



## Efficient removal of uranium from aqueous solution by zero-valent iron nanoparticle and its graphene composite



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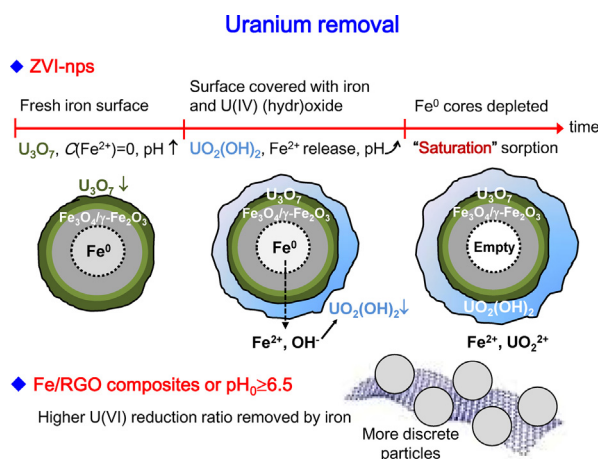
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### HIGHLIGHTS

- Uranium removal by ZVI-nps: independent of pH, the presence of  $\text{CO}_3^{2-}$ , humic acid, or mimic groundwater constituents.
- Rapid removal kinetics and sorption capacity of ZVI-nps is 8173 mg U/g.
- Two reaction mechanisms: sufficient  $\text{Fe}^0 \rightarrow$  reductive precipitation as  $\text{U}_3\text{O}_7$ ; insufficient  $\text{Fe}^0 \rightarrow$  hydrolysis precipitation of U(VI).
- Fe/graphene composites: improved kinetics and higher U(VI) reduction ratio.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 23 October 2014

Received in revised form 23 January 2015

Accepted 9 February 2015

Available online 11 February 2015

#### Keywords:

Zero-valent iron nanoparticles

Graphene composites

Uranium removal

Reductive precipitation

Hydrolysis precipitation

### ABSTRACT

Zero-valent iron nanoparticle (ZVI-np) and its graphene composites were prepared and applied in the removal of uranium under anoxic conditions. It was found that solutions containing 24 ppm U(VI) could be completely cleaned up by ZVI-nps, regardless of the presence of  $\text{NaHCO}_3$ , humic acid, mimic groundwater constituents or the change of solution pH from 5 to 9, manifesting the promising potential of this reactive material in permeable reactive barrier (PRB) to remediate uranium-contaminated groundwater. In the measurement of maximum sorption capacity, removal efficiency of uranium kept at 100% until  $C_0(\text{U}) = 643$  ppm, and the saturation sorption of 8173 mg U/g ZVI-nps was achieved at  $C_0(\text{U}) = 714$  ppm. In addition, reaction mechanisms were clarified based on the results of SEM, XRD, XANES, and chemical leaching in  $(\text{NH}_4)_2\text{CO}_3$  solution. Partially reductive precipitation of U(VI) as  $\text{U}_3\text{O}_7$  was prevalent when sufficient iron was available; nevertheless, hydrolysis precipitation of U(VI) on surface would be predominant as iron got insufficient, characterized by releases of  $\text{Fe}^{2+}$  ions. The dissolution of  $\text{Fe}^0$  cores

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was assigned to be the driving force of continuous formation of U(VI) (hydr)oxide. The incorporation of graphene supporting matrix was found to facilitate faster removal rate and higher U(VI) reduction ratio, thus benefitting the long-term immobilization of uranium in geochemical environment.

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## 1. Introduction

Uranium occurs in nature in primary deposits, U(IV)O<sub>2</sub>. Currently, uranium is being used as a typical nuclear fuel to enhance electrical production ability. With uranium ore mining, processing, fuel manufacture, spent fuel reprocessing and other related activities, more and more highly mobile U(VI) is released into the environment, making uranium a common contaminant to soils, surface and groundwater [1]. The concentration of uranium in some acid mine water and contaminated areas around waste disposal sites can even attain as high as several tens of ppm [2,3]. On the other hand, the allowed maximum level of uranium for drinking water is only 30 µg/L, recommended by EPA [4]. It is well known that intakes of uranium from food and/or drinking water can lead to internal irradiation and/or chemical toxicity. Long term exposure to uranium may result in cancer, kidney and liver damages, or all.

Permeable reactive barrier (PRB) technology has been successfully utilized to *in situ* remediate contaminated groundwater. Compared to conventional pump-and-treat, dig-and-treat, and containment technologies, PRB technology has many advantages, by which reactive media filled can adsorb, degrade, and/or precipitate various pollutants as contaminant plumes flow through the subsurface treatment wall. Therefore, it has been regarded to be technically attractive and cost effective [5,6]. Zero-valent iron, metallic iron (Fe<sup>0</sup>), as the reactive material, has been extensively investigated to remove heavy metals such as Pb<sup>2+</sup>, Cu<sup>2+</sup>, AsO<sub>4</sub><sup>3-</sup>, CrO<sub>4</sub><sup>2-</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ba<sup>2+</sup> [7], radionuclides, e.g., TcO<sub>4</sub><sup>-</sup> [8] and UO<sub>2</sub><sup>2+</sup> [7,9], and to degrade halogenated-hydrocarbon compounds from contaminated areas. Removal mechanism of uranium by Fe<sup>0</sup> was generally described as (i) Fe<sup>0</sup> and structural Fe(II) ions reduce U(VI) ions to sparingly soluble UO<sub>2</sub>, precipitating on the surface of iron, (ii) physical and/or chemical adsorption of U(VI) on corrosion products of iron [7,10], and (iii) probable formation of U(VI) (hydr)oxide precipitate [10].

