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Nanoscaled zero valent iron/graphene composite as an efficient adsorbent for Co(II) removal from aqueous solution

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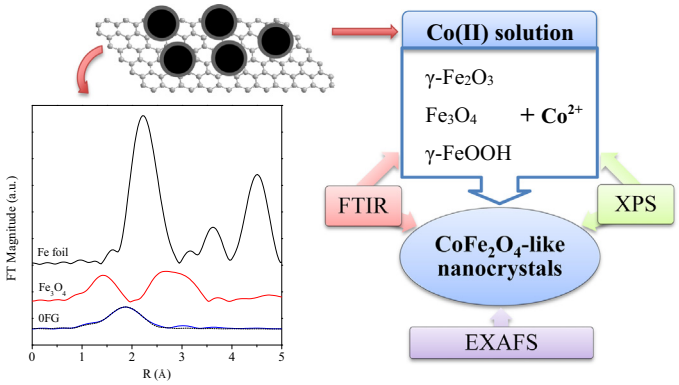
GRAPHICAL ABSTRACT



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ABSTRACT

A magnetic graphene, i.e., nanoscaled zero valent iron/graphene (0FG) composite, was prepared, characterized and applied for the removal of Co(II) from aqueous solution. The magnetic graphene (0FG) was synthesized through reduction of graphene oxide (GO) and ferrous ions by potassium borohydride. The kinetics and isotherms of Co(II) adsorption onto 0FG were investigated. The mechanism for Co(II) removal was proposed based on the Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and the X-ray absorption fine structure (XAFS) analysis. The results showed that pseudo second-order models and the Freundlich isotherm model fitted well with the data obtained. The adsorption capacity of 0FG was calculated from the Langmuir isotherm, which was 65.58, 101.60 and 134.27 mg/g at 10, 20 and 30 °C, respectively. Thermodynamic parameters suggested that the adsorption process was endothermic and spontaneous. Co^{2+} was stabilized by γ-FeOOH/γ-Fe_2O_3/Fe_3O_4 on the surface of graphene sheets, forming $CoFe_2O_4$-like nanocrystals. The coordination numbers and interatomic distances indicated that Co^{2+} mainly occupied the octahedral site, while pseudo-tetrahedral coordination may occur by dehydroxylation of $Co(O,OH)_6$. Magnetic graphene is a potential adsorbent for Co^{2+} removal.

1. Introduction

The treatment of radioactive wastes has been received increasing attention all over the world, especially after Fukushima

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accident. The presence of radionuclides and their fission products can pose serious chemical and radiological toxicity threats to ecological systems and human health. ^{60}Co and ^{57}Co are radioisotopes of cobalt and known as γ-emitters, which have relatively long half-lives [1,2].

Different technologies have been developed for treating the liquid radioactive waste, such as evaporation, precipitation, adsorption, ion exchange, membrane separation, solvent extraction and electro-coagulation [3–9]. Among them, adsorption is regarded as one of the most effective processes [10–12].

Graphene, a single layer of sp^2-hybridized carbon atoms found in graphite—is now well known for its large surface area and possible application in adsorption. Graphene and graphene oxide were widely used in the adsorption process to remove pollutants from aqueous solutions, such as heavy metal ions (Cu, Pb, Cd, Hg, Zn, Ni) [13,14], radionuclides (Co, Sr, U, Eu, Am) [15], and many cationic or anionic dyes [16]. To improve the separation performance of graphene materials, magnetic nanoparticles such as nanoscaled zero valent iron (nZVI), Fe_3O_4 and $CoFe_2O_4$ were loaded onto graphene via chemical reduction [17], coprecipitation [18], solvothermal synthesis [19] and hydrothermal method [20]. The application of nZVI/graphene composite for removing pollutants has been studied, for example, Wang et al. [21] synthesized nanoscale zero valent iron-reduced graphite oxide for removing As(III) and As(V), they found that the adsorption capacity of As(III) and As(V) was 35.83 and 29.04 mg/g, respectively. Jabeen et al. [17] found that iron nanoparticle decorated graphene could enhance the magnetic property, surface area and Cr(VI) adsorption capacity. Nano zero valent iron nanoparticles-graphene composite was also used as an efficient adsorbent for Pb(II) removal [22]. Furthermore, iron nanoparticles modified graphene composite were successfully used for the decolorization of methyl blue [23] and for the adsorption of polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs) and phthalates [24]. The temperature of sodium borohydride reduction reaction reported in these studies was 80–90 °C [17,21,22,24]. To our knowledge, there were a few reports on the removal of radioactive nuclides from aqueous solution by nZVI/graphene composite synthesized at room temperature using a facile chemical reduction. It is needed to investigate more details of the adsorption kinetics, thermodynamics and mechanisms of radioactive nuclides on nZVI/graphene composite.

