



Removal of pyridine from its wastewater by using a novel foam fractionation column



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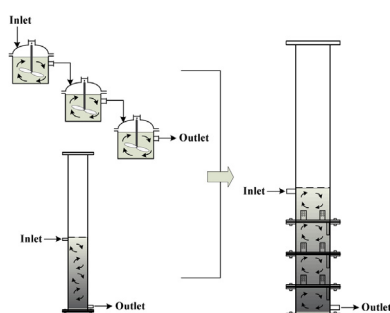
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HIGHLIGHTS

- Foam fractionation was used to remove pyridine.
- A novel foam fractionation column was designed.
- Bubble diameter was monitored to control foam fractionation process.
- A high enrichment ratio and a high removal percentage of pyridine were obtained in continuous foam fractionation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 20 January 2017

Received in revised form 17 March 2017

Accepted 18 March 2017

Available online 20 March 2017

Keywords:

Foam fractionation

Foam fractionation column

Interfacial adsorption

Foam drainage

Pyridine

ABSTRACT

Many of pyridine compounds are considered as typical hazardous refractory organics due to their acute toxic properties and teratogenic effects. Therefore, it is great significant to develop a separation technology with the characters of low energy consumption and environmental compatibility to efficiently remove pyridine from its wastewater. In this work, foam fractionation was used to remove pyridine from its wastewater and a novel foam fractionation column was designed for enhancing interfacial adsorption by vertical sieve tray and strengthening foam drainage by floating tongue type tray, in which bubble diameter was monitored for adjusting feeding flow rate and air flow rate in the continuous foam fractionation process. By comparing the foam properties and the adsorption properties of three anionic surfactants (sodium dodecyl sulfate, sodium alcohol ether sulfate and sodium alpha-olefin sulfonate), sodium dodecyl sulfate was chosen as the optimal collector to remove pyridine at pH 4.5. Under the optimal operating conditions, the enrichment ratio and removal percentage of pyridine could reach as high as 34.5 and 90.2%, simultaneously. Above results indicated that foam fractionation was a practicable technology to efficiently remove a hazardous material from its wastewater by designing an effective foam fractionation column.

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1. Introduction

Foam fractionation is a promising adsorption separation technology and it is regarded as a cost-effective early recovery step

in industrial downstream processing. In the recent decades, it has exhibited potential applications in the fields of chemical engineering, food engineering, pharmaceutical engineering, environment engineering and others for its advantages of low energy consumption, simple equipment, small investment and environmental compatibility [1–5]. Many researchers have engaged in the study on the intensification of the foam fractionation process for achieving a high enrichment ratio and a high recovery percentage of a target

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material, in which the enrichment ratio and the recovery percentage are two important parameters in evaluating the performance of foam fractionation.

The process of foam fractionation consists of two essential steps, namely, interfacial adsorption and foam drainage. Lots of works have been performed to enhance the interfacial adsorption of soy whey protein in the liquid phase through designing the foam fractionation columns [6,7]. From their results, the interfacial adsorption could be effectively enhanced by prolonging the residence time of bubbles and promoting mass transfer in the liquid phase, resulting in a high recovery percentage. However, at the same time, the enrichment ratio decreased. In fact, it was a challenging work to increase the enrichment ratio of a desired material. Thus, a series of foam fractionation columns have been designed to strengthen foam drainage by accelerating bubble coalescence, optimizing foam flow directions and increasing wall area in the foam phase [8–10]. Their results have indicated that the novel foam fractionation columns could accelerate the coalescence of bubbles and decrease the liquid holdup of foams leading to a higher enrichment ratio while the recovery percentage was significantly decreased at the same time. Obviously, it is very meaningful to design an efficient foam fractionation column which can enhance interfacial adsorption and strengthen foam drainage, thus achieving a high enrichment ratio and a high recovery percentage of a target material simultaneously.

Pyridine is the parent of a series of N-heterocycles and it has been recognized as a typical hazardous refractory organic material due to its acute toxic properties and teratogenic effects [11,12]. It is widely used as a solvent or an intermediate in the production of agricultural chemicals, drugs, dyestuffs and textile water-repellents. Therefore, a large amount of wastewaters containing pyridine is discharged from various industries. The concentration of pyridine in wastewater produced in an intermediate product plant is in the range of 20–300 mg/L. Many of pyridine compounds are difficult to degrade by indigenous microorganisms, leading to a long duration in environment [13]. Even the concentration of pyridine compounds is low, the polluted soil and groundwater can constitute a severe threat to human health. Therefore, it is of great importance in the removal of pyridine from its wastewater. It is reported that the methods of distillation, extraction and adsorption methods have been used for removing pyridine from its wastewater. Among these methods, distillation and extraction are not suitable because the concentration of pyridine is too low. Then, adsorption by utilizing activated carbon and other adsorbents has been investigated to remove pyridine at a low concentration [14,15]. Zhu et al. investigated the adsorption kinetics of pyridine by polymeric adsorbent MN 500 and the equilibrium adsorption capacity of pyridine could achieve 82.4 mg/g at temperature 55 °C and the initial pyridine concentration 150 mg/L. However, it is difficult to use the method of adsorption in an industrial scale because the volume of wastewater is huge but the concentration of pyridine is low. Thus, it is necessary to develop a novel technology for effectively removing pyridine from its wastewater.