Zero-valent iron nanoparticles (ZVI-nps) are believed to have improved performances because of increased specific surface area and more reactive sites on the surface. Additionally, nanoscale metal particles could be applied through direct injection of particle suspensions to contaminated sediments and aquifers instead of constructing metal walls [11]. Bare ZVI-nps tend to agglomerate into larger aggregates due to magnetic properties. Incorporation of nanoparticles into carbon or polymer matrix can prevent the aggregation and their susceptible oxidation, therefore activated carbon-, chitosan-, and bentonite-based hybrid materials have been developed [12,13]. Graphene is a new generation of carbon material and can be regarded as a single layer of graphite. Graphene oxide (GO) can be easily prepared by several classical methods from cheap natural graphite, introducing oxygen-containing functional groups such as carboxyl and hydroxyl groups into carbon sheets. GO has been demonstrated to be a promising adsorbent to remove heavy metals such as uranium [14,15] from aqueous solution. In this regard, it is expected that the removal performance of ZVI-nps for uranium could be improved by attaching GO sheets. Jabeen et al. reported the successful synthesis of nanoscale iron-decorated graphene sheets and their applications in Cr(VI) removal. Higher maximum sorption capacity and higher reduction ratio of Cr(VI) adsorbed were achieved with the composites compared to that in

bare ZVI-nps [12]. Moreover, Fe/graphene composites were also used to decolorize methyl blue solution. Higher removal capacities of the composites are due to the increased sorption sites, which originate from the inhibition of the particle aggregation and the reduction of the Fe particle size [16].

In this work, ZVI-np and its graphene composite were prepared successfully and applied in the removal of uranium from aqueous solution in anoxic atmosphere. The influences of solution pH, the presence of NaHCO<sub>3</sub>, synthetic groundwater constituents, and humic acid on removal efficiencies of uranium were investigated systematically in order to evaluate the efficacy of Fe<sup>0</sup> to remediate uranium-contaminated groundwater. Sorption kinetics and capacities were studied as well to clarify reaction mechanisms with the help of various analytical techniques, e.g., SEM, XRD, and XAS, analyzing the reacted adsorbents after sorption processes.

## 2. Experimental

### 2.1. Reagents

All common chemicals used in this study were purchased from Aladdin (Shanghai, China) and are of analytical grade. A 10 mM uranium stock solution was prepared by dissolving appropriate amount of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich Co.) in Milli-Q water (18.2 MΩ cm, Millipore Co.). Synthesized groundwater consists of 0.29 mM Ca(NO<sub>3</sub>)<sub>2</sub>, 0.31 mM CaBr<sub>2</sub>, 0.53 mM MgSO<sub>4</sub>, 0.45 mM Na<sub>2</sub>SO<sub>4</sub>, 0.011 mM Na<sub>2</sub>CO<sub>3</sub>, 0.60 mM NaHCO<sub>3</sub>, and 0.43 mM KHCO<sub>3</sub> [17].

### 2.2. Synthesis of ZVI-nps, reduced GO(RGO), and Fe/RGO composites

Fe<sup>0</sup> was obtained according to a NaBH<sub>4</sub> reduction method [16] under the protection of N<sub>2</sub>. Single-layered GO sheets, prepared from graphite according to the previously described procedure [14], were used as supporting matrix. In the synthesis of Fe/RGO composites (containing ~50% Fe by mass), a concentrated FeCl<sub>3</sub> solution (724 mg FeCl<sub>3</sub>·6H<sub>2</sub>O) was dropwise added into 300 mL of 0.5 mg/mL GO solution with ultrasonication. The mixed solution was magnetically stirred overnight, then NaBH<sub>4</sub> powder (406 mg) was incrementally added into the mixture to simultaneously reduce Fe<sup>3+</sup> and GO to Fe<sup>0</sup> and RGO, respectively [12,16], resulting in a black homogenous dispersion. After 30 min shaking, Fe/RGO composites were recovered by vacuum filtration, and the solid was totally washed by deoxygenated ethanol prior to the formation of a liquid meniscus so as to prevent iron rust [18]. Finally, the black solid was vacuum-dried at 70 °C for 4 h, broken up with a spatula, and stored in a common desiccator. The accurate Fe content was determined to be 47.1% by dissolving the composites in 5% HNO<sub>3</sub> and measuring Fe<sup>2+</sup> quantity. Additional composite materials with ~20% and ~80% Fe loading were also attempted, and the morphology and removal performances for uranium are shown in Figs. S1 and 2, (Supporting information).

ZVI-nps and RGO were prepared according to the aforementioned method in the absence of GO and FeCl<sub>3</sub>, respectively. It was noted that newly formed ZVI-nps were prone to aggregating in comparison with the Fe/RGO composites.

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