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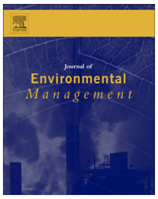

Research article

Evaluation of activated carbon fiber supported nanoscale zero-valent iron for chromium (VI) removal from groundwater in a permeable reactive column

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ABSTRACT

An activated carbon fiber supported nanoscale zero-valent iron (ACF-nZVI) composite for Cr(VI) removal from groundwater was synthesized according to the liquid phase reduction method. The techniques of N_2 adsorption/desorption, FESEM, EDX, XRD and XPS were used to characterize the ACF-nZVI composite and the interaction between the ACF-nZVI composite and Cr(VI) ions. Batch experiments were conducted to evaluate the effects of several factors, including the amount of nZVI on activated carbon fiber (ACF), pH value, initial Cr(VI) concentration, and co-existing ions on Cr(VI) removal. The results indicate that presence of ACF can inhibit the aggregation of nanoscale zero-valent iron (nZVI) particles and increase its reactivity, and the Cr(VI) removal efficiency increases with increasing amounts of nZVI on ACF and a decrease in the initial Cr(VI) concentration. In acidic conditions, almost 100% of Cr(VI) in solution can be removed after 60 min of reaction, and the removal efficiency decreases with increasing initial pH values. The Cr(VI) removal is also dependent on the co-existing ions. Reusability experiments on ACF-nZVI demonstrate that the ACF-nZVI composite can keep a high reactivity after five successive reduction cycles. The removal mechanisms are proposed as a two-step interaction including the physical adsorption of Cr(VI) on the surface or inner layers of the ACF-nZVI composite and the subsequent reduction of Cr(VI) to Cr(III) by nZVI.

1. Introduction

Toxic heavy metal pollution is a significant environmental and occupational concern because of the tendency of heavy metals to enter the food chain (Sikder et al., 2014; Chowdhury et al., 2016). Among metals of concern, chromium (Cr) is a commonly identified contaminant in soils and groundwater and is widely applied in various industries including metal electroplating, metal finishing, steelworks manufacturing, chromite mining, leather tanning, and synthesis of pigments (Sun et al., 2014; Dong et al., 2016a,b,c; Gong et al., 2017). Due to inadequate storage and improper disposal, Cr ions enter the environment and have caused many incidences of groundwater contamination (Mohan and Charles, 2006; Li et al., 2008). In the natural environment, Cr exists primarily in the form of Cr(III) and Cr(VI). The Cr(III) species are relatively stable and have low solubility and mobility in soils and aquifers (Lv et al., 2011). In fact, it is an essential microelement for organisms at low concentrations (Sarkar et al., 2010; Villacis-Garcia et al., 2015). In contrast, the Cr(VI) species (approximately 1000 times more toxic than Cr(III)), such as chromate (CrO_4^{2-}, $HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$), are highly soluble and mobile in aqueous solutions. These species could cause a series of problems for humans and animals because they could form non-biodegradable compounds that affect aquatic life and cause serious health issues such as digestive tract cancer, anemia, neurological damage, circulatory shutdown and death (Nriagu and Nieboer, 1988; Costa and Klein, 2006; Boni and Sbaffon, 2009; Saha et al., 2012). Since the last century, the USEPA has adopted a maximum permissible limit of 0.1 mg/L for Cr in groundwater (USEPA, 1992), and in 2014, the state of California established a maximum contaminant level (MCL) of 10 μg/L for Cr(VI) under the increased concern for Cr(VI) effects on human health (Kaprara et al., 2015). The removal of Cr from groundwater is mostly focused on Cr(VI). To date, there has been increasing interest

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in developing effective measures to remove Cr(VI) from Cr-contaminated groundwaters.

In recent years, nanoscale zero-valent iron (nZVI) technology has received much attention for the treatment of Cr-contaminated water due to its high reduction capacity and open structure, and it shows a high efficiency and low economic and environmental costs (Qiu et al., 2013; Dong et al., 2016a,b,c). Additionally, the reaction products (ferrous and ferric ions) of nZVI technology are harmless. Therefore, nZVI technology is believed to be a promising, cost-effective, and environmentally friendly for Cr(VI) removal. However, nZVI particles are prone to aggregation and inactivity in aqueous solution due to their properties of a high surface energy, magnetization and high reactivity, which result in a decrease in their reactivity and limit the application of nZVI particles in groundwater remediation (Guan et al., 2015; Dong et al., 2016a,b,c; Xie et al., 2017). To solve these issues, stabilize and support nZVI, and decrease particle agglomeration, researchers have attempted using different materials including bentonite (Shi et al., 2011a,b), mesoporous silica (Petala et al., 2013), kaolinite (Uezuem et al., 2009), sepiolite (Fu et al., 2015), activated carbon (Zhu et al., 2009), multiwalled carbon nanotubes (Lv et al., 2011) and biochar (Dong et al., 2017). These approaches can effectively combine the benefits of treatment under flow conditions with the high reactivity and the high degree of nanoscale iron utilization (Toli et al., 2016). Moreover, when nZVI is fixed on a porous matrix, the potential risks due to the accidental release of nanoparticles in the environment are minimized. In comparison to other materials, activated carbon fiber (ACF) is a readily available porous and carbon-rich material with the higher specific surface area, more stable structures capacity, and greater adsorption. Furthermore, the ACF surface can hold a large number of oxygen-containing groups, which is quite effective for the adsorption of heavy metal ions (Faur-Brasquet et al., 2002; Chen and Wang, 2004). However, according to the literature, there has been little research on the use of ACF as a carrier of nZVI.

