



Degradation of ciprofloxacin and sulfamethoxazole by ferrous-activated persulfate: Implications for remediation of groundwater contaminated by antibiotics



Yuefei Ji^{a,b}, Corinne Ferronato^b, Arnaud Salvador^c, Xi Yang^{a,*}, Jean-Marc Chovelon^{b,**}

^a State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, PR China

^b Université Lyon 1, UMR CNRS 5256, Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON), 2 Avenue Albert Einstein, F-69626 Villeurbanne, France

^c Université Lyon 1, CNRS, Université de Lyon, 69622 Villeurbanne cedex, Institut des Sciences Analytiques, France

HIGHLIGHTS

- Degradation of ciprofloxacin and sulfamethoxazole by Fe(II) activated persulfate.
- Hydroxyl and sulfate radical were major reactive species.
- EDTA showed promoting effect on SMX degradation at neutral pH.
- Degradation of antibiotics was nearly the same in Milli-Q and river water.
- Heterocyclic ring in sulfonamides strongly influenced the degradation.

ARTICLE INFO

Article history:

Received 4 September 2013

Received in revised form 1 November 2013

Accepted 1 November 2013

Available online 15 December 2013

Keywords:

Antibiotics

Ciprofloxacin

Sulfamethoxazole

Ferrous-activated persulfate

In situ chemical oxidation (ISCO)

ABSTRACT

The wide occurrence of antibiotics in groundwater raised great scientific interest as well as public awareness in recent years due to their potential ability to spread antibiotic resistant gene and pose risk to humans. The present study investigated the ferrous ion (Fe(II)) activated decomposition of persulfate ($S_2O_8^{2-}$), as a potential in situ chemical oxidation (ISCO) approach, for remediation of groundwater contaminated by antibiotics. Fe(II)-persulfate mediated ciprofloxacin (CIP) degradation was found to be more efficient than sulfamethoxazole (SMX) at near neutral pH (pH 6.0), probably due to the higher electric density in CIP molecule and its ability to form complex with Fe(II) as a ligand. Hydroxyl ($HO\bullet$) and sulfate radical ($SO_4\bullet^-$) were determined to be responsible for the degradation of CIP and SMX in Fe(II)-persulfate system by molecular probes. No enhancement in the degradation of CIP was observed when citrate (CA), ethylenediaminetetraacetate (EDTA) and (S,S)-ethylenediamine-N,N'-disuccinate (EDDS) were used as Fe(II) chelating agents in Fe(II)-persulfate system. For SMX, CA and EDTA accelerated the degradation by Fe(II)-persulfate. Degradation of antibiotics in river water matrix was nearly the same as that in Milli-Q water, implying the possibility of using Fe(II)-persulfate for antibiotics depletion under environmentally relevant condition. A comparison of the degradation efficiency of SMX with other sulfonamides and sulfanilic acid indicated that the heterocyclic ring has a large impact on the degradation of sulfonamides. Transformation products of CIP and SMX by Fe(II)-persulfate were analyzed by solid phase extraction–liquid chromatography–mass spectrometry (SPE–LC–MS) technique. Based on the intermediate products, Fe(II)-persulfate mediated CIP degradation pathways were tentatively proposed.

© 2013 Published by Elsevier B.V.

1. Introduction

Antibiotics are chemotherapeutic agents that inhibit or abolish the growth of microorganisms, such as bacteria, fungi, or protozoa. Recently, the wide occurrence of antibiotics in groundwater raised concerns

about potential adverse effects on human health and aquatic ecosystems (Sarmah et al., 2006; Kümmerer, 2009; Barber et al., 2009; Lapworth et al., 2012; Jurado et al., 2012). Municipal sewage treatment plants effluents, animal waste and landfill leachates are regarded as the primary pathways for antibiotics release into groundwater (Barber et al., 2009; Lapworth et al., 2012). The environmental fate of antibiotics in groundwater is mainly controlled by sorption to organic matter and clay minerals, and microbial degradation or transformation (Tolls, 2001; Gao and Pedersen, 2005; Gu and Karthikeyan, 2005; Li and Zhang, 2010). However, owing to the relatively long residence times

