



Reductive removal of Cr(VI) by starch-stabilized Fe⁰ nanoparticles in aqueous solution

L. Alidokht^{a,b}, A.R. Khataee^{a,*}, A. Reyhanitabar^b, S. Oustan^b

^a Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

^b Department of Soil Science, Faculty of Agriculture, University of Tabriz, Tabriz, Iran

ARTICLE INFO

Article history:

Received 4 October 2010

Received in revised form 13 November 2010

Accepted 15 November 2010

Available online 8 December 2010

Keywords:

Zeravalent iron

Fe₃O₄ nanoparticles

Chromium removal

Wastewater treatment

Chemical reduction

ABSTRACT

A comparative study of hexavalent chromium (Cr(VI)) removal from aqueous solution using Fe⁰ and Fe₃O₄ particles in nano and micro-scale was performed. Our results indicated that the Cr(VI) removal efficiency using starch-stabilized Fe⁰ nanoparticles, nonstabilized Fe⁰ nanoparticles, Fe₃O₄ nanoparticles, Fe⁰ and Fe₃O₄ microparticles was 99.25%, 60.4%, 9.13%, 6.92% and 6.17%, respectively. Results revealed that the Cr(VI) removal efficiency using Fe₃O₄ particles was highly dependent on pH with maximum removal efficiency at pH 3. The stabilized Fe⁰ nanoparticles efficiently remove Cr(VI) from aqueous solution in a wide pH range. In the present of Fe⁰ nanoparticles, increasing the initial Cr(VI) concentration from 10 to 50 mg/L decreased removal efficiency and observed pseudo-first order rate constant (*k*_{obs}) from 100% to 56.4%, and 0.101 to 0.015 min⁻¹, respectively. Increasing Fe⁰ nanoparticles dosage from 0.1 to 2 g/L increased *k*_{obs} value from 0.028 to 0.110 min⁻¹ and led to a 60% increase in the removal efficiency. The reaction rate constant decreased from 0.075 to 0.043 min⁻¹ with increasing pH from 3 to 9, respectively. Our results suggest that stabilized Fe⁰ nanoparticles may serve as an effective agent for reductive removal of Cr(VI) from contaminated waters.

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1. Introduction

Chromium is considered as a priority pollutant by the US Environmental Protection Agency [1], and its compounds have been classified as potential carcinogen and acutely toxic for humans, animals, plants, and microorganisms [2]. Chromium is widely used in many industrial processes such as metallurgical (steel, ferro- and nonferrous alloys), refractories (chrome and chrome-magnesite) and chemicals (pigments, electroplating, tanning and others) [3]. Leakage, unsuitable storage and/or improper disposal practices are the main reasons for releasing the significant quantities of chromium to the environment [4]. The permissible limit of Cr(VI) for inland surface waters is 0.1 mg/L and for potable water is 0.05 mg/L [5]. Chromium exists in various oxidation states ranging from +6 to -2, however; only the +6 and +3 oxidation states are stable under most natural environments [6,7]. Hexavalent chromium (Cr(VI)), such as chromate [CrO₄²⁻, HCrO₄⁻] is a highly soluble reactive and mobile species in aquatic systems [2], and exerts toxic effects on biological systems due to its strong oxidizing properties [8]. On the other hand, trivalent chromium (Cr(III)) is essential for the proper functioning of living organisms [3] and is not hazardous compared with Cr(VI) due to its low solubility (<10⁻⁵ M) over a wide pH range [2] and much stability with respect to redox potential (*E*_h), except in the presence of

