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Adsorption thermodynamics and kinetics of yohimbine onto strong acid cation exchange fiber

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ABSTRACT

The strong acidic cationic exchange fiber (SACEF) was used to adsorb yohimbine from alcoholic solution. Batch experiments were performed to examine the effects of adsorbent dosage, solution pH and temperature in the adsorption process. The thermodynamics and kinetics of adsorption were also analyzed. The optimum yohimbine adsorption onto the SACEF was found at pH = 5 of solution and equilibrium could be attained within 20 min. The equilibrium adsorption data were preferably modeled with the Freundlich isotherm model and the thermodynamic parameters were calculated to be: 11.99 kJ/mol < ΔH < 13.72 kJ/mol, −21.17 kJ/mol < ΔG < −17.87 kJ/mol and 63.18 J/mol K < ΔS < 65.60 J/mol K. The results demonstrated that the adsorption was an endothermic, spontaneous and feasible process of physisorption. Meanwhile, yohimbine adsorption on SACEF fitted well to the pseudo-second-order kinetic model and the adsorption rate was limited by film diffusion. The activation energy *Ea* was calculated to be 14.39 kJ/mol. Furthermore, the surface morphologies of the SACEF before and after yohimbine adsorption were analyzed by SEM and the adsorption mechanism was discussed by FTIR analysis. SACEF could effectively adsorb yohimbine from alcoholic solution and could be used repeatedly for more than five cycles.

1. Introduction

Yohimbine (structure as Fig. 1) is a well-known indole alkaloid primarily acting as a monoamine oxidase enzymeinhibitor [1] and a selective antagonist of α_2-adrenoceptors which increase brain noradrenaline cell firing and release [2]. And the predominant use is that yohimbine has been used for the treatment of male erectile dysfunction (ED) [3]. Yohimbine was firstly extracted from the bark of the *Pausinystalia yohimbe* in West African [4], and now it is usually extracted from *Rauvolfia* species in China [5–9]. However, yohimbine shares the similar physicochemical properties of the indole alkaloids in many plants of *Rauwolfia* species, and its content in the roots of *Rauwolfia* species is very low (about 0.1002–0.2195%, dry wt) [10]. Both its low content and similar physicochemical properties make yohimbine difficult to be isolated and purified from *Rauwolfia* species.

A survey in scientific literature revealed that the papers in English about yohimbine almost focused on the pharmacological activities, but the research about separation of yohimbine from *Rauvolfia* species was not enough, except a few papers in Chinese [5–9]. The conventional method for extracting and isolating yohimbine from *Rauvolfia* species usually consisted of the following steps [11]: maceration in methanol, evaporation, dissolution in HCl, filtration, basification to the neutral pH, extraction in chloroform, evaporation and finally dissolution in methanol with subsequent filtration. However, the conventional method had been weeded out because of low yield, large dosage of organic solvent, serious pollution and time-consuming procedure. Recently the macro-porous adsorption resins [6,7] and ion exchange resins [8,9] have been applied to separate and purify yohimbine from *Rauwolfia* species. However, these resins have some shortcomings including cracking easily and poor recycle rate, and they also could be easily poisoned by some organic or inorganic compounds when the pores were clogged by the colloids in the treated solution [12]. Therefore, to develop a method which should be more efficient, more stable and longer using life for isolating yohimbine from *Rauwolfia* species is highly desired.

Ion exchange fiber (IEF) is a fibrous ion exchange and adsorption material. Compared with the traditional ion exchange resin (IER), IEF shows potential adsorption performance due to the larger effective specific surface area, shorter transit distance, higher exchange rate, stronger adsorption ability, and longer using life [13].

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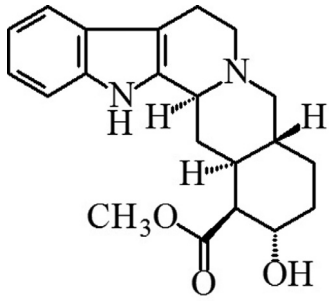

Fig. 1. Structure of yohimbine.

In addition, it's more easily to be regenerated, which reduces the industrial cost. Due to these favorable features, IEF has been widely applied in wastewater purification [14] and metal recovery [15]. Currently, IEF has also been used to isolate active ingredients from herbal raw materials, such as baicalin [16], dihydrocapsaicin [17], berberine [18], salvianolic acid B [19] and catechin [20]. However, the application of IEF for separation of yohimbine from *Rauvolfia* species has not been reported.

In this study, the strong acidic cationic exchange fiber (SACEF) was chosen as the adsorbent. The adsorption behavior of yohimbine onto SACEF was investigated. Adsorption thermodynamics and kinetics studies had been performed and the results had been analyzed. The adsorption mechanism was discussed by FTIR analysis and the surface morphology of the SACEF before and after yohimbine adsorption was analyzed by SEM. The results proved that SACEF was an efficient adsorption material for yohimbine. A theoretical basis for isolation of yohimbine from *Rauwolfia* species is provided through this study.

