Catalytic ozonation of nitroimidazole antibiotics using nano-magnesium hydroxide as heavy-metals free catalyst

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ABSTRACT

In this study, nano-magnesium hydroxide (nano-$Mg(OH)_2$) was prepared and first applied for the catalytic ozonation of the widely used nitroimidazole antibiotics. Most of nitroimidazole antibiotics were rapidly removed within 10 min. The removal rate constant of metronidazole in the catalytic ozonation treatment was four times higher than that without catalyst. Persistent high catalytic activity of nano-$Mg(OH)_2$ maintained after three runs. The severe inhibition of hydroxyl radical scavenger (TBA) on the catalytic ozonation suggested that hydroxyl radical reaction served as the predominant process. The removal of nitroimidazole antibiotics followed a pseudo-first order kinetic model. Increase in the dosage of catalyst and reaction temperature within certain range could enhance the degradation of metronidazole, tinidazole, and dimetridazole while increase in the initial concentration of nitroimidazole antibiotics led to the decrease in the removal efficiency. All anions (Cl^-, HCO_3^-, and SO_4^{2-}) and cations (Ca^{2+} and Mg^{2+}) had negative influence on the removal efficiency of nitroimidazole antibiotics. Due to the unique features such as low cost and heavy-metals free, high efficiency and persistent high catalytic activity of the nano-$Mg(OH)_2$ in the catalytic ozonation of nitroimidazole antibiotics demonstrated that nano-$Mg(OH)_2$ is a promising environment-friendly ozonation catalyst in terms of antibiotic removal.

Keywords: Nano-scale magnesium hydroxide; Nitroimidazole antibiotics; Catalytic ozonation; Degradation

1. Introduction

Various antibiotics have been widely and extensively used in the treatment of bacterial infections for both humans and animals as well as in the promotion of growth for livestock and aquaculture [1]. It has been reported that the antibiotics consumption in developing countries increased substantially 36% between 2000 and 2010 [2]. These antibiotics are discharged directly or indirectly into water bodies due to their continuous usage, incomplete metabolism, and absorption [3,4]. As a result, they have been frequently identified in the secondary wastewater effluents and natural aquatic systems around the world [5,6]. Among these antibiotics, nitroimidazole antibiotics are widely used and frequently detected in waters with concentrations ranging from 0.1 to 90.2 μg L^{-1} [7]. The continuous input of nitroimidazole antibiotics may cause potential harm to human and terrestrial organisms in a long term [8]. Furthermore, nitroimidazole antibiotics possess low biodegradability [9], high solubility in water [7], high toxicity [10], and mutagenic and

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carcinogenic characteristics [11]. These antibiotics are not completely removed by traditional wastewater treatment processes so as to be finally released into surface water. Therefore, it is necessary to develop efficient treatment method to control these contaminants.

In order to remove nitroimidazole antibiotics, various chemical methods including photo-catalytic oxidation method [12,13], nanoscale zero-valent iron technology [7], and ozonation [14–16] have been used for degradation of nitroimidazole antibiotics. The catalytic ozonation has been widely accepted as an efficient degradation approach for various antibiotics with short reaction time and high oxidation rate [17–19]. In this process, a catalyst is applied to enhance ozone decomposition to generate highly reactive and non-selective hydroxyl radicals. The radicals are able to oxidize toxic and resistant organic compounds into final inorganic products and convert them into less toxic and readily biodegradable compounds [20]. It has been reported that various materials including $Ce_{0.1}Fe_{0.9}OOH$ [17], hetero-atoms doped graphene [19], carbon materials [14,15,21,22], Fe_3O_4 [18], and Fe_2O_3/CeO_2-loaded activated carbon [23] have been examined so far for catalyzing the ozonation process of various classes of antibiotics. Although these catalysts have shown considerable catalytic performance, their cost is higher and transition or heavy metal ions will be introduced into some catalysts to cause secondary pollution. Magnesium hydroxide ($Mg(OH)_2$) has obtained attention as potential promising catalyst due to its unique features such as low cost, heavy-metals free, high stability in water, more environment-friendly, and less toxicity [24–26]. Various contaminants including phenol, nitrobenzene, and aniline have been successfully removed during the catalytic ozonation process in the presence of brucite [25,26]. These studies suggest that brucite can alter the pH of solution and the dissolved hydroxyl ions can accelerate the production of hydroxyl radicals to subsequently enhance the degradation rate of these pollutants [25,26]. In addition, the use of brucite can avoid secondary pollutant because Mg^{2+} is beneficial to the organisms in water [25,26]. However, with the development of nanotechnology, nanomaterials used as ozonation catalysts have shown high catalytic performance due to high surface area and numerous active sites on surface of the nanoparticles [12,16,27,28]. It is regretful that rare investigations are available on the oxidation of antibiotics in the catalytic ozonation with nano-$Mg(OH)_2$ as catalyst that is an environment-friendly and economically feasible catalyst.

In this study, nano-magnesium hydroxide (nano-$Mg(OH)_2$) was synthesized and first used as the catalyst for the catalytic ozonation of widely used nitroimidazole antibiotics. Three widely used nitroimidazole antibiotics including metronidazole (MNZ), tinidazole (TNZ), and dimetridazole (DMZ) were chosen as representative compounds of antibiotics to discuss catalytic ozonation effects because of their low reactivity to ozone and high affinity for hydroxyl radicals [15]. The removal of MNZ, TNZ, and DMZ using nano-$Mg(OH)_2$ as catalyst in catalytic ozonation was first investigated. The influence of different factors on the removal of MNZ, TNZ, and DMZ was also evaluated. The aims of this study were to provide a promising green catalyst and develop a new understanding on catalytic ozonation of wastewater containing antibiotics.

