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Recovery of Butyl Acetate in Wastewater of Penicillin Plant by Solvent Sublation I. Experimental Study

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Abstract: Recovery of butyl acetate (BA) in the wastewater from solvent extraction of penicillin by solvent sublation into n-nonane is studied. Emulsification at water-solvent interface in the sublation was discussed, and nonpolar n-nonane was representatively used as the immiscible organic solvent to minimize the emulsification. Effects of operation variables, such as gas flow rate, Q_a, and initial solvent volume, v_{oi}, were explored. Gas flow rate, Q_a, was an important operation parameter and initial volume of solvent, v_{oi}, had a little effect on the sublation efficiency, E_{ss}, which could be more than 65% under optimal operation conditions with semibatch sublation after

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about 180 min operation. Experimental results also showed the axial concentration of BA along the column height first increased and then decreased from bottom to top because of the mutual effect of diverse mass transports. With initial concentration of BA in the wastewater of about 1%, the volume of solvent, v_o, could be increased by more than 30% at the end of the sublation. Qualified butyl acetate could be obtained through distillation and n-nonane obtained could be recycled in the solvent sublation. Air stripping was not so effective as sublation in the recovery of BA. The sublation was carried out in a sieve plate column. Experimental results showed the sieve plate could increase the axial Peclet number of water in sublation column, or minimize the back mixing of the aqueous phase in the sublation.

Keywords: Solvent sublation, butyl acetate, penicillin, sieve plate column, wastewater, back mixing

INTRODUCTION

Penicillin, a widely used biosynthesized antibiotic, is usually extracted from the filtered ferment broth with butyl acetate (BA) as solvent. In the extraction operation, butyl acetate dissolves into the aqueous phase to cause wastewater containing BA of about 1% by weight (1). Subsequent recovery of BA from the wastewater is obligatory from ecological and economical points of view. Conventional recovery of BA in the wastewater is by azeotropic distillation (or stripping) (2). Distillation is not only costly and energy consuming, but also part of BA can be hydrolyzed to butanol and acetic acid at high temperature, leading to the corrosion of equipments. Both the plate or packed column and heat exchanger can often be clogged by filth after a period of operation because of biological materials dissolved in the wastewater. So there is need to develop a new and better separation process to recover BA in the wastewater from penicillin production.

Solvent sublation is a nonfoaming adsorptive bubble separation process suggested first by Sebba (3). In the separation process, organic compounds, ions, or particles are adsorbed or attached to the air-water interfaces of ascending bubbles, and then collected into an immiscible and stagnant organic solvent layer floating on the top of the aqueous phase. The removal of inherent hydrophobic compounds by solvent sublation has been explored in recent years (4, 5). In the 1980s, Wilson and his coworkers (6–8) carried out solvent sublation for the removal of refractory organics, such as methyl chloroform, naphthalene, phenanthrene, and indene, from water, to further our understanding of the process. Smith, Valsaraj et al. studied the effect of sparger design on the hydrodynamics of sublation column and the pilot-scale solvent sublation of pyrene and pentachlorophenol from simulated wastewater (9, 10). Thoma and Bowen et al. carried out solvent sublation for the treatment of oil-field produced water by dissolved air precipitation (11). Valsaraj et al. published a pilot-scale study of solvent sublation for the removal of naphthalene from an industrial water stream based on their previous work (12).

There are a number of advantages that make the solvent sublation an attractive separation process. Different from solvent extraction, intimate contact between organic solvent and aqueous phase is minimized in solvent sublation. The mixing of the two phases only occurs at the water-solvent interface in the cross-section of column, thus preventing the undesired emulsification and residual solvent in water, which often occurs in conventional solvent extraction. Furthermore sublation process is not limited by thermodynamics, but is mostly limited by kinetics, therefore ensuring separation efficiency up to 100%.

Solvent sublation is a potential separation process to recover hydrophobic organics from their dilute solutions. In this work, the recovery of BA in the wastewater of a biological ferment process from solvent extraction of penicillin by semibatch solvent sublation was studied. Biological materials, diverse surfactants, and penicillium chrysogenum in the wastewater (13) made it unnecessary to add additional surfactants to assist the sublation and had advantageous effect on the sublation of BA. n-Nonane was used as the organic solvent for the sublation. The axial concentration of BA along the column height was also studied. The process was carried out in a sieve plate column to improve the hydrodynamics and decrease the scale-up effect. The Peclet number based on one-dimension dispersion model was also determined to study the effect of the sieve plates on the back mixing of the aqueous phase. The semibatch solvent sublation is very useful for the further research and development work on continuous sublation process.

