



Activation of persulfate by homogeneous and heterogeneous iron catalyst to degrade chlortetracycline in aqueous solution

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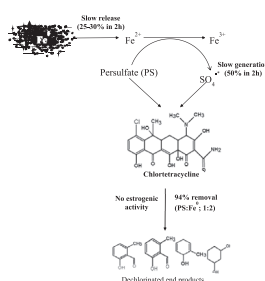
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HIGHLIGHTS

- Higher EDTA concentration was used to break CTC-Fe complexes.
- Low ZVI dose and slow activation of persulfate resulted in efficient degradation.
- Dechlorinated end products were seen by sulfate radical degradation.
- No estrogenic effects were observed for the treated CTC solution.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the removal of chlortetracycline (CTC) antibiotic using sulfate radical-based oxidation process. Sodium persulfate (PS) was used as a source to generate sulfate radicals by homogeneous (Fe^{2+}) and heterogeneous (zero valent iron, ZVI) iron as a catalyst. Increased EDTA concentration was used to break the CTC-Fe metal complexes during CTC estimation. The influence of various parameters, such as PS concentration, iron (Fe^{2+} and ZVI) concentration, PS/iron molar ratio, and pH were studied and optimum conditions were reported. CTC removal was increased with increasing concentration of PS and iron at an equal molar ratio of PS/Fe^{2+} and PS/ZVI processes. PS/Fe^{2+} and PS/ZVI oxidation processes at 1:2 (500 μM PS and 1000 μM) molar ratio showed 76% and 94% of 1 μM CTC removal in 2 h. Further increased molar ratio 1:2 onwards, PS/Fe^{2+} process showed a slight increase in CTC degradation whereas in PS/ZVI process showed similar degradation to 1:2 (PS/Fe) ratio at constant PS 500 μM concentration. Slower activation of persulfate which indirectly indicates the slower generation of sulfate radicals in PS/ZVI process showed higher degradation efficiency of CTC. The detected transformation products and their estrogenicity results stated that sulfate radicals seem to be efficient in forming stable and non-toxic end products.

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1. Introduction

Continuous detection of contaminants in water sources demands their efficient removal. Currently, advanced oxidation

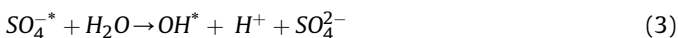
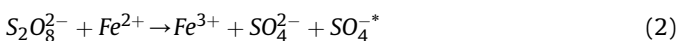
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processes (AOPs) have been competently used in the removal of emerging contaminants in wastewater. AOPs such as ozonation (Michael-Kordatou et al., 2017), Fenton (Munoz et al., 2016), ultrasonic (Mecha et al., 2016), photo-Fenton (Miralles-Cuevas et al., 2014), photocatalytic (Paul et al., 2007; Qin et al., 2016), and persulfate (Anipsitakis and Dionysiou; Lin et al., 2016) oxidation processes have proven to be efficient in degrading recalcitrant emerging pollutants. Continuous and trace detection of pollutants demands technological advances in AOPs to meet current environmental regulations. Almost all AOPs involves generation of hydroxyl radicals (OH^\bullet) which are non-selective towards most of the organic contaminants (Lee and von Gunten, 2010). The oxidants used for the generation of OH^\bullet , such as ozone, hydrogen peroxide, and permanganate have selective reactivity towards unsaturated compounds such as fatty esters, unsaturated alcohols, etc. This property makes these oxidants inefficient in the complete mineralization of recalcitrant contaminants having complex structure due to their selective oxidation (Gogate and Pandit, 2004).

PS oxidant has recently drawn much attention from researchers to overcome these limitations of oxidants producing OH^\bullet . PS has higher solubility and stability at room temperature and has high oxidation potential ($E^0 = 2.01 \text{ V}$) (Liang et al., 2004; Zhou et al., 2013). And activation of PS produces high redox potential and non-selective sulfate radical ($\text{SO}_4^{\bullet-}$, $E^0 = 2.6 \text{ V}$) similar to OH^\bullet (Vicente et al., 2011). Moreover, $\text{SO}_4^{\bullet-}$ induces hydroxyl radical's generation as per Eq. (3). Generation of OH^\bullet along with sulfate radicals having similar oxidation potential might increase the efficacy of the system to degrade the contaminants.