2. Materials and methods

2.1. Materials and reagents

The analytical grade metronidazole (MNZ, purity ≥99.0%), tinidazole (TNZ, purity ≥99.0%), and dimetridazole (DMZ, purity ≥98.0%) were purchased from Macklin (Shanghai, China). Magnesium chloride ($MgCl_2 \cdot 6H_2O$), polyethylene glycol (PEG 400), and ammonium hydroxide obtained from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China) were used as the raw materials for synthesizing $Mg(OH)_2$ catalyst. Acetonitrile used for high performance liquid chromatography was HPLC grade (Mreda, USA). Sodium chloride, sodium bicarbonate, anhydrous sodium sulfate, and calcium chloride were of analytical grade and used without further purification. Sodium thiosulfate and tert-butanol (TBA) with analytical purity grade were used as quenching agent and radical scavenger, respectively. The ultrapure water made by Thermo Scientific (Smart 2 Pure 3 UV, Sweden) with a resistivity of 18.2 MΩ cm was used to prepare all experimental solutions at room temperature.

2.2. Preparation of nano-Mg(OH)₂ catalyst

The $Mg(OH)_2$ catalyst was prepared according to the literature [29]. The $MgCl_2 \cdot 6H_2O$ (10.165 g) was dissolved in 100 mL ultrapure water to form a clear solution, followed by the addition of 10 mL polyethylene glycol (PEG 400). Then, the mixture was placed in a 50°C constant temperature bath. With constant magnetic stirring, the 8 mL ammonium hydroxide was added dropwise to the above prepared solution at 50°C through a dropping funnel. The mixture was stirred vigorously for 1.5 h, and then allowed to cool down to room temperature and held at room temperature for another 1.5 h. The attained precipitates were centrifuged at 4,000 rpm for 10 min, and then filtered and washed several times with ultrapure water and ethanol. The washed white products were dried at 60°C for 12 h under air atmosphere.

2.3. Catalytic ozonation of nitroimidazole antibiotics using nano-Mg(OH)₂

The catalytic ozonation experiments were carried out in bench-scale reactors. The reactor was composed of O_3 supply system and exhaust treatment system. Ozone was produced by an ozone generator (Wohuan Co., Ltd.) fed with pure oxygen. The flow rate of O_3 during experimental process was kept at 0.1 L min⁻¹. When the gas ozone flow rate remained stable, the gas ozone concentration was controlled by the current knob on the ozone generator. In all experiments, the gas ozone concentration was controlled at 0.5 g h⁻¹. The gaseous product from the reactor was led to a terminator, where the remaining ozone was absorbed by 20% KI solution. All the experiments were conducted at 25°C ± 2°C. In each catalytic ozonation experiment, certain concentrations of nano-$Mg(OH)_2$ catalyst and 100 mL antibiotic solution (initial concentration of MNZ, TNZ, and DMZ was set at 50 mg L⁻¹) were well-mixed in the flask under magnetic stirring. During the run, 5 mL sample was rapidly taken out from the flask at every certain time interval and quenched quickly by adding 0.025 mol L⁻¹ sodium thiosulfate solution to prevent further reaction. Then, the

suspension of each sample was filtered using 0.22 μm filter and the filtrate was analyzed for the target parameters. Moreover, the ozone generator was switched off and the pure oxygen was diffused into the flask under the same conditions to discard the effect of adsorption of nano-Mg(OH)$_2$ during the experiments. For comparative purposes, single ozonation experiments were performed as controls in the same system, under identical experimental conditions.

To investigate the catalytic ozonation performance of the synthesized nano-Mg(OH)$_2$, the removal assays of nitroimidazole antibiotics in aqueous solution were carried out at catalyst dosage of 0.15 g L^{-1}, the initial antibiotics concentration of 50 mg L^{-1}, ozone flow rate of 0.1 L min^{-1}, and ozone gas concentration of 0.5 g h^{-1}. The reaction time for the experiment was set for 15 min since all the target compounds could be totally removed within this period. To evaluate the persistent catalytic activities of the synthesized nano-Mg(OH)$_2$, the three-run assay was conducted for each target compound. The TBA (0.1 mol L^{-1}) was added to catalytic ozonation system to investigate the influence of radical scavenger on the removal of MNZ, TNZ, and DMZ. The temperature was adjusted by constant temperature bath to 15°C, 25°C, and 35°C to determine the degradation rate of MNZ, TNZ, and DMZ. The multiple initial concentrations of 10, 30, 50, 100, 200, and 500 mg L^{-1} were used to explore the effect of initial concentrations of target antibiotics on removal efficiency. Sodium salt with the corresponding concentrations (0, 0.005, 0.05, 0.2, and 0.5 mol L^{-1}) was added into the aqueous solution in order to evaluate the effect of anions (Cl$^-$, HCO$_3^-$, and SO$_4^{2-}$) on degradation of MNZ, TNZ, and DMZ. Similarly, the effect of cations (Ca^{2+} and Mg^{2+}) on removal efficiency of antibiotics was investigated by the addition of the certain concentration (0, 0.005, 0.05, 0.2, and 0.5 mol L^{-1}) of chloride. The catalyst dosage was set as 0, 0.15, 0.3, 0.6, and 1.0 g L^{-1} to evaluate the effect of catalyst dosage. The experiments were conducted in triplicate and the average results were presented.

