



Heavy metal release due to aging effect during zero valent iron nanoparticles remediation



Blanca Calderon*, Andres Fullana

Chemical Engineering Department, University of Alicante, San Vicente del Raspeig Road, 03690 San Vicente del Raspeig, Alicante, Spain

ARTICLE INFO

Article history:

Received 19 January 2015

Received in revised form

28 May 2015

Accepted 2 June 2015

Available online 21 June 2015

Keywords:

Zero-valent iron

Nanoparticles

Heavy metals

Aging effect

Immobilization

Delivery

ABSTRACT

Zero valent iron nanoparticles (nZVI) represent a promising agent for environmental remediation. Nevertheless, their application presents some limitations regarding their rapid oxidation and aggregation in the media. The aim of this study was to determine the effect that nZVI aging has in heavy metal remediation in water. Contaminants studied were Zn, Cd, Ni, Cu and Cr, which are typical elements found in ground and wastewater. Results show a high contaminant removal capacity by the nZVI in the first 2 h of reaction. Nevertheless, for longer reaction times, some of the metal ions that had already been adsorbed in the nZVI were delivered to the water. Cd and Ni show the maximum delivery percentages (65 and 27% respectively after 21 days of contact time). The starting delivery time was shortened when applying lower nZVI amounts. No re-dissolution of Cr was observed in any circumstance because it was the only element incorporated into the nanoparticles core, as TEM images showed. Contaminant release from nZVI is probably due to nanoparticles oxidation caused by aging, which produced a pH decrease and nZVI surface crystallization.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

1.1. nZVI for environmental remediation of heavy metals

Zero valent iron nanoparticles (nZVI) have been shown in the last 15 years to be effective for environmental remediation of a wide variety of organic and inorganic contaminants present in groundwater and wastewater. Some examples include heavy metals, nitrate, chlorinated organic solvents and azo-dyes (Cundy et al., 2008; Yan et al., 2013; Fu et al., 2014). Due to their large surface area and high number of active sites, nZVI enhance the remediation efficiencies of those contaminants remarkably (Boparai et al., 2013; Wang et al., 2010a,b; Karabelli et al., 2008; Li and Zhang, 2006).

Heavy metals are one of the groups of contaminants which can be removed by nZVI with high rates and capacities (Li and Zhang, 2007). The mechanisms that undertake the removal are complex, as they involve the actuation of the core and shell of the nanoparticles. A ≈ 3 nm layer of iron oxide (Yan et al., 2010; Martin et al., 2008) is spontaneously produced during nZVI synthesis, creating a

core-shell structure in the nanoparticles (Crane and Scott, 2012). The core is composed of metallic iron and acts as an electron donor source, promoting reduction of compounds. Shell layer composition depends on the synthesis method and nanoparticles environment (Nurmi et al., 2005). In general, it is composed of Fe^{2+} , Fe^{3+} and O, having a structure similar to that of the coating of iron oxides immersed in water (Li and Zhang, 2007). nZVI shell enables sorption, surface complexation and electron transport from and to the core. It is extremely reactive due to its amorphous structure, the presence of defective sites and the small size of nZVI. The main compound present at the surface when nanoparticles are synthesized by precipitation of iron salts is hydrated oxide $\text{FeO}(\text{OH})$ (Sun et al., 2006; Li et al., 2008; Olegario et al., 2010). Due to their dual structure, nZVI can present characteristics of both metallic and oxide iron, acting as reductant and adsorbent.

Several authors have proposed that removal processes depend on the type of contaminant and its interaction with the nanoparticles (Nurmi et al., 2005; Zhang et al., 2013). The mechanisms proposed have been (Yan et al., 2010; Crane and Scott, 2012): surface mediated reduction and precipitation in the nanoparticles core (Cr^{6+} , Hg^{2+} , Cu^{2+} , etc.), adsorption plus precipitation or surface complex formation (Zn^{2+} , Cd^{2+}), sorption plus partial chemical reduction (Ni^{2+} , Pb^{2+}) and surface mineralization (H_2S). Moreover, some studies affirm that nZVI can degrade contaminants by

* Corresponding author.

E-mail address: blanca.calderon@ua.es (B. Calderon).

oxidation. In the presence of dissolved oxygen, nZVI reduces O_2 to H_2O_2 , which combines with Fe^{2+} to produce hydroxyl radicals ($\bullet OH$). Those radicals have strong oxidizing capability towards a variety of organic compounds (Fu et al., 2014). Thus, nZVI can act through multiple mechanisms to trap compounds, which make them unique in their application in contaminant remediation (Greenlee et al., 2012).

1.2. Aging effect of nZVI on removal processes

The wide majority of studies regarding environmental remediation with nZVI are performed during a short timescale and with a single element. Such systems are far away from real applications in environmental waters and could lead to an overestimation of the nZVI performance. nZVI rapidly age in water due to corrosion and interactions with both dissolved oxygen (DO) and water. Corrosion originates changes in nZVI structure and chemical properties depending on environmental conditions. Several works dealing with this subject have been published in the last 5 years. For example, Wang aged nZVI under highly humid atmosphere (85%) and dry air (Wang et al., 2010a,b). It was proved that water content enhanced nZVI oxidation, developing the growth of a thicker shell and generating ordered crystalline structures. This phenomenon has been described by other authors and has demonstrated to be favored by increasing pH (Kanel et al., 2006; Ford et al., 1997). Compounds found at the nZVI surface after aging are lepidocrocite, magnetite, goethite and maghemite (Kanel et al., 2005) depending on the conditions under which nZVI have been oxidized. Additionally, the reactivity of nZVI towards non-target dissolved oxygen and water showed to produce a passive Fe^{3+} oxide shell which entailed to a complete loss of reducing capacity (Xie and Cwiertny, 2012). The crystalline structure obtained by nZVI aging is created when they react with O_2 , which liberates heat and leads to the recrystallization of nZVI. Thus, nZVI gradually crystallize over time to more ordered forms which present reduced surface area and less reactivity with target contaminants.

