Separation and Purification Technology 69 (2009) 71–77

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

# Caprolactam recovery by a column packed with polysulfone microcapsules containing 1-octanol

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ARTICLE INFO

*Article history:*
Received 11 May 2009
Received in revised form 24 June 2009
Accepted 25 June 2009

*Keywords:*
Microcapsule
Extraction
Caprolactam
Fixed bed column
1-Octanol

ABSTRACT

Caprolactam recovery from its dilute aqueous solution is a challenging task in industry. To save resources and protect environment, a caprolactam recovery technology based on extractant microcapsules as the separation material was introduced. In this new technology, polysulfone microcapsules containing 1-octanol were packed in a column. In the extraction process, recovery ratio of 0.99 was achieved within 0.6 bed volume. More than 10 theoretical plates per meter microcapsule column were realized. In the regeneration process, sulfuric acid aqueous solution was introduced as the stripping agent. Accordingly the new technology can be integrated with existing caprolactam production process because the eluent could be returned to $NH_3$ causticization section. Caprolactam was successfully stripped and concentrated. Caprolactam concentration of 112 g/L in the eluent was obtained. New technology based on extractant microcapsules shows high efficiency in caprolactam recovery.



## 1. Introduction

The production of caprolactam and its polymers will generate a large quantity of wastewater in which caprolactam mass fraction is usually less than 0.1 [1]. Directly discharging the wastewater containing low concentration caprolactam will cause both economy and environmental losses. Solvent extraction is an effective way to recover caprolactam massively [2]. Benzene, the most widely used extractant in industry, its extraction capacity is small when caprolactam content in aqueous phase is low [3]. Therefore, high theoretical plate number is required to ensure the recovery ratio of caprolactam. 1-Octanol is recommended as the substitutional extractant with larger extraction capacity and much lower toxicity than benzene [4]. But 1-octanol is easy to form an emulsion in liquid-liquid extraction due to its relatively high viscosity and low interfacial tension between water [5]. Therefore 1-octanol is suggested to be immobilized before caprolactam extraction [6].

Microcapsules or resins containing extractants have been successfully applied to extract metal ions and organic compounds [7–9]. There are several merits to use immobilized extractants as a substitute for conventional liquid-liquid extraction. First, the immobilization of extractants is an effective way to solve the problems in phase mixing and phase separation [10,11]. It indicates extractants with high viscosity or very large molecular weight can be employed without diluent [12,13], such as ionic liquids [14,15], polymers [16] or proteins [17]. Second, extraction process can be more energy saving. Microcapsules or solvent impregnated resins are packed in a fixed bed column when used in extraction. There is no energy consumed in stirring or other methods to contact the two phases. It also means the possibility to treat massive solutions with very dilute solutes [18,19]. Third, it is also much easier to operate a microcapsule column than a conventional extraction column because of less influencing factors. Fourth, the height of a transfer unit in a microcapsule column can be less than 0.01 m, which leads to a high theoretical plate number [20]. It is very helpful to obtain high recovery ratio when dealing with wastewater. It also indicates the possibility to separate compounds with very similar characteristics, such as chiral compounds [21]. In addition to these, in the stripping process, by selecting suitable stripping solution, solutes can be concentrated. In Ruiz et al.'s work [22], maximum concentration factor of valeric acid can reach 19 when the stripping solution was 0.5 mol/L NaOH. By using gradient elution, solutes extracted in microcapsule column can be separated completely, especially in the separation of metal ions [23]. In Zhang et al.'s work, more than 20 metal ions were separated with the usage of different solvent impregnated resin columns and gradient elution [24–26].

In this work, polysulfone (PSF) microcapsules containing 1-octanol were packed in a column to recover caprolactam from dilute solution. Caprolactam absorbed was stripped with aqueous solution of sulfuric acid. The influences of feed solution concentration and flowrate on the shape of breakthrough curves were investigated and modeled. The characteristics of flow and mass transfer were analyzed too.

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doi:10.1016/j.seppur.2009.06.019

**Nomenclature**

| | |
|---|---|
| $D$ | distribution coefficient between microcapsule phase and aqueous phase |
| $D_{eff}$ | apparent diffusion coefficient of caprolactam in microcapsules [$m^2/s$] |
| $D_S$ | caprolactam distribution coefficient between sulfuric acid phase and 1-octanol phase |
| $D_w$ | diffusion coefficient of caprolactam in water [$m^2/s$] |
| $H$ | height of microcapsule bed [m] |
| $H_{ox}$ | height of a transfer unit [m] |
| $dh$ | the height of infinitesimal element in microcapsule bed [m] |
| $d_{mc}$ | the diameter of a microcapsule [m] |
| $e_x$ | axial diffusion coefficient [$m^2/s$] |
| $K_x$ | overall mass transfer coefficient in column [m/s] |
| $k_{ext}$ | external mass transfer coefficient [m/s] |
| $k_{int}$ | internal mass transfer coefficient [m/s] |
| $N_{ox}$ | number of mass transfer unit |
| $Pe$ | $u_xH/D_A$, the axial Peclet number |
| $R$ | the radius of a microcapsule [m] |
| $Re$ | $d_{mc}u_0\rho/\mu$, Reynolds number |
| $t$ | time [s] |
| $u_0$ | superficial velocity [m/s] |
| $u_x$ | interstitial velocity [m/s] |
| $W_A$ | caprolactam mass fraction in aqueous phase |
| $W_O$ | caprolactam mass fraction in organic phase |
| $x$ | caprolactam concentration in aqueous phase in column [$kg/m^3$] |
| $x_i$ | caprolactam concentration in feed solution[$kg/m^3$] |
| $x^*$ | caprolactam concentration in aqueous phase which is in equilibrium with $y$ [$kg/m^3$] |
| $y$ | average caprolactam concentration in microcapsules packed in column [$kg/m^3$] |
| $z$ | spatial coordinate |
| $\varepsilon$ | porosity of microcapsule bed |