2.4. Analytical methods

The crystal phase of synthesized nano-Mg(OH)$_2$ catalyst was detected by an XRD analyzer (Rigaku, Japan) using Cu-Kα (λ = 0.154056 nm) at 2θ between 5° and 80°. The morphology of the obtained nano-Mg(OH)$_2$ was analyzed with Quanta-400F field emission scanning electron microscopy (FESEM, PerkinElmer, USA). The concentration of MNZ, TNZ, and DMZ in water sample was determined using high-performance liquid chromatography (HPLC, EX1600, Shanghai) consisting of a reverse-phase column (Waters SunFire C18, 2.1 × 150 mm, 3.5 μm) and a UV detector (EX1600 UV). The mobile phase was a mixture of 15% (v/v) acetonitrile and 85% (v/v) water at the flow rate of 0.2 mL min^{-1}. The injection volume was 5 μL, and the detection wavelength was 315 nm. The gas ozone concentration was measured by iodometric method [30,31]. To better illustrate the removal behaviors of nitroimidazole antibiotics in the presence of nano-Mg(OH)$_2$, the removal kinetics of nitroimidazole antibiotics was investigated. The following pseudo-first-order kinetic model (Eq. (1)) was used to fit the experimental data:

$$\ln C_t = \ln C_0 - kt \tag{1}$$

where C_0 and C_t are the concentrations of nitroimidazole antibiotics at time 0 and t min, respectively; k is the pseudo-first-order degradation rate constant.

3. Results and discussion

3.1. Characterization of synthesized nano-Mg(OH)$_2$ catalyst

The morphologies of the synthesized Mg(OH)$_2$ powders with low and high magnification views are shown in Figs. 1a and b, respectively. Fig. 1 exhibits that the obtained powder had a better morphology of regular nano-plates and the size of Mg(OH)$_2$ varied from 50 to 200 nm. In addition, the obvious agglomeration of Mg(OH)$_2$ was not observed, indicating that the synthesized Mg(OH)$_2$ nanoparticles had a rather good dispersion. The phase structure of nano-Mg(OH)$_2$ sample was analyzed by XRD patterns (Fig. 2). Crystal planes of (001), (100), (101), (102), (110), (111), (103), and (201) could be indexed as the hexagonal crystal structure of magnesium hydroxide, which matched with the standard (JCPDS 7-239). The sharp peaks indicated that the synthesized sample possessed good crystallinity. No extraneous peaks were detected in the pattern, indicating the high purity of the obtained sample.
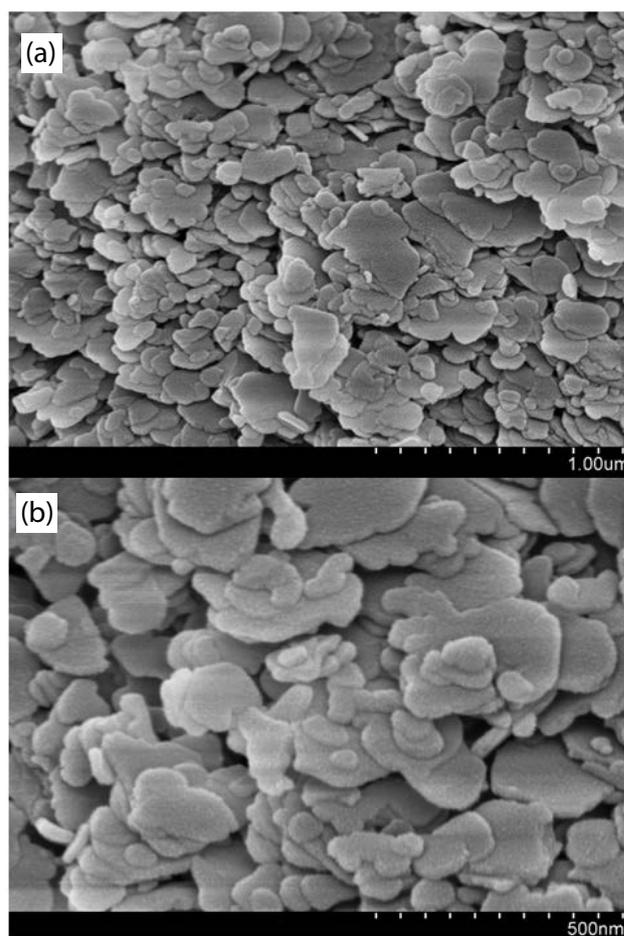

Fig. 1. Scanning electron microscopy (SEM) images of the synthesized nano-Mg(OH)$_2$ at low magnification (a) and high magnification (b) view.
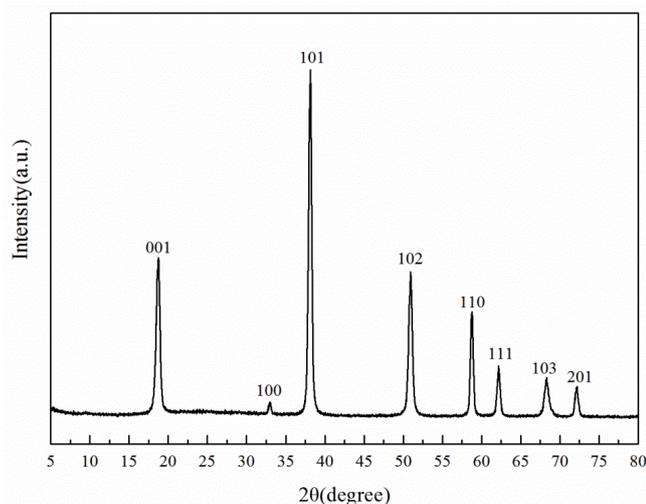
Fig. 2. X-ray diffraction (XRD) patterns of the synthesized nano-Mg(OH)$_2$.

