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## Adsorption equilibrium of citric acid from supercritical carbon dioxide/ethanol on cyano column

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## ABSTRACT

Supercritical adsorption equilibrium has a significant role in defining supercritical adsorption behavior. In this paper, the adsorption equilibrium of citric acid from supercritical CO<sub>2</sub>/ethanol on a cyano column was systematically investigated with the elution by characteristic point method. Equilibrium loading was obtained at 313.15 K and 321.15 K with supercritical CO<sub>2</sub>/ethanol densities varying from 0.7068 g·cm<sup>-3</sup> to 0.8019 g·cm<sup>-3</sup>. The experimental results showed that the adsorption capacity of citric acid decreased with increasing temperature and increasing density of the supercritical CO<sub>2</sub>/ethanol mobile phase. The adsorption equilibrium data were fitted well by the Quadratic Hill isotherm model and the isotherms showed anti-Langmuir behavior. The monolayer saturation adsorption capacity of citric acid is in the range of 44.54 mg·cm<sup>-3</sup> to 64.66 mg·cm<sup>-3</sup> with an average value of 56.86 mg·cm<sup>-3</sup>.

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## 1. Introduction

Citric acid (CA, 2-hydroxy-1,2,3-propanetricarboxylic acid, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) is one of the most important organic acids used massively worldwide because of its low toxicity compared with other acidulants [1]. It can be used as an additive to add an acidic taste to food and soft drinks, and also as an ingredient in detergents and cleaning products [2]. However, there is very limited natural supply of citric acid and the high demand for it can only be met by biotechnological fermentation processes [3]. Carbohydrates, including sucrose and molasses, are usually adopted as raw materials to produce citric acid. The fermentation process is relatively easy to achieve a high yield, whereas it is difficult to separate citric acid from the fermentation broth. The conventional method of precipitation by calcium salt suffers from disadvantages of high cost and considerable amount of environmentally harmful waste. The other possible methods such as solvent extraction, electro-dialysis, membrane separation, supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>) extraction and ion-exchange [2] also have more or less inherent drawbacks.

In recent years, the incentive of employing green, sustainable technologies in industrial processes is increasing [4]. Supercritical fluid chromatography (SFC), with its mobile phases generally using environmental friendly and less expensive solvent, presents strong economical and ecological advantages and gains more and more attention in refining processes. Applications range from micro-scale analysis of complex mixtures to macro-scale purification of chiral enantiomers in a variety of industries, such as pharmaceuticals, foods, cosmetics, agrochemicals,

petrochemical and natural products. The inherent speed, efficiency, and versatility of SFC have transformed the perceptions of the technology from novelty to integral tool for the modern labs, especially for those expecting to maximize throughput [5]. Patel *et al.* have successfully adopted packed column SFC for the separation of two-pairs of water soluble peptides of identical mass, composition and charge that differ only in amino acid sequence [6]. Desmorteux *et al.* have studied the separation of furocoumarins of essential oils by SFC with a green mobile phase of CO<sub>2</sub>/ethanol. The results obtained showed that SFC was a perfectly suitable method to investigate the essential oil composition because of the great number of compounds separated in a reduced analysis time (about 10 min) with a very short time for re-equilibration of the system at the end of the gradient analysis [7]. Based on the advantages and wide application of SFC, it is thought to be an attractive method for the separation of citric acid from the fermentation broth.

During the SFC separation process, the optimization of separating conditions in terms of production rate, yield, and costs is of much importance. In general, the knowledge of the shape of adsorption isotherms of components is necessary to understand the retention mechanism, to establish optimal conditions and to design the whole chromatographic separation process [8]. Adsorption isotherms are considered like “working curves” whose knowledge is required to maximize the yield of product purification [9]. In spite of the increasing importance and necessity, the knowledge of adsorption behavior under high pressures is still scarce [10]. Only a few researches have been reported on adsorption isotherms from supercritical fluid. The adsorption equilibrium of some solutes, such as benzoic acid and acetylsalicylic acid [11], salicylic acid [12], ethyl benzene [13], toluene and ethyl acetate [14,15], α-tocopherol and δ-tocopherol [16,17],

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terpene [18,19], furfural [20], and eicosane and 1,2-hexanediol [21], from sc-CO<sub>2</sub> has been studied. However, because of the complex nature of adsorbent–adsorbate interactions, it is hard to theoretically predict adsorption isotherms. Therefore, isotherms of the supercritical fluid adsorption process have to be determined experimentally. For the operation and development of SFC adsorption processes, especially for adsorption systems with sc-CO<sub>2</sub>, the measurement of thermodynamic data and the determination of adsorption equilibrium are important.

The present work was focused on the adsorption equilibrium of citric acid from sc-CO<sub>2</sub>/ethanol with a cyano column as the stationary phase. Firstly, citric acid was separated from simulated fermentation broth (citric acid, glucose and aconitic acid) and the effect of temperature on *R*<sub>C-A</sub> (the Resolution of citric acid to aconitic acid) was studied. The molecular dynamic simulation (MD) method was used to predict the density of the sc-CO<sub>2</sub>/ethanol binary mobile phase at different temperatures and pressures. The influence of temperature, pressure and density of sc-CO<sub>2</sub>/ethanol on adsorption capacity was studied. The method of elution by characteristic point (ECP) was used to analyze the adsorption isotherm of citric acid from sc-CO<sub>2</sub>/ethanol on a ZorBaxSB-CN column. The data were modeled with the Quadratic Hill isotherm model. In our work, the preparative SFC (pre-SFC) was first introduced to the separation of citric acid from simulated fermentation broth and for adsorption isotherm measurements. Data from this work can be applied for engineering design and optimization of separation of citric acid with SFC.

