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Efficient removal of fluoride by hierarchical Ce–Fe bimetal oxides adsorbent: Thermodynamics, kinetics and mechanism

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HIGHLIGHTS

- Efficient hierarchical Ce–Fe bimetal oxides were synthesized for defluoridation.
- Ce–Fe bimetal oxides exhibited high fluoride uptake capacity of 60.97 mg/g.
- Ce–Fe bimetal oxides showed high efficiency over a wide range of pH (2.9–10.1).
- Ion exchange of fluoride with the hydroxyl could be responsible for defluoridation.

GRAPHICAL ABSTRACT
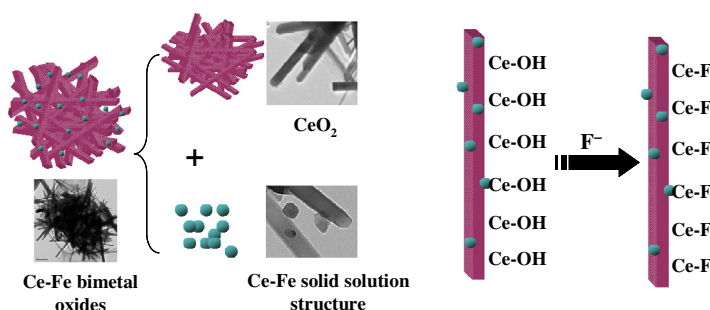
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ABSTRACT

Ce–Fe bimetal oxides with hierarchical pore structure were successfully prepared by a facile approach and used as efficient adsorbent for fluoride removal. The existence of Fe(III) and Ce(IV) in the as-obtained adsorbent was determined by XRD, XPS and HRTEM. The BET surface area of the optimized adsorbent is 164.9 m^2/g, and the corresponding hierarchical pore size centers at 1.68, 3.41 and 9.54 nm. Batch fluoride adsorption experiments were carried out to investigate the influence of various factors such as adsorbent dosage, contact time, initial solution pH and co-existing anions on the fluoride adsorption. Results show that the maximum adsorption capacity of the optimized adsorbent is as high as 60.97 mg/g. Furthermore, it shows high adsorption capacity over a wide range of pH from 2.9 to 10.1. The adsorption kinetic is well described by the pseudo-second-order model and the fluoride adsorption on the adsorbent agrees well with the Langmuir model. The effects of co-existing anions on the fluoride sorption followed the decreasing order of CO_3^{2-} > HCO_3^- > SO_4^{2-} > NO_3^- > Cl^-, which was found to be closely correlated with the charge–radius ratio values (z/r) of the anions. Fluoride adsorption on the Ce–Fe bimetal oxides could be attributed to ion exchange between fluoride and Ce-OH groups.

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1. Introduction

As one of the essential trace elements in the human body, fluoride is closely related to human life activities. However, it has been reported that an excess intake of fluoride can lead to dental fluorosis and many other bone diseases [1]. Fluoride contamination in drinking water has been a global problem since more than 200 million people worldwide suffer from high fluoride concentration drinking water [2]. Driven by the need to overcome the problem, many defluoridation methods have been proposed such as adsorption [3,4], membrane process [5], electrochemical technique [6] and so on. Among the methods, adsorption is found to be effective,

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environmental friendly and economical. Activated alumina has been the most commonly used adsorbent for fluoride removal, but low adsorption capacity, narrow available pH range and aluminum dissolution restrict its application for water treatment [7]. Thus, numerous modified adsorbents have been developed such as modified activated alumina, calcium based materials, iron based materials, and carbon based materials, metal oxides as well as many other natural materials [8].

It has been reported that rare earth metals have strong tendency to dissociate OH groups into hydroxyl ions because of their relatively small ionic potential and strong basicity, which results in promising potential for defluoridation [9]. Tokunaga et al. [10] investigated the fluoride removal by Al(III), Ca(II), Y(III), La(III), Ce(III/IV), Nd(III), Sm(III), Gd(III), Si(IV), Ti(IV) and Zr(IV) in the forms of oxides, hydrous oxides and basic carbonates, and only Ce(IV) hydrous oxide was effective in removing fluoride ions without a significant dissolution at pH 2. However, the high cost of cerium has been a big problem for its utilization [11]. Lou et al. [12] reported that the high electronegativity and small ionic size of the fluoride ion result in its strong affinity toward multivalent metal ions including Al(III), Fe(III) and Zr(IV). Therewith, hybrid materials of cerium and these cheaper metals have been reported for defluoridation [13–15]. For all we know, the hybrid of Ce(IV) and Fe(III) used for defluoridation has hardly been investigated.

In this study, Ce–Fe bimetal oxides were synthesized by a facile co-precipitation method and the preparation condition was also optimized. Besides, the effects of key operation parameters, such as adsorbent dosage, contact time, fluoride solution pH and co-existing anions on fluoride removal were also investigated in this work. In addition, thermodynamics and kinetics studies were carried out to investigate the fluoride adsorption process by Ce–Fe bimetal oxides. The proper mechanism of defluoridation by the obtained adsorbent was also proposed based on the FT-IR and XPS analysis results.