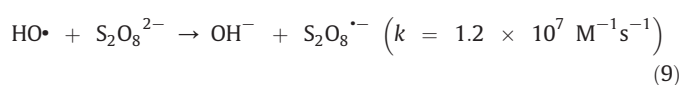
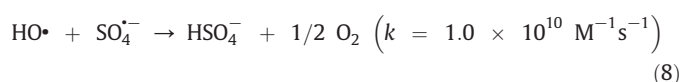
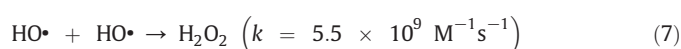
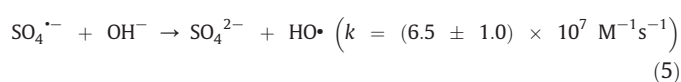
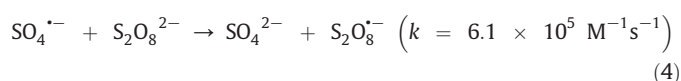
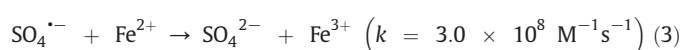
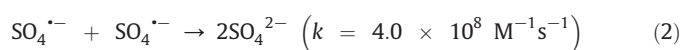
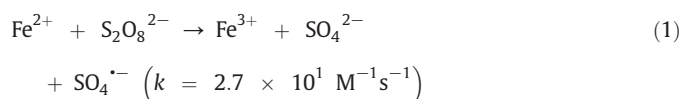
* Corresponding author. Tel./fax: +86 2589680357.

** Corresponding author. Tel.: +33 472432638; fax: +33 472448114.

E-mail addresses: jiyuefei2731@126.com (Y. Ji), yangxi@nju.edu.cn (X. Yang), jean-marc.chovelon@ircelyon.univ-lyon1.fr (J.-M. Chovelon).

and persistence due to reducing chemistry and relatively low microbial rates in groundwater, a growing number of antibiotics with considerably high levels have been detected worldwide (Sarmah et al., 2006; Kümmerer, 2009; Barber et al., 2009; Lapworth et al., 2012). The long term exposure to antibiotic contaminated groundwater is believed to cause chronic effects on human beings as well as ecological systems (Isidori et al., 2005; Kümmerer, 2009). In addition, the presence of antibiotics in natural waters may contribute to the spread of antibiotic resistance in microorganisms (Kümmerer, 2009). Thus, developing effective treatment technology for elimination of antibiotics in groundwater is of great scientific, regulatory and public interest.

In situ chemical oxidation (ISCO) is an emerging technology for groundwater remediation due to its applicability to a wide range of contaminants, relatively fast treatment, potentially enhanced post-oxidation microbial activity and cost effectiveness (Tsitonaki et al., 2010). The ISCO technology is mainly based on the generation of reactive species arising from the decomposition of oxidants such as persulfate ($S_2O_8^{2-}$) and hydrogen peroxide (H_2O_2). Among all commonly used ISCO oxidants, persulfate receives wide attention, and generally shows promising results because it can be activated by various approaches to generate free sulfate radical ($SO_4^{\bullet-}$, $E^0 = 2.6$ V). It is also easily delivered for long distances in aquifers due to its relatively high stability (Tsitonaki et al., 2010). Even though persulfate can be effectively activated by heat, UV and alkaline pH, transition metal based activation is the most viable method for field application of this oxidation technology (Zhao et al., 2013; Anipsitakis and Dionysiou, 2004; Rastogi et al., 2009b; Nfodzo and Choi, 2011). Fe(II) and Fe(III) are the most commonly used metal activators due to their natural abundance in porous media and benign nature (Tan et al., 2012; Xu and Li, 2010). Similar to the Fenton's reaction, the Fe(II)-persulfate reagent is composed of the transition metal and oxidant. Thus, Fe(II) activated persulfate bears a lot of similarity to Fenton systems and the knowledge from that technology can help us better understanding the mechanism. Once the $SO_4^{\bullet-}$ is generated, it can propagate a series of reactions involving the formation of other active species, particularly the hydroxyl radical ($HO\bullet$) (Eqs. (1)–(9)).