3.2. Degradation of nitroimidazole antibiotics in the presence of nano-Mg(OH)$_2$

The removal efficiency of MNZ, TNZ, and DMZ increased to 87.8%, 92.1%, and 98.2% within 10 min in the presence of nano-Mg(OH)$_2$ (Fig. 3). Compared with the catalytic ozonation treatment, the removal efficiency of MNZ, TNZ, and DMZ could only reach 51.9%, 87.8%, and 93.2% after 10 min in the pure ozonation process. The ultimate concentration of antibiotics (MNZ, TNZ, and DMZ) was very close to the original concentration in the adsorption experiments of nano-Mg(OH)$_2$, suggesting that the removal of antibiotics was mainly due to the ozonation process while the nitroimidazole antibiotics were hardly adsorbed on the catalyst. These results suggested that synthesized Mg(OH)$_2$ was favorable for the degradation of above-mentioned antibiotics. The ozonation of nitroimidazole antibiotics fitted the pseudo-first-order kinetic model (R^2 = 0.97–0.99). The removal rate constant of MNZ in the catalytic ozonation treatment (k_{MNZ} = 0.374 min^{-1}) was four times higher than that in the single ozonation treatment (k_{MNZ} = 0.093 min^{-1}). The degradation rate constant of TNZ increased by 31.2% from 0.266 to 0.349 min^{-1} by nano-Mg(OH)$_2$. Similarly, the degradation rate constant of DMZ increased by 39.2% from 0.319 to 0.444 min^{-1} when nano-Mg(OH)$_2$ was added. These results also confirmed the high catalytic performance of synthesized Mg(OH)$_2$ in the ozonation process of target antibiotics. The pH of the solution changed after the addition of nano-Mg(OH)$_2$ catalyst. The solution pH was 6.53 in the absence of catalyst while the solution pH became 10.2 after the addition of catalyst. More hydroxyl radicals which have stronger oxidation capacity will be produced as pH increases with the addition of catalyst [32,33]. These may also increase the removal rate of antibiotics. Additionally, the catalytic ozonation of MNZ by synthesized Mg(OH)$_2$ was better than that of TNZ and DMZ.

The high efficiency for the catalytic ozonation of nitroimidazole antibiotics using nano-Mg(OH)$_2$ as catalyst, indicated that the nano-Mg(OH)$_2$ is a promising ozonation catalyst. The removal efficiency of nitroimidazole antibiotics
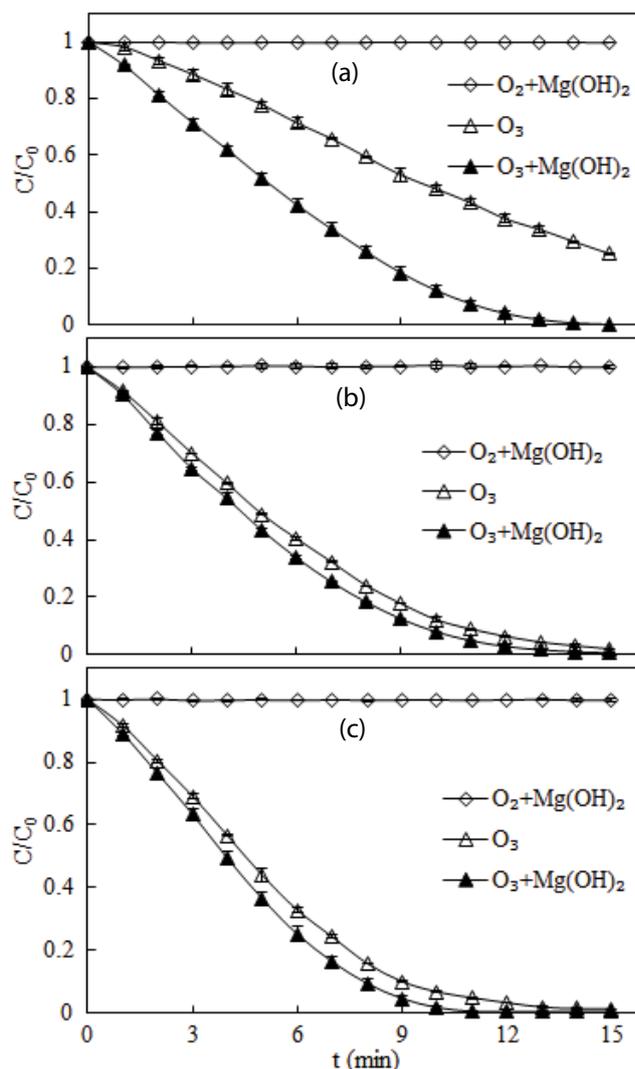

Fig. 3. Degradation of metronidazole (a), tinidazole (b), and dimetridazole (c) in different oxidation treatments.

did not sharply change after three runs in the presence of nano-Mg(OH)$_2$ (Fig. 4). The persistent high catalytic activity of the synthesized nano-Mg(OH)$_2$ indicated that the nano-Mg(OH)$_2$ is a kind of sustainable catalyst. The removal rate constant of MNZ, TNZ, and DMZ after three runs shifted to 0.326, 0.342, and 0.481 min^{-1}, respectively. The catalytic ozonation of MNZ and TNZ in the presence of other catalysts such as activated carbon, nano-MgO, and brucite have been investigated [13,16,34]. However, rare evaluation has been conducted on the degradation of MNZ, TNZ, and DMZ in the catalytic ozonation process using nano-Mg(OH)$_2$ as catalyst except this investigation.

