



Synergetic effect of pyrite on Cr(VI) removal by zero valent iron in column experiments: An investigation of mechanisms



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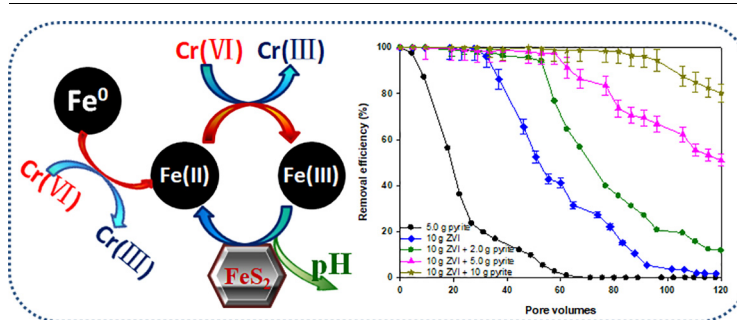
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HIGHLIGHTS

- Synergetic effect of pyrite on Cr(VI) removal by ZVI was observed.
- More Fe²⁺ was regenerated in the columns using ZVI/pyrite mixture.
- Pyrite could suppress the pH increase and retard surface passivation.
- The by-product SO₄²⁻ also contributed to the enhanced removal efficiency.
- Utilization efficiency of pyrite and ZVI was enhanced in the mixed system.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Pyrite
Enhance
Zero-valent iron
Reduction
Hexavalent chromium

ABSTRACT

In this work, a novel combination of pyrite with zero valent iron (ZVI) was used to enhance the efficiency of Cr(VI) removal in column experiments, simulating the operation of permeable reactive barriers (PRBs). The influence of pyrite dosage, initial pH, and the mixing manner on the removal efficiency were evaluated. The synergetic effect between pyrite and ZVI was found to contribute to enhanced Cr(VI) removal in column experiments using the ZVI/pyrite mixture, by which the Cr(VI) removal could be kept at > 90% for 50–100 PVs in comparison with ~30 PVs by using ZVI alone. The Cr(VI) removal efficiency by the ZVI/pyrite mixture was also much higher than the sum of those by ZVI and pyrite separately in the batch experiments. Mechanism investigations indicated that the synergetic effect was principally attributed to the more reactive Fe²⁺ regenerated in the columns using the ZVI/pyrite mixture, due to reaction of pyrite with Fe³⁺ produced during Cr(VI) reduction. In addition, pyrite could suppress the pH increase and retard the surface passivation of active materials. The by-product SO₄²⁻ from pyrite oxidation is also beneficial for enhanced removal efficiency. X-ray photoelectron spectroscopy (XPS) and Scanning electron microscopy-Energy dispersive spectrometry (SEM-EDS) studies confirmed the reduction of Cr(VI) into Cr(III), and that more pyrite was consumed in the Cr(VI) reduction by the ZVI/pyrite mixture. These findings are useful for developing cost-efficient methods for enhancing the removal of pollutants by ZVI-PRBs.

1. Introduction

Chromium (Cr) is a toxic pollutant that has often been discharged

into water from a variety of industries including electroplating, leather tanning, etc. Cr(VI) is the most toxic and mobile Cr species due to its high solubility in water, so most remediation technologies involve in

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<https://doi.org/10.1016/j.cej.2018.05.133>

Received 4 April 2018; Received in revised form 18 May 2018; Accepted 21 May 2018

Available online 23 May 2018

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transformation of Cr(VI) into relatively insoluble, immobile, and less harmful Cr(III) species [1–3]. In recent years, permeable reactive barriers (PRBs) using zero valent iron (ZVI) as active materials have been shown to be feasible in the remediation of many kinds of pollutants in groundwater, and laboratory studies, using both continuous column and batch experiments, have confirmed the good performance of ZVI technologies for Cr(VI) removal [4–6]. However, one of the main challenges facing the development of ZVI-PRBs for the remediation of pollutants in groundwater is the gradual increase of pH in the reaction media, which results in the passivation of ZVI surface by the deposition of iron (hydr)oxides [7,8]. Consequently, electron transfer from an Fe⁰ core to surface-adsorbed pollutants will be inhibited, and the reactivity and longevity of ZVI-PRBs will gradually decline. Over recent decades, many methods have been developed to overcome this drawback. The representative measures include employing bimetallic materials [9,10], and fabrication of supported nanoscale ZVI using adsorptive carriers such as clays [11,12] and carbons [13,14]. Generally, most of these carriers did not participate in the reduction of Cr(VI), which leads to an increased material cost or reduced hydraulic permeability.

Pyrite (FeS₂) is the most common species of iron sulfide minerals on Earth, and is widely distributed in anaerobic environments as the major product of sulfate reduction by bacteria [15,16]. Because of the reduction potential of both Fe(II) and S₂²⁻, pyrite has been applied to transform many oxidizing pollutants, such as chlorinated organic compounds [17,18], selenate and selenite [19], as well as Cr(VI) [20–22]. Similar to that observed on ZVI-PRBs, the rate of Cr(VI) reduction by pyrite is strongly dependent on pH [22–24]. However, pyrite possesses a special property that makes it distinct from ZVI: the reaction of pyrite with some oxidants (e.g. O₂ and Fe³⁺) is accompanied by H⁺ generation. For example, the reaction with O₂ (Eq. (1)) results in the generation of acid mine drainage that is considered to be an environmental issue related to pyrite [25,26], so pyrite has been thought to be an unwelcome waste in coal and metal mining industries.



