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Synthesis of magnetic Fe_3O_4/CFA composites for the efficient removal of U(VI) from wastewater

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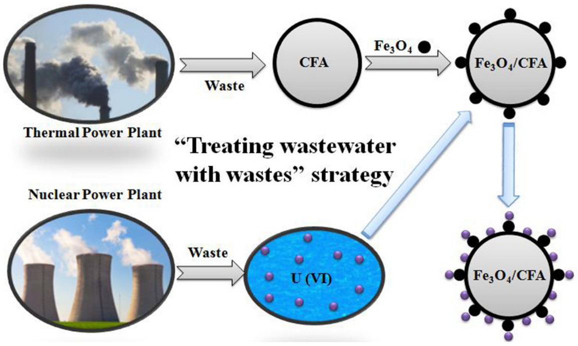
HIGHLIGHTS

- Fe_3O_4/CFA was successfully synthesized using liquid phase deposition method.
- Fe_3O_4/CFA has high removal ability for U(VI) from solutions.
- Maximum sorption capacity of U(VI) on Fe_3O_4/CFA was 1.380 mmol/g.
- Sorption of U(VI) on Fe_3O_4/CFA was mainly contributed by Fe—O bond and U(VI).
- This work highlighted the strategy of "treating wastewater with wastes".

GRAPHICAL ABSTRACT



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ABSTRACT

The application of thermal power plant waste (coal fly-ash, CFA) for the potential retention of U(VI) from wastewater was crucial in radionuclide contaminant management. In this work, magnetic Fe_3O_4/CFA composites were synthesized and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transformed infrared (FTIR) and energy dispersive (EDS) spectroscopy techniques. The as-synthesized Fe_3O_4/CFA composites were applied to remove U(VI) from aqueous solutions and the results showed that U(VI) sorption was mainly dominated by inner-sphere surface complexation at low pH values, and by outer-sphere surface complexation at high pH values. According to the results of X-ray photoelectron spectroscopy (XPS) and FTIR analysis, the high sorption of U(VI) on Fe_3O_4/CFA composites was mainly attributed to Fe—O bond. Compared with CFA ($Q_{max} = 0.254$ mmol/g), Fe_3O_4/CFA composites exhibited excellent U(VI) sorption capacity ($Q_{max} = 1.380$ mmol/g), relative high and stable U(VI) sorption ability under high pH values (pH 6∼10) in 0.1 M NaCl. The investigation was meaningful for the "treating wastewater with wastes" strategy implementation, especially in the aspect of reducing the environmental pollution caused by thermal power plant waste and their application in nuclear pollution management.

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1. Introduction

Uranium (U(VI)) was a common radioactive contaminant with potential toxic and carcinogenic threats to aquatic organism and human health, which was usually derived from nuclear energy production, weapon research and manufacturing activities, and could be released to natural water easily [1–3]. Therefore, the high efficient removal and safety treatment of U(VI) from aqueous solutions have become a world-concerned public issue. It has been demonstrated that the mobility of U(VI) in groundwater was mainly dependent on the sorption of U(VI) at water-mineral interfaces [4–6]. Therefore, the sorption of U(VI) from aqueous solutions have been widely investigated on variety kinds of adsorbents like clay minerals [4,7] and nanomaterials [8,9]. However, natural clay minerals usually have relatively low sorption ability, while most nanomaterials are inevitably high-cost, both of the two drawbacks would surely limit their widely practical applications. Hence, it is highly desirable to explore new materials with both high sorption capacity and low-cost.

Since coal fire plant brought into wide scale service in 1920s, million tons of coal fly-ash (CFA) and its related by-products have been released into the environment. It was estimated that around 500 million tons of CFA were released by factories and thermal power plants annual world widely [10]. It would cause soil and water pollution, ecological cycle's disruption and pose environmental hazards. So far, less than 50 percent of CFA has been putted into reuse such as concrete production, road base construction, zeolite synthesis, soil amendment, filler in polymers and so on. The remainder of CFA is waste, and is discharged into ash ponds, lagoons or landfills [11]. The disposal of such large amount of pollutants has become a serious environmental problem [12]. Nowadays, recycling techniques for CFA, such as the utilization of waste fly ash in new products is an economically viable and environmental friendly method to solve this problem. Recently, the "treating wastewater with wastes" strategy in China has been considered as an inspiring method for the treatment of waste [13]. Investigations showed that the physicochemical characteristics of CFA, such as bulk density (0.54–0.86 g/cm^3), particle size (<20 μm), porosity, water holding capacity and surface area (300–500 m^2/kg), make it suitable for the removal of heavy metal ions [11]. However, the relatively low sorption ability and difficult separation from solutions restricted the widely application of CFA in real applications. Therefore, it is necessary to make the CFA with high sorption efficiency and easy separation properties for its practical applications.

