



Plasma-enhanced amidoxime/magnetic graphene oxide for efficient enrichment of U(VI) investigated by EXAFS and modeling techniques

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HIGHLIGHTS

- Amidoxime/magnetic graphene oxide (AO/mGO) was well synthesized by plasma method.
- AO/mGOs displayed high selective enrichment for U(VI)
- Inner-sphere surface complexation and reduced precipitation dominated U(VI) adsorption.

ARTICLE INFO

Keywords:

U(VI)
Magnetic graphene oxide
Amidoxime
EXAFS
Modeling

ABSTRACT

The highly efficient enrichment of amidoxime/magnetic graphene oxide (AO/mGO) for U(VI) was elucidated by batch, EXAFS and modeling techniques. The characteristic results indicated that AO groups were successfully grafted to surface of mGO by plasma-grafting method. The batch experiments showed that AO/mGO composites presented the high enrichment performance (approximate 435, 55, 69, 43, 108 and 32 mg/g for U(VI), Th(IV), Eu(III), Sr(II), Pb(II) and Cs(I), respectively) and rapid adsorption rate (adsorption equilibrium within 30 min). The maximum enrichment capacity of AO/mGO composites for U(VI) from seawater of south China sea was 2.85 mg/g, indicating the potential for capturing U(VI) from seawater. The EXAFS analysis indicated that highly effective enrichment of AO/mGO composites for U(VI) was attributed to inner-sphere surface complexation due to the occurrence of U-Fe shell even at low pH. The results of surface complexation modeling indicated that U(VI) adsorption from simulated seawater on AO/mGO can be satisfactorily simulated by two inner-sphere surface complexes such as SOUO_2^+ and $\text{SOUO}_2(\text{CO}_3)_2^{3-}$ species. These findings are crucial for the application of AO-based composites in the preconcentration of U(VI) from aqueous solution in environmental cleanup and the recovery of uranium from seawater.

1. Introduction

Nuclear energy has become one of new energy resource, thus the rapid development of nuclear energy is extensively considered a feasible method for resolving the global energy crisis and improving air pollution [1–4]. Uranium (U(VI)) as raw materials of nuclear energy has been extensively exploited nowadays. The generous use of U(VI) will inevitably lead to the release of U(VI) into sub-surface environments, which could pose the potential threat to the human health and the ecological environment. Therefore, a large number of studies

concerning the removal of U(VI) from aqueous solutions have been extensively investigated on various adsorbents such as clay minerals [5–9] and Fe/Al-oxides [10–13]. Sun et al. found that the maximum adsorption capacity of alumina for U(VI) was only 3.99 mg/g at pH 6.8 and 293 K [14]. Such low adsorption capacities of these natural adsorbents limit their actual application at environmental cleanup.

Recently, nanomaterials have been extensively utilized in environmental cleanup due to the huge surface area and strong chemical activity [15–17]. Generally, routine nanomaterials have no resistance to irradiation and/or acidic erosion [18–26]. Graphene oxide (GO) as one

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<https://doi.org/10.1016/j.cej.2018.09.140>

Received 17 July 2018; Received in revised form 16 September 2018; Accepted 18 September 2018

Available online 19 September 2018

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of carbon-based nanomaterial with strong irradiation resistance and high thermal stability has been demonstrated the high adsorption performance for U(VI) [27–33]. In order to increase the separation efficiency and high selectivity, decoration of GO by grafting a variety of functional groups is an effective approach [34]. It is found that amidoxime (AO) presents the highly selective enrichment for U(VI) due to its strong chelating ability [35]. In our previous studies, it is demonstrated the maximum adsorption capacity of AO/carbon nanofibers for U(VI) was 588 mg/g, which was significantly higher than that of other radionuclides such as Th(IV) (167.34 mg/g), Am(III) (40.79 mg/g), Sr (II) (57.57 mg/g) and Cs(I) (42.61 mg/g) [36]. mGO has been widely demonstrated as an excellent adsorbent due to the high adsorption performance of GO and the strong reducing capacity of magnetic nanoparticles [4,37,38]. However, few studies regarding the mechanistic investigation of U(VI) on AO/mGO by EXAFS and modeling techniques are available [39].

The objectives of this manuscript were to (1) synthesize AO/mGO by plasma-grafting method and characterize it by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and Zeta potentials; (2) elucidate the effect of environmental factors (e.g., reaction time, pH, ionic strength, temperatures, initial U(VI) concentration) on efficient adsorption of U(VI) on AO/mGO by batch techniques; (3) demonstrate the interaction mechanism of U(VI) on AO/mGO by extended X-ray absorption fine structure (EXAFS) and surface complexation modeling (SCM). The highlight of this study is to apply AO-based nano-materials in the efficient adsorption of U(VI) from uranium-bearing wastewater and from seawater.

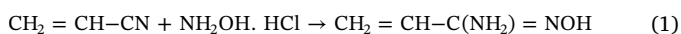
2. Experimental section

2.1. Materials

A stock solution of U(VI) (1.0 mol/L) was prepared by dissolving $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (analytical reagent, Hubei Chushengwei Chemical Co. Ltd) into DI water under glovebox conditions. Flake graphite was obtained as a gift from Qingdao Yanhai Carbon Materials Co., LTD. Chemicals (acrylonitrile (CH_2CHCN , AN), methanol (CH_3OH), N,N-dimethylformamide (DMF), ethanol($\text{CH}_3\text{CH}_2\text{OH}$), potassium carbonate (K_2CO_3), nitric acid (HNO_3), sodium hydroxide (NaOH), hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), ferrous chloride (FeCl_2), ferric chloride (FeCl_3)) were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents of analytical grade were used without further purification.