EXPERIMENTAL

Materials

Wastewater samples from solvent extraction of penicillin were supplied by the North China Pharmaceutical Corporation Limited (Shijiazhuang). n-Nonane, butyl acetate, potassium nitrate, and n-hexane were purchased from Beijing Chemical Reagent Company, China. They were all of analytical grade purity.

Equipments and Method

Semibatch sublation experiments were performed in a glass cylindrical column with sampling ports at 10, 45, 80, 115, 150, and 185 cm from the bottom, respectively. The glass column is 200 cm tall with inner diameter of 10 cm. Nitrogen was dispersed by a sintered titanic plate with the mean pore size of 20 μm (Beijing General Research Institute for Nonferrous

Metals) at the bottom of the sublation column. Five plates with sieve pores of 3–5 mm diameters were located in the glass column. The schematic diagram of the experimental equipments is shown in Fig. 1. The butyl acetate was further purified by distillation in a packed distillation column.

During the sublation process, 15 L of wastewater were pumped into the sublation column by peristaltic pump, and then about 300 mL of n-nonane were carefully added to the top of water in the column. About 300 mL/min of cylinder nitrogen measured by manometer and rotameter were introduced into the column bottom through the titanic plate. Experiments were all done with a stagnant aqueous layer and a stagnant solvent layer while gas was used in a once-pass-through mode. Liquid samples (about 10 mL) were taken from the ports along the column for analysis at given time intervals.

Aqueous sample of 5 mL was taken and diluted two times with deionized water, and then mixed with 2 mL n-hexane, which was then stirred with electric stirrer for 2 min. After that, the sample was centrifuged (3000 r/min) for 2 min. Finally the organic phase was collected and analyzed by gas chromatography (GC). A sample of 0.3 μL was injected into GC with FID as detector, and the capillary column is HP-5 (30 m × 0.32 mm × 0.5 μm) (HP6890 Agilent Technologies, USA) (14). Distillation product was also analyzed by GC.

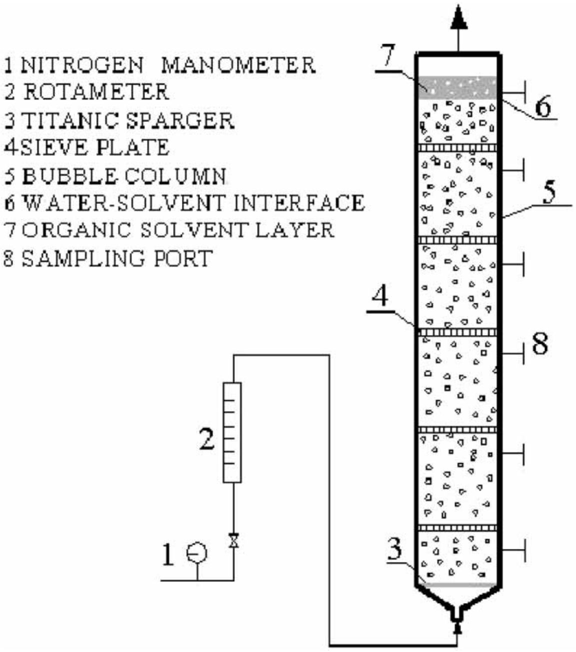

Figure 1. Schematic diagram of the experimental apparatus.

The wastewater used in experiments was directly collected from discharged water in penicillin plant with residual concentration of BA of about 1% by weight. The concentration of BA was relatively steady in experiments. For the sake of comparing data, the efficiency of sublation E_{ss} or air stripping E_{as} at time t is defined as:

$$E_{ss(as)} = \frac{c_{wi} - c_w}{c_{wi}} \times 100\% \qquad (1)$$

The Peclet number (P_e) based on one-dimension dispersion model is defined as shown in Eq. (2). It is a character of axial back mixing of the aqueous phase. Smaller value of Peclet number shows the back mixing of the aqueous phase is more serious. The point source pulse injection technique and the online analysis of conductance by computer were used. The tracer was potassium nitrate, and the simulated liquid phase was tap water. The experiments were carried out in continuous sublation process performed in the glass cylindrical column of 10 cm inner diameter but just 100 cm tall to simplify the process. For a "closed-closed" system, the relation between variance (second moment) of the response to a pulse signal and Peclet number is given by Eq. (3) (15–17). According to the measured residence time distribution (RTD) data, variance was first calculated, and then the corresponding Peclet number was calculated with the iterative method. All of the work was done by using a computer program.

