Weak magnetic field for enhanced oxidation of sulfamethoxazole by Fe^0/H_2O_2 and Fe^0/persulfate: Performance, mechanisms, and degradation pathways

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HIGHLIGHTS

- Weak magnetic field (WMF) enhanced sulfamethoxazole (SMX) removal by Fe^0/H_2O_2 or Fe^0/persulfate (PS).
- WMF accelerated SMX removal by Fe^0/H_2O_2 or Fe^0/PS with sulfate, nitrate, and chloride anions.
- WMF did not change the type of reactive oxygen species but accelerated the release of dissolved iron.
- Two transformation pathways of SMX in Fe^0/H_2O_2/WMF and Fe^0/PS/WMF systems were similar.
- Hydroxylated SMX was formed by the attack of $\cdot OH$, but the S-N bond of SMX was easily attacked by $\cdot SO_4^-$.

ARTICLE INFO

ABSTRACT

In this study, effects of the nonuniform weak magnetic field (WMF) on sulfamethoxazole (SMX) degradation rate by H_2O_2 and persulfate (PS) coupled with different zero-valent iron (Fe^0) samples were investigated. The k_{obs} value (pseudo-first-order rate constant) of SMX degradation by Fe^0/H_2O_2 or Fe^0/PS was accelerated by WMF irradiation. Meanwhile, the release rate of dissolved iron was increased in the presence of WMF which indicated WMF irradiation could promote Fe^0 corrosion in Fe^0/H_2O_2 and Fe^0/PS systems. Effects of WMF on SMX degradation kinetics by Fe^0/H_2O_2 or Fe^0/PS in the initial system pH (pH_{ini}) range of 3.0–7.0 were studied. Although WMF accelerated SMX removal by Fe^0/H_2O_2 at pH_{ini} 3.0 and 4.0, WMF did not exhibit advantages at higher pH_{ini}. In Fe^0/PS systems, WMF could promote SMX removal during the investigated pH range of 3.0–7.0, and k_{obs} of SMX removal depended on the form of aquatic SMX which suggested that $\cdot SO_4^-$ could selectively degrade dissociated or protonated SMX. Although SO_4^{2-}, Cl^-, and NO_3^- showed different effects on SMX degradation by Fe^0/H_2O_2 or Fe^0/PS, WMF could accelerate SMX degradation in the presence of these common anions. Chemical quenching experiments and electron paramagnetic resonance (EPR) studies identified that main reactive oxygen species (ROS) generated in Fe^0/H_2O_2/WMF and Fe^0/PS/WMF systems were $\cdot OH$ and $\cdot SO_4^-$, respectively. Meanwhile, the detection of ROS proved that WMF did not change the type of ROS in Fe^0/H_2O_2 or Fe^0/PS systems. Finally, degradation pathways of SMX by Fe^0/H_2O_2/WMF and Fe^0/PS/WMF were proposed based on transformation products.

1. Introduction

Since the synthesis of prontosil in 1932, sulfonamide drugs have been widely used in treating and preventing bacterial infections in human or animals [1]. Sulfamethoxazole (SMX), as an important sulfonamide drugs, was considered as the successful broad-spectrum antimicrobial agents in clinical use [2]. But SMX has been excreted in unchanged form and glucuronide conjugates by human or animals and then released to aquatic environments following the effluent and sludge from domestic wastewater [3,4]. Generally, the measured concentrations of SMX detected in surface water and ground water of China ranged from ng L^{-1} [5,6] to μg L^{-1} [7,8] level. On the one hand, SMX could directly damage human organism for its carcinogenicity to humans (IARC 3) [9]. On the other hand, more concerns from the social public on antibacterial resistant genes induced by SMX have brought a new challenge for traditional water treatment technologies [10,11]. Thereby, it is necessary to destruct SMX in aquatic environments by developing efficient technologies.

