Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–7

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Zero-valent iron-aluminum for the fast and effective U(VI) removal

Shuhong Xiang[a,b], Wencai Cheng[a,b,*], Xiaoqin Nie[a,b], Congcong Ding[a,**], Facheng Yi[a], 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 21 December 2017
Revised 25 January 2018
Accepted 26 January 2018
Available online xxx

Keywords:
Zero-valent iron
Aluminum
Uranium
Removal
Reduction

ABSTRACT

In this study, zero-valent iron-aluminum (NZVI-Al) bimetallic particles formed from Al(0) core and nanoscale Fe(0) shell were synthesized for highly effective U(VI) removal. The NZVI-Al bimetallic particles were characterized by SEM-EDS, FT-IR, XRD, and XPS. Batch experiment demonstrated that the reactivity of NZVI-Al bimetal was greatly improved relative to single zero-valent iron or aluminum. The enhanced U(VI) removal capacity up to 575 mg/g (but not to saturation at pH 5.0 and $T = 30$ °C) could be attributed to stronger reduction ability of NZVI-Al from the galvanic cell effect. XRD and XPS results indicated that U(VI) was immobilized via the reduction as $UO_{2(s)}$ and surface sorption as U(VI). The NZVI-Al bimetallic particles are promising for further testing to achieve the rapid and effective removal of U(VI) from polluted water.

1. Introduction

The uranium-bearing waste from legacy mining and milling activities has been a serious problem with the rapid development of nuclear energy and increasing demand of uranium resource [1–3]. Uranium contamination is of great concern due to its deleterious effects on humans and other organism even at very low exposure level [4–6]. Therefore, deep purification for uranium polluted aqueous solutions is urgent to be solved.

Numerous in situ zero-valent iron (ZVI) permeable reactive barriers (PRBs) have been in successful operation for many years [7, 8]. Our previous reports found the effective performance of nanoscale zero-valent iron (NZVI) toward U(VI) with removal capacity up to 215 mg/g [7]. The application of NZVI for U(VI) removal has been proved to be a low cost, high efficiency, and environmentally friendly approach [9]. However, there is an inevitable fact that the reducing activity of NZVI is limited with the formation of passivation layer (*i.e.*, the production of iron hydroxides or oxides) on the surface over time, eventually shortening the longevity of PRBs [10–12]. Additionally, agglomeration of NZVI particles also hindered their reducing performance and a field scale application [13–15]. On account of these intrinsic drawbacks, we turned to the introduction of second metal to form an iron based bimetal, which is an effective way to improve the reactivity of NZVI [16]. For NZVI, if electron can be continually supplied to maintain zero valent of Fe, more active reducing sites will be exposed to U(VI), thus enhancing the removal capacity of U(VI). Although this potentially shortens the lifetime of NZVI due to be vulnerable to the reaction with water, the reactivity of NZVI is greatly improved. Zero-valent aluminum (ZVAl) is one of the most abundant elements on earth, and its potential (−1.66 V) is far higher than that of NZVI (−0.44 V), thus presenting stronger reducing ability [17]. However, aluminum oxidation film formed more quickly and hindered further reduction process under neutral conditions. Wang et al. [18] reported that the cooperation with other metal can relieve the formation of oxidation film on ZVAl surface. Therefore, iron-aluminum bimetallic metal (NZVI-Al) is manufactured to improve the reducing ability of NZVI, where ZVAl is regarded as the electron supplier to prevent the iron hydroxides or oxides precipitates formed on the surface of NZVI.

Some papers reported the use of NZVI-Al bimetal in degradation of organic pollutants (*i.e.*, 4-chlorophenol and carbon tetrachloride) or in removal of heavy metals (*i.e.*, As(III) and Cr(VI)) [11,17,19]. So far, little is known regarding the reduction performance and mechanisms of NZVI-Al with U(VI). Especially the reduction efficiency of NZVI-Al toward U(VI) and the electron transfer between Al^0, Fe^0 and U(VI) were not clear.

