Colloids and Surfaces A 555 (2018) 548–557

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

Magnetic γ-Fe_2O_3/Fe-doped hydroxyapatite nanostructures as high-efficiency cadmium adsorbents

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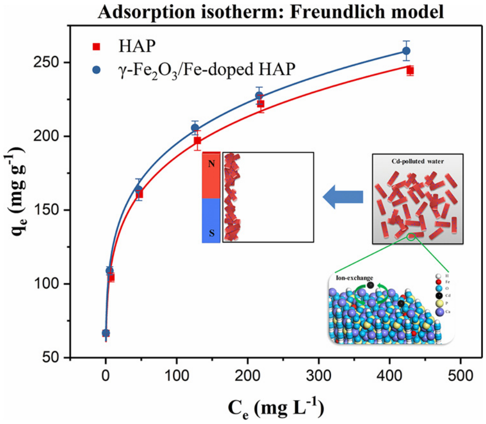
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Cadmium
Adsorption
γ-Fe_2O_3/Fe-doped HAP nanostructures
Magnetic separation

ABSTRACT

Nowadays, water pollution by industrial waste water that contains heavy metal elements, such as Cd, has become an urgent concern to be solved. In this work, magnetic γ-Fe_2O_3/Fe-doped hydroxyapatite (HAP) nanostructures are realized as Cd(II) adsorbents with outstanding adsorption performance. The Vibrating Sample Magnetometer (VSM) analysis and magnetic separation experiments reveal that γ-Fe_2O_3/Fe-doped HAP nanostructures can be effectively separated by external magnet. Compared with pure HAP, the γ-Fe_2O_3/Fe-doped HAP nanostructures show higher adsorbed concentration and adsorption rate. The maximum adsorbed concentration at the equilibrium is 258 mg g^{-1} (under initial concentration of 500 mg L^{-1}, temperature = 25 °C and pH = 5.0), which is higher than values reported for most of HAP-based adsorbents. The adsorption data could be well fitted by the Freundlich model, and the adsorption kinetic follows the pseudo-second-order model. Furthermore, the study of adsorption mechanism reveals that both ion-exchange and electrostatic interaction are involved in process of Cd(II) adsorption.

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https://doi.org/10.1016/j.colsurfa.2018.07.036
Received 28 May 2018; Received in revised form 18 July 2018; Accepted 19 July 2018

1. Introduction

Nowadays, discharging industrial waste water without proper treatment is greatly threating human beings due to the soil and water pollution by heavy metal ions [1]. Cd(II) ions are commonly contained in industrial effluent from mining, metallurgy and electroplating, which is a hazardous heavy metal pollutant for water and soil ecosystems [2,3]. Cd(II) shows high carcinogenicity to human beings, the intake of Cd(II) can cause endocrine disorder, calcium deficiency in bones and renal dysfunction [4]. Therefore, Cd(II) and other heavy metal ions have to be removed from the effluent before discharging, which rises urgent demand of applicable effluent purifying methods in industry. Cd(II) can be removed from the wastewater by various methods including ion-exchange [5], chemical precipitation [6], membrane filtration [7], *in-situ* solidification [8] and adsorption [9], among which, adsorption is regarded as one of the most promising processes for practical applications due to its relatively high efficiency, low cost and reusability [10].

Hydroxyapatite (HAP)-based materials have been extensively studied as Cd(II) adsorbents because they are eco-friendly and easily to be prepared. Moreover, the surface Ca(II) of HAP could be easily exchanged by Cd(II) ions [11], leading to high adsorption capacity around 200 mg g^{-1} [12,13]. Such high adsorption capacity makes HAP superior to other engineered adsorbents such as active carbons [14,15], zeolites [16], clays [17], TiO_2/STNWs [18] and carbon nanotubes [19] with adsorption capacities ranging in the extent of 10–150 mg g^{-1} [20]. However, to promote the industrial applications of HAP-based adsorbents, two issues have to be addressed: (1) the Cd(II) adsorption capacity and rate of HAP need to be further enhanced to meet the industrial requirements; (2) the spent HAP-based adsorbents should be easily separated from the treated water. To achieve so, the HAP-based materials should be rationally designed.

In this study, γ-Fe_2O_3/Fe-doped HAP nanostructures are synthesized via a facile wet chemical method to develop a high performance, magnetically separable Cd(II) adsorbent. The as-prepared products show a high maximum adsorbed concentration at the equilibrium is 258 mg g^{-1} (under initial concentration of 500 mg L^{-1}, temperature = 25 °C and pH = 5.0). Comprehensive characterizations have been done to analyze the average grain sizes, specific surface area, Zeta potential and the surface bonding state to reveal the underlying mechanism. The adsorption kinetics and adsorption isotherms analysis could be described by the Freundlich model and the pseudo-second-order equation [13]. Moreover, the magnetic ultra-fine γ-Fe_2O_3 particles are found attaching on the surface of Fe-doped HAP, which enables the spent γ-Fe_2O_3/Fe-doped HAP nanostructures easily to be separated from the solution by applying external magnet. This study proposes an effective strategy to develop high-efficiency adsorbents for heavy metal ions via nanostructure engineering and magnetic separation technique, which are promising in industrial applications.