$$P_e = \frac{uL}{D_L} \qquad (2)$$

$$\sigma_\theta^2 = \frac{2}{P_e} - \frac{2}{P_e^2}[1 - \exp(-P_e)] \qquad (3)$$

RESULTS AND DISCUSSION

Emulsification at Water-Solvent Interface and in Solvent

Although the serious mixing and turbulence between water and solvent is kept low in solvent sublation, sometimes emulsification would occur at the water-solvent interface or in solvent phase as shown in Fig. 1, especially under high gas flow rate. Holding the water-solvent interface stable, especially nonemulsification, is important to solvent sublation (3). In the solvent extraction of penicillin, de-emulsifier containing various surfactants should be added to filtered ferment broth to minimize disadvantageous emulsification (13). Most of the surfactants would dissolve in the aqueous phase. Furthermore in the wastewater from a ferment process, there were some biological materials, such as proteins and sugars. BA is an organic solvent with some inherent polarity. So it is not a surprise that surfactants, biological materials, and BA would result in emulsification at the water-solvent interface or in the solvent phase in the sublation of BA from the wastewater.

When polar solvents, such as octanol, were used as organic solvents in the sublation, experimental results showed that emulsifications at the water-solvent interface and in solvent were serious. Under such emulsification condition, water-solvent interface was too unstable to be controlled successfully. But if nonpolar straight alkyl hydrocarbons, such as n-nonane, were used as organic solvents, emulsification at the water-solvent interface wouldn't occur. In addition, the difference of boiling points between BA and n-nonane is large enough to make it economical to recycle the solvent and purify BA by distillation. n-nonane is a non-volatile organic solvent and has very low water solubility. BA and n-nonane can be dissolved in each other. So n-nonane is a representative solvent to further our understanding of the sublation and choosing of other more suitable solvents.

Effect of Gas Flow Rate

Gas flow rate, Q_a, directly affects the area of air-water interface per unit volume of the aqueous bulk in unit time, so it is a very important operation parameter in solvent sublation. The effect of gas flow rate, Q_a, on sublation efficiency, E_{ss}, is shown in Fig. 2. Under the same gas flow rate, sublation efficiency increases with the increase of time, but the rate of increase slows down with the increase of time and approaches asymptotically its maximum value. At the same sublation time, sublation efficiency with low gas flow rate is lower than that with a high one. Mass transfer of solute to air-water interface of

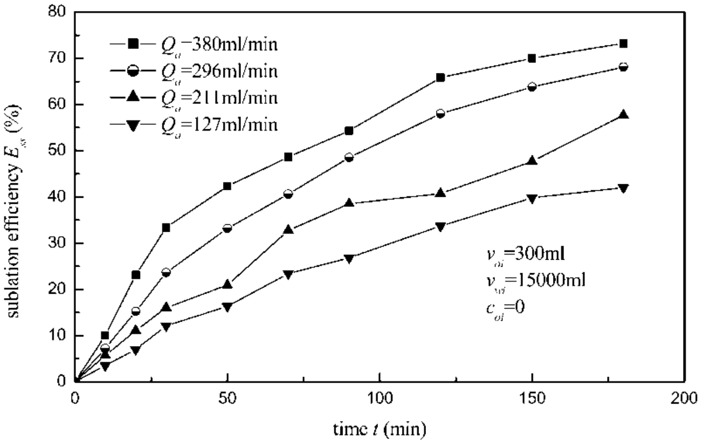

Figure 2. Effect of gas flow rate, Q_a, on sublation efficiency.

rising bubble in the aqueous phase is the dominant transport process strongly affecting the separation efficiency in solvent sublation. Under invariable mean radius of bubbles, air-water interface area of the same air volume at high gas flux is larger than that at the low one. As a result, more solute would be adsorbed or attached to the interface and entrained to solvent with high gas flow rate, resulting in better sublation efficiency. But under higher gas flow rate, emulsification as just mentioned at water-solvent interface and in solvent would be unavoidable. Under gas flow rate up to 500 mL/min, emulsified organic solvent layer of O/W (n-nonane in water) or W/O (water in n-nonane) in droplets and pieces would be back-mixed into the aqueous phase. In order to minimize the undesired back mixing, the desired gas flow rate is typically 300 mL/min.

