



Degradation of trichloroethene by nanoscale zero-valent iron (nZVI) and nZVI activated persulfate in the absence and presence of EDTA



Haoran Dong*, Qi He, Guangming Zeng, Lin Tang, Lihua Zhang, Yankai Xie, Yalan Zeng, Feng Zhao

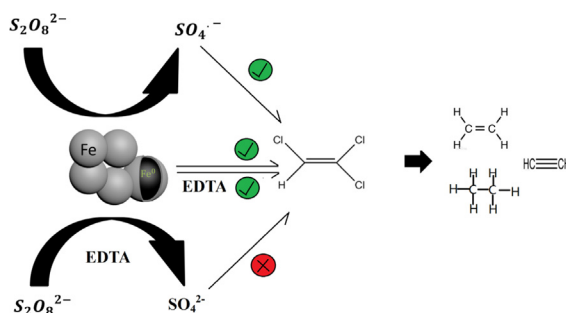
College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, China

Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha, Hunan 410082, China

HIGHLIGHTS

- The kinetics of TCE degradation by nZVI/nZVI activated persulfate were compared.
- The final products of TCE degradation in both the two systems were analyzed.
- The effects of EDTA on TCE degradation by nZVI and nZVI/persulfate were examined.
- Either positive or negative effect of EDTA was observed in different systems.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 11 November 2016

Received in revised form 18 January 2017

Accepted 30 January 2017

Available online 1 February 2017

Keywords:

Persulfate

Nanoscale zero-valent iron

EDTA

ISCO

Trichloroethene

ABSTRACT

This study investigated the degradation of trichloroethene (TCE) by nanoscale zero-valent iron (nZVI) w/o persulfate (PS) in the absence and presence of ethylenediaminetetraacetic acid (EDTA). In the absence of EDTA, the degradation of TCE obeyed the pseudo-first-order kinetics, and the rate constants increased exponentially with increasing molar ratio of PS and nZVI. Ethene was found to be the main reaction products in either the single nZVI system or nZVI/PS system. The presence of EDTA increased TCE degradation by nZVI in a short reaction period (within 360 min), whereas the TCE degradation was almost ceased after 1 day in a long-term (6 days) experiment, resulting in a lower TCE degradation than that in the absence of EDTA. However, EDTA drastically decreased TCE degradation in nZVI/PS system. The positive effect of EDTA in the nZVI system should be attributed to its possible inhibition of the precipitation of $\text{Fe}^{2+}/\text{Fe}^{3+}$, which could reduce the surface passivation of nZVI. On the other hand, the adverse effect should be due to the rapid corrosion of nZVI by EDTA and the generation of a large amount of Fe^{2+} ions in short time, which could possibly lead to a rapid consumption of sulfate radicals originally for the degradation of TCE.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

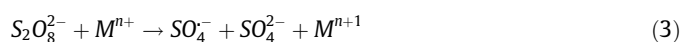
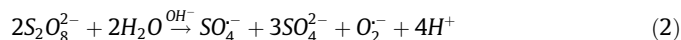
In recent years, the persulfate-based in-situ chemical oxidation (ISCO) technologies have been widely applied in the remediation of contaminated soils and groundwater [1–4]. Activation of persulfate

(PS) can be achieved by a variety of reactions, including heat, base, or transition metals (Eqs. 1–3) [5–8]. Sulfate radicals ($\text{SO}_4^{\cdot-}$) are generated from the activation of persulfate, and they are very reactive with a wide range of contaminants, such as trichloroethene (TCE) and many other halogenated organic contaminants (HOCs) [9].

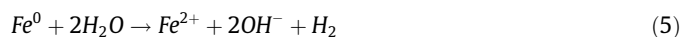


* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, China.

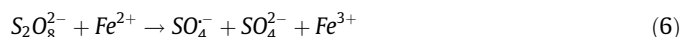
E-mail address: dongh@hnu.edu.cn (H. Dong).



Recently, zero-valent iron (ZVI) and nanoscale zero-valent iron (nZVI) have been reported to be able to activate persulfate for the degradation of contaminants [10–17]. Firstly, Fe⁰ corrosion occurs via reaction with persulfate (Eq. (4)) [10] and can also be initiated by waters under anaerobic conditions (Eq. (5)) [18–20], resulting in the release of Fe²⁺:



Then, the Fe²⁺ ions released from Fe⁰ corrosion can activate persulfate to generate sulfate radicals (Eq. (6)) [10,13,19,20]:



However, Fe⁰ corrosion usually occurs rapidly and can produce a large amount of Fe²⁺ ions in a short time. The high Fe²⁺ concentration in the system of persulfate activation could possibly induce the scavenging of sulfate radicals (SO₄^{·-}), and thus result in the decrease in the removal of contaminants (Eq. (7)) [10,13,19]:



To prevent the sulfate radical scavenging due to the presence of excess Fe²⁺, Fe²⁺ can be chelated by some organic ligands to form a stable metal chelate, which is effective in activating persulfate [21–24]. Among a variety of chelating agents, ethylenediaminetetraacetic acid (EDTA) is most widely used in industrial processes such as metal finishing, textile manufacturing, pulp and paper production [25–27]. EDTA is a well-known chelating agent with six potential sites (four carboxyl and two amino groups) available for binding with metal cations. It has been successfully used as a chelating agent to avoid the rapid conversion of Fe²⁺ to Fe³⁺ and to provide a Fe²⁺–Fe³⁺ redox couple to facilitate persulfate activation [23]. Besides, it was reported that the organic ligands (e.g., EDTA) could prevent the formation of passivation layer of Fe³⁺ (hydro)oxides on the external surface of microscale ZVI through chelating of EDTA with Fe³⁺, which maintained the exposure of active sites on the ZVI surface [25]. Accordingly, it is expected that EDTA could influence the performance of both nZVI and nZVI/persulfate systems. However, no studies have yet systematically investigated the influence of EDTA on the degradation of organic contaminants by nZVI or nZVI activated persulfate.