These highly reactive species can oxidize a wide variety of organic and inorganic compounds. However, the low efficiency and competition for $SO_4^{\bullet-}$ due to excess of Fe(II) or oxidant in Fe(II)-persulfate system have also been highlighted recently (Tsitonaki et al., 2010). In addition, the rapid conversion of Fe(II) to Fe(III) limits the ultimate oxidizing capability of ferrous-persulfate system (Anipsitakis and Dionysiou, 2004; Liang et al., 2004). In order to stabilize the amount of Fe(II) in solution, chelating agents are usually employed (Liang et al., 2004; Tan et al., 2012). For example, ethylene diamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) have been widely used as Fe(II) chelators. However, their unbiodegradability in the environment have also been highlighted recently (Sillanpaa and Pirkanniemi, 2001). Therefore, there is a need to search environmentally safe and highly effective chelating agents for persulfate activation.

The constituents of water matrix may more or less influence the removal efficiency of organic compounds by ISCO as observed in Fenton process and other AOPs (Sirtori et al., 2010; Hu et al., 2007). It is generally accepted that $SO_4^{\bullet-}$ reacts more selectively with organic compounds than $HO\bullet$ through one electron transfer mechanism. Thus, $SO_4^{\bullet-}$ -based oxidation could be less influenced by water matrix composition. For example, Liang et al. (2006) observed that at a neutral pH, persulfate oxidation of trichloroethylene (TCE) was not affected by the presence of bicarbonate/carbonate concentrations within the range of 0–9.20 mM. A more recent study has reported that $SO_4^{\bullet-}$ -based technologies showed promising results for the removal of diclofenac and sulfamethoxazole from wastewater treatment plant effluents because of the higher selectivity of $SO_4^{\bullet-}$ over $HO\bullet$, limiting radical scavenging by natural organic matter and allowing for higher abatement and mineralization rates (Mahdi Ahmed et al., 2012). However, data on the effect of natural water matrix on Fe(II)-persulfate mediated decomposition of organic compounds are still scarce.

In the present study, we assess Fe(II) activated persulfate as a potential ISCO approach for destructing ciprofloxacin (CIP) and sulfamethoxazole (SMX) in water. CIP and SMX have been chosen as model compounds of antibiotic agents because they are among the most frequently detected worldwide (see Table 1) (Kümmerer, 2009; Lapworth et al., 2012). Generally, groundwater may also be contaminated by other pollutants belonging to the same group (e.g., sulfonamide). Thus, comparison of the degradation efficiency and elucidation of the discrepancy among these structurally related compounds are of great interest. Therefore, the main goals of this study are (1) to investigate the kinetics and predominant reactive species responsible for the decomposition of CIP and SMX by Fe(II)-persulfate; (2) to study the effect of water matrix, Fe(II) chelating agents on Fe(II)-persulfate mediated antibiotics degradation and compare the decomposition of SMX with other sulfonamide drugs; (3) to identify the transformation intermediates and elucidate the degradation pathways of CIP and SMX by Fe(II) activated persulfate.

2. Materials and methods

2.1. Chemicals

Potassium persulfate ($K_2S_2O_8$, 99+%) was obtained from Aldrich. Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, $\geq 99.0\%$) was obtained from Sigma-Aldrich and was used as the catalytic Fe(II) species. Ciprofloxacin (CIP, $\geq 98.0\%$) and sulfamethoxazole (SMX, 99.0%) were purchased from Fluka. Other sulfonamides, sulfisoxazole (SIX, 99.9%) and sulfachloropyrazine (SCP, 99.9%) and sulfanilic acid (SAA, 97.0%) were purchased from Sigma-Aldrich. These compounds were used in comparison to SMX to assess if structural difference alters degradation efficiency. Three metal-chelates: citric acid (CA, 97%), ethylenediaminetetraacetic acid (EDTA, 99.5%), (S,S)-ethylenediamine-N,N'-disuccinic acid trisodium salt (EDDS, $\sim 35\%$ in H_2O) were all supplied by Sigma-Aldrich. HPLC or LC-MS grade acetonitrile (ACN), methanol

Download English Version:

<https://daneshyari.com/en/article/6331262>

Download Persian Version:

<https://daneshyari.com/article/6331262>

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