Chemosphere 193 (2018) 702–710

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Effect and mechanism analysis of MnO_2 on permeable reactive barrier (PRB) system for the removal of tetracycline

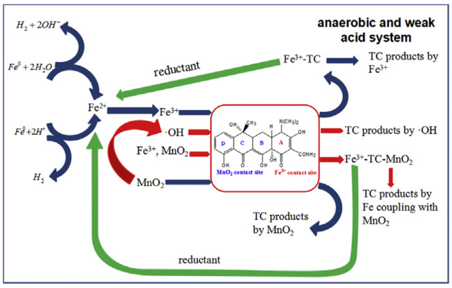
Guihua Dong [a], Lihui Huang [a, *], Xueyuan Wu [a], Chuang Wang [a], Yangyang Liu [a], Gaofeng Liu [a], Lisha Wang [a], Xiaowei Liu [a], Haibing Xia [b, **]

[a] *Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan, 250100, China*
[b] *State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, China*

HIGHLIGHTS

- MnO_2 could accelerate the transformation of Fe^{2+} into Fe^{3+} and it also could combine with Fe^{3+} to degrade TC.
- Hydroxyl radicals (·OH) were produced in this process, which played a key role in the degradation of TC.
- A-ring of TC was the main reaction site for interaction with Fe^{3+} and the BCD rings were crucial for interactions with MnO_2.
- The ring structure of TC was opened, and low-molecular-weight compounds were produced in ZVI-MnO_2 PRB system.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 July 2017
Received in revised form
14 November 2017
Accepted 16 November 2017
Available online 17 November 2017

Handling Editor: Hyunook Kim

Keywords:
Tetracycline
MnO_2
PRB
Reaction mechanism
Degradation products

ABSTRACT

Effect of manganese dioxide (MnO_2) on tetracycline (TC) removal/degradation in zero-valent iron (ZVI) based permeable reactive barrier (PRB) system was investigated. To analyze the role of MnO_2, three different PRB columns packed with ZVI, ZVI and a layer of MnO_2, and MnO_2 were set up to investigate the removal effect and reaction mechanism of ZVI coupling with MnO_2 on TC removal, respectively. The results show that the removal efficiencies of three PRB columns are 65%, 85%, and 50%, respectively. MnO_2 could accelerate the transformation of Fe^{2+} into Fe^{3+} and combine with Fe^{3+} to degrade TC in different reaction sites in the ZVI-MnO_2 PRB system. Hydroxyl radicals (·OH) were produced in this process, which contributed to about 58.3% for the TC degradation. The UV–Vis spectrum demonstrated that A ring of TC was the main reaction site for interaction with Fe^{3+} and the BCD rings were crucial for interactions with MnO_2. On the basis of intermediates identified by LC-ESI-MS, the ring structure of TC was opened, and low-molecular-weight compounds were produced in ZVI-MnO_2 PRB system.

1. Introduction

Tetracycline (TC) has been widely used as an antibiotic in medication, animal husbandry and food industry (Daughton and

---

* Corresponding author.
** Corresponding author.
E-mail addresses: 963722867@qq.com (G. Dong), huanglihui409@126.com (L. Huang), 137900873@qq.com (X. Wu), 372651040@qq.com (C. Wang), 1160043323@qq.com (Y. Liu), ttt234@126.com (G. Liu), 531858952@qq.com (L. Wang), 840667381@qq.com (X. Liu), hbxia@sdu.edu.cn (H. Xia).

https://doi.org/10.1016/j.chemosphere.2017.11.085
0045-6535/

Ternes, 1999; Liu et al., 2013; Teka et al., 2015). In recent years, overuse of TC and presence of TC in environmental media (e.g., soil, surface water, and groundwater) are of great concern. TC can enter crops in many ways, including irrigation and application of manure (Kumar et al., 2005; González-Pleiter et al., 2013; Li, 2014). It has been reported that TC concentrations were around 0.15 μg L^{-1} in polluted groundwater and surface water (Lindsey et al., 2001). Removal of TC from contaminated aquifers that are being used as sources of drinking water and/or irrigation is very important to ensure food security.

There are many alternatives to remove organic pollutants from groundwater, including pump-and-treat, permeable reactive barriers (PRBs), air sparging (AS), chemical oxidation (ISCO), electrokinetics remediation and bioremediation. PRB technology, as an in-situ approach to remedy contaminated groundwater aquifers, has been widely studied and used in the past two decades (Statham et al., 2016) because it is convenient, effective, inexpensive and durable (Thiruvenkatachari et al., 2008; Obiri-Nyarko et al., 2014). It can remove inorganics (e.g., heavy metals, nitrate, and sulfate) and organics (e.g., halogenated hydrocarbons, petroleum hydrocarbons and antibiotics) in aquifers. Due to the characteristics of non-toxic, abundant, inexpensive, and having a high reduction potential ($E^0 = -0.44$ V), zero-valent iron (ZVI) has been widely studied and employed as the main reactive component of many PRBs (Henderson and Demond, 2007; Fu et al., 2014). However, some researchers reported weakness of ZVI-based PRB in their durability to maintain its permeability and effectiveness in contaminant removal (Fu et al., 2014). ZVI could be readily oxidized to form FeO(OH) or $Fe(OH)_3$ solids, with increases in alkalinity and iron ion concentrations in the pore fluid, that would result in clogging of the media and masking ZVI to reduce its reactivity (Parbs et al., 2007). To overcome these limitations, pumice, activated carbon, metal oxides and other materials have been added to ZVI-based PRB as additives (Moraci and Calabrò, 2010; Obiri-Nyarko et al., 2014; Priebe and Lee, 2014). However, reaction mechanism and degradation pathways of TC removal using metal oxides assisted ZVI-based PRB have not been delineated.