Effect of Initial Volume of Organic Solvent

The effect of initial volume of organic solvent, v_{oi}, on sublation efficiency is shown in Fig. 3. Conventional liquid-liquid extraction is usually a process controlled by thermodynamics, so extraction efficiency is determined by the initial aqueous-to-organic phase volumetric ratio, v_{wi}/v_{oi}, and phase partition constant, K_{ow}. But in solvent sublation, liquid-liquid extraction process only exists in solvent layer. As air bubbles with thin water film around them penetrate into the solvent layer and break, the water in the film flows back to the aqueous phase as small droplets by gravity. In the

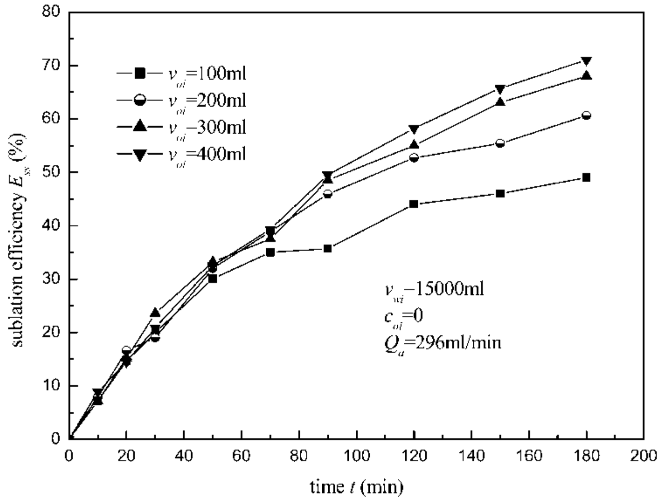

Figure 3. Effect of initial volume of organic solvent, v_{oi}, on sublation efficiency.

process, solute in water film is entrained into the solvent, and the equilibrium amount of solute with solvent phase will return to the aqueous phase. But this is usually not the predominated mass transport pathway. When molecular diffusive transport at the solvent-water interface (determined by the aqueous phase overall mass transfer coefficient K_l) is weak, solvent sublation is a process controlled by kinetics, not by thermodynamics. Thus sublation efficiency is almost independent of initial volume of solvent because predominate mass transport is the entrainment of solute or particles to solvent phase based on the adsorption to air-water interface from water. K_l for BA is low (9.03×10^{-4} cm/s), so the initial volume of organic solvent had a little effect on sublation efficiency when the initial solvent volume was more than 200 mL as shown in Fig. 3. It is one of the important advantages of solvent sublation over the conventional solvent extraction.

In other solvent sublation, organic solute concentration is usually in the order of 10^{-6} g/g. Different from them, the initial concentration of BA in the wastewater is about 1% by weight. Therefore the concentration of BA in the solvent would increase as BA was sublated into the solvent. Under solvent volume of 100 mL, the reverse mass transports at water-solvent interface (driven by the concentration gradient between solvent and water) and in the solvent layer by water film increased with the increase of sublation time as shown in Fig. 3. The initial aqueous-to-organic phase volumetric ratio had better not be more than 75 to minimize the disadvantageous effect. But under very small phase ratio, the concentration of BA in solvent would be too low to economically recycle solvent and purify butyl acetate by distillation. Desired initial aqueous-to-organic phase ratio is typically between 50 and 70.

As shown in Fig. 2 and Fig. 3, sublation efficiency can be higher than 60% at 150 min and 70% at 180 min under optimal conditions during the semibatch sublation of BA in the wastewater in penicillin production.

Axial Concentration Distribution of BA along the Column

Wilson and his coworkers proposed a batch-sublation model including the effect of the rate of solute mass transfer from the aqueous into the gas phase (6). In their model, the aqueous column was partitioned into some slabs. Simulation results showed to take the number of slabs more than five has little additional effect on the behavior of the model. The mixing of liquid phase is usually serious, so the water column was often considered as one well-mixed stage. Shin and Coughlin simply discussed the concentration profiles along the column with a middle sampling port during the solvent sublation of toluene (18). In our sublation, axial concentration distribution of BA along the column was studied. The typical experimental results were shown in Fig. 4. The concentration of BA increased along the column from

