



# Ultrasound-enhanced magnetite catalytic ozonation of tetracycline in water



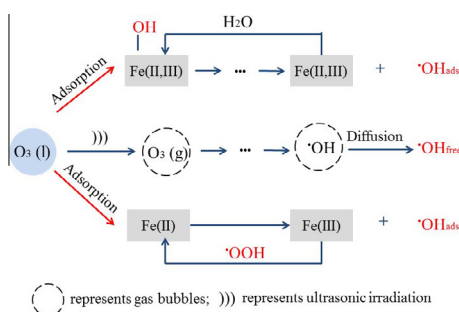
Liwei Hou, Hui Zhang\*, Ligu Wang, Lu Chen

Department of Environmental Engineering, Hubei Biomass-Resource Chemistry and Environmental Biotechnology Key Laboratory, Wuhan University, Wuhan 430079, China

## HIGHLIGHTS

- The mechanism of sono-catalytic ozonation of tetracycline was proposed.
- Ultrasound enhanced the catalyst activity in the sono-catalytic ozonation process.
- The acute toxicity of tetracycline was reduced after sono-catalytic ozonation.
- Significant improvement in biodegradability was achieved after 120 min reaction.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The degradation of tetracycline was investigated using the ultrasound-enhanced magnetite catalytic ozonation process (US/Fe<sub>3</sub>O<sub>4</sub>/O<sub>3</sub>). Thorough assessments of the operational parameters, biodegradability and acute toxicity were performed. The results indicated that the TC degradation rate was strongly influenced by the initial pH and the ultrasonic power density over the range investigated, but it was almost independent of the dosage of Fe<sub>3</sub>O<sub>4</sub> in the range of 0.3–1.0 g L<sup>-1</sup>. The TC degradation rate was diminished in the presence of *tert*-butanol, isopropanol and NaF. Under the optimal conditions, TC was almost completely removed after 20 min of treatment, and the COD removal reached 41.8%. The COD removal further increased to 89.1% when the reaction time was extended to 120 min, and the corresponding biochemical degradability (BOD<sub>5</sub>/COD) rose to 0.694. The acute toxicity reached its maximum value after 60 min treatment and then decreased with the prolonged reaction time. The catalyst stability was evaluated by measuring the TC removal rate and iron leaching for three successive cycles.

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## 1. Introduction

Over the past decades, contaminated water has been treated in biological treatment plants using biological and physico-chemical methods. However, conventional treatment processes are ineffective for antibiotic agents, both in their parent form and as metabolites, which are widely detected in wastewater, surface and ground waters and have been observed to be resistant to the conventional sewage treatment process [1,2]. Furthermore, considerable volumes of toxic by-products may be produced during the

treatment process. Advanced oxidation processes (AOPs) such as Fenton and photo-Fenton-like oxidation, have been extensively applied to address this problem [3,4]. Some of the AOPs are based on the use of ozone to degrade toxic compounds in wastewater [2,5]. Ozone is a powerful oxidizing molecule that can either react directly with organic pollutants or decompose to free radicals to attack the organic compounds with a very high rate constant. However, when ozone is used alone, it does not often lead to high level of mineralization and toxicity removal [6,7]. The use of ozone also has limitations with respect to the high implementation cost and the poor mass transfer rate. Consequently, ozone is usually combined with other technologies to improve its utilization and application [8,9]. In recent years, heterogeneous catalytic ozonation has

\* Corresponding author. Tel.: +86 27 68775837; fax: +86 27 68778893.  
E-mail address: [eeng@whu.edu.cn](mailto:eeng@whu.edu.cn) (H. Zhang).

become a powerful treatment method for the degradation of refractory organic pollutants, and high removal and mineralization can be achieved correspondingly [10–13]. The catalysts include MgO [10], alumina [11], alumina based catalysts [12], activated carbon supported catalyst ( $\text{MnO}_x/\text{GAC}$ ) [14],  $\alpha\text{-FeOOH}$  [15], cobalt oxides [16],  $\beta\text{-MnO}_2$  [17], perovskite [18], and brucite [19]. Although some catalysts have shown considerable catalytic activity in the ozonation process, their production might be problematic and cost-intensive from an industrial viewpoint. Moreover, the separation step is often unfavourable. Considering this information, the application of magnetite particles ( $\text{Fe}_3\text{O}_4$ ) in the pollution control has received great attention in the recent years [20–22]. Magnetic particles can be separated from the solution using a simple magnetic process, which shows its superiority to the other metal oxides (such as  $\alpha\text{-FeOOH}$ , and  $\alpha\text{-Fe}_2\text{O}_3$ ) [15,23]. In addition, as one of transition metal oxides,  $\text{Fe}_3\text{O}_4$  with multiple accessible oxidation states is a good catalyst for ozone decomposition [24,25]. Despite the promising results of catalytic ozonation using magnetic as the catalyst, the deactivation of the catalyst due to the organic intermediates accumulation on the surface of the catalyst is still a major obstacle for its application. In the meanwhile, the release of metal ions decreased the stability and activity of the catalyst. Therefore, the development of an effective approach to improve the catalytic efficiency and durability remains an important issue that needs to be urgently addressed.