---

[*] Corresponding author at: Fundamental Science on Nuclear Wastes and Environmental Safety Laboratory, Southwest University of Science and Technology, Mianyang 621010, PR China.
[**] Corresponding author.
E-mail addresses: chwc712@163.com (W. Cheng), dingc_3650483@163.com (C. Ding).

https://doi.org/10.1016/j.jtice.2018.01.039

Please cite this article as: S. Xiang et al., Zero-valent iron-aluminum for the fast and effective U(VI) removal, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.01.039

Herein, NZVI-Al bimetallic particles consisting of a core aluminum and surface iron nanoparticles were prepared to test their reactivity with U(VI). We focused on the following purpose in this study: (1) to successfully synthesize NZVI-Al bimetals; (2) to investigate NZVI-Al performance for U(VI) removal under different environmental conditions; (3) to characterize NZVI-Al bimetals before and after reaction with U(VI) using scanning electron microscope (SEM) combined with energy dispersive spectrometer (EDS), X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS), and to identify U(IV) and other products in the reduction process. Finally, an interaction mechanism between NZVI-Al and U(VI) was elucidated based on the obtained evidence.

2. Material and methods

2.1. Materials and reagents

All chemicals used in this study were of analytical grade and available from Shanghai Chemical Reagent Co. Ltd. ZVAl particles (~5 µm, 99% purity) were used in synthesis of NZVI-Al bimetallic particles. U(VI) stock solution (500 mg/L) was obtained by dissolving uranyl nitrate ($UO_2(NO_3)_2{\bullet}6H_2O$, analytical reagent) into deionized water.

2.2. Preparation of NZVI-Al bimetallic particles

NZVI-Al bimetallic particles were synthesized by depositing the NZVI nanoparticles on the ZVAL surface through the reaction of $Fe^{2+}$and BH_4^-as presented in Eq. (1) [20]. Briefly, 0.1 g ZVAL particles and 0.1 g $FeSO_4{\bullet}7H_2O$ were dissolved in 80 mL distilled water at 80 °C, and then the pH was adjusted to 7.0 by using 4 mol/L NaOH. After that, 20 mL of $NaBH_4$ solutions (15 g/L) were added drop by drop under $N_2(g)$ protection. The suspensions were kept at 80 °C for 4 h to guarantee the completion of the reaction. The NZVI-Al products were harvested by centrifuging for 10 min at 6000 rpm and washed three times using distilled water and dried in a vacuum freeze desiccator under oxygen-free condition. The color of NZVI-Al particles was dark grey. NZVI was synthesized in the same way except addition of ZVAl particles.

$$Fe^{2+} + 2\ BH_4^- + 6\ H_2O = Fe + 2\ B(OH)_3 + 7\ H_2 \qquad (1)$$

2.3. Batch experiment

All experiments were conducted under the protection of $N_{2(g)}$. The initial concentration of U(VI) and NZVI-Al particles were 100 mg/L and 0.36 g/L, respectively, at various initial pH values, temperature, and ionic strength. The initial pH values of the U(VI) and NaCl solutions were adjusted by adding negligible volume of 0.5 mol/L Na_2CO_3 or 0.1 mol/L HCl, and pre-equilibrated in glass containers for 24 h, and then NZVI-Al particles were added to initiate the reaction. Ionic strength of the system ranged from 0.01 to 0.1 mol/L NaCl. Sorption isotherms were investigated with U(VI) concentration in the range of 50–200 mg/L at pH = 5.0 and T = 303–325 K. More details on the experimental process and the calculation of U(VI) removal percentage (R, %) and removal capacity (Q_e (mg/g)) can be seen in supporting information (*SI*).