In the study, to enhance the dispersibility and stability of nZVI particles in the air, ACF was used to support the nZVI particles for Cr(VI) removal from aqueous solution. The primary objectives are to (1) synthesize and characterize the new and stable activated carbon fiber supported nanoscale zero-valent iron (ACF-nZVI) composite, (2) evaluate the Cr(VI) removal efficiency of ACF-nZVI in a permeable reactive column under different experimental conditions, (3) assess the reuse of ACF-nZVI and (4) test the role of ACF during the remediation process and investigate the elemental composition of the final products to reasonably conclude the Cr(VI) removal mechanism of ACF-nZVI.

2. Materials and methods

2.1. Materials and chemicals

ACF (20 mm × 20 mm × 1 mm) with a specific surface area of 737.9 m^2/g was purchased from Jiangsu Sutong Carbon Fiber Co., Ltd. Prior to use, the ACF was pretreated as follows: first, the ACF was soaked with 5% (wt%) hydrochloric acid for 24 h; next, the ACF was washed with deionized water until the pH of the supernatant was close to neutral; and finally, the ACF was dried at 378 K for 24 h. The clean ACF was stored in a desiccator for later use.

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, ≥99.0%) was used as the precursor of nZVI and purchased from Tianli Chemical Reagent Co., Ltd. (Tianjin, China). Sodium borohydride ($NaBH_4$, ≥97.0%) was obtained from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Potassium dichromate ($K_2Cr_2O_7$, ≥99.8%) was supplied by Xilong Chemical Industry Co., Ltd. (Guangdong, China). Quartz sand (grain size 0.2–0.3 mm) and other chemical reagents were obtained from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). All chemicals were analytical grade and used without further purification.

2.2. Preparation of ACF-nZVI

In this study, nZVI particles were synthesized according to the reduction method using $NaBH_4$ as the reducing agent, which reduces Fe^{3+} to nZVI. The specific reaction equation is as follows (Zhang et al., 2014):

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0\downarrow + 3BO_3^- + 12H^+ + 6H_2\uparrow \quad (1)$$

The ACF-nZVI composite was assembled according to a typical process as follows: 1.2163 g of $FeCl_3 \cdot 6H_2O$ was dissolved in 100 mL of ethanol aqueous solution (ethanol:deionized water = 3:7, V/V) in a three-neck flask, followed by the addition of 0.20 g of ACF with vigorous magnetic stirring for 15 min to form a composite of ACF and iron. Next, a freshly prepared $NaBH_4$ solution (1.8915 g of $NaBH_4$ in 100 mL) was added dropwise (at a rate of 0.167 mL/s) to the stirred mixture in an ultrasonic environment operating at 40 kW until no significant H_2 was produced, and the solution was then sonicated for 5 min (Xiao et al., 2015; Zhang et al., 2015; Zhou et al., 2015). Finally, the composite was separated from the solution by vacuum filtration (0.22 μm microporous membrane filter) and quickly rinsed three times with anhydrous ethanol. The composite was then dried at 60 °C under a vacuum.

2.3. Characterization

The microstructures of the prepared nZVI and ACF-nZVI composite were analyzed using an N_2 adsorption instrument (Gold APP V-Sorb 2800P, China). The morphological analyses and elemental composition of ACF, nZVI and ACF-nZVI were performed using a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan) with an energy dispersive X-ray (EDX). The X-ray diffraction (XRD) patterns of the nZVI and ACF-nZVI were acquired using an X-ray powder diffractometer (Bruker, D8 Advance A25, Germany) with the Cu-Kα radiation source operating at 40 kV and 40 mA. An X-ray photoelectron spectroscopy (XPS, Amicus, Shimadzu, Japan) analysis was used to detect elements such as C, O, Fe and Cr before and after the ACF-nZVI reacted with wastewater.

2.4. Batch experiments

The batch experiments were conducted in a permeable reactive column made of organic glass. The high and inner diameters of the column were 300 mm and 36 mm, respectively. The column was filled with 200 g of quartz sand. The wastewater with Cr(VI) was circulated through the ACF-nZVI composites on the top of the permeable reactive column using a peristaltic pump. To shade the reactive column from light, it was wrapped in tinfoil. Each reaction occurred in a beaker agitated on a magnetic stirrer with 500 mL of Cr(VI) solution. In the absence of special note, the nZVI loaded amount on ACF, pH value of solution and the initial Cr(VI) concentration are 0.40 g, 5.0 and 10.0 mg/L, respectively. The samples were filtered through a 0.22 μm membrane filter at different time intervals. The measurements were conducted at ambient temperature, and all the experiments were run in duplicate or triplicate. The residual Cr(VI) in aqueous solution was analyzed according to the 1,5-diphenylcarbazide method with an UV1901 UV–Vis spectrophotometer (Yoke, China) at a wavelength of 540 nm. The determination of total Cr was tested using a Z-2000 polarized Zeeman atomic absorption spectrometer (Hitachi, Japan) with an air-acetylene flame. The detection limits of both methods for determination of Cr concentration are less than 0.01 mg/L.