## 2. Experimental

### 2.1. Chemicals

Caprolactam (>99.9%) was kindly provided by Shijiazhuang Chemical Fiber Plant, SINOPEC (China). PSF (intrinsic viscosity: 0.56) was purchased from Beijing Trihigh Membrane Technology Co. Ltd. (China). Ethanol (>99.7%), methanol (>99.5%), aqueous ammonium (25–28%), 1-octanol (>99.8%), sulfuric acid (95–98%) and N-methyl-2-pyrrolidone (NMP, >99.0%) were purchased from VAS Chemical Co., Ltd (China). All materials were used as received without any further purification.

### 2.2. Measurements of liquid-liquid equilibrium

Liquid-liquid extraction experiments were carried out in a conical flask at 25 °C. The mixture of caprolactam and 1-octanol was contacted with sulfuric acid aqueous solution. After agitation for 10 h, the equilibrium state was considered to be reached. The liquid mixtures then were allowed to settle for at least 10 h until the two phases separated completely. Samples with a volume of 200 μL were taken out from two phases. After causticized with excessive aqueous ammonium, the samples were diluted with methanol in a 10 mL volumetric flask. Caprolactam concentration in methanol then was determined by the gas chromatography method (Agilent 6890, Agilent).

### 2.3. Preparation of microcapsule column

Microcapsules were prepared with a micro-dispersion process described in previous work [27]. For better comprehension, the experimental setup for preparing PSF microspheres is shown in Fig. 1. PSF was dissolved in NMP to form a polymer solution with a weight ratio of 8%. The PSF solution, as the dispersed phase, was pumped into the microdevice by a syringe pump (TS2-60, Lange). The outside diameter of the dispersed phase channel is 0.7 mm. The inner diameter of the main channel for gas flow is 2.6 mm. The flowrate of $N_2$ and the polymer solution were 200 L/h and 300 μL/min, respectively. Under the co-action of the rupture of $N_2$ and the gravity force, droplets of PSF solution were formed and solidified when they dropped into a solidification solution. The solidification solution was a mixture of 500 mL of ethanol and 1500 mL of deionized water. PSF microspheres were kept in solidification solution for 1 h before filtered out. After that, the microspheres were washed with deionized water for five times and dried at 110 °C for 5 h. PSF microspheres then were immersed in 1-octanol and subjected to ultrasonic treatment for 3 h. The power of the ultrasonic cleaner (SB3200DTD, Ningbo Scientz Biotechnology Co., Ltd.) was 180 W. The prepared PSF microcapsules then were kept in 1-octanol for 24 h. Finally, the microcapsules full of 1-octanol were filtered out and packed in a glass column with a dry column-packing process. The column was 107.9 cm in length, 9.9 mm in inner diameter. The bed porosity was 35.3%.

### 2.4. Characterization of microcapsules

The structures of the microspheres were characterized by scanning electron microscopy (SEM) (Model JSM-7401F, JEOL) micrographs. The mass transfer performances of the microcapsules were performed by contacting caprolactam aqueous solutions. When determining the maximum uptake of caprolactam, microcapsules were contacted with 25 mL caprolactam aqueous solutions with different concentrations under stirring for 24 h to reach the extraction equilibrium state. The caprolactam aqueous solution was saturated with 1-octanol before experiments. After extraction, the microcapsules were taken out and contacted with 2 mL of ethanol for 10 h, to ensure that all the caprolactam and 1-octanol in microcapsules were dissolved in ethanol. The caprolactam content in ethanol and aqueous phase then were determined with gas chromatography. A method of suspended microextraction was applied to determine the extraction kinetics, as described in previous work [27]. To control the temperature, the microextraction apparatus was placed in a dry oven (CS101-2A, Chongqing Yinhe Experimental Instrument Co., Ltd.). Several microcapsules and 5 mL of caprolactam aqueous solution saturated with 1-octanol were placed in a sample bottle at 30 °C. The bottle rotated at 850 rpm and formed a steady rotating flow field to reduce the mass transfer resistance in the outer aqueous phase. After extraction, microcapsules were taken out and contact with 1 mL of ethanol for 10 h to ensure that all the caprolactam and the 1-octanol in the microcapsules were dissolved in ethanol. Caprolactam concentration in ethanol then was determined with gas chromatography. The breakthrough curves of microcapsule column were determined at room temperature. In the extraction process, caprolactam solution saturated with 1-octanol was pumped into the microcapsule column. Samples with a volume of 100 μL were collected in the outlet solution from time-to-time. After diluted with ethanol in a 10 mL volumetric flask, caprolactam concentration of the samples was determined with gas chromatography. In the stripping process, sulfuric acid saturated with 1-octanol was pumped into the microcapsule column. The outlet solution was also collected. Before analyzed with gas chromatography, samples with a volume of 100 μL were causticized