



Adsorption behavior and kinetics for L-valine separation from aqueous solution using ion exchange resin

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ABSTRACT

Separation of L-valine (L-val) using ion exchange resins from a aqueous solution was successfully performed. Multifactor equilibrium isotherm, adsorption mechanism and kinetics were systematically studied. A multifactor empirical isotherm model was constructed and could demonstrate the equilibrium experimental data at different pH values well. A theoretical model integrating both ion exchange and proton transfer reactions was developed to describe the adsorption capacity of resin, and the theoretical model allowed us to verify the multilayer adsorption at a higher concentrations. Meanwhile, the results of quantum chemistry confirmed the existence of proton transfer reaction and multilayer adsorption on resin. The adsorption of L-val on resin was a spontaneous and endothermic process. Adsorption amount of L-val on cation exchange resin increased with increasing the L-val solution concentration and the temperature but decreased with increasing the diameter of resin. The rate constant (k_0) and the apparent reaction coefficient (α) of lumping kinetics and the apparent activation energy of reaction (E_a) were also determined by analyzing the mass transfer process from the main liquid to the active sites of resin.

1. Introduction

L-valine (L-val) is an important and indispensable amino acid which is widely applied in the fields of pharmaceuticals, food and feed [1, 2], and can be produced by both the chemical synthesis and the biological fermentation [3, 4]. At present, the market-purchasable L-val product is mainly obtained by the biological fermentation because it requires a relatively mild operation condition and produces fewer by-products. However, this technique has to experience many operation units, e.g., biological fermentation, centrifugal separation, purification and crystallization [5]. Moreover, the residual mother liquor obtained after crystallization still contains a certain amount of L-val. For many factories, the residual mother liquor is always sold as a liquid fertilizer at a much low price. Obviously, such treatment greatly devaluates the important product of L-val and certainly lowers the profit for a company, which drives us to adopt a feasible and low-cost technique for separation of the L-val from the residual mother liquor.

Although several technologies for the separation of amino acid from the residual liquor are available by using membrane separation [6], solvent extraction [7] and active carbon adsorption [8, 9], still some drawbacks will be faced to, for example, membrane fouling, residual extractant and poor selectivity. Ion exchanger, a kind of polymeric

absorbent with functional group, can adsorb the ionized substance via the ion exchange process and is used for separation of natural product [10, 11]. Many attempts have been made in studying separation of amino acid using ion exchangers, e.g., ion exchange fiber [12] and resin [13]. In previous studies, researchers have studied the parameters effect on the separation [14], the optimization of separation process [15], the breakthrough curve model of the fixed-bed column [10] and the adsorption kinetics (e.g., pseudo-first and pseudo-second order kinetics) [16]. Their works are beneficial to master the separation performance of resins and to attain the fundamental rules of amino acid separation, which certainly give a boost to the L-val separation from the residual mother liquor. For example, Mareia et al. [17] separated phenylalanine and tyrosine in the fixed-bed column using the PA 316 anion exchange resin, and Xie et al. [18] studied kinetics, equilibrium and thermodynamic of L-tryptophan using the 001 × 7 cation exchange resin.

The operation parameters and the kinetics are of great significant to determine the control scheme of separation unit of amino acid, which plays a fundamental role in enhancing separation efficiency and capacity of ion exchange resin. In addition, ionic form of amino acid could affect its adsorption behavior on ion exchange resin and also lead to the occurrence of different separation effects [19, 20]. Meanwhile, the interaction energy of functional groups also is an important factor for

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understanding the adsorption behavior of amino acid on ion exchange resin and the mass transfer process of amino acid from the main fluid to the resin interior [21]. The adsorption behavior and the equilibrium characteristics of amino acid on ion exchange resin, to the best of our knowledge, are fragmentary and incomplete. The interaction energy of functional groups is rarely addressed to explain the adsorption behavior of amino acid on ion exchange resin, and even the lumping kinetics model containing multiple parameters for the separation of amino acid has been reported less. The problems mentioned above are undoubtedly disadvantageous to the separation of L-val from the residual mother liquor using ion exchange resin.

In order to further investigate and to deeply understand the adsorption behavior of L-val on ion exchange resin and the adsorption kinetics for the L-val separation from the residual mother liquor, we herein carried out the related studies on the separation of the L-val using ion exchange resins, and an improved equilibrium isotherm and a lumping adsorption kinetics were carefully developed and the adsorption behavior of L-val was studied in detail. The main purpose of this work was to study the adsorption behavior of the L-val on resin by both the experimental exploration and the theoretical computation, and to establish a multi-factor diffusion model of the L-val molecule through a hypothesis of moving boundary layer. Two types of resins including cation and anion exchange resins were used because of both acidic and basic groups in the L-val molecule. This study not only elucidates adsorption behavior of L-val on a resin, but also provides a guideline for the L-val separation with an ion exchange resin.

