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Novel iron metal matrix composite reinforced by quartz sand for the effective dechlorination of aqueous 2-chlorophenol

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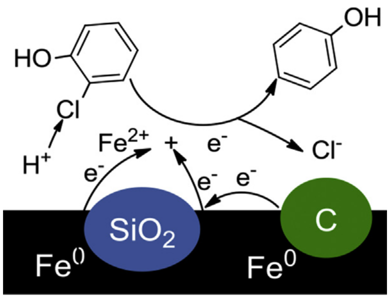
HIGHLIGHTS

- A novel iron matrix was mechanically synthesized for rapid dechlorination.
- The prepared SiO_2–Fe MMC performed higher reactivity than some Pd/Fe bimetals.
- It was proposed for the dechlorination mechanism at the SiO_2/Fe interface.
- This reduction material posssessed long service life for dechlorination.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we tested a novel iron metal matrix composite (MMC) synthesized by mechanically introducing quartz sand (SiO_2) into an iron matrix (denoted as SiO_2–Fe MMC). The pseudo-first-order reaction rate constant of the SiO_2–Fe MMC (initial pH 5.0) for 20 mg/L of 2-chlorophenol (2-CP) was 0.051×10^{-3} L/m^2/min, which was even higher than that of some reported Pd/Fe bimetals. This extraordinary high activity was promoted by the quick iron dissolution rate, which was caused by the formation of Fe–C internal electrolysis from carbonization of process control agent (PCA) and the active reinforcement/metal interfaces during the milling process. In addition, pH has slight effect on the dechlorination rate. The SiO_2–Fe MMC retained relatively stable activity, still achieving 71% removal efficiency for 2-CP after six consecutive cycles. The decrease in dechlorination efficiency can be attributed to the rapid consumption of Fe^0. A dechlorination mechanism using the SiO_2–Fe MMC was proposed by a direct electron transfer from Fe^0 to 2-CP at the quartz sand/iron interface.

1. Introduction

Given their natural abundance, low cost, and environmentally benign nature, zero-valent iron (ZVI) particles have been widely used for the reductive dechlorination of chlorinated organic compounds (COCs) under both laboratory and field conditions (El-

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Temsah and Joner, 2013, Jiao et al. 2009; Kocur et al. 2014; Velimirovic et al. 2013). For example, the short-chain COCs in groundwater are effectively degraded into hydrocarbons when they passes through the permeable reactive barriers constructed by ZVI (FePRBs) (Furukawa et al. 2002; Ma and Zhang, 2008, Yin et al. 2015). Despite the successful application of FePRBs in treating short-chain COCs, the dechlorination rate for chlorinated aromatics using only ZVI is slow because of their recalcitrant properties, with half-lives of days or longer as calculated by pseudo-first-order kinetics (Cheng et al. 2007). Several studies have exerted efforts to successfully enhance the dechlorination activity of Fe^0, but they only focused either on lessening the particles size to nanoscale (nZVI) (Cheng et al. 2007; Kocur et al. 2014) or on doping a second metal (e.g., Pd, Pt, Ni, and Cu) to form bimetals (Xu et al. 2012; Zhu and Lim, 2007). Limitations in field application remain because of the thermodynamically unstable nature of nZVI in solution and potential leaching problems of the second metal in bimetals (Huang et al. 2013; Zhang et al. 2013; Zhu and Lim, 2007).

In recent years, particulate-reinforced metal matrix composites (MMCs) have attracted considerable attention in industries application (Li et al. 2014; Zhong et al. 2011). MMCs are synthesized by embedding a reinforcing material into a monolithic metal matrix to improve the raw material properties. Those reinforcement materials include carbides (e.g., SiC, B_4C), nitrides (e.g., Si_3N_4, AlN), and oxides (e.g., $A1_2O_3$, quartz sand) (Li et al. 2014; Zhong et al. 2011). On the other hand, high-energy ball milling (BM) has been considered as a promising technology to homogeneously distributed reinforcement into metal matrix by repeated welding, fracturing, and rewelding of the solid materials (Li et al. 2009). Usually, organic process control agent (PCA, such as methanol, ethanol and hexane) was often added to prevent the excessive cold welding of the milled powders (Pilar et al. 2007). However, with the proceeding of the milling process, the organic PCA tended to decompose into carbon; moreover, previous studies indicated that the addition of the quartz sand would accelerate the carbonization process (Zhang et al. 2014). So, the produced MMC was often contaminated by the carbon when using quartz sand (SiO_2) as the reinforcement. As a result, the mechanically synthesized SiO_2 reinforced iron MMCs (SiO_2–Fe MMC) can form two interfaces: (i) iron–carbon (Fe–C) interface and (ii) Fe–SiO_2interface.