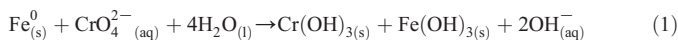
oxidized Mn [9]. Several methods are available for the decontamination of waters contaminated with Cr(VI) compounds. Some of these methods are reduction followed by chemical precipitation, adsorption, electro-kinetic remediation, membrane separation processes, and bioremediation [10]. Among these methods, chemical redox followed by precipitation has been considered the most common technique for the removal of Cr(VI) from wastewater [5]. After reduction, Cr is removed from solution as (Cr(OH)₃), or when dissolved iron is present, as a chromium-iron hydroxides (Cr_xFe_{1-x}) (OH)₃ [11]. To chemically reduce Cr(VI) to Cr(III) various reducing agents have been employed including H₂S [12], dissolved organic compounds, such as oxalate and citrate [13], sodium dithionite and ferrous sulfate [14]. The ability of iron to act as an electron donor is utilized in decontamination of several soil and groundwater pollutants, based on reductive technologies [15], and Fenton treatment techniques [16]. Over the last several years, there has been great interest in using zerovalent iron (Fe⁰) to mitigate chromium (VI) contamination [8]. Zerovalent iron is an available and innocuous low cost reducing agent extensively used to remove several kinds of contaminants such as chlorinated solvents [17], nitrate [18], and heavy metals like As⁵⁺ [19,20], U⁶⁺, V⁵⁺, Zn²⁺ [20], Pb²⁺ and Cr⁶⁺ [21] from aquatic systems. Aqueous Cr(VI) also can be reduced to Cr(III) through its interaction with solids containing Fe(II) in the near surface region such as magnetite (Fe(II)Fe(III)₂O₄) [22]. Kendelewicz et al. [22] have reported that the sorption of aqueous Cr(VI) on the magnetite surface results in a substantial reduction of Cr(VI) to Cr(III), and the Cr(VI) reduction has a significant correlation with presence of

* Corresponding author. Tel.: +98 411 3393165; fax: +98 411 3340191.

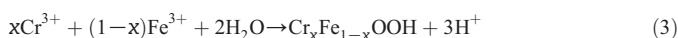
E-mail addresses: a_khataee@tabrizu.ac.ir, ar_khataee@yahoo.com (A.R. Khataee).

Fe(II). Magnetite have shown favorable activities for the adsorption/reduction of a few heavy metal ions (e. g., Ni^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , and Cr^{6+}) and the catalytic degradation of some organic contaminants [23–26]. Magnetite nanoparticles have been reported to have better adsorption and reduction activities than their traditional macro or micro-counterparts [27].

Powell et al. [28] have suggested that the remediation occurs via reductive processes associated with surface corrosion of the iron metal. Removal of Cr(VI) is achieved by a coupled reduction-oxidation reaction according to the following stoichiometry [29]:



In addition, Cr(III) can also be incorporated onto the surface FeOOH structure and precipitated as Fe(III)–Cr(III) hydroxide (Eq. (2)), or Fe(III)–Cr(III) oxyhydroxide (Eq. (3)) at the surface ($0 < x < 1$) [30]:



Nanoscale Fe^0 particles may complement the conventional zerovalent technology by providing a mobile and reactive iron. Diminutive size and large specific surface area of Fe^0 nanoparticles translate to enhanced reactivity for contaminant remediation [30]. However, Fe^0 nanoparticles prepared using conventional methods tend to either agglomerate rapidly or react quickly with the surrounding media (e. g., dissolved oxygen or water), resulting in much larger chains and loss of reactivity and transfer in contaminated sites [31]. Therefore, dispersion of Fe^0 nanoparticles is a critical factor to improve their reaction efficiency. In this case, various particle-stabilizing agents have been employed (e. g. resin [21], starch [32], chitosan [33] and carboxymethyl cellulose [34]). Starch is a nontoxic, biodegradable, and inexpensive substance that can be used as an effective dispersant for iron nanoparticles. Although a number of researchers have examined the ability of Fe^0 nanoparticles for the removal of Cr(VI) [21,33], Cr(VI) removal efficiency using stabilized Fe^0 nanoparticles affected by environmental factors, and in comparison with magnetite particles has not been reported in details. In the present work, zerovalent iron nanoparticles (ZVIN) were prepared using sulfate method [35], and water soluble starch was used as a stabilizer. Removal efficiency of Cr(VI) by using synthesized stabilized Fe^0 nanoparticles was studied in comparison with Fe^0 microparticles, and magnetite nano and micro-particles to evaluate their performance for the remediation process.