This special property of pyrite can compensate H⁺ consumption during the reaction of ZVI with some pollutants, which inspires a novel idea: that ZVI and pyrite may be used together for Cr(VI) removal. In this way, pyrite may suppress the pH increase in reaction media, and in addition, pyrite can react with Fe³⁺ to produce more reactive Fe²⁺ [22]. Until now, the application of a ZVI/pyrite mixture for Cr(VI) removal has never been reported, and little is known about the underlying mechanisms. So, the objectives of this work include: i) validation of the performance of the ZVI/pyrite mixture for Cr(VI) removal in column experiments simulating the operation of PRB technology; ii) comparison of the efficiency of ZVI/pyrite mixture with ZVI or pyrite alone; and iii) exploration of the underlying mechanisms related to the synergetic effect of ZVI and pyrite for Cr(VI) removal.

2. Experimental

2.1. Materials

Zero valent iron (ZVI) powders (98.0% purity) were purchased from Aladdin Inc., and ground to a size between 200 and 300 meshes before use. Pyrite (FeS₂) was prepared by purification of pyrite ore purchased from Yingde, Guangdong Province of China. The ore was pulverized to the same size as the ZVI and rinsed with pure water and anhydrous ethanol successively. The clean ore was soaked in 0.1 mol/L HCl solution for 24 h, rinsed with pure water and acetone, successively, and finally freeze-dried in a vacuum to produce the pyrite sample. The pyrite sample is composed of 46.0% of Fe and 52.2% of S by mass, equivalent to 98.2% of pure FeS₂, according to the X-ray fluorescence (XRF) analysis (XRF-1800, Shimadzu, Japan). The X-ray diffraction (XRD) pattern of the pyrite sample agrees with that reported by JCPDS

(No. 06-0710). BET specific surface areas of the pyrite and ZVI samples were measured to be 0.183 and 0.415 m²/g, respectively, through N₂ adsorption at 77 K (Autosorb IQ, Quantachrome Instruments, USA).

Sand was collected locally in the Cao'e River (Zhejiang Province, China), sieved and rinsed with tap water. The sand, measuring between 20 and 80 mesh, was used in the column experiments, after soaking in 1.0 mol/L HCl solution for 12 h and rinsing with pure water (18.2 MΩ·cm) repeatedly until neutral. Cr(VI) solution was prepared by dissolving potassium dichromate (K₂Cr₂O₇) of analytical grade in 0.01 mol/L sodium chloride (NaCl) solution, and the initial pH (pH₀) of Cr(VI) solution was adjusted by adding 0.1 mol/L HCl or 0.1 mol/L NaOH solution.

2.2. Column experiments

The Cr(VI) removal studies were primarily carried out in columns packed with 100 g of a mixture of sand and active materials, each containing different doses of ZVI and pyrite. The column used was 25 cm long with a 2.2 cm internal diameter. Except in the column experiments with specifically designed packing manner, the sand and two active materials (ZVI and pyrite) were uniformly mixed and filled into the columns. The packed columns were purged with deoxygenated pure water in an upward manner for 24 h. Then the Cr(VI) solution of 20 mg/L (C₀) with pH₀ = 4.0 (unless otherwise specified in the experiments using different pH₀) was continuously fed in the column at a rate of 0.5 mL/min by a peristaltic pump, with a required time of ~1.0 h for one pore volume (PV). The feeding Cr(VI) solution flowed upward through the column, with the container of Cr(VI) solution being connected to pure nitrogen gas to retain an anaerobic condition. This procedure lasted for 120 PVs. The Cr(VI) concentrations of the effluent sample at time *t* (C_{*t*}, mg/L) were determined. The average removal efficiency of duplicates was calculated by the following equation:

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

2.3. Batch removal experiments

The batch experiments were conducted in a conical flask containing 150 mL of Cr(VI) solution (pH₀ = 4.0, C₀ = 20 mg/L) to evaluate the role of Fe(II) for Cr(VI) removal and to compare the reaction rate of various active materials. The Cr(VI) solution was deoxygenated by a N₂ stream for 20 min before the addition of ZVI (10.0 g/L), pyrite (5.0 g/L) and 1,10-phenanthroline (5.0 mmol/L), and was kept sealed with a stopper during the reaction. The experiments were carried out by putting the flask in a thermostatic shaker bath at 25.0 ± 0.1 °C, with a rotation speed of 200 rpm. At given time intervals, 1 mL of the solution was sampled with a syringe and filtered through a 0.22 μm membrane, and the Cr(VI) concentration (C_{*t*}, mg/L) in the supernatant was measured. For comparison studies, the batch removal experiments without the addition of 1,10-phenanthroline were conducted using the same procedure. The batch experiment results were obtained in triplicates.

2.4. Analysis methods

The Cr(VI) concentration in the effluent was measured by the diphenyl carbazide method on a UV-vis spectrophotometer (UV-2800, UNICO, China) at a wavelength of 540 nm [27]. The Fe²⁺ concentration in the effluent was measured with the phenanthroline photometric method [28]. The total Cr and Fe concentrations in the effluent were determined using an atomic absorption spectrometer (AA-7000, Shimadzu, Japan), and the detection limit for both Cr and Fe was 0.05 mg/L. The Cr(III) contents were estimated based on the difference between the total Cr and Cr(VI) concentrations, and the Fe(III) contents were calculated by the difference between the total Fe and Fe²⁺ concentrations. The concentration of SO₄²⁻ in the effluent was determined using

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