In the field of environmental technology, the Fe–C micro electrolysis has been widely used in wastewater treatment including dyes, landfill leachate, and coking wastewater (Zhang et al. 2015). When iron and carbon particles are in contact, massive microscopic galvanic cells will be formed spontaneously between the iron (anode) and carbon (cathode) (Zhang et al., 2015). Therefore, it is reasonable to expect that the SiO_2–Fe MMC produced by BM had faster corrosion ability than common ZVI or monolithic matrices because of the following reasons: (i) the formation of micro-electrolysis of Fe–C, (ii) the unstable interfacial phase between the reinforcement and the matrix, and (iii) microstructural changes of the iron during the milling process (Bakkar and Ataya, 2014). So the application of SiO_2–Fe MMC should be promising for removing COCs owing to its corrosion attribute. However, to our knowledge, SiO_2–Fe MMC has not yet to be used to explore the dechlorination of COCs.

Additionally, ZVI was often reported as a reductive material in previous decades, but the interfacial process involved in its dechlorination mechanism was not thoroughly investigated. For example, whether or not direct reduction by iron (Eq. (2)) or indirect reduction via atomic hydrogen (H^*) (Eq. (4)) is the underlying interfacial mechanism remains controversial. Some studies claimed that COCs are mainly reduced through direct electron transfer from Fe^0 to the adsorbed COCs; however, this viewpoint contradicts the results that the reductive dechlorination of COCs highly correlates with aqueous pH (Li and Farrell, 2000). Some reports proposed that dechlorination mainly relies on the highly active H^* formed through iron corrosion (Eq. (3)). They also suggested that the galvanic couple formed between iron and the doped metal is not the primary reason behind the rate enhancement for the bimetals (Cwiertny et al. 2007; Farrell et al. 2000b; Li and Farrell, 2000). In fact, an inherent relevance should exist between the iron corrosion rate and its dechlorination rate because iron was the ultimate electron donor (Eq. (1)).

$$Fe - 2e^- \rightarrow Fe^{2+} \tag{1}$$

$$RCl + 2e^- + H^+ \rightarrow RH + Cl^- \tag{2}$$

$$2H^+ + 2e^- \xrightarrow{Pd(Ni)} H^* \tag{3}$$

$$RCl + 2H^* \rightarrow RH + H^+ + Cl^- \tag{4}$$

In this work, a highly active particulate-reinforced Fe^0–MMC was conveniently synthesized through BM for the dechlorination of aqueous COCs. 2-chlorophenol (2-CP) was selected as the target pollutant because it has the highest water solubility (up to 28.5 g/L) among chlorophenol homologs and its single dechlorination product is phenol (Yang et al. 2014). SiO_2–Fe MMC was characterized through scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The effects of the initial pH and longevity of SiO_2–Fe MMC on dechlorination were also examined. A dechlorination mechanism was proposed for the reductive process at the quartz sand/iron interface.

2. Materials and methods

2.1. Materials

Iron powder (>99%, 100 mesh) and iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) were purchased from Aladdin, Inc. Analytical-grade quartz sand (>99%, 10–20 mesh), NaOH (98.0%), and HCl (36–38%) were obtained from Tianjing Tianli Chemical Reagent Co., Ltd., Tianjin Guangfu Technology Development Co., Ltd., and Dongguan Dongjiang Chemical Reagent Co., Ltd., respectively. 2-CP (99.9%) and phenol (99.9%) were procured from AccuStandard, Inc. HPLC-grade methanol and ethanol were acquired from TEDIA Co. All solutions were prepared using water with a resistance of 18.2 MΩ from a Millipore-Q system.

2.2. SiO_2–Fe MMC prepared using BM

BM was carried out with a planetary ball mill (QM-3SP04, Nanjing University Instrument Corporation) at a rotation speed of 550 rpm without inert gas protection. Stainless vials (100 mL) as grinding container were fitted with two different sizes of stainless steel balls: 16 large balls (Φ10 mm) and 100 small balls (Φ6 mm). For each BM process, the materials added into the vial included 156 g of steel balls and 5 g of iron and SiO_2 mixture. The weight ratio of iron powder to SiO_2 was 9:1. Ethanol (0.3 mL) served as a control agent during BM. To prevent spontaneous combustion of the energetic powder, the container was cooled down to room temperature before opening the container lid in air at the end of ball milling.

2.3. Characterization

Particle morphologies, elemental mapping of the select zone,