2. Experimental

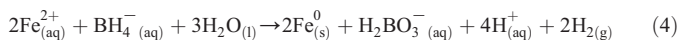
2.1. Materials

Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), sodium borohydride (NaBH_4), starch, 1,5-diphenylcarbazide, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), and iron microparticles (about $10 \mu\text{m}$) were of laboratory reagent grade (Merck Co.). Magnetite (Fe_3O_4) microparticles (98%, $\leq 5 \mu\text{m}$) and nanoparticles ($\geq 98\%$, about 30nm) were purchased from Sigma Aldrich. Magnetite and iron particles were used without any chemical and mechanical pretreatment.

2.2. Preparation of zerovalent iron nanoparticles

The nonstabilized and starch-stabilized Fe^0 nanoparticles were prepared by the sulfate method. In brief, stabilized Fe^0 nanoparticles were synthesized by adding 100 mL of 0.5 M sodium borohydride solution drop-wise into a three neck flask containing 0.14 M ferrous sulfate solution (1:1 volume) and 0.2% (w/w) starch as a stabilizer

with magnetic stirring and under argon gas bubbling to remove dissolved oxygen. In this process, the addition rate of borohydride lasted approximately for 2 h to help control particles size. After addition of all of the NaBH_4 solution, the mixture was stirred for further 30 min to complete the reaction. Ferrous iron was reduced to zerovalent iron by borohydride according to the following reaction:



The precipitated Fe^0 nanoparticles were separated using a centrifuge at 5000 rpm for 5 min, and washed three times with ethanol. Prepared particles were then dried under vacuum over night. Synthesis procedure of nonstabilized Fe^0 nanoparticles was the same as stabilized Fe^0 nanoparticles without using starch.

2.3. Characterization methods

X-ray diffraction (XRD) analysis was performed using a Siemens D5000 (Germany) diffractometer with $\text{Cu-K}\alpha$ radiation (40 kV, 30 mA, $\lambda = 0.15418 \text{nm}$), to identify the structure and the composition of freshly synthesized Fe^0 nanoparticles and purchased magnetite nanoparticles. Each sample was scanned within the 2θ range of $25\text{--}85^\circ$. Crystallite size of nanoparticles was calculated from the line broadening of X-ray diffraction peak according to the Sherrer formula [36]. Scanning electron microscopy (SEM) characterization was performed by a Hitachi S 4160 model (Japan) instrument to identify surface morphology and size distribution of Fe^0 and Fe_3O_4 particles in nano and micro-scale range.

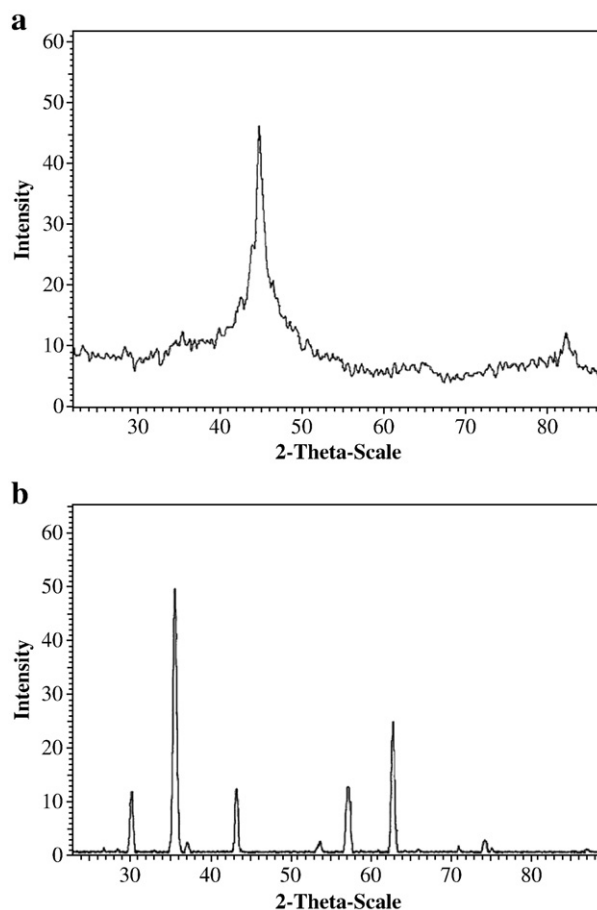


Fig. 1. XRD patterns of (a) synthesized starch-stabilized Fe^0 nanoparticles, and (b) magnetite nanoparticles.

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