Different approaches have been used to activate PS, such as increasing temperature (Luo, 2014), addition of transition metal ions (Anipsitakis and Dionysiou, 2004) or chelation agents (Liang et al., 2009), or by ultraviolet irradiation (UV) (Lau et al., 2007). Among these, iron (Fe) based metal activation was most studied and reported for efficient $\text{SO}_4^{\bullet-}$ production (Oh et al., 2009; Monteagudo et al., 2015). Moreover, an iron-based catalyst has both homogeneous (Fe^{2+} ; soluble) and heterogeneous (Fe^0 , insoluble) ways to activate persulfate (Gao et al., 2016). Cost-effectiveness, natural presence, and high activity of iron making it as a promising catalyst to activate the PS and generate sulfate radicals (Liang et al., 2004; Romero et al., 2010). Overall reactions involved in the process of generating $\text{SO}_4^{\bullet-}$ by activation of PS by ZVI and Fe^{2+} are described by Eqs. (1)–(7) (Wilmarth et al., 1962; McElroy and Waygood, 1990; Liang et al., 2007; Triszcz et al., 2009).



Tetracycline antibiotics are largely used in humans, veterinary, and aquaculture applications either for diseases prevention or for growth promotion due to their broad-spectrum activity. Researchers reported the omnipresence of tetracyclines around 0.11–48 $\mu\text{g/L}$ (Miao et al., 2004; Karthikeyan and Meyer, 2006; Puicharla et al., 2014) in water and wastewater sources. Chlortetracycline (CTC) is the first tetracycline antibiotic has a four-ring system with multiple O- and N-containing ionizable functional groups which form strong complexes with metals including iron (Pulicharla et al., 2015; Wang et al., 2015). Fig. 1 shows the binding site of Fe^{2+} metal in CTC structure. CTC-Fe complex affects CTC redox reactions by decreasing the availability of lone pair electrons ($-\text{OH}$ and $-\text{NH}_2$) which are susceptible to oxidative reactions. Until date, many oxidation technologies were developed to degrade CTC in the aqueous solution such as ozonation, UV and photocatalysis treatments and were efficient to remove 90% of CTC (Daghrir et al., 2012, 2013; Guo and Chen, 2012; Kim et al., 2012; Hammad Khan et al., 2013). However, to our knowledge, PS/ Fe^{2+} (homogeneous) and PS/ZVI (heterogeneous) processes have never been attempted to degrade CTC. According to studies, $\text{SO}_4^{\bullet-}$ can be rapidly scavenged by excess Fe^{2+} in the case of PS/ Fe^{2+} process (Eq. (4)), which decrease the pollutant degradation efficiency (Liang et al., 2004). Use of ZVI powder alternative to Fe^{2+} has been reported in the literature to overcome this disadvantage (Liang and Guo, 2010; Deng et al., 2014). Further, ZVI is able to produce and regenerate Fe^{2+} by reduction of PS (Eq. (7)) and Fe^{3+} (Eq. (8)), respectively. Even though persulfate ($\text{S}_2\text{O}_8^{2-}$) transforms into an undesired product (SO_4^{2-}) (Eq. (7)), still Fe^0 generation from Fe^{2+} is necessary to activate persulfate to produce sulfate radicals.

The scope of this study is to evaluate the degradation efficiency of CTC by PS/ Fe^{2+} and PS/ZVI processes; specifically focuses on 1) method development to estimate the free CTC after complexation with iron using ultra high-pressure liquid chromatography-mass spectrometry (UHPLC-MS/MS); 2) PS/ Fe^{2+} and PS/ZVI ratio optimization to produce sulfate radicals by PS activation to degrade CTC; 3) comparison of degradation efficiencies of CTC by PS/ Fe^{2+} and PS/ZVI processes; 4) identification of degradation products and pathways; and 5) toxicity measurement of degraded CTC by determining estrogenicity. Estrogenicity is defined as the effect of CTC and its by-products on the fauna to develop female secondary sex characteristics, growth, and maturation of long bones.

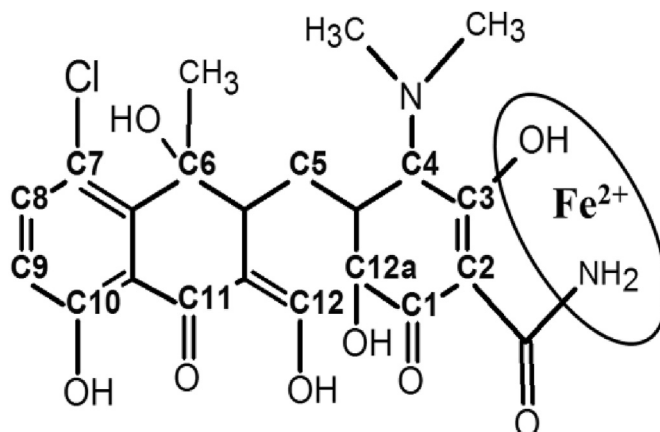


Fig. 1. Chlortetracycline structure showing the iron binding site.

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