



## Research article

# The catalytic destruction of antibiotic tetracycline by sulfur-doped manganese oxide (S–MgO) nanoparticles

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## ABSTRACT

The present study evaluates the efficacy of S-doped MgO (S-MgO) as compared with the plain MgO as a catalyst for destructive removal of tetracycline (TTC) in aqueous solutions. The S-MgO had around 6% S in its structure. Doping MgO with S caused increase in surface oxygen vacancy defects. Adding S-MgO (12 g/L) to a TTC aqueous solution (50 mg/L) caused removal of around 99% TTC at the neutral pH (ca. 5.1) and a short reaction time of 10 min. In comparison, plain MgO could remove only around 15% of TTC under similar experimental conditions. Diffusing O<sub>2</sub> into the TTC solution under the reaction with S-MgO resulted in a considerable improvement of TTC removal as compared to diffusing N<sub>2</sub>. Complete removal of TTC and 86.4% removal of its TOC could be obtained using 2 g/L S-MgO nanoparticles. The removal of TTC increased with the increase in solution temperature. The presence of nitrate, sulfate and chloride did not considerably affect the removal of TTC using S-MgO while TTC removal significantly decreased at the presence of bicarbonate and phosphate. The S-MgO was a stable and reusable catalyst exhibiting much higher catalytic activity than plain MgO for the TTC destruction. Accordingly, S-MgO is an emerging and efficient catalyst for catalytic decomposition and mineralization of such pharmaceutical compounds as TTC under atmospheric temperature and pressure.

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## 1. Introduction

Tetracycline (TTC) is among the most widely used pharmaceutical antibiotics for treatment of human and veterinary infectious as well as for growth promoter in the aquaculture (Mahamallik et al., 2015). Therefore, wastewater from the residential communities and animal farms as well as effluent from the pharmaceutical manufacturing plants may largely contain considerable amount of pharmaceuticals including antibiotics as parent or metabolite. The conventional treatment methods are not able to efficiently removing the pharmaceuticals compounds and thus they released mainly untreated to the receiving water bodies. Therefore, pharmaceuticals are considered as a new emerging class of water contaminants. The most accepted technique for treating wastewater streams is the biological process. In the other hand, TTC as an antibiotic is a xenobiotic compound that resists to the

biodegradation (Mahamallik et al., 2015; Moussavi et al., 2015) and thus is a recalcitrant compound.

The degradation of TTC has been investigated using different variations of advanced oxidation processes (AOPs). For instance, the degradation of TTC in the catalytic ozonation process using goethite catalyst (Wang et al., 2011) and in the photocatalysis process combined with hydrodynamic cavitation (Wang et al., 2017a) was evaluated. Although these processes provided considerable TTC degradation, they are complex and expensive oxidation processes. In comparison to AOPs, the tetracycline hydrochloride degradation by highly porous MnO<sub>2</sub> nanosheet was investigated and around 75% degradation was obtained under controlled pH (Mahamallik et al., 2015). It reveals that selecting an appropriate material having the catalytic potential is the preferred technique of TTC elimination from the contaminated water under mild catalytic reaction conditions.

The high surface reactivity and thus high catalytic potential pose magnesium oxide (MgO) as an efficient candidate for catalytic destruction of such recalcitrant compounds as TTC. It has been

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reported that MgO has high potential for destructive removal of synthetic dyes (Moussavi and Mahmoudi, 2009) as well as of aromatic compounds (Moussavi et al., 2013). The oxygen vacancy defects of MgO contribute to the catalytic activity of MgO in reactions (Scorza et al., 1997). Therefore, the catalytic potential of MgO can be increased through doping with nonmetal elements including sulfur (S) due to increasing the surface defects as oxygen vacancies (Li et al., 2015). Therefore, the structure of MgO need be modified to increase the intensity of surface defects as oxygen vacancy thus to enhance its catalytic properties for the degradation reactions. The oxygen vacancy defects of MgO can be increased as the substitution of an atom of O in MgO lattice by S atom. Oxygen vacancy acts as active centers and gives the material a high catalytic activity in generating reactive oxygen species (ROSs) (Richards, 2006).

Accordingly, the main purpose of the present study is the evaluation of S-doped MgO (S–MgO) for catalytic destruction of TTC as an emerging water contaminant. The effect of solution pH, catalyst and TTC concentrations, solution temperature, and water anions was investigated on TTC removal from the aqueous solution by plain MgO and S–MgO catalysts. The contribution of decomposition in the TTC removed from the solution by S–MgO and thus its mineralization degree was determined. The potential of durability and reusability of the prepared catalyst was also examined.

