Journal of Industrial and Engineering Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Reactivity of carbonized fungi supported nanoscale zero-valent iron toward U(VI) influenced by naturally occurring ions

Congcong Ding[a], Wencai Cheng[a,b,*], Xiaoqin Nie[a,b,*], Facheng Yi[a], Shuhong Xiang[a,b], Abdullah M. Asiri[c], Hadi M. Marwani[c]

[a] Fundamental Science on Nuclear Wastes and Environmental Safety Laboratory, Southwest University of Science and Technology, Mianyang 621010, PR China
[b] School of National Defence Science & Technology, Southwest University of Science and Technology, Mianyang 621010, PR China
[c] Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Article history:
Received 8 October 2017
Received in revised form 28 November 2017
Accepted 10 December 2017
Available online xxx

Keywords:
Zero-valent iron
Fungi
Uranium
Removal
Reduction

ABSTRACT

More discrete and active nano-scale zero-valent iron (NZVI) particles were obtained by assembling them on the surface of carbonized fungi (F) in this study. NZVI/F composites can totally remove 0.25 mmol/L U(VI) in 0.5 h at pH 6.5. Both sorption and reductive precipitation of U(VI) resulted in the high removal. Preliminary evidence showed that the influence of ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, and $CO_3{}^{2-}$) on NZVI/F composites reactivity varied with system pH. Our findings could provide an essential start in the treatment of water containing U(VI) and multiply coexistent ions, and open the doorways for the application of NZVI/F composites.

Introduction

The occurrence of uranium in groundwater and soils is of serious environment concern due to the chemical toxicity and radioactivity [1–3]. The in situ remediation is a preferable method among various strategies due to directly accessing and targeting the contaminants. Nanoscale zero-valent iron (NZVI) has been widely employed as one of the most promising permeable reactive barrier (PRB) materials for degrading or removing organic and inorganic contaminants in groundwater, due to the high surface area to volume ratio, environmentally benign nature, and low cost [4–6]. Recently, the direct injection of nanoscale zero-valent iron (NZVI) particles for the removal of uranium obtains great interest for their stronger activity to reduce mobile U(VI) to immobilized U(IV) such as $U^{(IV)}O_{2(s)}$ which tends to stay locked in soils [7,8]. Ding et al. [7] found that the maximum sorption capacity of NZVI toward U(VI) was 335.25 mg/g at pH 5.0. The effective removal of U(VI) by NZVI was evidenced via two process, sorption/incorporation of U(VI) on the corrosion products of NZVI and the reductive precipitation of U(VI) (UO_2(s)) by Fe(0) core [9–11]. However, the bare NZVI particles have a strong tendency to agglomerate due to their high surface energies and intrinsic magnetic interactions, which decreases their surface reactivity and transfer in contaminated sites, and consequently decreases their efficiency [12,13]. Thus, extensive efforts have been made to reduce NZVI aggregation and increase the dispersity, such as the use of surfactants [14], polymers [15], modified cellulose [16], and other supports [17–19]. The assembly of NZVI particles on stabilizers to enhance steric repulsions of particles is an effective method to prevent the aggregation [12].

Fungi are widespread microorganisms in soil environment. Due to the fast growth, low-cost and easy gain characteristics, fungi have been extensively employed to remove U(VI) and have exhibited the effective performance [20–22]. In related work from our laboratory [23,24], we have established the method for the assembly of nano-materials on fungi templates. The superior advantages of fungi carrier have been observed as compared with conventional carrier, such as effective mass transfer, low cost, efficient reduction of excess sludge and so on. Thus, it is feasible to make NZVI particles assemble on the fungi. To avoid the degrading and decomposing nature of fungi in aqueous solution, a facile method of hydrothermal carbonization (HTC) was adopted for the fabrication of carbonized fungi with better strength and stability [25]. Since carbonized fungi supported NZVI particles (NZVI/F) are essentially made with carbon and iron, they are environmentally friendly. The functional groups on carbonized fungal cell