2. Materials and methods

2.1. Materials

All the chemicals used in this study were of analytical reagent grade and were used as received without any further purification. Iron(II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), calcium hydroxide ($Ca(OH)_2$), phosphoric acid (H_3PO_4), Cd(II) chloride ($CdCl_2{\cdot}2.5H_2O$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and acetic acid (HAc) were all purchased from Chengdu Kelong Chemical Co. Ltd. (China). Milli-Q ultrapure water (18.25 MΩ cm) was used throughout the experiments.

The γ-Fe_2O_3/Fe-doped HAP nanostructures were synthesized via a wet chemical method. Briefly, an aqueous solution of H_3PO_4 (0.036 mol in 60 mL) was added dropwise into a basic aqueous suspension of $Ca(OH)_2$ (0.06 mol in 80 mL) containing Fe ions, under constant heating at 45 °C and stirring. A series of different quantity of $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ (0 mmol, 1.5 mmol, 3 mmol, 4.5 mmol in 15 mL) were added together as Fe(II) and Fe(III) sources before the neutralization process. The reaction product was kept in suspension by constant stirring and heating for 3 h after the neutralization reaction and then left to age for 24 h at room temperature without further stirring. The precipitate was separated from solution by vacuum filtration, then washed three times with water by filtration, dried at 80 °C, and grinded. Finally, all the precipitates were sieved to < 45 μm to reduce the effect of agglomeration after drying on the original adsorption performance of samples

2.2. Materials characterization

The phase composition and morphology of sample were analyzed by Powder X-ray Diffraction (XRD, Shimadzu XRD-6100), Scanning Electron Microscopy (SEM, FEI Inspect F50) and Transmission Electron Microscopy (TEM, JEOL JEM-2100 F, operating at 200 kV). The content and binding energy were investigated by XPS (EscaLab 250Xi). The Zeta potentials of the as-prepared adsorbents with variation of pH in adsorption were measured by Zetasizer Nano (Malvern Instrument). The magnetic properties of the γ-Fe_2O_3/Fe-doped HAP nanostructures were measured in a vibrating sample magnetometer (VSM, Lakeshore 735, USA). Brunauer-Emmet-Teller (BET) specific surface area was measured by N_2 adsorption and desorption isotherm, and the plot of the pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the isotherm by an Automated Specific surface area and Porosity Analyzer (ASAP 2020, Micromeritics). The concentration of Cd(II) was determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, IRIS Adv, USA).

2.3. Adsorption experiments

Considering the influence of the equilibration time, initial Cd(II) concentration and solution pH to the adsorption capacities of the γ-Fe_2O_3/Fe-doped HAP, adsorption experiments were performed by batch equilibration technique. Cd(II) solutions with concentrations ranging from 25 to 500 mg L^{-1} were prepared from $CdCl_2{\cdot}2.5H_2O$ by dissolution in deionized water. The desired pH of the Cd(II) solution was adjusted by diluted NaOH or HCl solution. The initial and residual Cd(II) concentration of solution was tested by ICP-AES.

The effect of pH on the Cd(II) adsorption was investigated by adjusting initial Cd(II) solution pH from 3.0 to 8.0 with initial concentration of 50 mg L^{-1} and adsorbent dose of 0.4 g L^{-1}.

The adsorption isotherms experiments were performed with an adsorbent loading of 0.4 g L^{-1} at pH 5.0 ± 0.1. In detail, 10 mg pure HAP or γ-Fe_2O_3/Fe-doped HAP were added in glass conical flask containing 25 mL of Cd(II) solution (25–500 mg g^{-1}), followed by shaking at 25 °C for 20 h to reach equilibrium. The solution containing pure HAP was separated by filtration, and the solution containing γ-Fe_2O_3/Fe-doped HAP was separated by external magnetic field. The adsorbed concentration (q_e, mg g^{-1}) was calculated using the following equations.

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

Where C_0 (mg L^{-1}) is the initial Cd(II) concentration, C_e (mg L^{-1}) is the equilibrium concentration, m (g) is the mass of adsorbent, and V (L) is the volume of the Cd(II) solution, respectively.

For adsorption kinetic experiments, 120 mg of adsorbents was added in 500 mL glass beaker containing 300 mL Cd(II) solution with 100 mg L^{-1} of initial concentrations, and the mixtures kept stirring at 25 °C by mechanical stirrer. 5 mL solution was taken from the suspension at a specified contact time, and then quickly separated by filtered using membrane (filtration precision = 0.22 μm). The residual Cd(II) concentration was measured.