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Separation of butyl acetate from model emulsions by solvent sublation

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ABSTRACT

Separation of butyl acetate from the O/W type model emulsion by solvent sublation with Span-80 as the emulsion surfactant was studied. The particle size and zeta potential were analyzed by particle size analyzer and emulsion stability was characterized by concentration measurement. The effects of gas rate, operating time, surfactant concentration, solute concentration, pH and cosolutes (NaCl and ethanol) on the removal efficiency and the particle size and zeta potential were investigated. It was found that only droplets with the diameter larger than 500 nm can be removed from the model emulsions by solvent sublation. Under that condition, the separation efficiency of solvent sublation was somewhat increased in comparison with that of solvent extraction when the solution was in emulsion type. Comparison of removal efficiency was made between the aqueous saturated solution and model emulsion. Results showed that the emulsion property of the solution improved the separation.

1. Introduction

Solvent extraction is used widely in petroleum refining, food processing, hydrometallurgical engineering, pharmaceutical manufacturing and cosmetic sectors for its easiness to operate and convenience to scale up. However, emulsion is commonly encountered in the solvent extraction process, which originates from the intimate contact of organic solvent with aqueous phase. The emulsion varied from unstable state to stable state depending on the presence of surfactants or surfactant-similar materials in the extraction system. In general, formation of emulsion will increase the difficulty of phase separation. The emulsion causes not only the loss of organic solvent but also the secondary contamination of aqueous phase. This is a disadvantage to the separation.

Penicillin G is one of the extremely important antibiotics and raw material of semi-synthetic penicillins. Solvent extraction is one of the most widely used separation techniques for the recovery of penicillin G. Despite the economic advantages of using butyl acetate (BA) as extractant to recover penicillin G, it has been limited due to environmental considerations. The concentration of BA dissolved in the wastewater (1% by weight) is much higher than the saturated concentration of BA in water [1]. Separation and recovery of BA from the wastewater is of economical, ecological and environmental importance. The conventional method used is azeotropic distillation. It not only is of high cost and energy consuming, but also leads to the corrosion of equipment as part of BA can be hydrolyzed to butanol and acetic acid at high temperature. Both the column and heat exchanger were often clogged by filth after a period of operation because of biological materials dissolved in the wastewater. Alternative method needs to be explored. Several methods have been introduced in the process of separation of BA from penicillin wastewater, e.g., air stripping [2,3], foam separation [1] and solvent sublation process [4] and the results indicated that solvent sublation has better separation efficiency.

In the previous work, Sun et al. found that the raw wastewater of penicillin plant was in emulsion form [5]. The emulsion properties of the wastewater have positive effect on the solvent sublation for BA recovery in the penicillin wastewater. Furthermore, they indicated that the mass transport of solute by attachment on the rising bubbles was an important pathway when the wastewater was in emulsion form [6]. However, the systems were very complicated and the final separation efficiency was the integrative result of interactions of various parameters. How the properties of emulsion and each of the individual process parameters affect the separation was not explored and clarified. In addition, the critical sizes of droplets that can be attached by bubbles were not known. Thus, knowledge and understanding of the relationship of properties of emulsion and process parameters with separation as well as that of how to improve the efficiency is very important.

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Some works related to the separation from emulsified wastewater by flotation have been conducted. Bubble attachment by oil droplets and the enrichment mechanism of bubble separation in the flotation process were examined by Moosai and Dawe [7] and Grattoni et al. [8,9]. The surface science of the gas flotation process, particularly the gas attachment to the oil droplet, was especially emphasized. The authors indicated that the adhesion of the gas bubble to the oil droplet was the crux of the flotation. Pal and Masliyah [10] studied the oil recovery from its aqueous emulsified solution by a flotation column. The column performance at various levels of feed oil concentration, gas flowrate and surfactant concentration was investigated. In another report, the effect of emulsified compound properties on flotation efficiency for the removal of partly soluble and slightly volatile hydrocarbons from their emulsions was explored [11]. Simulation indicates that different mechanisms should be selected when emulsions of different hydrocarbons were modeled. Chavadej et al. [12] reported the effect of microemulsion formation on clean-up of oily wastewater by froth flotation. They deduced that the maximum removal of *ortho*-dichlorobenzene could be obtained when a Winsor type III microemulsion was formed, especially in the microemulsion region in excess of the oil phase [13]. The increase in separation efficiency by the formation of emulsion was validated. Al-Shamrani et al. [14] focused on the electrochemical aspects involving the separation of oil from water by dissolved air flotation. The zeta potentials of the emulsified and flocculated oil droplets were determined. The authors indicated that it is important to decrease the magnitude of zeta potential by adding aluminium sulphate. The electrostatic repulsion decreased, so the emulsion was destabilized prior to flotation and then the separation became easier.