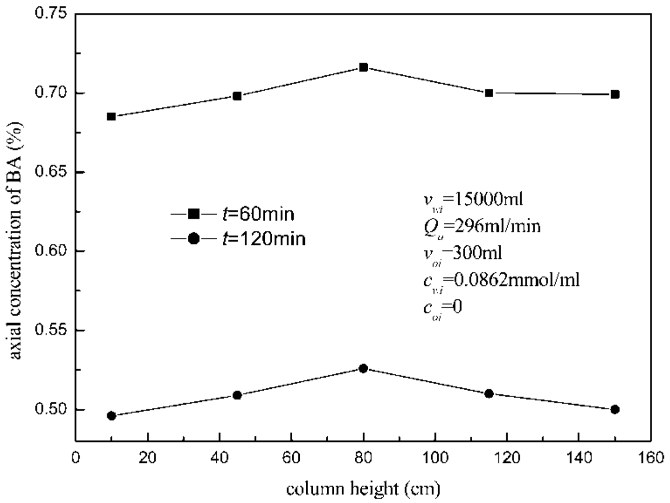

Figure 4. Axial-distribution of BA along column.

the bottom of the column, and there existed a maximal concentration at the column height of about 80 cm, then it would decrease a little. The axial concentration distribution shows that at the bottom of the water column, bubbles that carried BA at air-water interface were rising in the column, leading to the increase of BA concentration along the column. At the upper part of the water column, the decrease of BA concentration might be attributed to the extraction effect of n-nonane back-mixed to the water and the mass transfers occurring both at water-solvent interface and in solvent layer by water film.

Comparison with Air Stripping

In order to understand the solvent sublation for the recovery of BA in the wastewater better, air stripping was studied with the gas flow rate of 296 mL/min as used in solvent sublation. The only difference between them was the presence of solvent layer floating at the top of the stripping column. The experimental results are shown in Fig. 5. The efficiency of air stripping, E_{as}, was much lower than that of solvent sublation, E_{ss}. It could be explained as that air stripping is a separation process based on the volatility of organic, but BA has a low Henry's law constant (0.00829), which shows its vapor pressure is relatively low under the atmospheric pressure (19). Most of BA adsorbed at the air-water interface return into the aqueous phase as bubbles broke on the water-air interface at the top of the column. But in solvent sublation, most of them were entrained into the solvent layer to prevent BA from re-entering

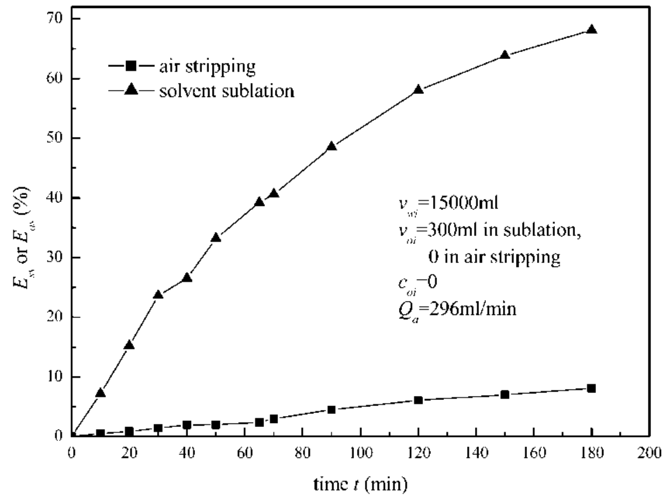

Figure 5. Efficiency of air stripping in comparison with solvent sublation.

into the aqueous phase. So the recovery efficiency of BA in solvent sublation is better than that obtained in air stripping.

Hydrodynamics of Sieve Plate Column in Solvent Sublation

The turbulent and eddy flow of the aqueous phase is usually serious because of the asymmetric dispersal of gas and the agitation of gas in the sublation. It would result in the back mixing of the wastewater in sublation column, with bad effect on the scale-up of the sublation, especially on the continuous sublation process. Therefore it is important to minimize the disadvantageous effect and improve the hydrodynamics of the sublation column. Valsaraj and his coworkers used the bubble column with an annular shear sparger to improve the hydrodynamics of the sublation column and applied an overflow reservoir to prevent the solvent from being entrained and mixing throughout the column (9). Wilson also suggested that axial dispersion could be controlled by baffles in the column and by dispersal of air uniformly across the cross-sectional area of the column (6). But little work has been carried out in recent years. On the other hand, solvent sublation has been explored to treat real industrial wastewater. It needs further studies on the hydrodynamics effect in solvent sublation. In our sublation experiments, sieve plates with pores of 3–5 mm inner diameters and 35 cm plate interval were applied. Experiments showed the turbulent and eddy flows were greatly mitigated. Experimental results showed the Peclet number based on one-dimension dispersion model for the flow with sieve plates was higher ($P_e = 5.795$) than that without sieve plates ($P_e = 3.651$). It shows the back mixing of the aqueous phase was minimized by sieve plates. It is very meaningful for the scale-up of the sublation process.

