Interfacial adsorption of methyl orange in liquid phase of foam fractionation using dodecyl dimethyl betaine as the collector

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A B S T R A C T

It is important to develop an environment-friendly collector for removing or recovering harmful non-surface-active materials using foam fractionation. Dodecyl dimethyl betaine (BS12) was used as the collector for studying the interfacial adsorption of methyl orange (MO) in the liquid phase. The maxima of the surface excess and the enrichment ratio of MO were 22.7% and 51.5%, respectively under pH of 5 and the BS12 concentration of 0.40 g/L. The results indicated that BS12 was an effective and environmental collector and it can promote the development and application of foam fractionation for the removal of harmful non-surface-active materials.

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Introduction

Water pollution is a serious worldwide problem and the prevention and treatment of wastewaters have attracted the attention of environmentalists and entrepreneurs in recent years [1–3]. Dyes used in pharmaceuticals, cosmetics and textile dyeing [4,5] are a kind of the most typical contaminants [6] due to coloring power with a low amount in their aqueous solutions [7], carcinogenicity [8] and high industrial discharge [9]. The common methods for dyeing wastewater treatment [10–12], such as adsorption, oxidation, coagulation-flocculation, membrane separation, photodegradation, nanotechnology and biological treatment, are limited on an industrial scale due to high cost and secondary pollution [13].

Foam fractionation is a technique that uses bubble interfaces to separate selected components from an aqueous solution based on the adsorption theory with the advantages of simple operation, low energy requirement and environmental compatibility [14,15]. Foam fractionation has been proved to be a desirable and cost-efficient separation technique for the removal of dyes using appropriate surfactants as collectors which can react with the non-surface-active dyes [16–18]. However, there are still a few subjects which should be studied in order to promote the industrial

application of recovering the dyes from their wastewaters using foam fractionation. First, the common collectors, such as sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), are toxic and lead to secondary pollution [19]. Second, the removal and enrichment of dyes using foam fractionation is a combined action of interfacial adsorption and foam drainage [33]. The previous researches almost dealt with the effect of foam drainage on the removal efficiency [16,18,20], but there have been few references on studying interfacial adsorption of dyes. The adsorption characteristics of dyes in the liquid phase affect not only the removal efficiency of dyes [21], but also the foam properties [22], thereby affecting foam drainage and enrichment efficiency [23]. Therefore, it is essential to develop a more environment-friendly collector to remove dyes from wastewaters and study the interfacial adsorption of dyes in the liquid phase.

Dodecyl dimethyl betaine (BS12, $C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$) is a mild zwitterionic surfactant with an excellent stability under the conditions of acidity and alkalinity and it is widely used as a detergent, a dispersant and an emulsifier due to free hazard, environmental benefit and reaction compatibility with several types of dyes, surfactants and cosmetic materials [24,25]. Furthermore, BS12 is favorable for dyeing homogeneity and dyeing acceleration of acid dyes [26]. Thus, the dyes recovered by foam fractionation using BS12 as the collector can be directly reused for dyeing and printing.

During the process of foam fractionation using a column without internals in the liquid phase, the bubbles leave the distributor and move upward along the axial direction due to
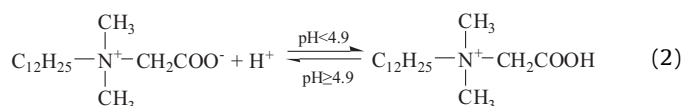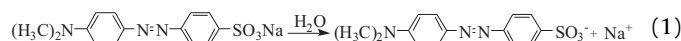
buoyancy and air-flow. It is difficult for such the motion of bubbles to improve the mass transfer in the liquid phase. In our previous research [27], the vertical sieve tray (VST) was developed and used as an internal in the liquid phase of foam fractionation column, and it had been proved to effectively enhance the interfacial adsorption of separated materials because the decrease of the flow area increased the velocity and the turbulence intensity of the bubbles in the liquid phase when the bubbles went through the pores of the VST internal.

In this study, methyl orange (MO) was adopted for the model dye and dodecyl dimethyl betaine (BS12) was used as the collector. The physical characteristics of BS12 and the complex formation of MO and BS12 were evaluated. The effects of pH and the BS12 concentration on the surface excess and the enrichment ratio of MO were investigated under a semi-continuous operation in the foam column with the vertical sieve tray (VST) internal and the foam column without any internals, respectively.