Since Fenton firstly reported reactions between Fe(II) and H_2O_2 in 1894 [12], Fenton reactions have been extensively applied to rapid remove organic contaminants. Hydroxyl radical ($\cdot$OH) was identified as main reactive oxygen species (ROS) in Fenton reactions [13], so Fenton reactions have shown high performance on the degradation and mineralization of various aquatic emergency organic pollutants. Besides, many advanced oxidation processes (AOPs) such as heterogeneous Fenton, ultrasonic-Fenton, and photo-Fenton reactions by producing $\cdot$OH have been also considered as superior strategies to destroy organic contaminants in industrial and domestic wastewater treatment [13]. Recently, new AOPs by producing sulfate radical ($\cdot SO_4^-$) have been widely investigated to destruct organic contaminants [14,15]. AOPs (e.g., Fe(II)/persulfate (PS)) based on $\cdot SO_4^-$ have attracted more interests in the degradation of organic pollutants include various antibiotics [16] in aquatic environment [17,18]. Theoretically, $\cdot SO_4^-$ possessed a higher redox potential of (E^0 = 2.5–3.1 V) than $\cdot$OH (E^0 = 1.9–2.7 V) which indicated that $\cdot SO_4^-$ is a stronger ROS [19]. Moreover, $\cdot SO_4^-$ selectively oxidized various organics by hydrogen/electron abstraction or addition which was very different from the non-selective oxidation of organics attacked by $\cdot$OH [14]. Consequently, Fe(II)/PS reactions have also attracted more interests in organic pollutants degradation [20,21].

Since the application of zero-valent iron (Fe^0) to water treatment in 1994 [22,23], Fe^0 also as an alternative of Fe(II) has been widely used to develop heterogeneous AOPs reactions by coupling with H_2O_2 or PS [13–17,24]. The addition of Fe^0 not only continuously supplied dissolved Fe(II) but also refrained the introduction of other anions [25]. The reactive ability of microscale Fe^0 was much lower, and some new measures such as the preparation of nanoscale Fe^0 samples [26,27] and bimetallic iron based systems [28–30] were conducted to improve the reactivity of Fe^0. However, the potential ecotoxicity of nano Fe^0 or bimetallic iron increased more considerable concerns on aquatic environment [25]. Most recently, Guan's group [31–35] have reported that the irradiation of weak magnetic field (WMF) remarkably enhanced degradation performances of various heavy metals such as Se(IV) [32], Sb(V) [36], Cr(VI) [37], As(V)/As(III) [38], and Cu(II) [39] by microscale ZVI by microscale Fe^0. Besides, premagnetized Fe^0 samples could also promote removal efficiency of various heavy metals [34]. Moreover, Guan's group [18,40] also studied effects of WMF on various organic contaminants degradation by Fe^0/H_2O_2 and Fe^0/PS, and WMF significantly improved removal performance of target organics both in Fe^0/H_2O_2 and Fe^0/PS processes. After Guan's remarkable work, Zhou's group [41,42] also proved that premagnetized Fe^0 samples showed higher removal performance of organics with H_2O_2 or PS than Fe^0 samples. Obviously, WMF is an effective and economic strategy to promote contaminants removal efficiency by Fe^0 activated H_2O_2 or PS. However, very few studies were conducted to study the universality of WMF enhancement on AOPs based on Fe^0 samples with different origin. Besides, effects of WMF on generation mechanisms and types of ROS which destroyed contaminants in Fe^0/H_2O_2 or Fe^0/PS systems were rarely investigated.

The objectives of this study are to (1) investigate effects of WMF on SMX removal performance by H_2O_2 or PS with different Fe^0 samples, (2) investigate effects of WMF on SMX degradation by Fe^0/H_2O_2 and Fe^0/PS at different initial system pH, (3) evaluate effects of WMF on SMX degradation by Fe^0/H_2O_2 and Fe^0/PS with several background anions, (4) identify ROS of $Fe^0/H_2O_2/WMF$ and $Fe^0/PS/WMF$, and (5) compare SMX degradation pathways in $Fe^0/H_2O_2/WMF$ and $Fe^0/PS/WMF$ processes.

2. Experimental materials and methods

2.1. Reagent

SMX was supplied by Sigma-Aldrich Co. LLC. (St. Louis, USA). H_2O_2, PS, *tert*-butyl alcohol (TBA), and methanol (METH) were purchased

Table 1
Characteristics of Fe^0 samples used in this study.