Though flotation was successfully applied in treating emulsified wastewater, few works were focused on the solvent sublation process. Solvent sublation, a nonfoaming adsorptive bubble separation method, has already found wide applications during the seventies and eighties of last century. In the last forty years, previous studies on the separation of organics by solvent sublation have been carried out mainly by Wilson and his coworkers, Valsaraj's group, Dong and co-workers, as well as Lu's group except for ours. According to the physiochemical properties and/or the formation of the sublate, the organic substances can be classified into the following four categories. (1) Dyes, such as methyl orange and methylene blue [15], bromophenol blue [16], methyl violet [17] and indigo carmine [18]; (2) surfactants or dye-surfactant ion complexes. For example, hexadecyl pyridinium chloride and dodecyl benzenesulfonic acid [19,20], hexadecyl trimethyl ammonium chloride [21] and bromocresol green [22]; (3) hydrophobic and refractory organics. For instance, indene and aldrin [23], alkyl phthalates [24], trichlorobenzenes [25], naphthalene and phenanthrene [26], chlorinated organics and nitrophenols [27]; (4) natural products, such as achyranthes bidentata [28], magnolol and honokiol [29]. It can be seen that the quantities of organic chemicals in the previous studies were relatively low. Moreover, most of the chemicals were removed from their aqueous solutions. Only recent work of Bi et al. [30] was conducted with the real system. Compared with these studies, the wastewater of penicillin plant is a complex system, in which the BA concentration is rather high. Besides, the effect of emulsion property on solvent sublation and separation of solute with such a high concentration by solvent sublation were also seldom reported. So, it is of great importance to study the solvent sublation process in treating simulating emulsion solutions with a higher concentration of BA.

In this paper, the O/W type of model emulsion was made by addition of a non-ionic surfactant, such as Span-80 into the aqueous solution of BA. The stability of the solution was examined. Separation of BA from the model emulsion by solvent sublation was investigated. The present work is aimed to investigate the influence of emulsion property and individual process parameters on the removal efficiency. Another objective was to find out the reason for the inability of separation after a period of operation from a small scale (by particle size analysis). The results of solvent sublation were also compared with those of solvent extraction.

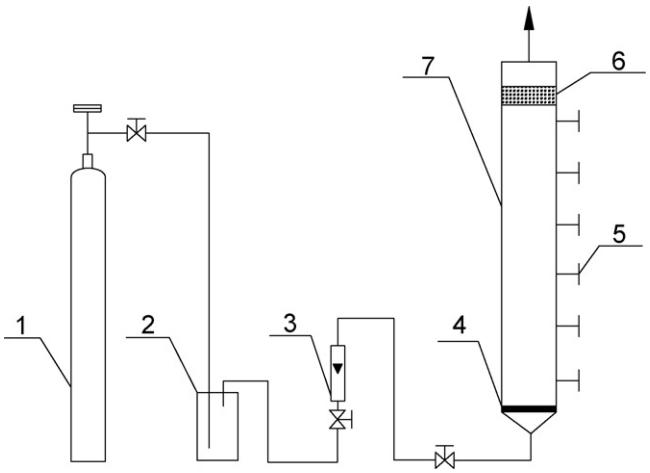

Fig. 1. Schematic diagram of the experimental apparatus. (1) Compressed gas cylinder; (2) Surge tank; (3) Rotameter; (4) Sintered glass disk; (5) Sampling port; (6) Organic solvent layer; (7) Bubble column.

2. Experimental

2.1. Materials

Butyl acetate (BA), n-nonane, sorbitan monooleate (Span-80), *n*-hexane, sodium chloride, ethanol, acetone, Sudan III and concentrated hydrogen chloride were purchased from Beijing Chemical Reagents Company (Beijing, China). All chemicals were of analytical grade and used as such without further purification.

2.2. Preparation of emulsion and feed

The model emulsion was prepared by adding 0.1-g Span-80 and 4-ml BA into 500-ml tap water in a jar. The mixture was stirred by a mixer with high speed for about 12 min, then the O/W type emulsion was formed and transferred into a separatory glass funnel immediately. After standing for a few minutes, the subnatant of the emulsion was drained and saved as the stock solution for sublation because the BA added was superfluous. The type of the model emulsion was checked by dying the emulsion with Sudan III and studied by optical microscope with oil lens (BX41, Olympus, Japan) [5]. The saturated solution was made by dissolving BA into the tap water at the room temperature.

2.3. Emulsion stability test

The emulsion stability test was conducted according to the method developed by Ham et al. [31]. The emulsion solution was put into a 2-l separatory funnel, samples of 5-ml volume were drained from the bottom of the funnel at different standing periods and the concentration of BA was followed.

2.4. Solvent sublation test

The experimental apparatus is the same to that described earlier by Sun et al. [4]. The schematic diagram of the experimental equipment is shown in Fig. 1. A glass cylindrical column 100 cm