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The uptake of europium by reduced graphene oxide-supported nanoscale zerovalent iron investigated by batch and modeling techniques

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ABSTRACT

The reduced graphene oxide-supported nanoscale zerovalent iron (NZVI@rGO) composites were synthesized towards the uptake of europium (Eu(III)) in environmental cleanup. In this study, the effect of environmental factors on the uptake of Eu(III) from aqueous solutions on NZVI@rGO composites was investigated under ambient conditions by batch techniques. The uptake kinetics indicated that the uptake of Eu(III) on NZVI@rGO composites can be satisfactorily fitted by pseudo-second order kinetic model. The uptake of Eu(III) on NZVI@rGO composites was independent of ionic strength at pH > 5.0, indicating that inner-sphere surface complexation dominated the uptake of Eu(III) on NZVI@rGO composites. It is demonstrated that the maximum uptake capacities of NZVI@rGO composites for Eu(III) calculated from Langmuir models was 96.675 mg/g at pH 5.0 and $T = 293$ K. The thermodynamic parameters indicated that the uptake of Eu(III) on NZVI@rGO composites was an endothermic and spontaneous process. Based on surface complexation modeling, the diffuse layer model gave an excellent fits to the uptake of Eu(III) on NZVI@rGO composites with cation exchange complexes (X_3Eu species) at pH < 4.5, mononuclear and monodentate complexes ($SOEu^{2+}$ species) at pH 5.0–7.0, and mononuclear and bidentate complexes ($(SO)_2Eu(OH)_2^-$ species) at pH > 7.0, respectively. The results indicated that NZVI@rGO composites can be considered as a promising adsorbent for the uptake of trivalent radionuclides from wastewaters in environmental cleanup.

1. Introduction

With the expansion of agricultural and industrial activities, the increasingly energy requirement becomes one of the most concerned issues to the public [1]. More and more nuclear power plants have been established worldwide to meet the humanity demands. Therefore radionuclide pollution will be faced in the future, which could be posed serious environmental problems due to its radioactivity, extremely low concentration and bioaccumulation. Compared with conventional chemical pollution, it is difficult for radioactive contamination to remove into the lower nontoxic substances in soil and water environment [2–4]. For the sake of public health ecosystem and stability, it is of great importance to eliminate radioactive contaminants from wastewater under the permissible limits before its discharge to the environment. The efficient removal of radioactive contaminants from wastewater in environmental cleanup has been investigated by various methods such as chemical precipitation, membrane filtration, biodegradation and redox reactions [5–7]. Among these techniques, uptake was considered as an efficient and promising method to move radioactive contaminants from aqueous solutions due to environmental friendly, low cost and easy operation [8].

The sorption of radioactive contaminants has been extensively investigated by a variety of adsorbents such as iron (hydr) oxides [9–11], clay minerals [12–14] and activated carbon [15–17]. In these studies, the uptake of radionuclides had been investigated under various environmental factors such as pH, ionic strength and initial concentration. It is determined that nanoscale zero-valent iron (NZVI) presents high efficient enrichments of radionuclides due to its high reduced reactivity [18–21]. Riba et al. found that the fast uptake of U(VI) by NZVI due to the reduction of

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U(VI) to U(IV), whereas re-oxidation of U(IV) to aqueous U(VI) species was observed after exposure to O_2 for 4 h at pH 4.0 [22]. Therefore, various NVZI composites have been employed to retard the reduction of U(IV) to U(VI) in aqueous solutions. Sun et al. found that the increased removal of U(VI) on reduced graphene oxide supported NZVI (NZVI@rGOs) due to the large number of reactive sites. The authors also found that the presence of rGOs inhibited the re-oxidization of U(IV) to U(VI) at ambient conditions [23]. However, few studies on the uptake of Eu(III) on NZVI@rGO composites are available [23,24].

In this study, Eu(III) was chosen as representative of trivalent radionuclide. The objectives of this paper are (1) to characterize the morphology and nanostructures of NZVI@rGO composites by scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray diffraction (XRD), magnetism measurement and zeta-potential analysis; (2) to elucidate the effect of content time, pH, ionic strength, initial Eu(III) concentration and temperature on the uptake of Eu(III) on NZVI@rGO composites by using batch technique; and (3) to demonstrate the uptake mechanism of Eu(III) on NZVI@rGO composites by using surface complexation modeling. NZVI was supported on rGOs in order to increase the dispersibility of NZVI in aqueous solution. The highlight of this study is the potential practical application of NZVI@rGO composites for the remediation of radionuclides in environmental wastewater management.

