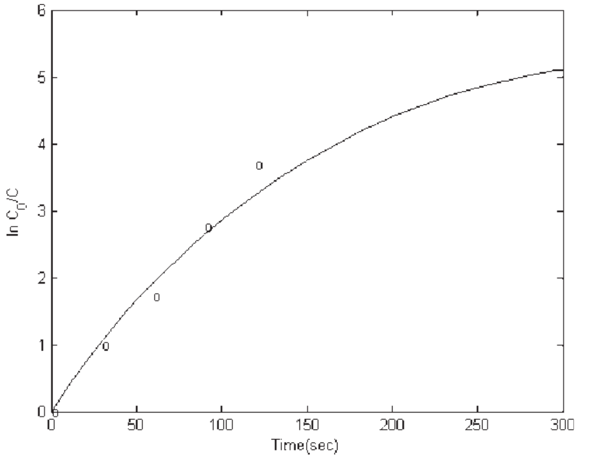

Figure 8. Simulation of experimental results for the solvent sublation of BG-HPC the line represents the theoretical result and the circle represents the experimental result $C_{BG} = 5.0 \times 10^{-5}$ mol/L; $C_{HPC} = 6.25 \times 10^{-5}$ mol/L; $K_e = 0.25$; $K_{a1} = 0.01$, $K_{a2} = 0.002\ s^{-1}$; $Q_a = 75$ mL/min; $K_{l1} = 0.001$cm/s; $K_{l2} = 0.004$; $K_{ow} = 800$; $V_w = 300$ mL; $V_o = 5$ mL; $r_c = 3.7$ cm; $d_i = 0.0001$ cm; $a = 0.1$ cm.

the model. By adjusting the value of other micro-parameters, the simulation results can be obtained.

The simulation of experimental results for the solvent sublation of BG-HPC is shown in Fig. 8. The symbols can be referred to in the literature (21). The results showed that the mathematical model can describe the solvent sublation of the BG-HPC system.

CONCLUSIONS

BG was removed effectively from the aqueous solution by solvent sublation with a cationic surfactant, HPC. A stoichiometric amount of surfactant (surfactant: dye, 1.25:1) was found to be the most effective in which over 99% of BG was removed within 5 min. The increased airflow rates enhance the process of solvent sublation, provided that the bubbles size is kept small. However, at high airflow rates, the generation of axial dispersion would compromise the efficiency of the solvent sublation.

The solvent sublation was somewhat independent on the organic volume.

The ethanol used as co-solute impairs the process of the solvent sublation for the solubility of sublate. The increase of the NaCl concentration would greatly decrease the removal rate of sublation and it made the ion-equation move towards the hydrophilic product direction. The pH value 3 to 4 is optimal to the higher removal efficiency, but the higher pH value decreased the removal efficiency.

The kinetics of the solvent sublation was followed by first-order kinetics. The apparent activation energy was put forward as a parameter of the solvent sublation resulting to be 1.3 Kj/mol.

The result, by simulating of the mathematical model and experimental data of BG-HPC, is quite satisfactory. Therefore, the mathematical model can describe accurately the real solvent sublation of the BG-HPC. Through the investigation of the experiment and the mathematical model, the adsorption process on the bubbles is the key step in the solvent sublation, and the sublation process of the BG-surfactant ion complex obeys a first order kinetics equation.

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