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# Degradation of sulfamethoxazole by a heterogeneous Fenton-like system with microscale zero-valent iron: Kinetics, effect factors, and pathways

Juanshan Du, Wanqian Guo\*, Xiaofan Li, Qi Li, Bing Wang, Yilin Huang, Nanqi Ren\*

State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, PR China

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## ABSTRACT

Five commercial microscale zero-valent iron (mZVI) samples showed different reactivity in sulfamethoxazole (SMX) removal in the presence of  $H_2O_2$ , which was independent of respective iron surface area but was consistent with the dissolved iron releasing rate. Of five mZVI samples, mZVI<sub>VF2</sub> possessed the highest reactivity in  $H_2O_2$  and the mZVI<sub>VF2</sub>/ $H_2O_2$  system could remove 97.9% SMX at room temperature within 10 min. The degradation curve of SMX by mZVI/ $H_2O_2$  at  $pH_{ini}$  3.0 could be divided into three phases: a lag phase, a rapid degradation phase, and a final stationary phase. Effects of  $pH_{ini}$ , mZVI loading, SMX concentration, and  $H_2O_2$  concentration on SMX degradation by mZVI/ $H_2O_2$  were analyzed. Removal rates of SMX by mZVI/ $H_2O_2$  dropped sharply upon increasing  $pH_{ini}$ . Increasing dosages of  $Fe^0$  ranged from 25 to 75 mg/L and  $H_2O_2$  at low concentrations (below 0.5 mM) both enhanced SMX degradation, but a higher concentration of  $Fe^0$  and  $H_2O_2$  also quickly decreased oxidative efficiency of SMX. Increasing dosages of SMX within the range of 5–100  $\mu$ M progressively decreased the oxidation rates of SMX by mZVI/ $H_2O_2$ . Furthermore, three degradation pathways of SMX by mZVI/ $H_2O_2$  process were proposed based on the combination of theoretical calculations and intermediates identification.

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## 1. Introduction

Antibiotics, an important category of pharmaceuticals and personal care products (PPCPs) [1], have been frequently detected in various environment mediums by increasing researches from different countries [2–4] and have become emerging contaminants in drinking water and wastewater [5]. Chinese antibiotics consumption has been widely used to treat and prevent bacterial diseases such as coccidiosis, diarrhea, and gastroenteritis since 1930s [6,7]. Generally, about 15.2%, 99.9%, and 28.8% of total sulfamethoxazole (SMX) usages have been excreted in unchanged form and glucuronide conjugates by human, pigs, and chicken and then released to the aquatic environments following the effluent and sludge from domestic wastewater treatment plants (WWTPs), hospitals, and livestock farms [6]. And conventional WWTPs usually exhibit a low removal rate of SMX between 20% and 30% for its antibacterial nature [8]. As a result, the widespread occurrence of SMX in WWTPs effluents and surface water has been reported in continuance by different countries and regions [9]. In China, the measured concen-

tration of SMX in different aquatic environments usually maintains at the ng/L to  $\mu$ g/L level which cannot directly show toxicity or side effects on human health [6]. But aquatic organisms can also been adversely affected by concentration addition toxicity [10]. Seriously, increasing bacterial resistance and resistant genes generated by residual SMX have raised serious concerns from the general public and bring a new challenge for traditional water treatment technologies [6]. Thereby, it is essential to control the concentration of SMX in aquatic environments by developing efficient technologies.

Since 1890s, Fenton-based advanced oxidation processes (AOPs) as alternative strategies for industrial and domestic wastewater treatment have been widely investigated the degradation of aquatic emergency organic pollutants including SMX [11,12]. Classical Fenton process ( $Fe^{2+}/H_2O_2$ ) has present potential efficiencies on rapidly reducing and even mineralizing SMX for the generation of highly reactive hydroxyl radicals ( $\bullet OH$ ), but a higher removal rate of SMX requires the continuous addition of dissolved  $Fe^{2+}$  in a homogeneous system. In the past few years, zero-valent iron (ZVI or  $Fe^0$ ) in lieu of  $Fe^{2+}$  could induce heterogeneous Fenton-like reactions in the presence of  $H_2O_2$  which also exhibited similar degradation effectiveness to contaminants due to reduction by  $Fe^0$ , oxidation by  $\bullet OH$  and co-precipitation–sequestration upon formation of iron corrosion products (ICPs) [13–17].