3.3. Effect of hydroxyl radical scavengers on the removal of nitroimidazole antibiotics

Ozone can oxidize organic pollutants via direct oxidation by molecular ozone and indirect radical oxidation by hydroxyl radical [35,36]. In order to understand which
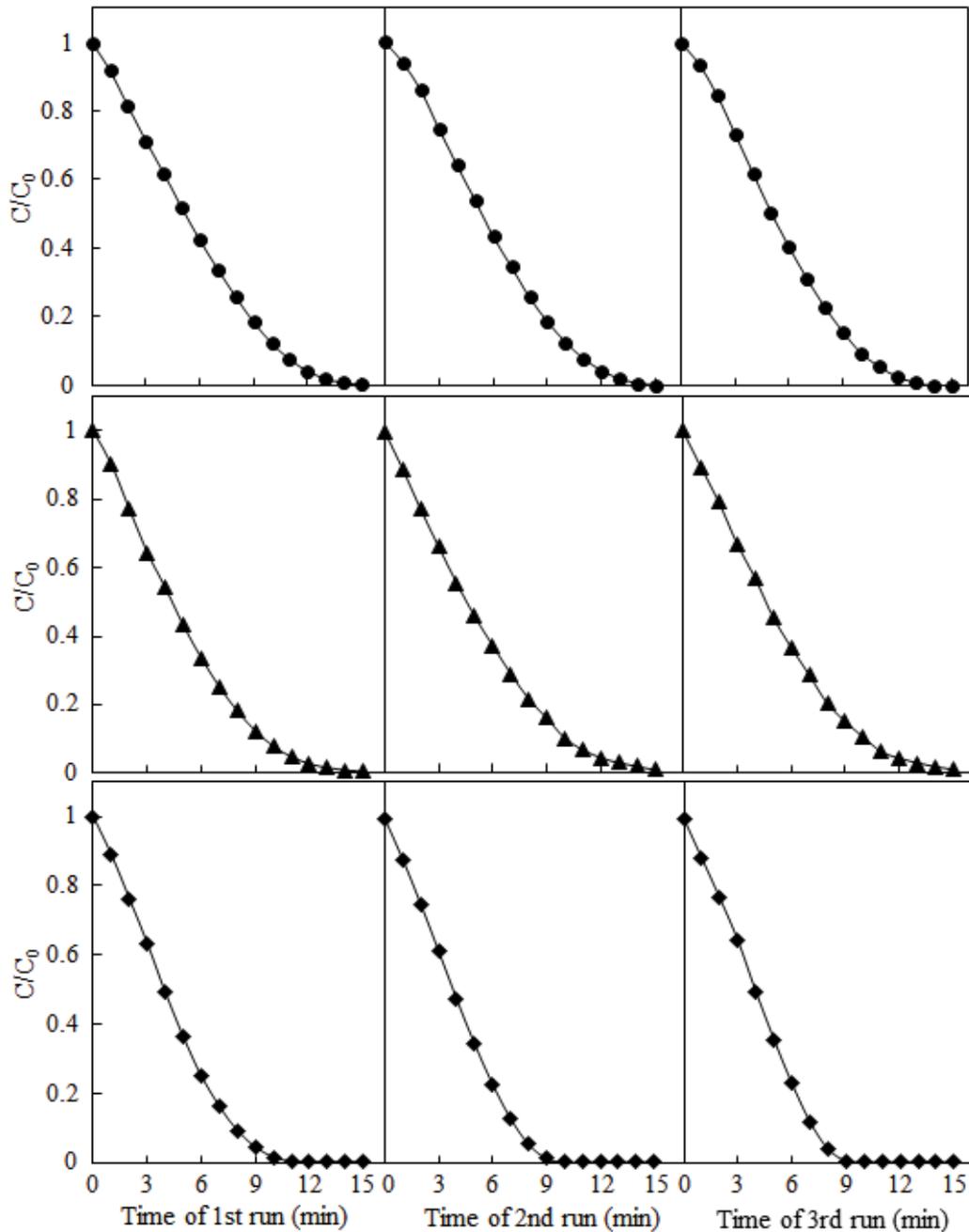
Fig. 4. Effect of run times on the removal of metronidazole (●), tinidazole (▲), and dimetridazole (◆) in the presence of nano-Mg(OH)$_2$.

oxidation type played a major role in the degradation of MNZ, TNZ, and DMZ in the catalytic ozonation system, the radical scavenger (TBA) was employed during the catalytic ozonation process following previous methods [37,38]. The presence of TBA inhibited the degradation of MNZ, TNZ, and DMZ in catalytic ozonation (Fig. 5). After 10 min, degradation rates of MNZ, TNZ, and DMZ reached 87.8%, 92.1%, and 98.2% in the absence of scavenger in catalytic ozonation. However, degradation rates of MNZ, TNZ, and DMZ decreased to 30.7%, 62.5%, and 80.5% in catalytic ozonation with the addition of TBA. This result indicated that the catalytic ozonation of target antibiotics was mainly through

the hydroxyl radical reaction process, which indicated the potential high removal efficacy of antibiotics using nano-Mg(OH)$_2$ as ozonation catalyst.

In order to further confirm the contribution of ozone molecule (f_{O_3}) and hydroxyl radicals ($f_{OH\bullet}$) to the removal of MNZ, TNZ, and DMZ in the catalytic ozonation with/without the presence of TBA, the following rate equations were used [39,40]:

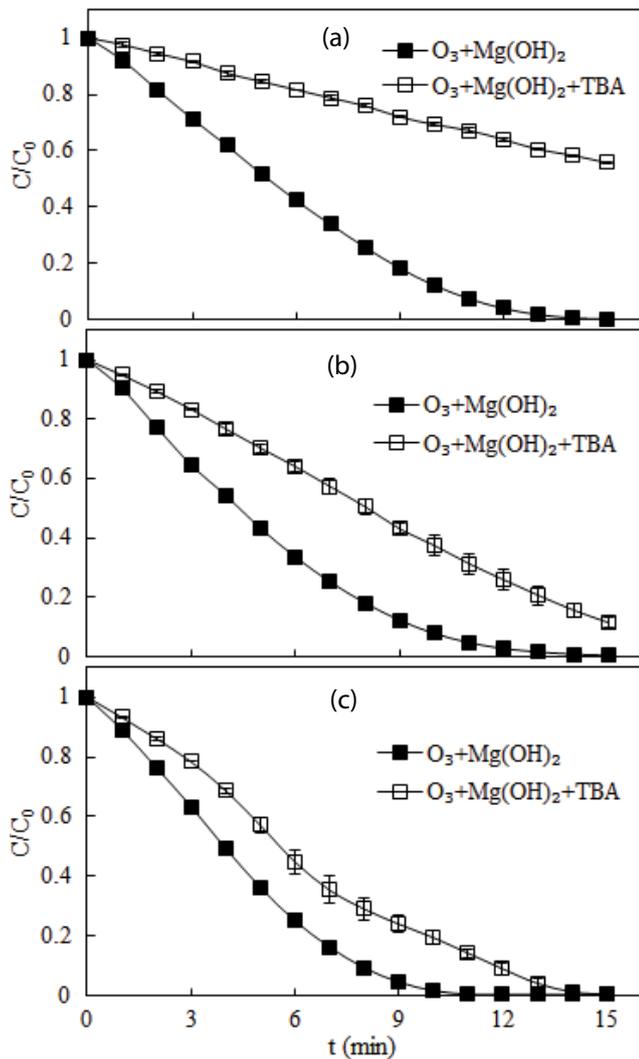$$-\frac{dC}{dt} = r_{homo} + r_{hetero} \qquad (2)$$

