The effects of flow rate and concentration on nitrobenzene removal in abiotic and biotic zero-valent iron columns

Weizhao Yin [a,b,c,d,e], Jinhua Wu [a,b,c,d,*], Weilin Huang [a,f], Yongtao Li [g], Gangbiao Jiang [h]

[a] School of Environment and Energy, South China University of Technology, Guangzhou 510006, PR China
[b] The Key Laboratory of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, PR China
[c] The Key Laboratory of Environmental Protection and Eco-Remediation of Guangdong Regular Higher Education Institutions, PR China
[d] Guangdong Environmental Protection Key Laboratory of Solid Waste Treatment and Recycling, PR China
[e] Department of Plant and Environmental Sciences, Faculty of Life Sciences, University of Copenhagen, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark
[f] Department of Environmental Sciences, Rutgers, The State University of New Jersey, New Brunswick, NJ 08901, United States
[g] School of Natural Resources and Environment, South China Agricultural University, Guangzhou 510642, PR China
[h] School of Materials and Energy, South China Agricultural University, Guangzhou 510642, PR China

HIGHLIGHTS

- Bio-iron column was employed to treat nitrobenzene-contaminated groundwater.
- Increasing NB loading at higher flow rate and NB concentration were tested.
- Better performance was achieved in biotic ZVI column.
- Co-precipitation and reduction removal were the two major mechanisms for NB removal.

GRAPHICAL ABSTRACT
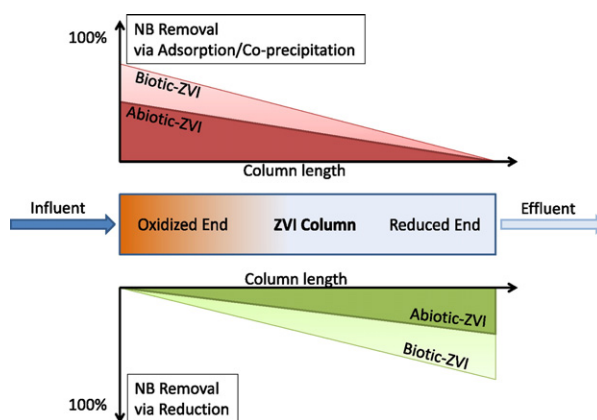
ARTICLE INFO

ABSTRACT

This study investigated the effects of varying nitrobenzene (NB) loadings via increasing flow rate or influent NB concentration mode on the removal efficiency in zero-valent iron (ZVI) columns sterilized (abiotic) or preloaded with acclimated microorganisms (biotic). It was shown that physical sequestration via adsorption/co-precipitation and reductive transformation of NB to aniline (AN) were the two major mechanisms for the NB removal in both abiotic and biotic ZVI columns. The NB removal efficiency decreased in both columns as the flow rate increased from 0.25 to 1.0 mL min^{-1} whereas the AN recovery increased accordingly, with relatively high AN recovery observed at the flow rate of 1.0 mL min^{-1}. At the constant flow rate of 0.5 mL min^{-1}, increasing influent NB concentration from 80 to 400 µmol L^{-1} resulted in decreasing of the overall NB removal efficiency from 79.5 to 48.6% in the abiotic column and from 85.6 to 62.5% in the biotic column. The results also showed that the sequestration capacity and chemical reduction capacity were respectively 72% and 157.6% higher in the biotic column than in the abiotic column at the same tested hydraulic conditions and NB loadings. The optimal flow rates and influent NB concentrations were at 0.5 mL min^{-1} and 80 µmol L^{-1} for the abiotic column and

* Corresponding author at: School of Environment and Energy, South China University of Technology, Guangzhou 510006, PR China.
E-mail address: jinhuawu@scut.edu.cn (J. Wu).

2.0 mL min-1 and 240 μmol L^{-1} for the biotic column, respectively. This study indicated that microorganisms not only enhanced overall reduction of NB, but also facilitated NB sequestration within the porous media and that the optimal loading conditions for overall removal, sequestration, and reduction of NB may be different. Optimal operation conditions should be found for preferred sequestration or transformation (or both) of the target contaminants to meet different goals of groundwater remediation with the ZVI-PRB systems.

1. Introduction

Among various remediation technologies (Anotai et al., 2009, Carlos et al., 2008, Zhao and Ma, 2008), iron-based permeable reactive barriers (PRBs) (Henderson and Demond, 2007, Cundy et al., 2008, Westerhoff, 2003) have been shown to be effective and efficient for the removal of organic pollutants including nitrobenzene (NB) from groundwater. Zero-valent iron (ZVI) was firstly proposed to be the reactive material of PRB for the removal of chlorinated chemicals from groundwater in 1990s because of its sufficiently high reducing capacity (Agrawal and Tratnyek, 1995, Yin et al., 2012a). In the Fe^0–H$_2$O system, pollutants can be removed via chemical reduction by accepting electrons from Fe^0 and Fe^{2+} (surface-bounded or structural) oxidation (White and Peterson, 1996). It is also shown that contaminants can be either removed primarily through adsorption and co-precipitation by secondary iron corrosion products (e.g., goethite, lepidocrocite and magnetite) (Noubactep, 2009, 2010), or enmeshed/encapsulated within the matrix of iron corrosion products. These adsorbed or encapsulated pollutants can be eventually sequestered in the growing oxide film at the surface of iron particles (Noubactep, 2011a). Even though the co-precipitation mechanism could beneficially contribute to the overall efficiency of contaminant removal, the passive corrosion products might adversely suppress the reactivity and permeability of the PRB system. In practice, there may be an optimal condition at which a maximal removal of pollutant can be achieved due to both physical sequestration and chemical reduction mechanisms. One of the two objectives of this study was to search for such an optimal condition with extensive laboratory tests using flow-through column systems.