\* Corresponding authors.

E-mail addresses: [guowanqian@hit.edu.cn](mailto:guowanqian@hit.edu.cn), [hitgwq@yeah.net](mailto:hitgwq@yeah.net) (W. Guo), [nrq@hit.edu.cn](mailto:nrq@hit.edu.cn) (N. Ren).

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However, reactions between  $\text{Fe}^0$  and  $\text{H}_2\text{O}_2$  are slow for the low reactivity of conventional  $\text{Fe}^0$  powder and the deposition of oxide layers on the surface of  $\text{Fe}^0$  inhibiting the release of  $\text{Fe}^{2+}$  [18]. Nanoscale zero-valent iron (nZVI) is employed to enhance  $\text{Fe}^0$ -based Fenton like reactions, but the synthesis of nZVI has been considered too expensive for the costly reagents and complex processes [19,20]. Besides, nZVI surface passivation was carried out before handling due to its high reactivity, and the potential toxicity of nZVI and derivatives has arisen much concern [19]. Lee et al. [21] have reported that nZVI could rapidly inactivated *Escherichia coli* in aqueous solution and a strong linear correlation between log bactericidal inactivation and nZVI dose is found under deaerated conditions. Comparing to nZVI, microscale zero-valent iron (mZVI) shows lower reactivity which is also much higher than conventional iron powder or filings. More importantly, it can avoid the barriers of nZVI mentioned above in water treatment. Recently, Ghauch et al. [22,23] have reported that mZVI could be successfully utilized in other AOPs based on ultrasonic  $\text{H}_2\text{O}_2$  or persulfate to degraded PPCPs, thus the application of mZVI in AOPs might be effective in contaminants removal.

Therefore, in the present study, SMX was chosen as the target contaminant to investigate effects of selected factors on SMX degradation by  $\text{Fe}^0/\text{H}_2\text{O}_2$ . The objectives of this study are to (1) compare removal rates of SMX in Fenton-like systems with mZVI of different origin, (2) assess the effects of initial pH ( $\text{pH}_{\text{ini}}$ ), SMX concentration, mZVI loadings,  $\text{H}_2\text{O}_2$  concentration on SMX degradation by mZVI/ $\text{H}_2\text{O}_2$ , and (3) clarify SMX degradation pathways in the mZVI/ $\text{H}_2\text{O}_2$  system.

## 2. Materials and methods

### 2.1. Materials

SMX of 99% purity was purchased from Sigma-Aldrich Co. Ltd. (St. Louis, MO, USA).  $\text{H}_2\text{O}_2$  (30%, v/v) was obtained from Sinopharm Chemicals Reagent Co., Ltd. (Shanghai, China). Four mZVI samples including mZVI<sub>YF1</sub>, mZVI<sub>YF2</sub>, mZVI<sub>HT</sub>, mZVI<sub>SA</sub>, and mZVI<sub>GY</sub> samples of 99% purity were supplied by Shanghai Yunfu Nanotechnology Co. Ltd. (Shanghai, China), Shanghai Haotian Nanotechnology Co. Ltd. (Shanghai, China), Sigma-Aldrich Co. LCC., and Sinopharm Chemicals Reagent Co., Ltd., respectively. All chemicals were used without further purification and solutions were prepared with deionized (DI) water.

### 2.2. Batch experiments

The batch experiments were conducted in an organic glass reactor (14 cm height  $\times$  10 cm diameter) open to the air at  $20 \pm 1.0$  °C, and 0.5 L solution containing SMX was completely mixed by digital display electric blender under constant stirring rate (800 rpm). With the stirring intensity of 800 rpm,  $\text{Fe}^0$  could be distributed evenly in the solution and no aggregation of  $\text{Fe}^0$  was observed at the bottom of the reactor (comparative experiment at different rpm and in non-disturbed solutions was shown in the supplementary material, Fig. S1). The initial pH of solution was adjusted by NaOH and HCl, and then experiments were initiated after addition of ZVI into the reactor without the presence of any buffer. During the reaction process, the change of solution pH value was less than  $\pm 0.3$  (data were not shown). For the kinetic study, 15 mL sample, which was immediately quenched with 100  $\mu\text{L}$  of methanol at fixed time intervals, was rapidly transferred into a 25 mL beaker, filtered with 0.22  $\mu\text{m}$  membrane, and collected into sample vials quickly.