Fig. 5. Effect of tert-butanol (TBA) on the degradation of metronidazole (a), tinidazole (b), and dimetridazole (c).

where r_{homo} represents the homogeneous reactions occurring in the liquid bulk; r_{hetero} represents the heterogeneous reactions occurring on the catalysts surface.

So Eq. (2) can also be written as:

$$-\frac{dC}{dt} = \left(k_{homo} + k_{hetero}[S]\right)C = k_{overall}C \tag{3}$$

$$k_{homo} = k_1[O_3] + k_2[OH^\bullet] \tag{4}$$

$$k_{hetero} = k_3 + k_4[O_3] + k_5[OH^\bullet] \tag{5}$$

where $[S]$ is the concentration of catalyst; $k_{overall}$ is the pseudo-first-order degradation rate constant; k_{homo} represents the homogeneous reaction rate constant occurring in the liquid bulk; k_{hetero} represents the heterogeneous reaction rate constant occurring on the catalysts surface; parameters k_1, k_2, k_3, k_4, and k_5 are the degradation rate constants for the reaction

with molecular O_3, hydroxyl radicals, adsorption on the catalyst surface, molecular O_3 on the surface, and hydroxyl radicals on the surface, respectively. In the catalytic ozonation of target antibiotics, the addition of TBA suspended the reaction with hydroxyl radical, so the k_2 and k_5 can be omitted in Eqs. (4) and (5). The contribution of hydroxyl radicals ($f_{OH^\bullet}$) can be determined by Eq. (6):

$$f_{OH^\bullet} = 1 - f_{O_3} = \left(1 - \frac{k_{TBA}}{k_{overall}}\right) \times 100\% \tag{6}$$

The k_{TBA} for the MNZ, TNZ, and DMZ was 0.039, 0.138, and 0.224 min^{-1}, respectively (Table 1). The $k_{overall}$ for the MNZ, TNZ, and DMZ was 0.203, 0.349, and 0.444 min^{-1}, respectively. Therefore, the $f_{OH^\bullet}$ for the MNZ, TNZ, and DMZ was 80.8%, 60.5%, and 50.0%, respectively. These results indicated that the hydroxyl radical played a major role in the catalytic ozonation process of MNZ and TNZ. However, the hydroxyl radical and molecular O_3 had a roughly even split fraction in the catalytic ozonation process of DMZ.

3.4. Effect of temperature on the removal of nitroimidazole antibiotics

The influence of reaction temperature on catalytic ozonation of MNZ, TNZ, and DMZ was investigated at 15°C, 25°C, and 35°C (Fig. 6). The removal efficiency of the target antibiotics increased when the temperature increased. The removal rate constant of MNZ, TNZ, and DMZ sharply increased from 0.179, 0.268, and 0.206 min^{-1} to 0.374, 0.349, and 0.444 min^{-1}, respectively, when the temperature increased from 15°C to 25°C. However, the removal efficiencies were suppressed when the reaction temperature further increased to 35°C. The removal rate constant of MNZ, TNZ, and DMZ decreased by 50.0%, 20.3%, and 29.3% to 0.186, 0.278, and 0.314 min^{-1}, respectively, when the temperature increased from 25°C to 35°C. The same phenomenon was reported by Lan et al. [39] using Fe-MCM-41 as catalyst to assist ozonation of p-chlorobenzoic acid. It is generally accepted that the increase of temperature accelerates chemical reaction rate and mass transfer [41], which directly improves removal efficiency of target antibiotics. Apart from increased reaction rate, the increased reaction temperature would lead to a decrease in ozone solubility of aqueous solution [42], which lowered the concentration

Table 1
Contribution of hydroxyl radicals ($f_{OH^\bullet}$) to the removal of nitroimidazole antibiotics in the catalytic ozonation treatment with/without tert-butanol (TBA)

Name	Metronidazole	Tinidazole	Dimetridazole
k_{TBA} (min^{-1})	0.039	0.138	0.224
$k_{overall}$ (min^{-1})	0.203	0.349	0.444
$f_{OH^\bullet}$ (%)	80.8	60.5	50