2. Experimental

2.1. Materials

All reagents used in experiments were of analytical grade and purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The commercially available resins were provided by the Wuxi Green separation Applied Technology Institute Co., Ltd. (Jiangsu, China). The matrix of resins is composed of the polystyrene-divinylbenzene copolymer, and the detailed properties of resins are summarized in Table 1.

2.2. Resin pretreatment

Prior to use, the cation exchange resins (D001, HZ016) were sequentially washed with a 1 mol/L HCl and a 1 mol/L NaOH solutions, then further washed by the HCl solution for converting them into the H-type resins. After that, the H-type resins washed with the deionized water until the washing liquor was detected to be neutral. Experiencing similar procedures for the anion exchange resins but completely reverse sequence between HCl and NaOH solutions, the anion exchange resins (201 × 7, D296) were the OH-type ones. Finally, the obtained wet resins were filtrated by a vacuum suction pump for 10 min, and the pretreatment resins were further used to perform the related adsorption experiments of the L-val.

Table 1
Main of physicochemical properties of resins.

| Resin | Functional group | Particle size (mm) | Exchange capacity (mmol/g) | Divinylbenzene (%) |
|---------|---|--------------------|----------------------------|--------------------|
| D001 | –SO ₃ [–] | 0.32–1.25 | ≥ 4.35 | 8 |
| 201 × 7 | –N ⁺ (CH ₃) ₃ | 0.32–1.25 | ≥ 3.80 | 7 |
| D296 | –N ⁺ (CH ₃) ₃ | 0.32–1.25 | ≥ 3.85 | 7 |
| HZ016 | –SO ₃ [–] | 0.32–1.25 | ≥ 4.23 | 7 |

2.3. Equilibrium experiments

The adsorption experiment for a resin was conducted in a sealed Erlenmeyer flask placed in a thermostatic shaker (80 rpm) for evaluations of the adsorption capacity (q) and the selectivity coefficient (α) of the resin, and obtaining its adsorption equilibrium isotherm at various pH values (initial pH value of the solution, the same hereinafter) and temperatures. More specifically, a 100 mL L-val and/or L-leu solution with a known initial concentration (1.5 g/L – 10 g/L) was added into a flask with 4 g of a pre-placed resin. After the adsorption equilibrium, the mixture of liquid phase and solid phase was simply filtered to separate the resin, and the concentration of L-val and/or L-leu remained in the filtrated was analyzed by a high-performance liquid chromatography (HPLC).

The adsorption capacity q (mg/g resin) and the selectivity coefficient α of resins were calculated according to Eqs. (1) and (2), respectively.

$$q_e = \frac{(c_0 - c_e) \cdot v}{m} \quad (1)$$

$$\alpha = \frac{q_A \cdot c_B}{q_B \cdot c_A} \quad (2)$$

where c_0 and c_e are the initial and the equilibrium concentrations, respectively, of both the L-val and the L-leu (g/L); v is the solution volume (L), m is the mass of resin (g); q_A and q_B represent the resin phase equilibrium concentrations of both the L-val and the L-leu (g/g dry resin), c_A and c_B are the liquid phase equilibrium concentrations of both the L-val and L-leu (g/L).

2.4. Kinetics experiments

The procedure of kinetics experiment for determining the adsorption rate of resin is similar to that of the equilibrium experiment, and the experimental parameters include the temperature and the concentration of the L-val as well as the diameter of resin. The experimental setup consisted of several 250 mL Erlenmeyer flasks, was hermetically sealed and placed in a thermostatic shaker (80 rpm). Within 12 h of continuously shaking the flasks (4 g resin, 100 mL of the known initial concentration of the L-val solution), 0.5 mL of small aliquots was taken out from flask at the pre-set intervals for analyzing the concentrations of the L-val. The sample amount was not considered in liquid phase for following steps.

2.5. Analytical method

The concentrations of L-val and L-leu in an aqueous solution were determined by HPLC equipped with a Wonda Cracts ODS-2 column (4.6 mm × 250 mm, Shimadzu) and an evaporative light-scattering detector (ELSD 6000, Alltech, America) at a flow rate of 0.7 mL/min. The mobile phase was a mixture of methanol and water (30:70, v/v), and the column temperature was maintained at 298 K. An entire run time was 9 min, the retention times of L-val and L-leu were 4.5 min and 5.5 min, respectively.

2.6. Theoretical computation

The density functional theory (DFT) is a really powerful theoretical tool for a wide range of chemical interests. DFT associates accuracy with low computational cost in such a way that it constitutes an attractive alternative to other procedures. The potential for the computational investigations using DFT method to guide experiment has been clearly established. Therefore, the DFT with the B3LYP mode was applied for the calculation of geometric characterization and understanding of interaction mechanism [22]. The amino and the carboxylic groups of the L-val (or the L-leu) could be in a protonated or dissociated

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