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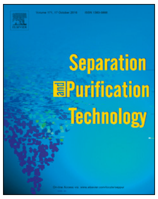

Mass transfer of molybdenum in L35 + sodium sulfate + H_2O aqueous two-phase system with a packed column

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ABSTRACT

The mass transfer characteristics of molybdenum in a packed extraction column using a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymer surfactant (L35) + sodium sulfate + H_2O aqueous two-phase system was studied. The hold up of dispersed phase (ε_D) and the overall volumetric mass transfer coefficient of the dispersed phase (K_Da) were measured with three kinds of packings, such as ceramic rasching rings, metal θ rings and glass springs under different conditions. The experimental results showed that the hold up of dispersed phase increases with increasing the flow rate of the dispersed phase, and decreases with the increase of the tie line length (*TLL*), and increases as increasing the void fraction of the packings. The mean residence time and the Peclet number of the dispersed phase decrease, showing that the axial diffusion extent of the dispersed phase become more serious with increasing the rate of dispersed phase and *TLL*, and increase with the increase of the void fraction of packing bed according to the sequence of ceramic raschig rings – glass springs – metal θ rings. The overall volumetric mass transfer coefficient of dispersed phase increases with the increase of the rate of dispersed phase and continuous phase and the specific area of three kinds of packings, and decreases with increasing *TLL* and operating temperature. The mass transfer resistance of two phases is not disregarded.

1. Introduction

Molybdenum is a kind of rare mental, which is broadly distributed in China. Molybdenum and its compounds are important materials in industrial and agricultural applications such as steel and iron industry, military industry, chemical industry and fertilizer production industry et al [1–4]. Currently, the main methods in extracting molybdenum include organic solvent extraction, ion exchange and adsorption, chemical precipitation and so on [5–8]. But, low partition coefficient makes traditional liquid–liquid extraction inefficient, and a large number of waste water produces for ion exchange and adsorption method, and chemical precipitation technique requires to consume massive chemical reagent and only is suitable to aqueous media containing low molybdenum concentration. The appearance of aqueous two-phase system (ATPS) has attracted increasing attention [9]. Different from traditional organic solvent liquid-liquid extraction, ATPS is an excellent alternative for the selective extraction of metals in hydrometallurgical procedures, which has advantages of nontoxic, low cost, easy recovery of extractant and salt, short phase separation time and easy scale up [10–13].

The metal ions extraction in PEG-salts aqueous two-phase systems depend on (i) the formed aqueous two-phase system characteristics (determined by the type and molecular mass of PEG, type of inorganic salt and their concentrations, system pH, temperature, presence of neutral or charged inert species) and (ii) the properties of metallic extracted species (hydration degree, charge, dimension, etc.) [14]. Beside suitable selection of the chemical characteristics of ATPS components, the mass transfer process also should be focused on industrial application in aqueous two-phase system, because mass transfer performance is not only an important factor to measure mass transfer process, but also important parameters in designing extraction equipment [15]. Therefore, it is of great significance to research the mass transfer characteristics of aqueous two-phase system by continuous countercurrent extraction process [16,17]. Compared with the research of mass transfer performance on bioactive substance with ATPS in all kinds of extraction equipment, such as spray column [18,19], packed column

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[20,21], perforated rotating disk contactor [22,23], mixed settler [24], karr reciprocating-plate extraction column [25], pulsed sieve plate column [16], and pulsed caps column [26], et al.

Spray columns are simple in construction and easy to operate, but spray columns suffer from the drawback of having a high degree of backmixing in the continuous phase. This arises due to intense circulation of the continuous phase. The plate column is essentially a stack of several spray columns, but the mass transfer coefficient in plate columns essentially equals that in spray columns. This is because the forces which govern the drop size are the same in plate and spray columns. To achieve a reduction in drop size, the level of shear stress needs to be increased. This is usually done by providing packings in the column, or by providing agitation. The former method is simple. Further, the continuous phase circulation is dampened by the packings which results in a reduction in the continuous phase backmixing by a factor of 3–4 [27]. On the basis of the above advantages, packed columns require smaller floor space and can be used for aqueous two-phase extraction, and the operation is easier. Furthermore, the packing elements can reduce back mixing and provide tortuous pathways for the two phases, and increase the contact area strengthening the mass transfer [28].

In the present study, we have evaluated the mass transfer performance of molybdenum in a packed column by the continuous and counter-current extraction with ATPS composed of L35 + sodium sulfate + H_2O. The influence of different kinds of packing, tie line length, the rate of dispersed phase and continuous phase on the hydrodynamic characteristics and the mass transfer characteristics has been researched.