In recent years, magnetic nanoparticles (MNPs), like Fe_3O_4, have attracted more and more attentions for its outstanding low toxicity and easy separation properties [14–17]. However, because of the anisotropic dipolar attraction effect, naked MNPs usually easily aggregated in aqueous solutions, thereby reduces its sorption capacity and restricts its extensive use [18,19]. Hence, surface modifications of MNPs by covalent binding or physical coatings have been widely investigated, such as magnetic chitosan resins [20], magnetic corn stalk [21], mesoporous SBA-15 [22], MSFA/PPy [13] and so on. The results showed that the composites could be well coated with MNPs and easily separated from aqueous solutions. However, to the best of our knowledge, few research focused on the synthesis of magnetic CFA and their application in the efficient elimination of U(VI) from aqueous solutions.

In this work, the magnetic Fe_3O_4/CFA composites were synthesized by liquid phase deposition method. The sorption properties of Fe_3O_4/CFA composites for the efficient removal of U(VI) was investigated under different experimental conditions. The samples were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and Fourier transformed infrared (FTIR) spectroscopy. The interaction mechanism of U(VI) with Fe_3O_4/CFA and U(VI) was analyzed by X-ray photoelectron spectroscopy (XPS) and FTIR spectroscopy techniques.

2. Experiments

2.1. Chemicals and materials

Coal fly-ash (CFA) was obtained from Sanhe Power Plant of China Electric Power Company in Beijing, China. The CFA was firstly dried in an oven under 105 °C for 24.0 h, and then sieved to 200–300 mesh. Standard U(VI) stock solution (2000 mg/L, pH = 3.2) was prepared by dissolving 4.22 g $UO_2(NO_3)_2$ into 1 L deionized water at room temperature and then conducted ultrasound for 30 min. The solutions for different sorption experiments were prepared by appropriate dilution of the stock solution. All the chemicals and reagents were obtained from analytical purity from Sinopharm Chemical Reagent (Shanghai, China) and used in the experiments without any further purification.

2.2. Synthesis and characterization of Fe_3O_4/CFA

The magnetic Fe_3O_4/CFA composites were synthesized by liquid phase deposition method. In general, 4 mmol $FeCl_2 \cdot 4H_2O$ and 8 mmol $FeCl_3 \cdot 6H_2O$ were firstly dissolved in 50 mL deionized water, and then 2.0 g CFA was added into the solution. The suspension was stirred vigorously for 30 min, and then 40 mL of 10 wt% ammonia solution was added dropwise under nitrogen gas atmosphere. After continuous reaction for 3.0 h at room temperature (~298 K), the obtained Fe_3O_4/CFA solid was magnetically separated, washed with ethanol and deionized water for several times, and then dried under vacuum at 60.0 °C for 10.0 h.

The surface morphology was examined by SEM (Hitachi SU8010, Japan) image. An EDS analysis was conducted under the condition of 20 kV. The XRD (Bruker D8-FOCUS, Germany) patterns were performed on a powder diffraction system with Cu Kα radiation at 40 kV, 40 mA. FTIR (Shimadzu IRTracer-100, Japan) spectroscopy was measured using the standard KBr disk method.

2.3. Batch sorption experiments

The sorption of U(VI) on Fe_3O_4/CFA composites was carried out in 10.0 mL polyethylene tube. The Fe_3O_4/CFA stock suspension was pre-equilibrated with NaCl for 24.0 h before the addition of U(VI) stock solution. The solution pH was adjusted by adding negligible volume of 0.10 or 0.01 mol/L NaOH or HCl. Before and after U(VI) sorption, variances in pH were kept below 0.2. The pre-experiments confirmed that 24.0 h shaking time was enough to achieve sorption equilibrium. The liquid and solid phases were separated through centrifugation at 8000 rpm for 20.0 min. The sorption of U(VI) in the absence of Fe_3O_4/CFA composites, demonstrating that U(VI) sorption on the test tube walls was negligible.

The amount (q_e), percentage (%) and distribution coefficient (K_d) of U(VI) sorption on CFA or Fe_3O_4/CFA were calculated according to the following equations:

$$Sorption(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \tag{2}$$

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{3}$$