---

* Corresponding authors at: Fundamental Science on Nuclear Wastes and Environmental Safety Laboratory, Southwest University of Science and Technology, Mianyang 621010, PR China.
E-mail addresses: chwc712@163.com (W. Cheng), xiaoqin_nie@163.com (X. Nie).

https://doi.org/10.1016/j.jiec.2017.12.021

Please cite this article in press as: C. Ding, et al., Reactivity of carbonized fungi supported nanoscale zero-valent iron toward U(VI) influenced by naturally occurring ions, J. Ind. Eng. Chem. (2017), https://doi.org/10.1016/j.jiec.2017.12.021

contribute to the introduction of NZVI particles and enhance the dispersibility of the particles. Additionally, these functional groups also play an important role in that they serve as adsorbents for the uranium, thus bring U(VI) to the vicinity of the NZVI species and facilitating reaction. Concurrently, as a template, carbonized fungi can extend the length scale of NZVI to macro-scale level [26,27], which avoids the pollution from nanoparticles.

Reactivity of NZVI/F composites is, in part, controlled by the groundwater geochemistry [28,29]. Inorganic salts like bicarbonate and calcium are usually present in groundwater, which possibly inhibit U(VI) removal by NZVI/F composites. For example, bicarbonate are known to greatly influence U(VI) species, such as the formation of soluble U(VI)-carbonate species [7,10]. Recent studies have demonstrated that bicarbonate and calcium inhibited the reduction of U(VI) by NZVI [7,10]. The performance of NZVI particles or their composites toward U(VI) in different water types (especially referring to the presence of different inorganic ions) is the key issue for the actual field application. Therefore, we investigated the potential impact of common ions in groundwater on U(VI) removal by NZVI/F composites at different pH values. Herein, a kind of fungi (*Geotrichum* sp. dwc-1) was chosen to synthesize NZVI/F composites and studied their removal performance for U(VI) in the presence of other competing ions at different pH. The purposes of this study are to (1) prepare NZVI/F composites and characterize them by scanning electron microscope (SEM) combined with energy dispersive spectrometer (EDS), X-ray diffraction (XRD), and thermogravimetric analysis (TGA); (2) investigate the impacts of various common groundwater ions (e.g., sodium, magnesium, calcium, and bicarbonate) on the removal and reduction process of U(VI) by NZVI/F composites; (3) explore the removal mechanisms of NZVI/F composites by X-ray photoelectron spectroscopy (XPS). We highlight removal performance of NZVI/F composites toward U(VI) influenced by different ions commonly present in groundwater, which is expected to provide some meaningful information about NZVI/F composites for further engineering application in site remediation.

Experimental

Materials

U(VI) stock solution (1 mmol/L) was obtained by dissolving uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$, analytical reagent) into deionized water. The *Geotrichum* sp. dwc-1 was provided by the College of Life Science, Sichuan University. The culturing method of the fungal cells was provided in our previous reports [24]. The fungal cells were harvested by centrifugation (4000 rpm, 5 min) during the logarithmic phase and were washed three times using 0.05 mol/L NaCl solutions. All the chemicals used in this study were in analytical grade and available from Shanghai Chemical Reagent Co. Ltd. The groundwater (GW) was synthesized based on the modified method of previous reports [30]. The components of GW included 0.286 mmol/L $Ca(NO_3)_2$, 0.312 mmol/L $CaCl_2$, 0.529 mmol/L $MgCl_2$, 0.451 mmol/L NaCl, 0.0111 mmol/L Na_2CO_3, 0.604 mmol/L $NaHCO_3$, and 0.43 mM $KHCO_3$.

