



## Adsorptive removal of Cr(III) and Fe(III) from aqueous solution by chitosan/attapulgite composites: Equilibrium, thermodynamics and kinetics

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### ABSTRACT

Adsorption of Cr(III) and Fe(III) onto chitosan/attapulgite composites (CTS/ATP) was investigated with respect to pH, temperature, initial concentration and binary solution. Equilibrium data, at various temperatures, were described by the Langmuir, Freundlich isotherm models. The Freundlich isotherm model was fitted to the experimental data significantly better than the Langmuir isotherm. In a binary solution, the combined effect of adsorbing one metal ion in the presence of the other metal ion reduced the adsorption capacity of either metal ion. The kinetic data was well fitted to the intraparticle diffusion equation, which indicated that the three adsorption steps belonged to the pseudo-second-order adsorption process. Intraparticle diffusion increased with the increase in adsorbate concentration while film and pore diffusion decreased. The thermodynamics parameters (positive values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and negative values of  $\Delta G^\circ$ ) indicated the binding systems between CTS/ATP and adsorbate were endothermic, entropy gained and spontaneous in nature.

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### 1. Introduction

Human activities such as electro-plating, smelting contaminated the wastewaters with heavy metal ions, which would be harm to the environment [1]. The concentrations of traces of heavy metal ions in matrices as environmental samples are below the detection limit, a preconcentration–separation procedure is needed to improve the detection limits. The widely used preconcentration–separation methods for heavy metal ions include solvent extraction [2], co-precipitation [3], cloud point extraction [4,5], ion exchange [6], membrane filtration [7] and solid-phase extraction (SPE) [8,9]. Among the preconcentration–separation techniques mentioned above, SPE is one of the efficient techniques for the trace or ultratrace amount of heavy metal ions duo to its simplicity and economy [10].

Chitosan (CTS) has many reactive amino groups and hydroxyl groups, which is beneficial for the adsorption of metals from solution [11–13]. However, CTS is only soluble in few dilute acid solutions due to its crystalline nature, and it has drawbacks of swelling and unsatisfying mechanical property, which limits its applications. To improve the properties of CTS, abundant studies have been devoted to the modification of the CTS

surface by cross-linking with functional agents, such as glutaraldehyde, ethyleneglycol diglycidyl ether and epichlorhydrin [14,15]. Recent researches proved CTS-based inorganic composites could be applied to adsorptive remove of heavy metal ions. Various inorganic materials such as silica gel [16], clay minerals [17], zeolite [18], metallic oxide [19] and carbon nanotubes [20] have been used up to now.

Attapulgite (ATP) is a hydrated octahedral layered magnesium aluminum silicate mineral with large surface area, excellent chemical stability and strong adsorption [21,22]. Although ATP possesses high adsorption capabilities, the modification of its structure can successfully improve its capabilities. In this work, CTS/ATP composites are applied as an adsorbent for the removal of chromium and iron ions from aqueous solution of both single and binary systems. The adsorption properties such as equilibrium, kinetics and thermodynamics were demonstrated by batch mode adsorption experiments.

### 2. Experimental

#### 2.1. Instruments and apparatus

Scanning electron microscopy (SEM) images were obtained at 15.0 kV on the field emission scanning electron microscope (USA) after gold plating. X-ray diffraction (XRD) was performed on Siemens D5005 powder X-ray diffractometer. Infrared

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spectra (4000–400  $\text{cm}^{-1}$ ) was recorded on a Nicolet NEXUS 470 FT-IR apparatus (U.S.A.). The specific surface area, pore volume of the adsorbents were measured according to the Brunauer–Emmett–Teller (BET) model using single point analysis and a Flowsorb II 2300 from Micromeritics Instrument Corporation, Norcross, GA. A Varian Liberty 150 AX Turbo model inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used for the determination of Cr(III) and Fe(III) from aqueous solutions.

## 2.2. Reagents and materials

Ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and chromium chloride ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ) salts were used in the preparation of the salt solutions. Stock solutions of  $1000 \text{ mg L}^{-1}$  were prepared by dissolving the accurately weighed amounts of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  in 1000 mL distilled water. Experimental solutions were prepared by diluting the stock solution with distilled water. CTS with 98% deacetylation and an average molecular weight of  $6.0 \times 10^4 \text{ g mol}^{-1}$  (Yuhuan Biomedical Corp., China) was used as functional monomer. Attapulgite, with average size of 92 nm, was supplied by the Nanjing Yadong Aotu Mining Inc. in China. Prior to use, ATP was activated by baking 6.0 h at  $250^\circ\text{C}$  and then dispersing in the  $0.1 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$  for 10 h at room temperature. All the other chemicals used were analytical grade, and DDW was used throughout this work.

## 2.3. Preparation of CTS modified ATP

CTS solution was prepared by dissolving 4.0 g of CTS in 100 mL of 1% (v/v) acetic acid. An amount of 2.5 g ATP was dispersed in 100 mL of distilled water and then treated in ultrasonic bath for 1.0 h. The as-prepared CTS solution was slowly added into the ATP suspension with vigorous stirring. The mixture was treated at  $60^\circ\text{C}$  for 12 h. The CTS/ATP composites were washed with distilled water until the pH of the washed water became neutral. CTS/ATP composites were separated from water by centrifugation at 3500 rpm for 10 min and then dried at  $60^\circ\text{C}$  for 24 h [23].