In this study, we used nZVI to activate persulfate and examined its potential environmental application for the degradation of trichloroethene (TCE). EDTA as a chelating agent was added into the system to explore its influence on the removal of TCE. The specific research objectives were to (i) quantify the reaction kinetics and main products in the system of nZVI w/o persulfate; (ii) investigate the influence of EDTA on the degradation of TCE by single nZVI or nZVI activated persulfate; and (iii) gain insights into the reaction rates, pathways and underlying mechanisms of TCE degradation in different systems.

2. Experimental section

2.1. Chemicals and Materials

All chemical reagents used in this study, including sodium persulfate, TCE, *cis*-1,2-dichloroethene (*c*-DCE), *trans*-1,2-dichloroethene (*t*-DCE), 1,1-dichloroethene (1,1-DCE), vinyl chloride (VC), methanol, hexane, K₂Cr₂O₇, HCl, NaOH and EDTA were analytical reagent grade and used without further purification.

Pristine nZVI particles (Nanofer 25, produced from nanosized ferrihydrite) were purchased from the NANOIRON[®] Company (Czech Republic, EU). The mixed gas standards (8.10% acetylene, 12.3% ethylene, 3.11% ethane; argon was used as the balance gas) were prepared using gasses (the purities of these gases were >99.99%) purchased from Airchem Specialty Gases & Chemicals Co., Ltd. (Dalian, China). The chemical stock solutions were prepared by dissolving chemicals into ultrapure water. Ultrapure water was purged with argon for 30 min prior to usage.

2.2. Degradation of TCE

The TCE degradation was tested in a series of duplicated batch experiments. Batch experiments were conducted in 43 mL serum vials capped by Teflon Mininert valves. Each vial contained 20 mL of 2 g/L nZVI w/o EDTA (at molar ratio of 1:1) suspension (with 23 mL of headspace). All the samples were prepared in the anaerobic glovebox so the vial headspace was initially filled with argon. TCE degradation was initiated by spiking 0.1 mL of a TCE stock solution (48 g/L TCE in methanol) into the nZVI or nZVI-EDTA suspension, resulting in an initial TCE concentration of 240 mg/L at pH 7.3. After complete mixing, 0.3 mL of 23.5 M persulfate solution was quickly added into the vials. Then, the vials were sealed and kept shaking at 250 rpm on a reciprocating shaker at room temperature (22 ± 1 °C). Control experiments were also carried out with only persulfate or EDTA added into the TCE solutions.

During the reaction, 0.1 mL of the aqueous sample was withdrawn using a 250 µL gastight syringe at selected time intervals. The sample was then transferred into a 2 mL GC (gas chromatograph) vial containing 1 mL of hexane for the extraction of TCE. After phase separation, the TCE in the extract was analyzed by using a Shimadzu QP2010 ultra GC equipped with a mass spectrometer (MS) and a DB-5 capillary column. The gas samples (100 µL) in the headspace were withdrawn using a tight gas syringe for the analysis of the main gas products (using Shimadzu QP2010 ultra GC-MS). The scan range of MS was from 2 to 100 *m/z*, where the sum of these ions is referred to as the total ion count (TIC). Quantification of the gas products was performed by integrating the TIC and comparing the peak areas with the calibration curves obtained with the mixed gas standards (8.10% acetylene, 12.3% ethylene, 3.11% ethane; argon was used as the balance gas).

2.3. Removal of Cr(VI)

To compare the removal efficiency of Cr(VI) by nZVI in the absence and presence of EDTA, the kinetics experiments were conducted using a 500 mg/L nZVI suspension and 50 mg/L Cr(VI) in deionized water in the absence and presence of EDTA at pH 7.3. The final solutions (200 mL) were placed on a rotary shaker at 22 ± 1 °C and 250 rpm. At selected time intervals, the mixed suspensions were sampled and filtered immediately (through 0.45 µm membranes) for the measurement of Cr(VI) and soluble Fe concentration.

The Cr(VI) concentrations were measured following the 1,5-diphenylcarbazide method with a UV-visible spectrophotometer (UV-2550) at wavelength of 540 nm [28]. The concentration of soluble Fe ions in the samples was measured following a phenanthroline spectrophotometry method with UV-visible spectrophotometer (UV-2550) at wavelength of 510 nm [29]. The EDTA concentration was measured following the Standard Test Method for Tetrasodium Salt of EDTA in Water (ASTM D3113-80). Besides, the EDTA degradation was also determined by the measurement of the total organic carbon (TOC) with TOC-V_{CPH/CPN} (Shimadzu Corporation).

Download English Version:

<https://daneshyari.com/en/article/4763331>

Download Persian Version:

<https://daneshyari.com/article/4763331>

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