*k_{TBA}: degradation rate constant in the catalytic ozonation with the presence of tert butyl alcohol.
$k_{overall}$: degradation rate constant in the catalytic ozonation without the presence of tert butyl alcohol.
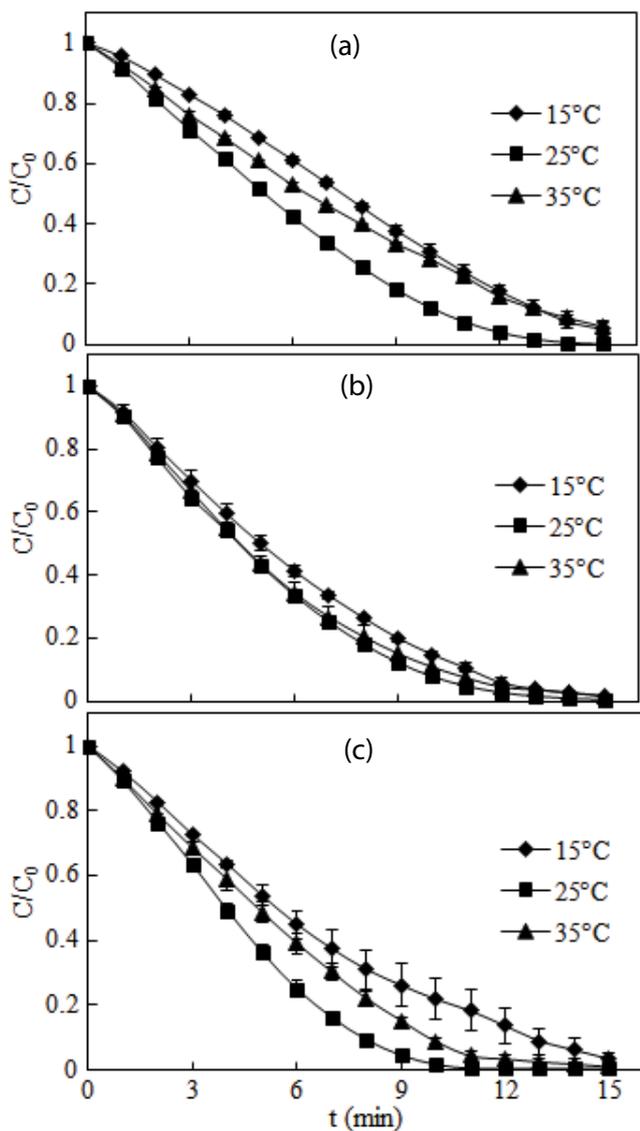
Fig. 6. Effect of temperature on the degradation of metronidazole (a), tinidazole (b), and dimetridazole (c).

Fig. 7. Effect of initial concentration of antibiotics on the degradation of metronidazole (a), tinidazole (b), and dimetridazole (c).

of ozone in aqueous solution and reduced the generation of hydroxyl radicals. The competition of the two opposite effects led to 25°C as the optimal reaction temperature for the catalytic ozonation of MNZ, TNZ, and DMZ. Therefore, 25°C was chosen as the reaction temperature in the following experiments.

3.5. Effect of initial concentration of antibiotics on the removal of nitroimidazole antibiotics

The effect of initial concentration on the removal of nitroimidazole antibiotics was investigated. A sharp decrease in removal efficiency of MNZ was observed when the MNZ initial concentration increased from 10 to 500 mg L^{-1} (Fig. 7). The removal efficiency of MNZ quickly reached up to 93.6% after 10 min of reaction with the initial concentration of 10 mg L^{-1} while those with initial concentrations of 30, 50, 100,
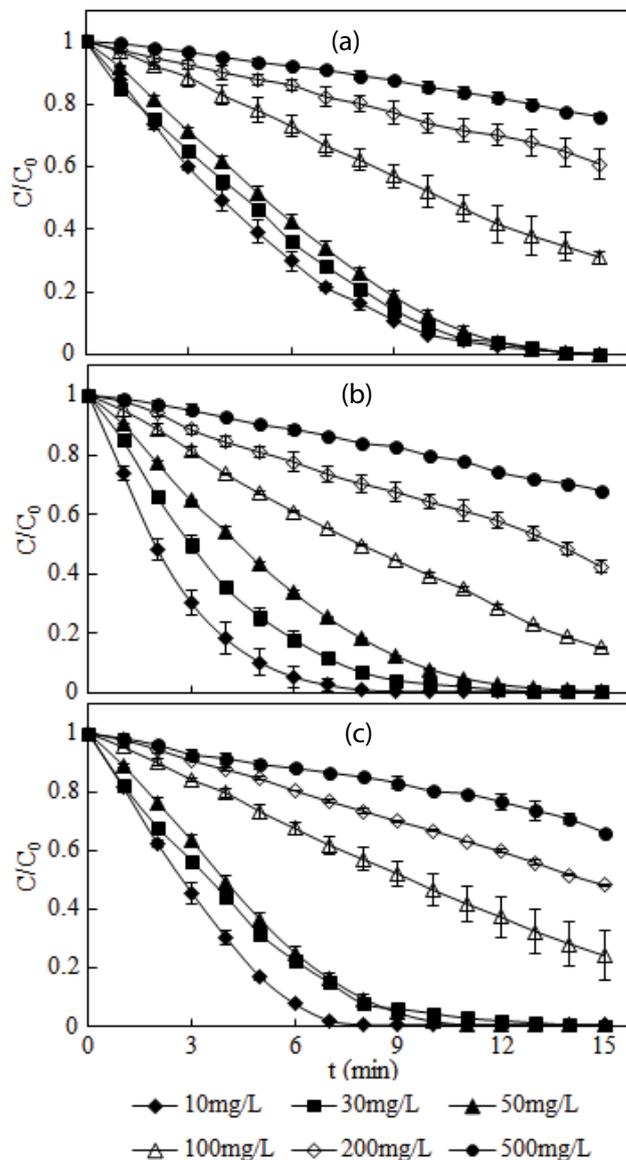
200, and 500 mg L^{-1} were only 91.1%, 86.6%, 47.9%, 26.2%, and 14.6%, respectively. Meanwhile, the degradation rate constant decreased by 20.7 times from 0.390 to 0.018 min^{-1} when the initial concentration of MNZ increased from 10 to 500 mg L^{-1}. Similar sharp drop trend was also observed when the initial concentration of TNZ or DMZ increased from 10 to 500 mg L^{-1}. The increase in the initial concentration of target compound led to the decrease in the removal efficiency of MNZ, TNZ, and DMZ. A possible explanation for this finding might be that the organic intermediates increased with an increase in the concentration of target compound and the competing reactions between antibiotics and their degradation products with ozone turned predominant to decrease the contact probability of contaminants with ozone [6,17,43,44]. Additionally, excessive antibiotics and

degradation intermediates can be adsorbed onto the surface of catalyst, which also inhibited the surface reactions to cause lower removal efficiency [17].

