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Adsorption characteristics of amino acids on to calcium oxalate

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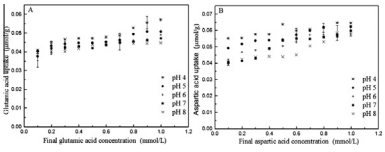
GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption of amino acids on to calcium oxalate found in urinary calculus has been studied and the adsorption characteristics were analyzed. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to fit the kinetics data. The pseudo-second-order model best described the dynamic behavior of the adsorption process. The uptake of glutamic acid and aspartic acid were found to decrease as solution pH increasing from 4 to 8. The experimental data obtained at different pH conditions were analyzed and fitted by Langmuir, Freundlich, Redlich–Peterson, Temkin and Sips isotherm models using linear and nonlinear regression analysis. Error analysis (correlation coefficient, residual root mean square error and chi-square test) showed that the Langmuir I isotherm model and the non-linear form of Sips isotherm model should be primarily adopted for fitting the equilibrium data. The maximum adsorption capacity of glutamic acid and aspartic acid onto calcium oxalate monohydrate crystals are 0.059 and 0.066 μmol/g at pH 4, respectively. These studies have the vital significance for research aimed at exploring the role of urinary amino acids effect the formation process of calcium oxalate crystals found in urinary calculus and for potential application in the design of synthetic peptides used for urinary calculi therapy.

1. Introduction

Attributing to multiple factors including changes in dietary habit and lifestyle, increments in the prevalence of obesity and diabetes mellitus, which have also been associated with the formation of kidney stones [1,2], and even possible changes associated to environmental factors [3,4], urolithiasis becomes a common health problem that produces heavy economic burden on society and serious damage on the quality of life [5]. The key characteristic of urinary stone disease is a high recurrence rate after initial treatment for the patients. Over the past few decades, about 70% of patients with experience nephrolithiasis will have recurrences, and the incidence and prevalence of this disease has steadily increased [6]. Urinary calculi are composed of organic and inorganic mineral matrix. Multiple studies show that calcium oxalate (CaOx) is the main composition of urinary calculi; about 70–80% of stones based on calcium are calcium oxalate stones [6–8].

Organic components in urinary calculi are mainly macromolecular compounds such as proteins and acid mucopolysaccharide. Among them, protein plays an important role in the process of stone formation [9,10], it is speculated that the number, types and sequence of amino acids that constitute the basic skeleton of

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protein structure have a significant effect on the process of CaOx crystallization [11]. Research has shown that osteopontin (OPN) [12,13] and urinary prothrombin fragment 1 (UPTF1) [14,15] are present in the organic matrix of CaOx stones [16], the most likely binding affinity of these proteins adsorbed on to CaOx crystal surfaces is the interaction between terminal amino acids residue and the calcium ions [11,17,18]. Considering that protein is constituted with amino acids, it is especially important to investigate the effects of urinary amino acids on the process of CaOx crystallization, including the process of CaOx crystals nucleation, growth, aggregation and solid phase transformation.

Urine amino acids are considered to be one of the important components that may influence the formation process of CaOx crystals [19,20]. Among the 20 native amino acids, acidic amino acids, such as the glutamic acid and aspartic acid can compete with oxalate for calcium ions in solution, and adsorb on to CaOx crystal surfaces preferentially, which will significantly inhibit the nucleation and the growth rates of CaOx crystals [21–24].

The adsorption of amino acids on inorganic surfaces including kaolinite [25], hydroxyapatite [26,27], polymer resin [28], TiO_2 [29,30], Al_2O_3 [31], SiO_2 [32–34], chitosan [35], zeolite [36–38], and so on, has been widely investigated in recent years [39]. Several mechanisms including electrostatic interactions, specific covalent bond formation, hydrogen bond formation, ligand-exchange and ion-exchange reactions, hydrophobic effects, and the superimposed interactions of several adsorption mechanisms are involved in the adsorption of amino acids on to inorganic surfaces [25,39]. However, to our knowledge, few studies have reported about the adsorption characteristics of glutamic acid and aspartic acid onto CaOx crystal surfaces. The main purpose of this paper is, therefore, to explore the adsorption characteristics of amino acids onto calcium oxalate monohydrate (COM, the most stable form of thermodynamics in all CaOx crystal forms [40]) under physiological urinary pH range using glutamic acid and aspartic amino as model amino acid. The adsorption kinetics was analyzed by fitting kinetic models (pseudo-first-order and pseudo-second-order and intraparticle diffusion models). Experimental equilibrium data were fitted to the adsorption isotherm equations (Langmuir, Freundlich, Redlich–Peterson (R–P), Sips (Langmuir–Freundlich) and Temkin) in linear and non-linear forms to determine the best-fit isotherm equation. Error analysis was also carried out to test the adequacy and the accuracy of the model equations. On this basis, the adsorption mechanisms of amino acid onto CaOx crystal surfaces were discussed.