2. Materials and methods

2.1. Materials

The strong acidic cation exchange fiber (SACEF, $-SO_3H$ ion-exchange group, exchange capacity ≥ 4.0 mmol/g, diameter $= 40 \pm 2\ \mu$m) was purchased from Guilin Zhenghan Sci. &Tech. Co., Ltd. (Guangxi, China). Yohimbine (purity > 99.8%) was purchased from Aladdin company (Shanghai, China). Acetonitrile (chromatographic grade) was bought from Merck (Germany). All the other chemicals used in this study were analytical grade, and the water used in the experiments was ultrapure water (the electrical conductivity < 0.1 μs/cm) made by ELGA Ultrapure Water Polishing System (model: CLXXUVFM2).

The stock solution of 2000 mg/L of yohimbine was prepared by dissolving the yohimbine powder in the acetonitrile. The desired test solutions of yohimbine were prepared using appropriate subsequent dilutions of the stock solution by 60% hydrous alcohol. The range of concentrations of desired test solutions varied between 100 and 300 mg/L. The pH of each test solution was adjusted to the required value with 0.1 mol/L NaOH or 0.1 mol/L HCl.

2.2. Pre-treatment of SACEF

The pre-treatment method of SACEF according to China National Standard GB/T5476-2013 (method for pretreating ion exchange resins) was described below. The fiber was washed for the removal of mechanical impurity with ultrapure water, and then dipped into 1 mol/L HCl, ultrapure water, 1 mol/L NaOH, ultrapure water, 1 mol/L HCl for 30 min, respectively. At last the fiber was washed repeatedly with ultrapure water until the pH of washings reached about 7 before it was dried in a vacuum oven at 60 °C for the later experiments.

2.3. Analysis

The concentrations of yohimbine in the solutions before and after equilibrium were determined [21] by HPLC (Waters 1525, USA) equipped with reversed phase C18 column (4.6 mm × 250 mm, 5 μm, Hypersil-ODS2, China). It was applicable to samples with a concentration between 2.6 and 208 mg/L or samples diluted to fall into this concentration range. The mobile phase was composed of acetonitrile-MKP solution (20 mmol/L) with *V*/*V* ratio of 55:45. The flow rate was 1 mL/min. The detector wavelength (UV) used was 270 nm. The temperature of column was adjusted to 30 °C. The injection dose was 10 μL. Under these chromatographic conditions, the standard linear regression equation was $A = 40521C + 12{,}586$ (*A*: peak area, *C*: concentration of yohimbine, mg/L), $R^2 = 0.9999$. Each determination was repeated three times and the results obtained were their average values.

The pH of solution was measured by the LEI-CI pH meter (pHS-25, INESA, China) with a combination electrode. Fourier Transform Infrared Spectrometer (FTIR, SHIMADZU, FTIR-8400S) analysis was used to identify different chemical functional groups presenting on the SACEF before and after yohimbine adsorption. The analysis was carried out using KBr tablet and the spectral range varied from 4000 to 400 cm^{-1}. The surface morphology of the SACEF before and after yohimbine adsorption was analyzed by scanning electron microscopy (SEM, HITACHI, S-3400N) at an accelerating voltage of 20 kV.

2.4. Preparation of SACEF for FTIR and SEM

The SACEF for FTIR and SEM was prepared in 500 mL conical flask filled with 200 mL yohimbine solution of 9.9300 g/L and 0.2000 g preprocessed SACEF. The pH value of the solution was adjusted to 5 by 0.1 mol/L HCl. The flask was placed in the Magnetic Heated Stirrer (DF-101S, Yuhua, China) at 100 rpm and 30 °C. A small amount of the SACEF was taken out from the conical flask at different contact time (1, 5, 10, 90 min), respectively. Then the above fiber was washed by ultrapure water until the pH value of washings reached to 7. At last the fiber was dried in a vacuum oven at 60 °C until the weight reached a constant. The adsorbed and dried SACEF was divided into two parts, one part for SEM and the other part for FTIR.

2.5. Batch adsorption experiments

To study the effects of parameters such as adsorbent dosage, solution pH and temperature for yohimbine adsorption onto the SACEF, the batch adsorption experiments were carried out in a series of 250 mL conical flasks with ground glass stoppers. Each flask was filled with 100 mL known initial concentration of yohimbine solution and accurately weighed quantity of pretreated SACEF. The flasks were placed in the Magnetic Heated Stirrer at a constant speed (100 rpm) and a desired temperature until the adsorption equilibrium was reached. And the equilibrium time was set as 20 min (found out from the kinetic studies). Samples were taken at the equilibrium time in above experiments. The equilibrium concentration of yohimbine (c_e) was determined by HPLC. All experiments were performed in triplicates and the results obtained were their average values. The equilibrium adsorption capacity of yohimbine onto the SACEF (q_e) was calculated as Eq. (1), and the percentage removal of yohimbine (removal%) was calculated as Eq. (2).

$$q_e = (c_0 - c_e)v/m \tag{1}$$

$$\text{Removal\%} = \frac{c_0 - c_e}{c_0} \times 100\% \tag{2}$$

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