## 2. Materials and methods

### 2.1. Materials

The MgO and S–MgO were prepared and fully characterized as described in detailed by Mashayekh–Salehi et al., 2017. The S–MgO was a nanocrystalline mesoporous nanoparticle with an average particle size of 13.6 nm and a BET specific surface area of 257.3 m<sup>2</sup>/g, composed of 36.4% magnesium, 57.3% oxygen and 6.3% sulfur (wt%). A high density of active surface functional groups was developed on the surface of S–MgO particles. Tetracycline (TTC), (C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>8</sub>), was obtained as powder from a local pharmaceutical company and used as received. A 0.1% TTC stock solution was prepared by dissolving 1 g TTC powder in 1 L of distilled water. The working solutions with desired concentration of TTC were prepared by sufficiently diluting the aliquots of the stock solution in distilled water. Terephthalic acid (TFA), (C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>), used as the probe of reactive oxygen species (ROSc), was of the analytical grade. All other chemicals used in the present work were of analytical grade purchased from Merck Co.

### 2.2. Experimental procedure and analysis

The TTC removal batch experiments were conducted in a 500-mL Pyrex Erlenmeyer flask. In each test, 250 mL of the reaction solution with a given TTC concentration and solution pH was transferred to the flask, the predetermined amount of catalyst was added, and then the suspension was magnetically stirred at 120 rpm for the specified time. The reaction solution was sampled at the known time intervals, filtered using 0.2 μm fiberglass filters to separate the catalyst particles and the filtrate was analyzed for the target parameters. The solution pH was adjusted at the desired level using NaOH or HCl normal solutions.

The amount of TTC destructed in each test was measured using mass balance analysis as explained below. First, the spent catalyst was separated from the suspension by the filtration at the end of the target test, air-dried and the TTC remained on that was desorbed. For desorption, the dried catalyst was weighed (M<sub>c</sub>) and then added to a flask containing 25 mL of HPLC mobile phase solution (60/40 (vol%) buffered phosphate and acetonitrile) and stirred at 120 rpm for 60 min. The concentrations of TTC and TOC in the

desorbed solution were then measured. Considering the volume of the working solutions (250 mL), the amounts of TTC in the solution before (M<sub>b</sub>) and after (M<sub>a</sub>) the catalytic reaction as well as in the desorbed solution (M<sub>d</sub>) were subsequently calculated. Finally, the removal and destruction efficiencies were calculated from below equations.

$$\text{TTC removal efficiency (\%)} = \left[ \frac{(M_b - M_a)}{M_b} \right] \times 100 \quad (1)$$

$$\text{TTC destruction efficiency (\%)} = \left[ \frac{(M_b - M_a) - M_d}{(M_b - M_a)} \right] \times 100 \quad (2)$$

$$\text{TTC removal capacity (mg/g)} = \left[ \frac{(M_b - M_a)}{M_c} \right] \times 100 \quad (3)$$

$$\text{TTC destruction capacity (mg/g)} = \left[ \frac{(M_b - M_a) - M_d}{M_c} \right] \times 100 \quad (4)$$

The formation ROSs in the reaction medium was evaluated by photoluminescence test (by photoluminescence spectroscopy at wavelength of 420 nm) using TFA solution (Charbouillot et al., 2011; Wang et al., 2017b). The formation of the ROSs were further confirmed by the comparison of TTC removal at presence and absence of p-benzoquinone as O<sub>2</sub><sup>•-</sup> scavenger (Wang et al., 2017b) and salicylic acid as •OH scavenger (Moussavi and Shekoohiyan, 2016; Mashayekh–Salehi et al., 2017). Moreover, to understand the stability and reusability of the S–MgO, the spent catalyst separated from the catalytic experiment was dried and its catalytic potential was retest for five consecutive cycles.

## 3. Results and discussion

### 3.1. Effect of initial solution pH

The effect of initial solution pH between 2 and 12 was investigated on the removal of 100 mg/L TTC using 2 g/L MgO or S–MgO at the contact time of 60 min and the results are shown in Fig. 1. The same trend is seen in Fig. 1 for the removal TTC using both MgO and S–MgO as a function of initial solution pH, although with a considerably higher rate in the case of S–MgO. Based on Fig. 1, the removal of TTC by S–MgO improved rapidly from 7.7% to 89.2% when the initial solution pH was increased from 2 to 5 while it remained almost unchanged at the solution pHs between 5 and 8. Further increase in initial solution pH from 8 to 12 caused suddenly

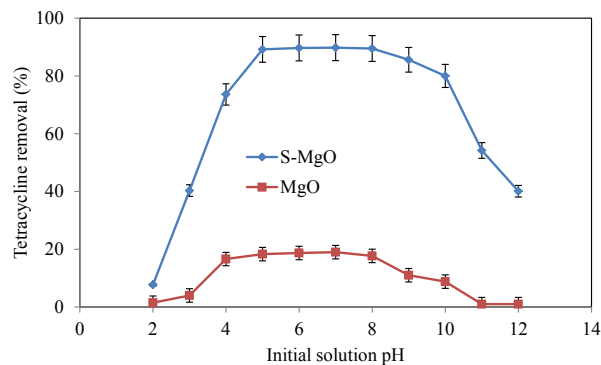


Fig. 1. Effect of initial solution pH (2–12) on TTC removal by MgO and S–MgO catalysts (TTC = 100 mg/L; catalyst = 2 g/L; reaction time = 60 min; solution temperature = 25 °C).

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