## 2. Theoretical Fundamentals

### 2.1. Elution by characteristic points (ECP method)

Determination of adsorption isotherms can be done by the ECP method. This method is simple and fast and only a small amount of sample is required. It is based on the use of a simple equation giving the rear diffusive part of an overloaded elution band. When a large amount of sample is injected into a chromatographic column packed with an adsorbent, an unsymmetrical band with a steep front and a diffuse rear profile or a steep rear and a diffuse front profile is obtained by elution. Assuming that the column efficiency is infinite and the instant adsorption equilibrium is reached between the adsorption phase and the mobile phase, the retention time (*t*<sub>R</sub>) at the concentration *C* can be expressed by the equation:

$$t_R(C) = t_p + t_0 \times \left( 1 + \frac{1-\varepsilon}{\varepsilon} \times \frac{dq}{dC} \right). \quad (1)$$

The equation is solved for *dq/dC*, giving the relationship [22]:

$$q(C) = \frac{1}{V_a} \times \int_0^C (V - V_0) dC. \quad (2)$$

### 2.2. Adsorption isotherms

Adsorption is a process in which molecules from the mobile phase attach themselves on the surface of the stationary phase. The adsorption equilibrium can be reached during the process and the adsorption isotherm is always applied to describe this process [23]. Adsorption equilibrium models including Langmuir, Freundlich and Brunner–Emmet–Teller (BET) are usually used. They are limited to model isotherms with a single curvature, either convex or concave. Isotherms exhibiting both curvatures cannot be described. For describing this type of isotherms, a more flexible model of Hill isotherms can be used [24].

$$q = \frac{q_s}{N} \times \frac{b_a c + 2b_b c^2 + \dots + nb_n c^N}{1 + b_a c + b_b c^2 + \dots + b_n c^N} \quad (3)$$

In the equation, for *N* = 1, the isotherm is identical to the Langmuir model. For *N* ≥ 2, isotherms of different curvatures with a point of inflection can be described. In this work the experimental data were fitted well by the Quadratic Hill model (*N* = 2).

$$q = \frac{q_s}{2} \times \frac{b_a c + 2b_b c^2}{1 + b_a c + b_b c^2} \quad (4)$$

## 3. Experimental Section

### 3.1. Experimental set-up and materials

The experimental set-up (Thar Company, USA) is illustrated in Fig. 1. The cyano column (ZorBaxSB-CN, 250 × 9.4 mm, i.d., 5 μm, purchased from Agilent, USA) was adopted for the separation of citric acid from simulated fermentation broth and also for the measurements of adsorption isotherms under specified conditions. The physical properties of the ZorBaxSB-CN column are listed in Table 1. The wavelength of UV detection was set to 215 nm. The sample of citric acid was filtered by a filter membrane of 0.45 μm before being injected into the chromatographic system.

Carbon dioxide with purity >99.9% (by mass) was purchased from Tianjin Liufang Ind., Tianjin China. Ethanol (analysis grade) and citric acid (analysis grade) were provided by Tianjin Jiangtian Chemical Technology Co.

### 3.2. Experimental method and procedure

#### 3.2.1. Separation of citric acid from simulated fermentation broth

Referring to the component of the fermentation broth produced in the plant, the simulated fermentation broth whose composition is citric acid, glucose and aconitic acid was prepared. Supercritical fluid chromatography (SFC) with ZorBaxSB-CN (cyano column) as the stationary phase was adopted for the purification of citric acid from simulated fermentation broth. According to West's classification of the stationary phases, three major groups have been defined: non-polar, moderately polar and very polar [25]. The cyanopropyl-bonded stationary phase (CN) is in the very polar group and is suitable for the separation of polar and medium- or small-sized molecules. The cyanopropyl-bonded stationary phase (CN) is able to obtain symmetric peak for acid and basic substances, and the selectivity for separation of double bond compound is satisfied. Considering the polarity and acidity of citric acid as well as aconitic acid and the property of the cyanopropyl-bonded stationary phase, ZorBaxSB-CN (cyano column) was chosen as the stationary phase in the experiment.

#### 3.2.2. Measurement of hold-up volume and column porosity

In preparative chromatography, the column porosity of the stationary phase is an important parameter. It can be calculated from the retention volume of an unretained substance, the so-called hold-up volume. 1,3,5 Tri-*tert*-butyl-benzene was adopted as the marker substance to quantify the hold-up volume of the cyano column. The density of the mobile phase changed from 0.7 to 0.8 g·cm<sup>-3</sup>. At these conditions, it was viewed that there is no dependency between hold-up volume and density of the mobile phase. The measured total porosity ( $\varepsilon_t$ ) of the cyano column was about 0.6. The particle porosity ( $\varepsilon_p$ ) was 0.38. According to the relationship  $\varepsilon_t = \varepsilon_b + (1 - \varepsilon_b)\varepsilon_p$ , it can be calculated that the bed void porosity ( $\varepsilon_b$ ) was 0.35.

#### 3.2.3. Calculation of the number of theoretical plates

High column efficiencies were required while the ECP method was used to determine the adsorption isotherm. The number of theoretical plates under experimental conditions has been measured. 10 μl citric acid aqueous solutions of different concentrations were injected into

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