2.2. Synthesis and characterization of AO/mGO

AO/mGO was synthesized by grafting acrylonitrile (AN) groups onto surface of mGO under N_2 -plasma conditions, and then AN groups were transformed to AO groups using $\text{NH}_2\text{OH}\cdot\text{HCl}$ as a reducing agent [36]. GO was firstly synthesized by modified Hummers' method [40], then mGO was obtained by co-precipitation of Fe(II) and Fe(III) on GO surface [4]. More details regarding the synthesis of GO and mGO were provided in the Supporting Information (SI). AN/mGO was treated by N_2 plasma in reactor for 30 min under vigorous stirring conditions. The power, N_2 pressure, electrical current and voltage were 120 W, 10 Pa, 20 mA and 600 V, respectively. Briefly, the reactor was heated to 60 °C after N_2 plasma treatment, and then 100 mL of (v/v, 50%) AN containing DMF solution were added and were reacted for 6 h under vigorous stirring conditions. The AN/mGO were obtained by washing with DMF and drying at 60 °C in vacuum for 24 h. Then as-prepared AN/mGO was provided into 50 mL of 3% (w/v) $\text{NH}_2\text{OH}\cdot\text{HCl}$ prepared by water/methanol (50/50, v/v) and was stirred at 80 °C for 6 h. The oximation reaction route can be described as Eq. (1):



The role of magnetite in AO/mGO was the enhancement of U(VI)

removal by simultaneous adsorption-reduction and the increase of U (VI) separation by using magnet.

The AO/mGO was obtained by washing with DI/ethanol and then drying at 70 °C in vacuum overnight.

The morphology of as-prepared AO/mGO was characterized by field emission SEM (S-4800 scanning electron microscope, Hitachi, Japan) and TEM (Titan™, G2 60-300 Transmission Electron Microscope, Hitachi, Japan). The surface functional groups of AO/mGO were demonstrated by FT-IR (PerkinElmer, USA) with a standard KBr pellet and XPS (Axis-Ultra, Kratos, UK) with Al-K α radiation ($h\nu = 1846.6$ eV) at 5 mA and 10 kV under 10^{-8} pa. The charging effects were calibrated using binding energy of C 1s (284.8 eV) as a reference. The surface area and pore sizes of AO/mGO were measured using Quantachorm QuadraSorb SI instrument (ASAP-2100, Quantachorm, FL, USA).

2.3. Batch adsorption

The effect of environmental factors (pH, contact time, ionic strength, temperature and initial concentration) on U(VI) adsorption on AO/mGO was investigated under glovebox conditions. Briefly, 5 mg of AO/mGO was provided in a conical flask, and then 10 mL of 10 mg/L U (VI) solution was gradually added to avoid generating schoepite under vigorous stirring conditions. The suspensions were reacted for 2 days to ensure adsorption equilibrium. The pH were adjusted the given values by NaOH or HCl solution. The adsorption of U(VI) without AO/mGO was also conducted to eliminate the effect of tube walls on U(VI) adsorption. After adsorption equilibrium, the solid and liquid phases were separated by centrifuging at 6000 rpm for 10 min, and then the supernatant was filtered by a 0.22- μm membrane. The adsorption of U (VI) and competitive ions (e.g., Na^+ , Mg^{2+} , Cl^- , CO_3^{2-} etc) was also conducted by adding certain amount of AO/mGO into seawater from China South Sea under the glovebox conditions. The concentration of uranium in supernatant was measured by ICP-MS (Bruker 820-MS, Germany). Each data were obtained by the average of three individual experiments and error bars ($\pm 5\%$) were provided.

2.4. XANES and EXAFS analysis

The samples for XANES and EXAFS analysis of U(VI)-bearing AO/mGO at pH 4.0 were prepared under room temperature in the glovebox. The AO/mGO and NaClO_4 (0.01 mol/L) were weighted into 150 mL flask bottles and then Milli-Q water (boiled then bubbled with Ar) was pre-equilibrated for 24 h. The CO_2 -free U(VI) solution was dropwise added under vigorous stirring conditions in order to avoid any precipitation, and the solution were adjusted to pH 4.0 by using neglected volume 0.01–1.0 mol/L HClO_4 or NaOH solution. Samples were then gently agitated on a shaker for 2 days. The wet pastes of U(VI)-bearing AO/mGO by centrifuging it at 9000 rpm for 30 min and then through 0.22- μm membrane filters. U L $_{III}$ -edge X-ray absorption spectra were recorded at Shanghai Synchrotron Radiation Facility using a 32-elements solid-state Ge detector. The spectra of XANES and EXAFS were collected in fluorescence mode. EXAFS data were firstly normalized using Athena mode of IFFEFIT 7.0 software [41,42]. The fitting of EXAFS data was performed based on theoretical crystalline of uraninite using Artemis mode [43]. The fitting of U-Oax, U-Oeq, U-Fe shells were derived from the crystal structure of Fe-substituted torbernite [44].

2.5. Surface complexation modeling

The surface complexation modeling has been extensively investigated to predict the adsorption of U(VI) under the varying geochemical conditions [45–47]. The adsorption of U(VI) on AO/mGO under different pH was fitted by diffuse double layer model with an aid of visual MINTEQ v. 2.6 [48]. The visual MINTEQ code has been extensively used to fit the adsorption behaviors at water-solid interfaces. The constants of protonation and deprotonation ($\log K^+$ and $\log K^-$

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