Manganese is a transition metal and one of the common elements in the earth crust. Via adsorption, catalysis, and redox activities, manganese dioxide (MnO_2) plays an important role in transport and transformation of organic pollutants in groundwater aquifers (Jiang et al., 2017). MnO_2 also participates in oxidation of aromatic amines (Li et al., 2003) and antibiotics in the soil and aquatic environmental media (Zhang et al., 2008). It can also function in a galvanic cell with iron to promote electron transfer on the surface of iron to alleviate the passivation.

In this study, we constructed laboratory columns to emulate PRBs, and compared the performances of different reactive media on removal of TC. The overall objective was to investigate degradation and removal mechanism of TC in the ZVI-based PRB containing MnO_2. Besides, we also studied the role of MnO_2 in ZVI PRB system in a weak acidic groundwater environment (pH = 6–6.5) for one month. Furthermore, transformation products were identified and degradation pathways of TC were proposed based on the results of liquid chromatography electrospray ionization mass spectrometry in tandem (LC-ESI-MS).

2. Materials and methods

2.1. Chemicals

Tetracycline hydrochloride (97.2% purity) was obtained from MDBio, Inc. (Qingdao, China), TC structures was composed of connected ring systems with multiple ionizable functional groups (denoted as A, B, C and D from right to left in Fig. 1). Iron filings (particle size = 1–3 mm) from Integrity of Metal Material Limited Co. (Hebei, China) was used with ZVI content ≥ 99.9%. MnO_2 (size = 0.5–2 mm) was purchased from Beijing Hongdaboyu Technology Co., Ltd (Beijing, China). MnO_2 was made following a national standard method (GB/T476-2008AR). Buffered solutions 2-(N-morpholino) ethanesulfonic acid (MES) and 4-morpholine propanesulfonic acid (MOPS), purchased from Shanghai Yuanye Bioscience Technology Limited Co. (Shanghai, China), were used to maintain the solution pHs within the range of 5.5–6.5 and 6.5–7.5, respectively. All the other chemicals were used as received without further purification.

2.2. Experimental setup and operation

Three Plexiglas columns (length = 20.0 cm; inner diameter = 4.0 cm) were packed with different types of media and they worked as the PRBs in this study (Fig. 2). For each column, water entered from the bottom and exited from the top. The first column was picked with 300 g quartz sand (particle size = 1–3 mm) and 120 g ZVI; the second 300 g quartz sand, 100 g ZVI and 3.4 g MnO_2 (the volume ratio of ZVI to MnO_2 = 5: 1); and the third column 300 g quartz sand and 20.4 g MnO_2. Peristaltic pumps (BT 100-2 J drive, DG-4 pump head, Baoding Longer Precision Pump Co., Ltd., Baoding, China) were used in the experiments to provide continuous feed to the columns. The influent concentration of TC was 20 mg L^{-1}, and the solution pH was in the range of 6–6.5. The flow rate was set to be 3.3 mL min^{-1} and the corresponding hydraulic detention time was 72 min. The experiments were conducted under room temperatures (22–25 °C).

2.3. Analysis of water samples

Effluent samples were first filtered through 0.45 μm membrane filters and the TC concentrations were analyzed using a Knauer high performance liquid chromatography (HPLC) instrument (Shimadzu, Japan). Total organic carbon (TOC) concentrations were measured by the burning oxidation-non-dispersive infrared absorption method using a Shimadzu TOC-VCPH analyzer (Shimadzu, Japan).

Intermediates of TC were analyzed by an LC-ESI-MS, a Thermo Ultimate 3000 HPLC system with a Thermo LCQ Fleet mass spectrometer (Thermo Fisher, USA) and an Agilent C18 HPLC column (2.1 × 150 mm, 2.1 μm). The mobile phase consisted of 15% water and 85% formic acid aqueous solution (1‰) at a steady flow rate of 0.2 mL min^{-1}. MS analyses were conducted in a negative ionization mode, over the full scan acquisition of m/z ranged from 100 to 500. An electrospray interface (ESI) was used with the following conditions: the spray voltage = 4 kV and the ion-transfer capillary temperature = 320 °C.

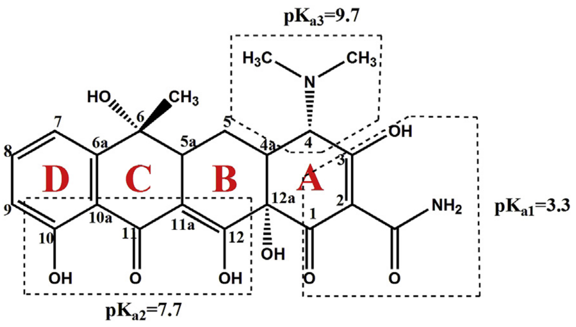


Fig. 1. Structures and properties of TC.