2.4. Characterization

The selected solid phase samples were prepared, stored and transported in an oxygen free environment prior to be characterized by SEM-EDS, XRD, FTIR and XPS techniques. SEM (Zeiss Ultra55, Germany) was used to examine morphologies of NZVI-Al bimetal. The combined EDS spectrum was carried out to determine the existence of element in NZVI-Al bimetal before and after reaction. XRD analysis was performed by an X-ray diffractometer (Thermo K-Alpha, US), and the diffraction pattern was recorded from 3° to 80° with a step length of 0.03342° and a count time of 8 s. The data was analyzed by the software of MDI Jade 6.0. FTIR analysis was carried out by Fourier transform infrared spectroscopy (Perkin Elmer spectrum one, US). The XPS spectra of the NZVI-Al before and after reaction were obtained using an X-ray photoelectron spectroscopy (Escalab 250Xi, Thermo Scientific). XPS spectra were recorded using normal Al Kα radiation (1486.8 eV) under a residual pressure of 2×10^{-9} Torr.

3. Results and discussion

3.1. SEM and EDS analysis

The surface morphology of ZVAl particles (Fig. 1a) and NZVI-Al bimetal before and after reaction with U(VI) (Fig. 1b, c) were studied by SEM combined with EDS spectrum. When compared with ZVAl particles, NZVI nanoparticles can be obviously seen on the surface of ZVAl in Fig. 1b. Accordingly, Fe peak appeared in the EDS spectrum of NZVI-Al. EDS spectrum showed that NZVI-Al bimetal consisted primarily of Al and Fe, with weight ratio of Fe/Al as 0.20. After reaction with U(VI), the surface of the NZVI-Al bimetal became more rough and unsmooth. Some floccus precipitants were observed on NZVI-Al surface, which might be attributed to U(VI) reduction to insoluble U(IV) species. Meanwhile, uranium element was testified by EDS spectrum. The presence of U(IV) species was further evidenced by our XPS result as well.

3.2. XRD and FTIR analysis

Fig. 2a showed XRD diffraction pattern of NZVI, ZVAl, and NZVI-Al. NZVI exhibited characteristic peaks at $2\theta = 44.8°$ (main diffraction peak) and 65.2°, which matched well with (110) and (200) planes of iron [7, 11]. The characteristic peaks of ZVAl appeared at the diffraction angle of 38.6° (main diffraction peak), 44.8°, 65.2°, and 78.5°, assigned to (111), (200), (220), and (311) diffraction of aluminum [21]. NZVI-Al had the characteristic peaks of both NZVI and ZVAl, suggesting the successful manufacture of NZVI-Al bimetal.

The XRD diffraction pattern of NZVI-Al after reaction with relatively low (50 mg/L) and high (1 g/L) concentration of U(VI) was also shown in Fig. 2a. The characteristic peaks of UO_2 at $2\theta = 27.8°$ and 32.2° (PDF card of mineral from the PDF-2 database of the International Center for Diffraction Data) can be obviously seen at high concentration of U(VI), and the main diffraction peak at $2\theta = 27.8°$ was also observed at low concentration of U(VI). The results demonstrated the removal ability of NZVI-Al can be attributed to U(VI) reduction to U(IV) as insoluble UO_2. Low abundance of UO_2 might result in the insignificant diffraction peaks at 50 mg/L U(VI). Interestingly, iron corrosion products such as lepidocrocite and magnetite failed to be detected after reaction with 50 mg/L U(VI), while similar iron corrosion products were observed in reacted NZVI surface with 36 mg/L U(VI) by XRD analysis in our previous reports [7]. When U(VI) concentration was up to 1 g/L, some tiny peaks at 49.29° and 65.11° matched with FeOOH appeared. The disappearance of diffraction peaks of iron or aluminum peaks can result from the consumption of NZVI or ZVAl during the reaction, or from the coverage of large abundance of $UO_{2(s)}$ on NZVI-Al surface which shielded the interior iron or aluminum signals. XRD results demonstrated the great reducing ability of NZVI-Al with U(VI).

The FT-IR spectra of ZVAl, U(VI)-free NZVI-Al bimetal, and U(VI)-loaded NZVI-Al bimetal were shown in Fig. 2b. A new peak

Please cite this article as: S. Xiang et al., Zero-valent iron-aluminum for the fast and effective U(VI) removal, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.01.039