**Table 1**  
Characteristics of mZVI samples used in this study.

Name	Meads BET surface area ( $\text{m}^2/\text{g}$ )	Particle size ( $D_{50}$ , $\mu\text{m}$ )
mZVI <sub>GY</sub>	0.15	37
mZVI <sub>SA</sub>	0.09	89
mZVI <sub>HT</sub>	0.14	37
mZVI <sub>YF1</sub>	0.14	41
mZVI <sub>YF2</sub>	1.08	3.9

### 2.3. Chemical analysis

A high-performance FE20-FiveEasy pH meter (Mettler-Toledo, Switzerland) was employed to measure solution pH and daily calibration with standard buffers (pH 4.00, 6.86 and 9.18) was necessary to ensure its accuracy. The concentrations of ferrous and ferric ion (after reduction to  $\text{Fe}^{\text{II}}$  with hydroxylamine hydrochloride) were determined by the Shimadzu UV-visible 2600 spectrophotometer (Kyoto-fu, Japan) at 510 nm after complexing with 1,10-phenanthroline (detection limit: 0.03 mg/L).

The BET surface area of all ZVI samples was determined by Quantachrome Instruments Quadrasorb SI-MP-21 (Boynton Beach FL, USA), and was illustrated in Table 1. The morphological analysis of granular ZVI, mZVI, and nZVI samples performed using a Philips-FEI Sirion 200 scanning electron microscopy (SEM), a Philips-FEI Quanta 200 SEM, (Eindhoven, the Netherlands) and a Merlin Compact SEM (Carl Zeiss, Germany) (Oxford Instrument, UK) are shown in Figs. S2–S6, respectively. The median particle size of granular ZVI and mZVI was analyzed by the Malvern Mastersizer 2000 (Malvern, United Kingdom) using ethanol as the dispersant. The median particle sizes of ZVI preparations are listed in Table 1 and the analytical results are shown in Figs. S2–S6.

SMX was analyzed by a Waters ACQUITY ultra-performance liquid chromatography (UPLC) system including a binary solvent manager (BSM) and a sample manager (SM) with a UV detector (TUV) (Milford MA, United States). Separation was accomplished with an UPLC BEH C18 column ( $2.1 \times 50$  mm, 1.7  $\mu\text{m}$ ; Waters) at  $35 \pm 1.0$  °C with a mobile phase of two effluents (effluent A: 30% acetonitrile with 0.1% formic acid; effluent B: 70%  $\text{H}_2\text{O}$  with 0.1% formic acid) at a flow rate of 0.1 mL/min. Concentrations of SMX were determined by comparing the peak area at 270 nm with that of standards. The intermediate products of SMX degradation were separated by the Waters ACQUITY UPLC but interfaced with a tandem quadrupole mass detector (Xevo TQD) (UPLC-MS-MS). Mass spectral analysis was conducted in positive mode electrospray ionization ((+)ESI) over a mass range of 50–500  $m/z$ . The cone voltage used was 30 V conducted in auto full scan mode (MS2). Details of the UPLC method description were similar to the conditions of SMX quantification mentioned above.

### 2.4. Methodology of chemical calculations

All theoretical calculations were performed with the Gaussian 09 package (Revision D.01) [24], using the density functional theory (DFT) M06-2X and B3LYP with the 6-31G+(d,p) basis set (including a single set of diffuse functions, a single set of diffuse functions and a set of d functions on nonhydrogenic atoms, and a set of p functions on hydrogen atoms) [25]. IEFFCM solvent model with UFF atom radii was carried out for aqueous solution calculations. All geometry optimization schemes of equilibrium structures were optimized with closed shell method and default convergence criteria. And values of condensed Fukui function ( $f_k^0$ ) in SMX molecule were obtained from NBO charges of atoms by Eq. (1) [26]:

$$f_k^0 = \frac{(q_k^{N-1} - q_k^{N+1})}{2} \quad (1)$$

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