Separation and Purification Technology 133 (2014) 335–342

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Technology of foam fractionation coupled with crystallization for the enrichment and purification of folic acid

Qian Zhang, Zhe Zhang, Yuecheng Zhang *, Zhaoliang Wu *

School of Chemical Engineering, Hebei University of Technology, No. 8 Guangrong Road, Dingzi Gu, Hongqiao District, Tianjin 300130, China

ARTICLE INFO

Article history:
Received 26 April 2014
Received in revised form 5 July 2014
Accepted 8 July 2014
Available online 18 July 2014

Keywords:
Foam fractionation
Crystallization
Coupling technology
Folic acid
Wastewater

ABSTRACT

A technology of foam fractionation coupled with crystallization was developed for effectively recovering materials from wastewaters with low concentrations. The wastewater containing folic acid (FA) was used as a system and cetyltrimethyl ammonium bromide (CTAB) was chosen as a collector to recover FA from its wastewater. The results showed that the technology could effectively enrich and purify FA with a low concentration of 6 mg/L from its wastewater. In foam fractionation, the enrichment ratio and recovery percentage of FA were 86.1% and 69.1%, respectively. CTAB could be reused using a two-stage foam fractionation. In crystallization, the recovered FA had 98.0% in purity and it met the quality standard (GB 15570-95). The total recovery percentage of FA was 66.0% by the technology of foam fractionation coupled with crystallization. The technology could be effective not only for recovering FA from its wastewater but also for recovering other trace materials from their wastewaters.

1. Introduction

It is very important and difficult to obtain renewable resources from wastewaters. Furthermore, the effective recovery of materials is a challenging work when their concentrations are very low in the wastewaters [1–3]. In pharmaceutical industry, lots of wastewaters containing materials such as pipemidic acid, methotrexate, folic acid, ubenimex, proglumide and enoxacin at low concentrations are produced. However, these wastewaters are often discharged without recovering the materials as much as possible, resulting in the waste of resources [4–7]. So it is necessary to effectively recover these materials from their wastewaters.

In this work, folic acid (FA) was adopted as a recoverable material from its wastewater because it could represent the typical properties of above materials. FA is a synonym of pteroylmonoglutamic acid [8] and an important kind of B-group vitamins and it is effective in the treatment of megaloblastic anaemia [9,10]. For example, women's risk of having a fetus or an infant with a neural-tube defect, such as spina bifida, can be reduced by the consumption of a multivitamin containing FA during the periconceptional period [10–12]. During the synthesis of FA, a lot of filtrate containing FA at a low concentration is produced [13]. On the basis of the literature, the ion-exchange resins were used for the recovery and purification of FA from its filtrate [14]. However, the efficiency of the ion-exchange resins was very low due to the extremely low concentration of FA in the filtrate. So it is necessary to develop an effective technology to recover and purify FA and even other materials from their wastewaters with low cost and environmental compatibility.

Foam fractionation is a technology with the advantages of simple equipment, small investment, low energy consumption and environmental compatibility [15], and it has been used for separating several minerals [16–18], organisms [19–22] and proteins [23–25]. In addition, foam fractionation is suitable for separating materials at low concentrations. Though foam fractionation can enrich the materials, there have been no any studies on a purification technology for obtaining these materials on the basis of foam fractionation. Therefore, the technology development of foam fractionation coupled with other techniques should attract much attention for the research and industrialization of recovering the trace materials from their wastewaters.

Taking a technology of foam fractionation coupled with crystallization as the example, foam fractionation can be used for enriching the materials from their wastewaters and crystallization can be used for purifying them in the foamate obtained by foam fractionation. In foam fractionation, materials without surface activity are enriched by chemical reactions using appropriate surfactants as collectors [26]. FA is ionized into carboxylate ion with negative electric charge. Therefore for enriching FA from the filtrate by foam

---

* Corresponding authors. Tel.: +86 22 60204279 (Y. Zhang), +86 22 26564304 (Z. Wu).

E-mail addresses: yczhang@hebut.edu.cn (Y. Zhang), zhaoliangwu_hebut@163.com (Z. Wu).

http://dx.doi.org/10.1016/j.seppur.2014.07.009
1383-5866/

fractionation, a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB), was chosen as a collector to form complexes with FA. Then, crystallization was used for purifying FA from its foamate on the basis of two properties of FA and CTAB. Firstly, the reaction between FA and CTAB is a reversible reaction [21]. Secondly, the solubility of CTAB is high in its aqueous solution and FA has a high solubility in alkaline aqueous solution and a low solubility in acidic aqueous solution [13]. For the crystallization of FA, a high difference of the solubility between FA and CTAB is in favor of the purification of FA. The discharged solution from the crystallization had CTAB and the unpurified FA and then it could be used as the feeding solution of foam fractionation. This is the technology of foam fractionation coupled with crystallization for the enrichment and purification of FA, and the materials with the similar properties as those of FA and CTAB may be purified using the technology.

Therefore in this work, the technology of foam fractionation coupled with crystallization was developed for the enrichment and purification of FA from its filtrate. Fourier transform infrared spectroscopy (FTIR) was used to determine the FA–CTAB complexes. In FA foam fractionation, the operational parameters on the performance parameters of FA foam fractionation were investigated, here the operational parameters were pH, liquid loading volume, volumetric airflow rate and the concentration of CTAB and the performance parameters were the enrichment ratio and recovery percentage. In FA crystallization, FA purification was investigated by the study on the effect of pH on the FA solubility and the analysis of the FTIR spectra of the recovered FA from the filtrate. On the basis of the studies above, the optimum technology of foam fractionation coupled with crystallization for the enrichment and purification of FA from wastewater was determined.