In this work, the feasibility of foam fractionation to remove pyridine from its wastewater was studied. In fact, pyridine had no surface activities. Based on electrostatic effect, the foam properties and adsorption properties of three surfactants (sodium dodecyl sulfate (SDS), sodium alcohol ether sulfate (AES) and sodium alpha-olefin sulfonate (AOS)) were evaluated to screen a suitable one to use as the collector for carrying pyridine onto the gas-liquid interface. A novel foam fractionation column was designed for enhancing interfacial adsorption by vertical sieve tray and strengthening foam drainage by floating tongue type tray, in which bubble diameter was monitored for adjusting feeding flow rate and air flow rate in the continuous foam fractionation process. This work was aimed at developing efficient equipment and providing

an effective method to control the foam fractionation process for the removal of hazardous materials from industrial wastewaters.

2. Materials and methods

2.1. Materials

Pyridine, SDS ($C_{12}H_{25}SO_4Na$), AES ($C_{12}H_{25}(CH_2CH_2O)_2OSO_3Na$) and AOS ($C_{12}H_{25}CH=CHCH_2SO_3Na$) were purchased from Tianjin Dengfeng Chemical Reagent Co. Ltd., China. The critical micelle concentrations (CMC) of SDS, AES and AOS were 8.2×10^{-3} mol/L, 0.5×10^{-3} mol/L and 1.1×10^{-3} mol/L, respectively. The wastewater with pyridine was provided by an environmental protection technology Co. Ltd., China and its properties were pH 7.2 and pyridine concentration 117 ~ 185 mg/L. Naphthalene, furan, benzene and its derivatives also existed in the wastewater and however, their concentrations were all lower than 10 mg/L. Sodium hydroxide and hydrochloric acid were used for adjusting pH and they were supplied by Tianjin Bodi Chemical Industry Co. Ltd., China. Methanol was used for the measurement of pyridine concentration and it was obtained from Tianjin Bodi Chemical Industry Co. Ltd., China. Deionized water was delivered using a Millipore Milli-Q system from Barnstead International, Dubuque, IA, USA.

2.2. Foam fractionation

Fig. 1 shows the schematic diagram of foam fractionation column in a continuous foam fractionation process. The foam fractionation column was constructed by a polymethyl methacrylate tube with height 1600 mm and inner diameter 100 mm. A gas distributor of sintered glass with a pore diameter of $380 \pm 20 \mu m$ was mounted at the bottom of the column to serve as a gas distributor. In each experiment, vertical sieve trays (VST) and floating tongue type trays (FTTT) were installed in the foam fractionation column. The VST was composed of a transparent polycarbonate plate of 2 mm in thickness and 100 mm in inner diameter with four vertical sieve caps of 14 mm in inner diameter and 50 mm in height. The FTTT was composed of a transparent polycarbonate plate of 2 mm in thickness and 100 mm in inner diameter with two floating tongue internals of 2 mm in thickness and 20° in maximum flare angle. Besides, the downcomer of 10 mm in inner diameter and 30 mm in height was installed on each side of the trays in order to form a backflow liquid. The aqueous solution of pyridine or its wastewater was injected into the column from the feed inlet nearby the gas-liquid interface. The interface between the foam phase and liquid phase was at a same position which was regulated by the liquid flow rate from effluent outlet. The air was sparged through the gas distributor to form numerous bubbles in the liquid phase and then a surfactant was quickly adsorbed on the bubble surface, resulting in a stable foam phase above the liquid phase. At the same time, pyridine could be adsorbed on the surface of the stable bubbles by electrostatic effect with the surfactant. With the foam rising, the interstitial liquid was returned in the liquid phase owing to foam drainage. Finally, the dry foam was discharged out from the column and collected in a foam collector. The solution after breaking the dry foam was called as the foamate, in which the target material (pyridine) was greatly enriched. The separation performances of continuous foam fractionation were evaluated by enrichment ratio (E) and removal percentage (R) and they are expressed as follows.

$$E = \frac{C_f}{C_0} \quad (1)$$

$$R = \frac{C_f \times V_f}{C_0 \times V_0} \times 100\% \quad (2)$$

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