2. Materials and methods

2.1. Materials

$Ce(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, NaF, NaOH and other chemicals used in the present study were all of analytical reagent grade, which were obtained from the China National Medicines Company (Beijing, China) and were used directly without further purification. A 1000 mg/L standard stock solution of fluoride was prepared by dissolving 0.221 g NaF into 100 mL of deionized water at ambient condition. The desired fluoride solution was prepared by appropriate dilution of the standard stock solution.

2.2. Preparation of Ce–Fe composites

A batch of Ce–Fe bimetal oxides were synthesized by co-precipitation method at ambient condition. In a typical synthesis, $Ce(NO_3)_3 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 400 mL of deionized water with 3:1, 1:1 and 1:3 mol ratios of Ce and Fe, respectively. Then the pH of the mixture was adjusted to 10 by dropwise adding 2 mol/L of NaOH aqueous solution under magnetic stirring. After 30 min of vigorously stirring, the precipitates were centrifuged and washed with deionized water for three times, and then were dried at 70 °C for 8 h. The products were denoted as CF31-10, CF11-10, and CF13-10, respectively. To determine the optimized synthesis condition, the adsorbents with 3:1 mol ratio of Ce and Fe were prepared under solution pH of 8.5, 10 and 11 respectively, which were noted as CF31-8.5, CF31-10, and CF31-11, respectively. Moreover, the CF31-10 sample was further calcined at 300, 450 and 600 °C for 4 h with a heat rate of

10 °C/min, which were denoted as CF31-10-300, CF31-10-450 and CF31-10-600, respectively. Besides, Ce oxide and Fe oxide were also synthesized under the same condition for comparison experiment, which were denoted as SC and SF.

2.3. Characterization of catalysts

The crystal structure and crystallinity of the as-prepared adsorbents were analyzed by powder X-ray diffraction (XRD, Rigaku, Japan) using Cu Ka radiation ($\lambda = 0.154056$ nm) with 40 kV of accelerating voltage and 50 mA of applied current. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) (JEM-2100F, Japan) were used to analyze the microstructure of the CF31-10 sample. The BET surface area and Barrett–Joyner–Halenda (BJH) pore size distributions of the optimized sample were measured through N_2 adsorption–desorption isotherms on a TriStar II 3020 V1.03 nitrogen adsorption apparatus (Micromeritics, USA). The surface chemical bonds of the as-prepared samples were detected by Fourier transform infrared spectroscopy (FT-IR, Thermo Nicolet, USA). The morphologies of the samples were examined using scanning electron microscope (SEM, JSM-5610LV). X-ray photoelectron spectroscopy (XPS) was carried out using an ESCALAB II XPS system with a monochromatic Mg Ka source and a charge neutralizer. All binding energies were referred to the C 1s peak at 284.5 eV of the surface adventitious carbon.

2.4. Fluoride adsorption experiments

All the fluoride adsorption experiments were carried out in a temperature controlled shaker at the fixed speed of 180 rpm. The effects of adsorbent dosage (0.3–1.5 g/L), contact time, fluoride solution pH (2.9–10.1) and co-existing anions (Cl^-, SO_4^{2-}, NO_3^-, HCO_3^- and CO_3^{2-}) were investigated with 100 mL fluoride solution (10 mg/L). The adsorption isotherms and kinetics of fluoride removal were also investigated under different temperatures and different initial fluoride concentrations. The fluoride concentration was determined by Ruosull (China) fluoride-ion-selective electrode according to the National Standard of the People's Republic of China (GB 7484-87).

3. Results and discussion

3.1. Characterization

Fig. 1 shows the XRD patterns of the samples prepared under different conditions. The diffraction peaks of the SC and SF samples
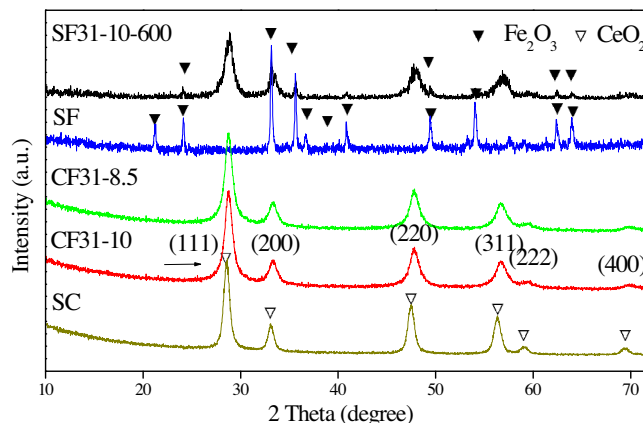

Fig. 1. The XRD patterns of the samples prepared under different conditions.