In this study, the nZVI/graphene (0FG) composite was synthesized by reducing ferrous ion and GO simultaneously with KBH_4 solution at room temperature. The composite was characterized by scanning electron microscopy (SEM), magnetization measurement, Raman analysis, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) analysis. The application of the magnetic 0FG composite for the removal of Co(II) from aqueous solution was investigated. The effect of dosage, as well as the adsorption kinetics and isotherms was studied. The possible adsorption mechanisms of Co(II) by 0FG composite were identified using FTIR, X-ray photoelectron spectroscopy (XPS) and XAFS analysis.

2. Materials and methods

2.1. Synthesis of adsorbents

All chemicals were of analytical grade. Graphite (EG-JF90-50N) was purchased from Beijing creative new biological engineering materials Co., Ltd.

Graphene oxide was synthesized using the modified Hummers method [25]. Briefly, 1.0 g of graphite and 106 mL of H_2SO_4 were mixed in a three-necked flask. Meanwhile, 5.0 g of $KMnO_4$ was slowly added in an ice-water bath. Once added, the solution was removed from the ice-water bath and stirred for 3 days. Deionized water was added with constant stirring in two steps: 40 mL of water was slowly added while the temperature was kept at 60 ± 1 °C for 1 h, then 80 mL of water was added and the temperature was raised to 90 ± 1 °C. The mixture was stirred for 0.5 h, and H_2O_2 (30%) was added slowly to remove the residual permanganate and manganese dioxide. The solution was centrifuged and washed with 1:10 HCl for several times. Finally, the deposit was dried via freeze drier.

The nZVI/graphene was synthesized according to the method of Xu and Wang [26,27]. 0.056 g of GO was dispersed in 80 mL of deionized water by 3 h ultra-sonication, then 20 mL 0.2 mol/L $FeSO_4{\cdot}7H_2O$ solution was added. The mixed liquid was transferred immediately to a three-necked flask and stirred for 3 h to form Fe^{2+}/GO composite. 100 mL of 0.2 mol/L KBH_4 solution was added drop-wise to the flask with violently stirring. Ferrous iron and GO were simultaneously reduced to form the nZVI/graphene (0FG) composite. The products were collected by centrifugation and washed two times with deionized water and ethanol, and then vacuum-dried at room temperature for instant usage.

2.2. Characterization

The morphology images of 0FG were obtained with a field emission scanning electron microscope (SEM, JSM-6301F, JEOL) with energy dispersive X-ray (EDX) detector. Magnetic hysteresis loops of adsorbents were studied on a Physical Property Measurement System (PPMS, 730 T, LAKESHORE, USA) at room temperature. Raman spectra were recorded on a Raman spectrometer (Horiba JY HR800) using a regular model laser operated at wavelength of 514 nm. The Fourier transformed infrared (FTIR) spectroscopy measurements were mounted using a Perkin-Elmer 100 spectrometer in KBr pellet at room temperature. X-ray diffraction (XRD) patterns were measured on a D8-Advance diffractometer (Bruker, 40 kV and 40 mA, Cu Kα) with a scan range from 5° to 90° of 2θ. The X-ray absorption fine structure (XAFS) was measured on the 1W1B baseline in Beijing Synchrotron Radiation Facility. The experimental data were analyzed and fitted using Athena and Artemis, respectively. The X-ray photoelectron spectroscopy (XPS) measurements were conducted with a PHI-5300 spectrometer, using a monochromatic Al Kα X-ray radiation at 1486.6 eV.

2.3. Adsorption experiments

Certain amount of adsorbents was dispersed in deionized water. The suspensions of 0FG and Co^{2+} were added in the flask and shaken in a vibrator (HZQ-F160, HDL) at 150 rpm. Effect of dosage (0.05–0.4 g/L), adsorption kinetic (0–24 h), adsorption isotherm (10–600 mg/L initial concentration) and thermodynamic studies (10–30 °C) were performed, without adjusting pH. The initial pH value of heavy metal solution was 5.7 by measurement. Furthermore, the adsorption property at different initial pH (3.0–9.0) was investigated, and pH was adjusted using 0.1 mol/L NaOH and HCl.

2.4. Analytical methods

The concentration of Co^{2+} was analyzed using atomic absorption spectrometric method with flame atomization (AAS 6 Vario). The adsorbed amount of metal ion per unit weight of adsorbent at time t, q_t (mg/g), was calculated from the mass balance equation as follows:

$$q_t = (C_0 - C_t)V/m \quad (1)$$

where C_0 and C_t (mg/L) are the initial metal ion concentration and the metal ion concentration at any time t, respectively; V is the volume of the metal ion solution; and m is the weight of 0FG.