Experimental

Materials

Methyl orange (chemically pure) was purchased from Tianjin Yingda Rare Chemical Reagents Factiry, China. Dodecyl dimethyl betaine (solid content ≥30%) was purchased from Linyi Lusen Chemical Co. Ltd., China. The chemical structures of MO and BS12 are shown in Fig. 1.

$$(H_3C)_2N-\!\!\!\bigcirc\!\!\!-N\!:\!N-\!\!\!\bigcirc\!\!\!-SO_3Na \xrightarrow{H_2O} (H_3C)_2N-\!\!\!\bigcirc\!\!\!-N\!:\!N-\!\!\!\bigcirc\!\!\!-SO_3^{\cdot}+Na^+ \quad (1)$$

$$C_{12}H_{25}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N^+}}-CH_2COO^- + H^+ \underset{pH\geq4.9}{\overset{pH<4.9}{\rightleftharpoons}} C_{12}H_{25}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N^+}}-CH_2COOH \quad (2)$$

The chemical equilibrium reactions of MO and BS12 in aqueous solutions are shown in Eqs. (1) and (2). The isoelectric point (pI) of BS12 is 4.9 [28], that is to say, for pH < 4.9, the positively charged BS12 is a cationic surfactant; for pH ≥ 4.9, electrically neutral BS12 is ionized to form a zwitterion or an internal salt.

The liquid feed was prepared by mixing the solutions of MO and BS12 and adjusting pH to several desired values using a pH meter (PHS-3 C, Hangzhou Orion Instrument Co. Ltd., China). Distilled water, HCl solution and NaOH solution were used in all experiments. All reagents were used without further purification.

Vertical sieve tray internal

The schematic diagram of the vertical sieve tray (VST) internal is shown in Fig. 2. The VST internal was made up of a transparent plexiglass plate of 3 mm in thickness and 48 mm in diameter and 4 vertical sieve caps of 14 mm in external diameter and 50 mm in height. Each vertical sieve cap had 3 rows of aligned pores of 3 mm in diameter, each row had 9 pores and the center distance between the adjacent two pores was 5 mm. A downcomer of 5 mm in diameter was located at the center of the tray to allow the liquid entrained by the rising bubbles to flow down.
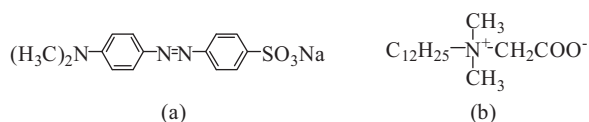
$(H_3C)_2N-\!\!\!\bigcirc\!\!\!-N\!\!=\!\!N-\!\!\!\bigcirc\!\!\!-SO_3Na$ $C_{12}H_{25}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N^+}}CH_2COO^-$

(a)   (b)

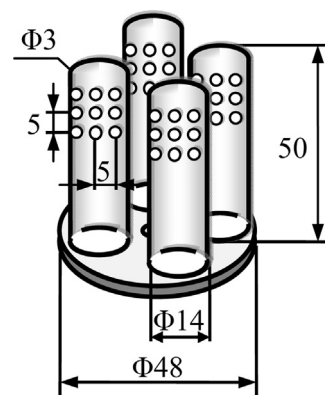**Fig. 1.** Chemical structures of (a) MO and (b) BS12.

Fig. 2. Schematic diagram of the vertical sieve tray (VST) internal.

Experimental procedure

All experiments were done at a semi-continuous operation. The foam column was constructed by a transparent plexiglass tube of 500 mm in height and 48 mm in internal diameter. The VST internal was installed at the midst of the column as shown in Fig. 3. A sintered glass filter of 0.18 mm in average pore size was installed at the bottom of the column as the gas distributor. The air was injected using an air compressor (ACO-318, Guangdong Hailea Group Co. Ltd., China) and controlled using a rotameter (LZB-3WB, Wuhuan Meter Factory, China). The operation temperature was 25 °C. The solution was consecutively charged into the bottom of the foam fractionation column using a peristaltic pump (YW03, Changzhou Yuanwang Fluid Technology Co. Ltd., China) at a given feeding rate. The liquid phase height was adjusted to arrive at 50 mm away from the top of the column by controlling the air flow rate and the liquid feed rate. The foam from the top of the column was collected using a foam collector every 15 min. The MO concentration was determined using a UV–vis spectrophotometer (GB7676, Shanghai Precision & Scientific Instrument Co. Ltd., China) [29]. The experiments were done until the MO concentrations in the consecutive three samplings were constant and then the system was considered to achieve the steady state. Then, collected the foam into another foam collector for a given time, measured the volumetric flux of the foamate, the MO concentrations of the foamate and the liquid pool, and the bubble diameter at a height of 20–30 mm above the surface of the liquid pool using a digital photographic camera (Nikon CooLPIX P6000) [30]. All of the experiments were at least triply repeated and the mean values were plotted in the resultant figures.

Determination of the surface excess of MO

The surface excess of MO has often been determined using Eq. (3) on the basis of material balance at a steady state [31,32].

$$C_f V_f = C_e V_f + A\Gamma \quad (3)$$

where C_f (mg/m^3) and C_e (mg/m^3) are the MO concentrations of the foamate and the liquid pool, respectively; V_f (m^3/s) is the volumetric flux of the formate; Γ (mg/m^2) is the surface excess; A (m^2/s) is the bubble surface area flux, which is determined using the following equation [33]:

$$A = \frac{6q}{D32} \quad (4)$$

where q (m^3/s) is the air flow rate; D_{32} (mm) is the Sauter mean bubble diameter and it is determined using Eq. (5) [34] and the