Distillation to Obtain Qualified BA

Through measuring the height of organic solvent layer during the sublation, we could find that solvent volume increased as BA was sublated into the organic solvent. The initial concentration of BA of about 1% is relatively high in conventional solvent sublation. The variation of the organic solvent volume during the sublation is shown in Fig. 6. At the end of the sulation, the solvent volume would increase by more than 30%, in agreement with the calculated result of overall mass balance of BA according to the analytical results of the concentration of BA in wastewater. After the sublation, there was about 30% of BA (by weight) in n-nonane. The mixture should be distilled to obtain qualified BA and recycle the n-nonane. It is different from other reported solvent sublation work (10, 12). Distillation results showed that qualified BA with a concentration in excess of 98% could be obtained. Compared with the results of the recovery by azeotropic distillation (or stripping), the acidity of BA from this work was much lower than that from stripping. The results confirmed that part of BA hydrolyzed to acetic acid in azeotropic distillation with heat increased the acidity of the product, which did not occur in solvent sublation. Experimental results also showed that

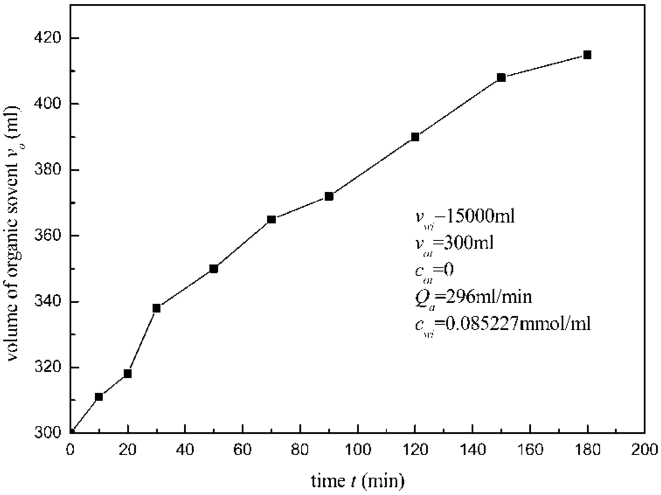

Figure 6. Variation of volume of organic solvent.

recycled n-nonane had little effect on the sublation. All of these prove that solvent sublation for the recovery of BA in the wastewater of penicillin plant is practical.

CONCLUSIONS

As an organic hydrophobic compound dissolved in the wastewater containing diverse surfactants, biological materials, and penicillium chrysogenum, butyl acetate could be sublated into organic solvent by solvent sublation. The nonpolar organic solvent, n-nonane, under optimal gas flow rate, could efficiently eliminate the undesired emulsification at the water-solvent interface. The sublation efficiency, E_{ss}, could reach 65% in 180 min. Desired gas flow rate is typically 300 mL/min, and initial aqueous to solvent volumetric phase ratio, 50–70. Qualified butyl acetate could be obtained and n-nonane can be recycled after distillation. Experimental results also showed air stripping was not so effective as sublation to the recovery of BA. A sieve plate column with 10 cm inner diameter and 200 cm tall was used to improve the hydrodynamics. The Peclet number of water in the sublation column with sieve plates was larger than that without sieve plates, proving that the back mixing of the aqueous phase could be minimized by sieve plates. It is very meaningful for the scale-up of the sublation process and continuous sublation process.

NOMENCLATURE

c_{oi}	initial solute concentration in solvent phase (mmol/mL)
c_w	concentration of solute in aqueous phase (mmol/mL)
c_{wi}	initial solute concentration in aqueous phase (mmol/mL)
D_L	liquid phase axial back mixing coefficient (cm^2/s)
E_{as}	efficiency of air stripping (%)
E_{ss}	sublation efficiency (%)
K_l	aqueous phase overall mass transfer coefficient (cm/min)
K_{ow}	phase partition constant (—)
L	characteristic length of the sublation column (cm)
P_e	Peclet number (—)
Q_a	gas flow rate (mL/min)
t	time (min)
u	liquid velocity (cm/s)
v_o	volume of organic solvent phase (mL)
v_{oi}	initial volume of solvent phase (mL)
v_{wi}	initial volume of wastewater (mL)

Greek

σ_θ^2 variance of a trace curve or square standard deviation (—)

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