It is expected that cathodic hydrogen generated in the anaerobic iron corrosion process can serve as a potential electron donor for various types of autotrophic bacteria. Several facultative hydrogen-consuming bacteria such as methanogenic, acetogenic, sulfate-reducing, denitrifying, and iron-reducing bacteria are able to degrade chlorinated hydrocarbons and nitro aromatics by either co-metabolism or using the contaminants as electron donor (Weathers et al., 1997, Oh et al., 2001, Field and Sierra-Alvarez, 2004). The presence of microorganisms in iron barriers could change the physic-chemical circumstances of the Fe^0–H$_2$O system. For example, hydrogen utilizers can consume entrapped hydrogen gas that would otherwise ameliorate hydraulic conductivities of the iron barriers and would provide stable hydrogen partial pressures for relevant contaminant transformation (Weathers et al., 1997). The existence of iron-reducing bacteria can clean up iron surface by reducing the ferric iron corrosion products to ferrous iron compounds (Gerlach et al., 2000, Huang and Zhang, 2006). In addition, iron-reducing and sulfate-reducing microorganisms usually generate highly reactive precipitates such as iron sulfides and green rusts (GRs). Unlike Fe^{III} bearing oxides, these iron sulfides and GRs can further react with chlorinated compounds (Van Nooten et al., 2008) or can serve as conductors for electron transfer between ZVI and contaminants (Karri et al., 2005). Hence, additional microorganisms might improve the performance of iron-based PRB and prolong its lifetime for groundwater remediation.

The beneficial effects of microorganisms presented in a Fe^0–H$_2$O system were evaluated in both batch and column experiments of our previous studies (Yin et al., 2012b, Wu et al., 2013, Yin et al., 2015). These studies, along with other published work, indicated that contaminant removal efficiency and life-span of ZVI materials could be enhanced via the following interactions between iron and microorganisms: i) reduction of Fe^{3+} to Fe^{2+} by certain iron-reducing bacteria that can facilitate electron transfer and iron redox cycling in the Fe^0–H$_2$O system; ii) formation of highly reactive iron precipitates such as iron sulfides and GRs in the bio-iron system; iii) biotic reduction of pollutants as iron serves as the electron donor. It is apparent that, in addition to the physical sequestration and chemical reduction mechanisms operating in abiotic Fe^0–H$_2$O systems, multiple physicochemical and biological mechanisms coexist in biotic Fe^0–H$_2$O systems. The second objectives of this study was thus to search for optimal conditions at which a maximal removal of pollutant can be achieved in biotic Fe^0–H$_2$O column systems.

It is known that pollutant removal efficiency in porous media is highly dependent upon the transport processes (i.e., flow velocity of fluid) and pollutant concentrations. In this study, incremental increases of the flow rate and the influent concentration of NB, the target pollutant, were chosen for evaluating the NB removal efficiencies in both biotic and abiotic ZVI columns. The recovery efficiencies of aniline (AN), the product of NB reduction via both biotic and abiotic processes, were also quantified for the contribution from biotic and abiotic reduction processes to the overall removal of NB in the column systems. The overall NB removal via both adsorption/co-precipitation and NB reduction under different conditions were compared for better understanding of NB removal mechanisms and the optimizing engineering design of ZVI-based PRB systems.

2. Materials and methods

2.1. Chemicals, microorganisms and groundwater preparation

We used NB as the target pollutant because it is widely found in polluted groundwater systems (Haigler and Spain, 1991) and because it is listed in many countries as a priority pollutant due to its widespread, toxicity and persistence in the environment (Latifoglu and Gurol, 2003). It is used for manufacturing aniline, pharmaceuticals, dyes and pesticides (Contreras et al., 2001) and is also used as an industrial solvent during production of paint, shoe, floor and metal polishes (Kuşçu and Sponza, 2009). Both NB and AN used in this study were purchased from Aladdin-reagent Company (Shanghai, China). The granular iron (1 mm) and coarse sand (1–2 mm) were obtained from Guangdong Metals Company and Yuexiu Company (Guangzhou, China), respectively. They were washed with 1 N HCl for 30 min, and then rinsed with deoxygenated deionized water until neutral, freeze-dried and stored in anaerobic containers before use. All other chemicals were analytical grade and obtained from Guangzhou Chemical Reagent Factory.

Before the column study, a mixed culture of NB-reducing bacteria was acclimated using NB containing water and following the method described in a previous study (Yin et al., 2015). The mixed culture was collected from the secondary sedimentation tank of a local sewage treatment plant, and then was transfer into a 5 L anaerobic bioreactor for acclimation. Before the acclimation process, the initial suspended solids (SS) and granular iron dosage of 5 g L^{-1} and 10 g L^{-1}, respectively. The feeding NB concentration was 50 mg L^{-1}, along with a nutrient medium containing glucose (150 mg L^{-1}), NH$_4$Cl (300 mg L^{-1}), K$_2$HPO$_4$ (175 mg L^{-1}), MgSO$_4$·7H$_2$O (200 mg L^{-1}), CaCl$_2$ (100 mg L^{-1}), NaHCO$_3$ (1500 mg L^{-1}) and trace metals (CoCl$_2$·5H$_2$O, CuCl$_2$·2H$_2$O, MnCl$_2$·4H$_2$O, NiCl$_2$·6H$_2$O, NH$_4$MO$_3$ and ZnSO$_4$, each at 0.5 mg L^{-1}). The hydraulic retention time was set at 1 day and NB and