It has been found that ultrasound can enhance the activity of the catalyst in the ozonation process without prejudice to the stability of the iron species [23,26]. During the ultrasonic process, the cavitation effect can clean the surface of the catalyst, and the catalyst can thereby avoid being poisoned during the ultrasonic irradiation process [23,27]. In addition, ultrasound accelerates turbulence, which can reduce the liquid film thickness and subsequently increase the mass transfer of reactants and by-products between the liquid and solid phases [27,29]. Furthermore, hydroxyl radicals will be generated in the vapour phase of cavitation bubbles during the ultrasonic process [29,30].

In this study, magnetic particles,  $\text{Fe}_3\text{O}_4$ , were selected as the catalyst to evaluate its catalytic activity with ozone. Tetracycline hydrochloride (TC), which is a typical class of antibiotics that is

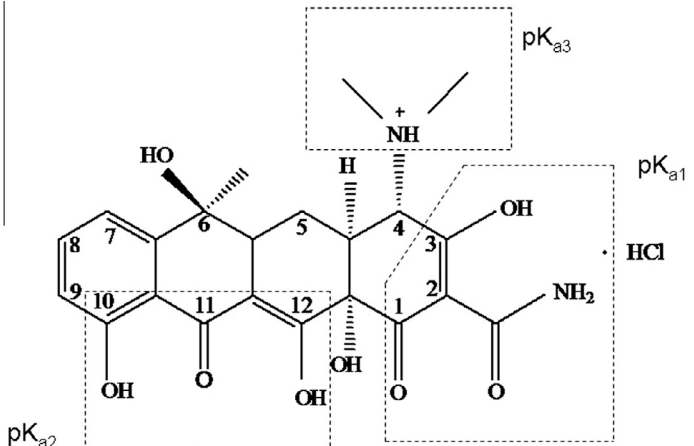
widely used for the treatment of infectious diseases in humans and in veterinary applications, was chosen as the target contaminant compound. An air-lift reactor was used owing to its efficient mixing with low shear stress and energy consumption and it provides the advantage of a high rate of gas–liquid mass transfer [23,28,30]. Comparative experiments were performed to investigate the degradation efficiencies and removal rates of TC, including experiments with ozonation alone, ultrasound-enhanced ozonation ( $\text{US}/\text{O}_3$ ), catalytic ozonation ( $\text{Fe}_3\text{O}_4/\text{O}_3$ ), and ultrasound-enhanced catalytic ozonation ( $\text{US}/\text{Fe}_3\text{O}_4/\text{O}_3$ ). The effects of the operating conditions on the removal of TC during the ultrasound-enhanced catalytic ozonation process were investigated. The mineralization and the variation of biodegradability and toxicity were also investigated in this study. The solubility and the reusability of the catalyst were critical parameters that were evaluated to investigate the stability of the catalyst.

## 2. Experimental section

### 2.1. Materials

Commercial tetracycline hydrochloride ( $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_8\text{Cl}$ , Sigma-Aldrich, >99%) with a molecular weight of 480.9 was used as received without further purification. The structure and relative data on TC are presented in Table 1. Magnetite was purchased from Prolabo (Paris, France). The structure of the catalyst and the spent samples were verified via X-ray diffraction using a Bruker D5005 diffractometer equipped with a  $\text{Cu K}\alpha$  radiation source ( $\lambda = 1.5406 \text{ \AA}$ ). The diffraction intensity data were recorded between  $20^\circ$  and  $80^\circ 2\theta$  with a recording step of  $0.05^\circ 2\theta$  each 3 s. Phase identification was performed by comparison of the diffraction results with those from the JCPDS database (Supplementary information, Fig. S1). The specific surface areas of the catalyst before and after the oxidation process were obtained using the  $\text{N}_2$  adsorption measurements. Furthermore, the primary physico-chemical properties of the fresh and spent samples were summarized in Table 2. *Tert*-butanol, isopropanol and NaF were purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). The other chemicals used in this study were of reagent grade.

**Table 1**  
Chemical structures and relevant data for tetracycline hydrochloride.

Name	Tetracycline hydrochloride
Formula	$\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_8\text{Cl}$
Structure	
Formula Weight ( $\text{g mol}^{-1}$ )	480.9
$\lambda$ (nm)	359, 270
$\text{pK}_a$	3.3, 7.68, 9.7

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