2. Materials and methods

2.1. Materials

Visible spectrophotometry analysis was carried out on a 752N UV–Vis spectrophotometer, purchased from Shanghai Precision & Scientific Instrument Corporation. L-glutamic acid and L-aspartic acid (99% purity) were purchased from CapitalBio Corporation. CaOx monohydrate was purchased from Tianjin Damao Chemical reagent Factory. All other reagents were of analytical reagent grade and Double-distilled water was used in all experiments. The glassware using in experiments must be soaked 12 h in 0.1 mol/L NaOH and then washed by double-distilled water.

2.2. Methods

2.2.1. Adsorption equilibrium experiments

A saturated aqueous solution of CaOx at pH 4 was prepared by adding 4 g of CaOx monohydrate to Erlenmeyer flask containing 100 mL distilled water. The flasks were agitated at 37 °C for 1 day in a rotary shaker, adjusting the pH to 4 using Mettler-Toledo DELTA 320 pH meter with 0.1 mol/L HCl or 0.1 mol/L NaOH solutions, then leaving the solutions to stand for a further 2 days to equilibrate. The residual CaOx crystals were separated by vacuum filtration through a 0.45 μm membrane filter (mixed cellulose ester) and discarded.

The adsorption experiments of glutamic acid and aspartic acid were carried out by batch studies. In 100 mL-stoppered Erlenmeyer flasks containing 20 mL aliquot of the saturated aqueous solutions of CaOx, 1 g of CaOx monohydrate adsorbent was added, and the glutamic acid and aspartic acid was added to a series of final concentration (0.1–1.0 mmol/L), independently. The initial solution pH was adjusted to the range from 4 to 8 with either 0.1 mol/L HCl or 0.1 mol/L NaOH. The flasks were placed in a rotary shaker and incubated at 37 °C with gentle stirring. The solutions were centrifuged by a centrifuge (Thermo Scientific Sorvall ST 16R, Germany) at different incubating time (during 24 h) and the supernatant were analyzed using a 752N UV–Vis spectrophotometer. All adsorption experiments were performed in replicate and average values were used for further calculations, and all the standard deviations were within 3%. The equilibrium adsorption capacity (q_e, μmol/g) was calculated as follows:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where C_0 (mmol/L) is the initial concentration of glutamic acid or aspartic acid, and C_e (mmol/L) is the concentration of glutamic acid or aspartic acid at equilibrium. V is the volume of the solution (L). m is the mass of CaOx monohydrate adsorbent (g).

2.2.2. Analytical measurements

Amino acid concentrations in the solutions were determined by UV–Vis spectrophotometry after chromogenic reaction according the method reported by Fleming et al. [11]. After the adsorption equilibrium, the CaOx crystal was collected by filtration, and then washed with 20 mL of 0.1 mol/L NaOH solutions and incubated at 37 °C for 2 h (the pilot experiments showed that the absorbed amino acid was completely desorbed by washing with alkaline solutions for 2 h). The alkaline solution containing amino acid was collected by centrifugation for 10 min at 12,000 rpm. 1 mL of the supernatant reacted with 1 mL of 1% ninhydrin agent for 15 min under boiling water to develop color, and then diluted with 3 mL of 60% ethanol. The amino acid concentration in the alkaline solution was detected by UV–Vis spectrophotometer at 570 nm. The calibration curve showed a linear variation up to 0.3 mmol/L amino acid concentration, and the correlation coefficient of glutamic acid ($y = 3.9529\ x + 0.0169$) and aspartic acid ($y = 3.5252\ \ x + 0.0039$) were achieved 0.9993 and 0.9995, respectively.

2.2.3. Modeling and error analysis

In this study, all experimental data were fitted by selected adsorption models (listed in Tables 2 and 3), and the model fitted parameters were evaluated by regression analysis using OriginPro 9.0 software, except for linearized Redlich–Peterson (R–P) and Sips isotherm models, which were evaluated by the *solver* add-in function of Microsoft Excel. Correlation coefficient R^2 is a common parameter to evaluate the goodness-of-fit of the equation to the experimental data [41]. Apart from the R^2, the chi-square test (χ^2) and the residual root mean square error (RMSE) were also applied to measure the goodness-of-fit and to test the adequacy and the accuracy. The χ^2 can be defined as:

$$\chi^2 = \sum_{i=1}^{n} \frac{(q_e - q_c)^2}{q_c} \quad (2)$$