There is limited research dealing with the influence of nZVI aging on contaminant removal. Moreover, most of the studies have been performed in a semi continuous way. I.e. nZVI are aged under certain conditions and are used afterwards to remove a target contaminant. In all those studies, nanoparticles aging has shown a remarkable decrease in removal efficiency (Liu and Lowry, 2006; Sarathy et al., 2008). For example, 80% decrease in trichloroethylene removal was recorded using nZVI suspensions which had been previously aged in air during 3 days (Xie and Cwiertny, 2010). Additionally, in the study of Sarathy et al. (2008), a decrease in efficiency of 25% and 70% in 5 days and 6 months, respectively, was determined for CCl_4 elimination. In that case, nZVI aging was produced with deoxygenated water. The decrease in nZVI reactivity was caused by the formation of a passivation shell, which was composed of more protective and less reactive magnetite rich oxides.

Nevertheless, studies are lacking in nanoparticles age effect on continuous experiments. If nanoparticles are employed to treat ground and wastewater, is important to determine if nZVI aging will affect the removal processes. There are very few studies covering this area. Two examples are the works of Crane et al. (2011) and Dickinson and Scott (2010) about uranium removal using nZVI, in which they proved the release of uranium into the water due to nZVI aging. A partial release of 20% of already retained U was observed after just one week, reaching values of 60% after 3 weeks. Uranium delivery was attributed to the re-dissolution of uranyl-carbonate complexes induced by CO_2 absorption from the atmosphere, but no more research was conducted to confirm it. It is not known if this phenomenon could happen with heavy metals or

other contaminants. Reacted nZVI usually remain unattended at treated sites, and what happens to the contaminants that have already been removed with nZVI has been slightly studied. Some desorption and remobilization of phenanthrene from nZVI was reported in groundwater due to pH variation or natural organic matter (NOM) (Grieger et al., 2010), but a lot more efforts have to be made in this area.

The aim of this work is to study the removal of heavy metal ion during long reaction times in order to determine the effect of nanoparticles aging on the process, which has not been studied before. This study will provide a new insight to the chemical behavior of nZVI in contaminant remediation and will help to better design ground and wastewater treatments. Metals chosen in the study have been Zn, Cd, Ni, Cu and Cr, which are common surface and wastewater contaminants coming from industrial processes as electroplating and metal finishing plants. Different conditions such as iron quantity, oxygen concentration in water and pH value will be assessed in order to determine their influence on the process.

2. Materials and methods

2.1. Chemicals

All chemicals used for both the synthesis of nZVI ($FeCl_3 \cdot 6H_2O$, $NaBH_4$, ethanol) and the contaminated solution preparation ($Ni(NO_3)_2 \cdot 6H_2O$, $Cd(CH_3COO)_2 \cdot 2H_2O$, $ZnCl_2$, $K_2Cr_2O_7$, $CuCl_2 \cdot H_2O$) were of analytical grade. All the solutions were prepared using purified water. Gaseous nitrogen employed to achieve the anoxic atmosphere was purchased from Air Products with analytical grade.

2.2. Nanoparticles synthesis

nZVI were synthesized by the borohydride reduction method (Wang and Zhang, 1997), which produces particles within the range of 50–100 nm. Briefly, 1.5 times molar excess of $NaBH_4$ was added to a stoichiometric $FeCl_3$ solution to produce the metallic iron nanoparticles. After synthesis, nanoparticles were separated magnetically and then washed four times with distilled water to remove the remaining borohydride. Nanoparticles were stored in a 5% of ethanol in water suspension at 6–8 °C during 24 h before use.

2.3. Batch tests

In order to approach actual water conditions, this study was performed with a solution containing a mixture of five heavy metals (Zn^{2+} , Cd^{2+} , Ni^{2+} , Cu^{2+} and Cr^{6+}) commonly found in contaminated ground and wastewater. The contaminated solution contained 100 ppm of each of the metals mentioned and had a pH of 3.9. No prior pH adjustment was performed throughout the experiments. Initial dissolved oxygen (DO) concentration in the contaminated water was around 7.5 mg/L, which corresponds to oxygen concentration in equilibrium with the atmosphere.

Experiments were performed in a 500 mL batch laboratory-scale reactor under continuous mixing. Volume of contaminated solution used in each experiment was 500 mL. A specific amount of nZVI was added to the reactor to start the reaction, and 2 mL samples from the reaction mixture were taken at different times. Water solution was separated from nanoparticles by using a neodymium magnet, followed by centrifugation and filtration with a 0.2 μm syringe to remove the remaining solid. Total metal concentration in water samples was determined by inductively coupled plasma mass spectrometry (ICP-MS). The solid surface was analyzed by XPS to determine the atomic percentage of the

Download English Version:

<https://daneshyari.com/en/article/6365722>

Download Persian Version:

<https://daneshyari.com/article/6365722>

[Daneshyari.com](https://daneshyari.com)