2. Experiments

2.1. Materials

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) tri-block copolymer nonionic surfactant (L35, $HO(EO)_{11}(PO)_{16}(EO)_{11}H$) with an average molar mass 1900 g/mol was brought from Haian Chemical Plant, Jiangshu, China. Sodium molybdate and sodium sulfate were obtained from Xilong Scientific Co. Ltd, Guangdong, China. Sulfuric acid was supplied by Tianjin Kemiou Chemical Reagent Co. Ltd., Tianjin, China. All reagents were of analytical grade. Distilled water was used in all experiments.

2.2. Tie line data

The tie-line determination started with the addition of five ternary mixtures within the immiscibility region of different known mass fractions to the breakers, the temperature was kept constant at 313.15 K and the mixture was stirred vigorously and left to settle for 24 h to ensure a complete phase separation. The water concentration was measured by vacuum drying, sodium sulfate concentration was determined by specific conductance, and L35 concentration was determined by mass balance for two phases. The measured deviation was controlled according to the sum of the amount of the top phase and bottom phase is equal to the added amount for composition *i*, as following Eq. (1):

$$\frac{m_i^t + m_i^b}{m_i} = 1.00 \pm 0.05(i = 1, 2, 3) \tag{1}$$

where m_i is the added mass of composition i in the systems, m_i^t is the mass of composition i in the top phase (L35-rich phase), and m_i^b is the mass of composition i in the bottom phase (salt-rich phase). The composition i represents L35, sodium sulfate and water, respectively.

The five corresponding tie line lengths (*TLL*) of L35 + sodium sulfate + H_2O system at 313.15 K were shown in Fig. 1. In this study, we choose the first three system compositions to prepare the dispersed and continuous phases, and the tie line data were listed in Table 1 and corresponding physical parameters, such as density, viscosity, interfacial tension and their difference in two phases, were shown in Table 2. The density, viscosity and interfacial tension in two phases were measured by densimeter, rotational viscometer and maximum bubble pressure method, respectively.

2.3. Packing

The choice of the packing elements is markedly important. The packing should be wet preferentially by the continuous phase, and its diameters limited to 1/8 ~ 1/10 of the column inner diameter to random packing. Consequently, ceramic Rasching rings, metal θ rings and glass springs were used in our experiments. The packing characteristics are listed in Table 3.

2.4. Equipment

The used packed column was designed by ourselves and fabricated by Jiaojiang Glass Instrument Plant, Taizhou, China. The packed column is a glass tube with an inner diameter of 50 mm, with 3 mm wall thickness, and with 600 mm total height. The packing depth is 250 mm for three kinds of packings. The equipment temperature was controlled by circulating water outer column. The grid plates used as packing support and packing clamp were placed the bottom and top of the packing depth, and the distributors of the continuous and dispersed phase are shower nozzle type being of 30 mm diameter and have six poles with 1 mm diameter on it. A schematic diagram of the experiment was shown in Fig. 2.

2.5. Experimental procedure

2.5.1. Hold up of dispersed phase

The solutions of the two phase forming components were prepared separately according to the equilibrium phase compositions given by the tie line data. The two phases were stirred respectively by two constant temperature heating magnetic stirrers (ZNCL-GS, Kesheng Instrument Company Limited, Shanghai, China) under the condition of 313.15 K. The continuous phase was firstly pumped to the packing height at the top of the column via a peristaltic pump (Pre-fluid Technology Co. Ltd., Changzhou, China) in order to wet the packing with that phase, then the dispersed phase was poured continuously into the bottom of the column by another peristaltic pump and was withdrawn at the top of the column. The hold-up was determined by operating the column until steady flow conditions were reached. The interface height was recorded when dispersed phase velocity and phase interface have been stable. The hold up of dispersed phase was calculated according to Eq. (2) [29,30].

$$\varepsilon_D = \frac{H_D - H_1}{H_D} \times 100\% \tag{2}$$

where ε_D is the hold up of dispersed phase (%) and H_1 and H_D represent packing height (m) and the phase interface height (m) under stable state, respectively.

2.5.2. Axial diffusion

The axial diffusion of the dispersed phase (L35-rich top phase) was determined by a stimulus/response method, using the pulse injection of rhodamine B as a tracer. The reason adapted rhodamine B as a tracer is that the distribution coefficient of rhodamine B is over 300 in the L35-rich phase by our partitioning experiments. The samples were taken out at intervals of 5 min from the top phase outlet, and the sample concentration was determined by absorbance using the spectrophotometer (UV–Vis 1800P, Shanghai, China). The residence time distribution and the mean residence time were determined according to equations given by Zhu [31]. The axial diffusion model was used to fit the experimental data with Peclet number or axial diffusion coefficient as model