2. Materials and methods

2.1. Materials and reagents

The FA filtrate with a concentration of 6 mg/L and FA with a purity of 98.0% were provided by a pharmaceutical factory located in Hebei, China. CTAB of 99.0% and ammonium hydroxide of 25.0% were analytical grade and provided by Tianjin Chemical Reagents Co. Ltd., Tianjin, China. Hydrochloric acid, sodium hydroxide, calcium hydroxide, methanol and potassium phosphate monobasic were analytical grade and provided by Beijing Chemical Reagents Co. Ltd., Beijing, China. All of the above materials were used without further purification and distilled water was used in all experiments.

2.2. Experimental equipment and procedure

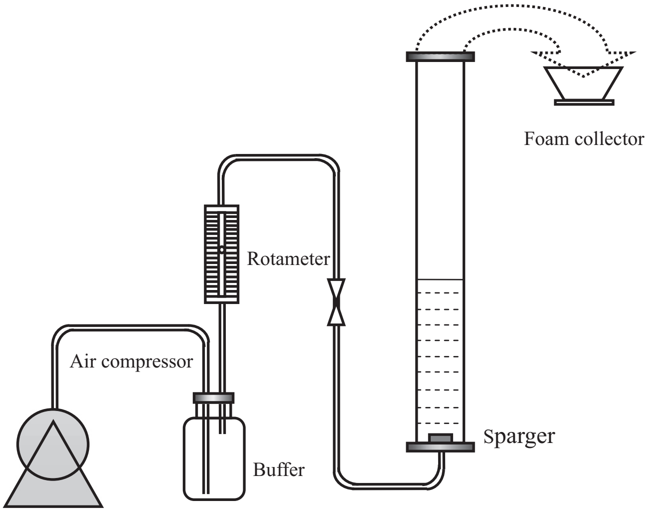

Fig. 1. Schematic diagram of the experimental setup.

Fig. 1 illustrates the schematic diagram of the experimental setup. The column was made of a transparent plexiglass tube of 1000 mm in height and 50 mm in inner diameter. A gas sparger made of a fritted glass of 0.125 mm in pore diameter was fixed at the bottom of the column. The experiments were done in batch operation at 25 °C. Furthermore, the first stage and the second stage of the two-stage foam fractionation were operated independently using batch fractionation [16,23,27,28]. CTAB weighted by an electronic balance (FA1024B, Shanghai Precision Scientific Instruments Co. Ltd., Shanghai, China) was added into the FA filtrate, which is the wastewater. The initial pH of the wastewater was then adjusted by a pH meter (pHS-25, Shanghai Precision Scientific Instruments Co. Ltd., Shanghai, China). The wastewater was then poured into the column. The air was bubbled into the bottom of the column by an electromagnetic air compressor (AC0-318, Guangdong Healy Group Co. Ltd., Guangdong, China) through a rotameter (LZB-3WB, Tianjin Meter Factory, Tianjin, China). The foam was collected by a foam collector and then changed into the foamate. The experiments were run until the foam stopped to exit from the outlet.

2.3. Determination of the FA–CTAB complexes

In this work, FTIR was used for determining the FA–CTAB complexes in the foamate. The foamate was obtained by foam fractionation. The foamate was freeze-dried (Eyela Fdu-1200, Tokyo Rikakikai Co. Ltd., Tokyo, Japan), and the obtained powder was collected as the sample of the FA–CTAB complexes. Moreover, FA (100 mg) and CTAB (100 mg) were mixed thoroughly to serve as the sample of the physical mixture. The FTIR spectra of FA, CTAB, the sample of the physical mixture and the sample of FA–CTAB complexes were determined between 4000 and 650 cm^{-1} on a Vector-22 infrared spectrophotometer (TENSOR 27, Bruker, Germany) with 256 scans at a resolution of 2 cm^{-1} using the KBr method. In addition, the data were recorded and processed using Opus software (Bruker, Germany).

2.4. Determination of FA concentration

FA 10 mg and ammonium hydroxide of 25% 2 mL were placed into a volumetric flask and diluted using distilled water to 50 mL and the obtained solution was used as the reference. A sample of FA aqueous solution 10 mL and ammonium hydroxide of 25% 2 mL were placed into a volumetric flask and diluted using distilled water to 50 mL. The obtained solution of 5 mL was filtered using a membrane filter of 0.45 μm in pore diameter to remove undissolved materials and then measured by HPLC. The sample of FA aqueous solution was analyzed under the conditions of a diode array detector (Agilent Technologies, Inc., USA), a symmetry C_{18} (250 mm × 4.6 mm, 5 μm, Shimadzu, Japan), a column temperature of 35 °C, a mobile phase of 0.01 mol/L potassium dihydrogen phosphate and methyl alcohol (89:11, V/V), a detection wavelength of 280 nm, a flow rate of 1.0 mL/min.

2.5. Determination of CTAB concentration

The concentration of CTAB was equal to the concentration of bromide ion in a dilute solution and was determined by a bromide selective electrode [29]. The instruments consisted of a bromide selective electrode (pBr-1-01, Shanghai Yueci Electronic Instruments, Co. Ltd., Shanghai, China), a double-junction Ag/AgCl