## 2.4. Determination of $\text{pH}_{\text{ZPC}}$

$\text{pH}_{\text{ZPC}}$  is the pH when the charge on the activated carbon surface is zero. The pH drift method was used to determine the  $\text{pH}_{\text{ZPC}}$  of the CTS/ATP composites surface using 10 mL of 0.1 M NaCl in a series of Erlenmeyer flasks whose pH was adjusted using 0.1 M NaOH and 0.1 M HCl in the range between 1.0 and 9.0. The initial pH of the solutions was determined and 0.03 g of the adsorbent was added to each of the flasks and after completion of 12 h, the final pH of the solutions was measured.  $\text{pH}_{\text{ZPC}}$  was noted at the pH in which the initial pH equals the final pH.

## 2.5. Batch experiments

All batch adsorption experiments were carried out by mixing 0.01 g CTS/ATP composites with 50 mL aqueous solution of copper acetate with the desired concentration and appropriate pH and shaking for 12 h at 298 K. The pH of Cr(III) or Fe(III) solution was adjusted to different pH values (1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0) with acetic acid or sodium hydroxide solutions. For equilibrium adsorption experiments, 50 mL of various initial concentration (from 10 to  $400 \text{ mg L}^{-1}$ ) of Cr(III) or Fe(III) solution was mixed with 0.01 g CTS/ATP composites, then shaken at 298 K until the equilibrium was established. Batch kinetic experiments were carried out by mixing 0.01 g CTS/ATP composites with 50 mL Cr(III) or Fe(III) solution ( $C_0 = 3.0 \text{ mg/L}$ , pH 5.0 or 3.0) and shaking at 298 K for predetermined intervals of time.

The Cr(III) or Fe(III) solution was separated from the adsorbent by centrifugation at 1500 rpm for 10 min. Both the initial and the final concentrations of Cr(III) or Fe(III) in the solution were measured by ICP-AES. The adsorption capacity of the composites for Cr(III) or Fe(III) was calculated through the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial and equilibrium concentration of Cr(III) or Fe(III), respectively.  $V$  (mL) and  $W$  (g) are the solution volume and the weight of sorbent, respectively.

## 2.6. Adsorption from binary solution

A series of binary solution where the concentration of Cr(III) was fixed at  $3.0 \text{ mg L}^{-1}$ , the concentration of Fe(III) was varied from 0 to  $10 \text{ mg L}^{-1}$  and the pH value of the binary solution was adjusted to 3.0. In another binary system, the initial concentration of Fe(III) was fixed at  $3.0 \text{ mg L}^{-1}$ , the concentration of Cr(III) was varied from 0 to  $10 \text{ mg L}^{-1}$  and the pH value of the binary solution was adjusted to 5.0. These binary solutions were agitated for 12 h at 298 K. Equilibrium concentrations of Cr(III) and Fe(III) in the various binary solutions were determined by ICP-AES.

## 2.7. Desorption studies

In order to search out an effective reagent for the CTS/ATP composites desorption, certain amount of the CTS/APT composites was prepared and its adsorption capacity for Cr(III) and Fe(III) was calculated. The influence of different acid solutions on desorption efficiency was studied by mixing 0.10 g CTS/APT composites with 5.0 mL 1.0 mol/L acid solutions (HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{CH}_3\text{COOH}$ ) and agitating for 12 h at room temperature. Desorption efficiency was calculated using the following equation:

$$\% \text{Desorption} = \frac{C_d \times V_d}{w \times q_e 1000} \times 100 \quad (2)$$

where  $C_d$  is the desorbed adsorbate concentration ( $\text{mg L}^{-1}$ ),  $V_d$  is the volume of the desorption solution,  $w$  is the mass of the pre-adsorbed adsorbent (g),  $q_e$  is the amount of the adsorbate pre-adsorbed on the adsorbent ( $\text{mg g}^{-1}$ ).

## 3. Results and discussion

### 3.1. Characteristic of CTS/ATP composites

The elemental analysis shows that the lignin had the following percentage composition (%): C, 2.625; H, 1.117; N, 9.651. The average pore diameter was 1.527 Å and the specific surface area of the CTS/APT composites was  $64.68 \text{ m}^2 \text{ g}^{-1}$  measured by the  $\text{N}_2$ -BET method.

To characterize the size and shape of the CTS/APT composites, SEM was conducted. Fig. 1 presents the typical SEM images of ATP and the CTS/APT composites, indicating that the products are well-dispersed with CTS. It is seen from the structure of ATP is maintained even after the combination with CTS.

The FT-IR spectrum of the CTS/ATP (Fig. 2) shows the combination of characteristic absorptions due to the CTS and ATP groups. The peak at  $1595 \text{ cm}^{-1}$  of the  $-\text{NH}_2$  group in the starting CTS was shifted to  $1559 \text{ cm}^{-1}$  in the CTS/ATP spectrum, corresponding to the deformation vibration of the amine group of CTS. Compared with ATP, the Si–O bands in CTS/ATP shift to  $1029 \text{ cm}^{-1}$ . The results suggested that CTS was bonded on the ATP, resulting in the composites CTS/ATP.

Fig. 3 shows the XRD patterns of ATP and the CTS/ATP composites. For the XRD spectrum of the CTS/ATP composites, the main

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