Name	BET surface area (m²/g)	Particle size (D_{50}, μm)	Wt%
Fe^0_{GY}	0.15	37	98.22
Fe^0_{SA}	0.09	89	100
Fe^0_{HT1}	0.14	37	96.77
Fe^0_{HT2}	1.08	3.7	96.74
Fe^0_{YF1}	0.14	41	94.81
Fe^0_{YF2}	1.08	3.9	96.4
Fe^0_{DK1}	0.091	7.9	99.1
Fe^0_{DK2}	0.093	8.0	100

from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). All stock solutions were prepared with deionized (DI) water. Deionized water was used throughout the whole experiment process. Eight commercial Fe^0 samples (Table 1) were purchased from Sinopharm Chemicals Reagent Co., Ltd. (Fe^0_{GY}, Shanghai, China), Sigma-Aldrich Co. LLC. (Fe^0_{SA}, St. Louis, USA), Haotian Nanotechnology Co., Ltd. (Fe^0_{HT1} and Fe^0_{HT2}, Shanghai, China), Yunfu Nanotechnology Co., Ltd. (Fe^0_{YF1} and Fe^0_{YF2}, Shanghai, China), and DK Nano Technology Co., Ltd. (Fe^0_{DK1} and Fe^0_{DK2}, Beijing, China), respectively. Commercial Fe^0 samples were used as received.

2.2. Kinetic procedures

Batch kinetic experiments were carried out in a wide mouth cylindrical plexiglass tube, 8 cm in internal diameter and 14 cm in height. Temperature of reactors was set at 20 ± 1.0 °C controlled by thermostatic bath. The reactor was fixed on a magnetic stirrer coinciding with the bottom side of the reactor. And WMF was generated by the magnetic stirrer owning two pieces of permanent magnet. The tests were initialled by simultaneously adding Fe^0 samples and H_2O_2 or PS into 500 mL reaction solution containing SMX, then working solution were rapidly stirred by an Dragon OS40-Pro LCD digital display electric blender (Beijing, China). Solution system pH were adjusted by H_2SO_4 and NaOH. About 5 mL sample was quickly filtered with 0.22 μm membrane at regular time intervals, then transferred into a 10 mL centrifuge tube containing 100 μL of sodium thiosulfate which could rapidly quench residual ROS and oxidants, then the sample was collected into a 2 mL sample vial.

2.3. Chemical analysis

A laboratory FE20-FiveEasy pH meter (Mettler-Toledo, Greifensee, Switzerland) was employed to monitor solution pH value. Surface areas of Fe^0 particles were characterized by the Quadrasorb SI Analyzer (Quantachrome Instruments, Boynton Beach, USA), and values of BET surface areas are summarized in Table 1. The morphological analysis of Fe^0 samples performed by a Philips-FEI Quanta 200 scanning electron microscopy SEM with an energy dispersive spectrometer (EDS) (Eindhoven, the Netherlands), and a Carl Zeiss Merlin Compact SEM with an EDS (Jena, Germany) are illustrated in Figs. S1–S8. The median particle sizes (D_{50}) of Fe^0 preparations were analyzed by the Malvern Mastersizer 2000 (Malvern, UK) using ethanol as the dispersant (Figs. S1–S8). Detail values of median particle sizes and weight fraction of iron particles are summarized in Table 1. Total dissolved iron was firstly reduced by hydroxylamine hydrochloride to Fe(II), then was complexed with 1,10-phenanthroline at a later stage for quantification. And concentrations of Fe(II) were measured at 510 nm by the Shimadzu UV–visible 2600 spectrophotometer (Kyoto, Japan). Electron paramagnetic resonance (EPR) experiments were performed on a Bruker A200 system (Billerica, USA).

SMX was analyzed by a Waters ACQUITY ultra performance liquid chromatography system (UPLC) (Milford, USA). Samples were separated in an ACQUITY UPLC BEH C18 1.7 μm column (2.1 × 100 mm) at