Synthesis of NZVI/F composites

The whole processes for the synthesis of NZVI/F composites are shown in Fig. 1. Carbonized fungi were obtained via mild hydrothermal treatment according to previous reports [25]. Typically, 5.0 g fungal cells were dispersed in 30 mL of 2.5% glutaraldehyde under ultrasound for 30 min, and then placed into a 50 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 8 h. Glutaraldehyde could strengthen the polysaccharide networks, thus avoiding the undesired breaking. After cool-down to a room temperature naturally, the puce products were collected by vacuum filtering, swilling, and drying at oven 60 °C overnight. As-prepared carbonaceous fungi and 2.5 g of $FeCl_3 \cdot 6H_2O$ were dissolved in 20 mL of water. After a reaction time of 12 h, a 10 mL $NaBH_4$ solution (1.0 mol/L) was dropwise added under $N_{2(g)}$ protection. The suspensions were kept at 80 °C for 4 h. The NZVI/F composites were obtained after the particles were centrifuged and washed by water thoroughly.

Kinetics experiment

All experiments were conducted at 298 K in glovebox with inclusion of atmospheric P_{CO_2}. The removal/reduction rates of U(VI) by NZVI/F composites were examined by batch experiment at different pH (4.5, 6.5, and 8.5, respectively) in the presence of various groundwater constituent (1 mmol/L NaCl, KCl, $CaCl_2$, $MgCl_2$ and Na_2CO_3, respectively) or synthetic groundwater. The initial pH of suspensions was adjusted by the drop-wise addition (<0.1 mL) of a 1.0 mol/L HNO_3/NaOH solution. The initial concentration of U(VI) and NZVI/F composites were 0.25 mmol/L and 2 g/L, respectively. Briefly, the bulk suspensions of NZVI/F composites and groundwater constituents were pre-equilibrated in tubes for 24 h, and then U(VI) stock solution was added to initiate the reaction. At various time intervals, Aliquots of the suspensions were withdrawn from the tubes by using a 6 mL polypropylene syringe. Subsamples containing 3 mL of the suspensions (solid plus aqueous phase) were used to extract surface-adsorbed U(VI) by using a 0.2 mol/L Na_2CO_3 solution. The remaining samples (3 mL) were centrifuged and filtered through a 0.1 μm syringe filter. The filtrate was used to determine the U(VI) concentration in the aqueous phase and the collected particles were freeze-dried for analysis of the solid phase. U(VI) concentrations were measured using a Fluorolog-3 fluorescence spectrometer (Johin-Yvon-SPEX instruments, New Jersey). This method cannot detect the U(IV) species because it does not emit fluorescence [7]. All of the experimental data were averages of triplicate data.

U(VI) removal ($[U]_{removal}$) could result from both the sorption ($[U]_{sorbed}$) and reduction ($[U]_{reduced}$) (i.e., $[U]_{removal} = [U]_{sorbed} + [U]_{reduced}$). The concentration of $[U]_{sorbed}$ (mg/L) can be extracted by using Na_2CO_3 solution [11]. In brief, equivoluminal Na_2CO_3

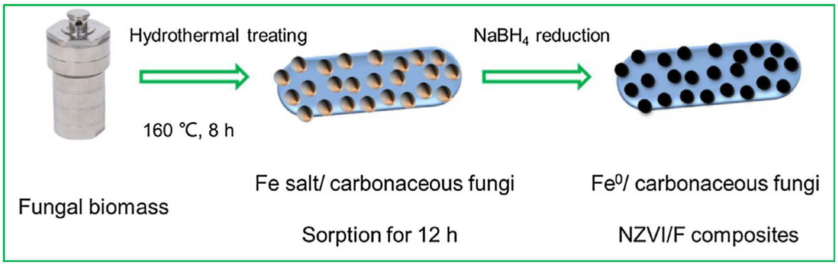

Fig. 1. Schematic of reaction for NZVI/F composite synthesis.

Please cite this article in press as: C. Ding, et al., Reactivity of carbonized fungi supported nanoscale zero-valent iron toward U(VI) influenced by naturally occurring ions, J. Ind. Eng. Chem. (2017), https://doi.org/10.1016/j.jiec.2017.12.021