2. Materials and methods

2.1. Synthesis of NZVI@rGO composites

The NZVI@rGO composites were synthesized by co-precipitation methods [25]. Firstly of all, the GO was synthesized by modified Hummers method [26]. Briefly, 2.0 g graphite powder (<200 mm, Tianhe graphite Co., Qingdao, China) and 0.5 g $NaNO_3$ were placed into concentrated H_2SO_4 under continuous stirring and ice-water bath conditions. Then 5.0 g $KMnO_4$ was slowly added and suspension were vigorous stirred for 5 days at room temperature. The residual MnO_4^- was removed by adding H_2O_2 solution. GO solution was obtained by centrifuging and ultrasonic treatment of aforementioned suspension several times. The NZVI/rGO composites were fabricated by the reduction of $FeCl_3$ solution with $NaBH_4$ under N_2 atmosphere in GO aqueous solution. In this study, GO also can be reduced by $NaBH_4$ completely [27]. The Eu(III) stock solution (1.0×10^{-3} mol/L) was prepared by dissolving $Eu(NO_3)_3 \cdot 6H_2O$ (99.99% purity) into Milli-Q water. All chemicals used in the experiments were purchased in analytical reagents and used without any purification.

2.2. Characterization

The morphology and nanostructure of NZVI@rGO composites were characterized using a scanning electron microscope (SEM

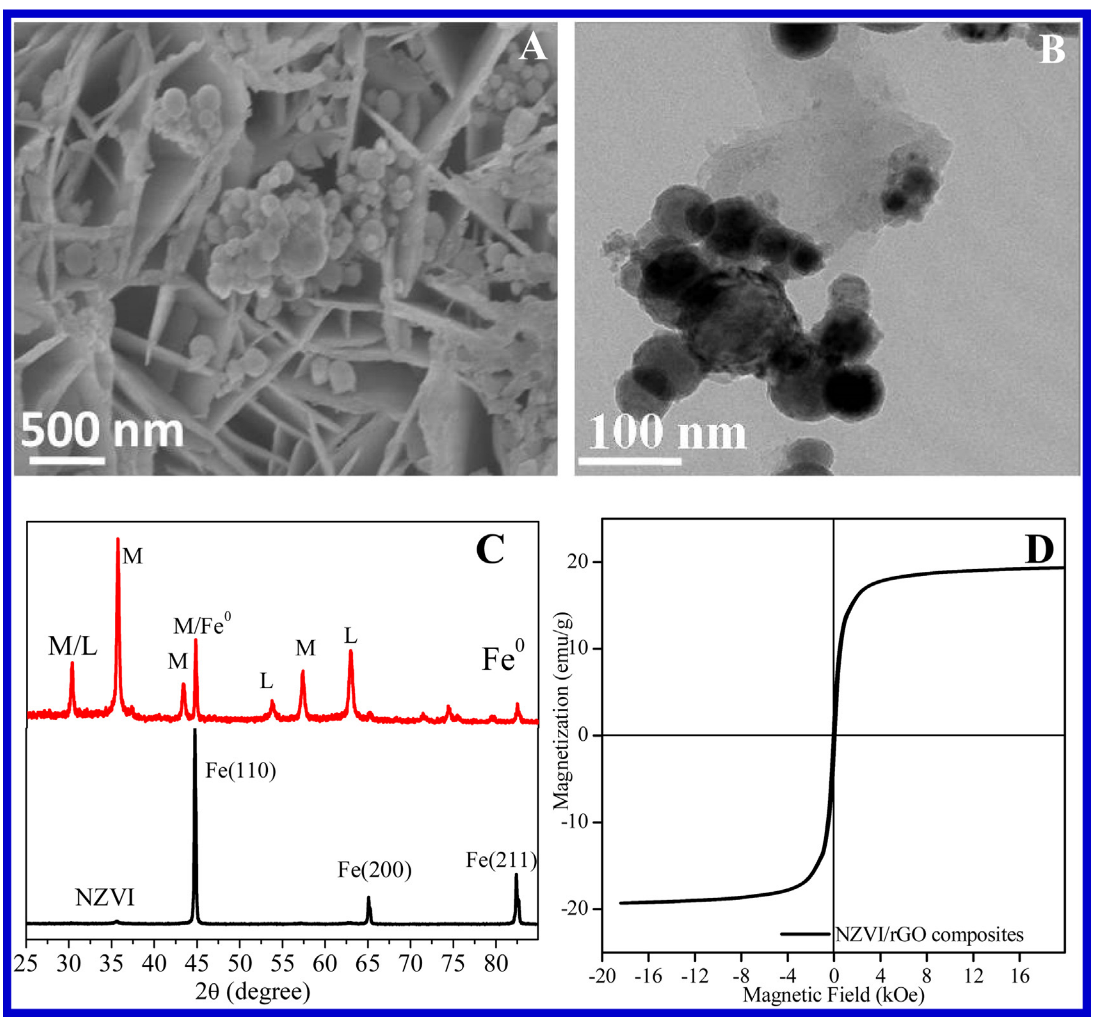

Fig. 1. The characterization of NZVI@rGO composites, A and B: SEM and TEM image, respectively; C:XRD patterns before and after Eu(III) uptake; D: magnetization curve.