3.6. Effect of anions on the removal of nitroimidazole antibiotics

Natural water is a complex system, in which there commonly exist a wide variety of inorganic anions such as Cl^-, HCO_3^-, and SO_4^{2-}. The concentrations of these anions in different water bodies are different so that it is necessary to study the removal of nitroimidazole antibiotics in the presence of different concentrations of anions. The study evaluated the effect of anions (Cl^-, HCO_3^-, and SO_4^{2-}) on the removal of nitroimidazole antibiotics in catalytic ozonation with the initial concentration of different anions ranging from 0 to 0.5 mol L^{-1} (Fig. 8). The results showed that these anions had great influence on the degradation of nitroimidazole antibiotics. The removal rate constant of MNZ, TNZ, and DMZ decreased by 66.8%, 61.9%, and 64.6%, respectively, when the initial concentration of Cl^- increased from
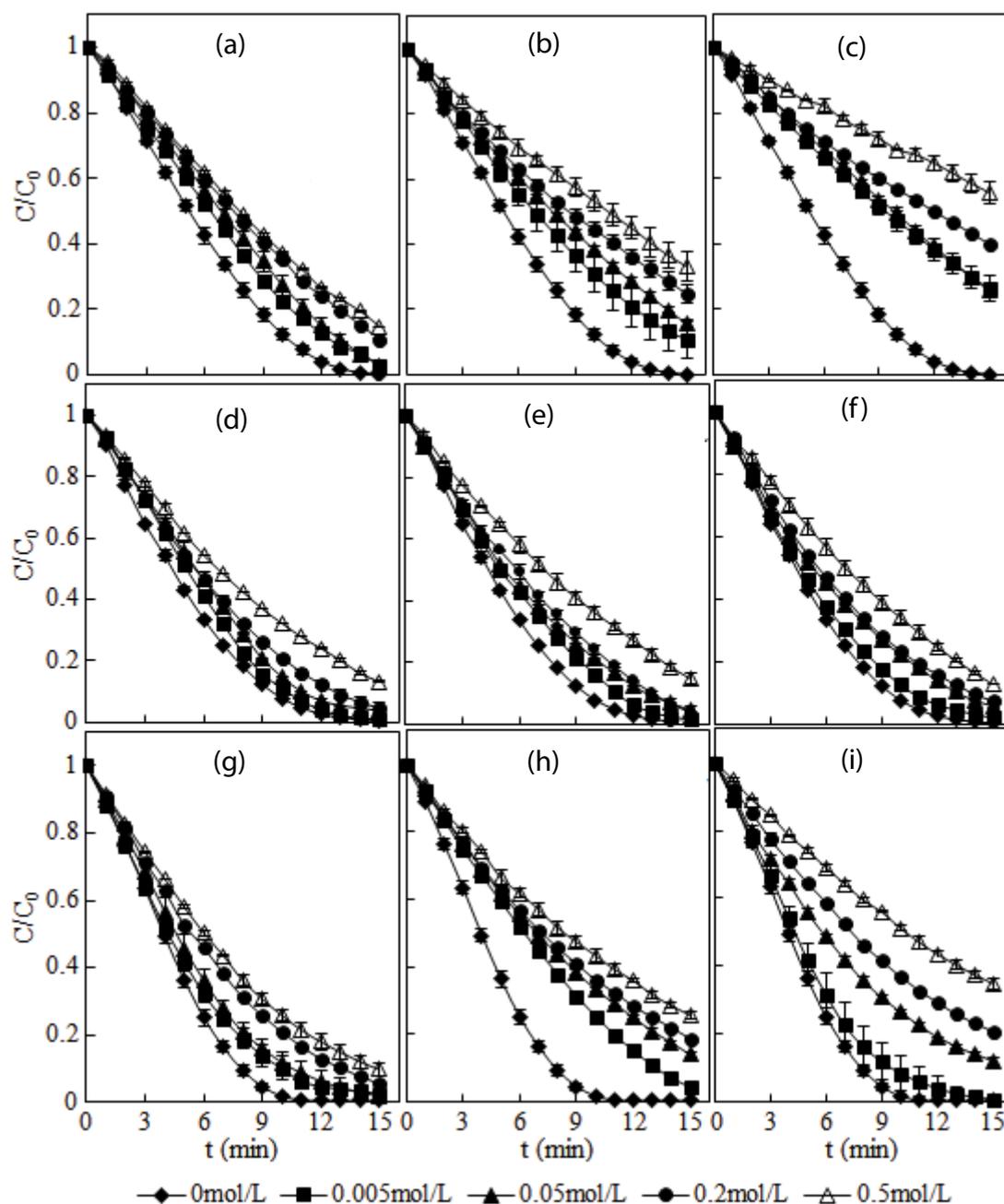

Fig. 8. Effect of anions on the degradation of nitroimidazole antibiotics. The a, b, and c refer to the effect of Cl^-, HCO_3^-, and SO_4^{2-} on the degradation of metronidazole, respectively. The d, e, and f refer to the effect of Cl^-, HCO_3^-, and SO_4^{2-} on the degradation of tinidazole, respectively. The g, h, and i refer to the effect of Cl^-, HCO_3^-, and SO_4^{2-} on the degradation of dimetridazole, respectively.

0 to 0.5 mol L⁻¹ while that of MNZ, TNZ, and DMZ decreased by 80.7%, 64.8%, and 79.7%, respectively, when the initial concentration of HCO_3^- increased from 0 to 0.5 mol L⁻¹. In the case of dianion, the removal rate constant of MNZ, TNZ, and DMZ decreased by 89.6%, 62.5%, and 83.8%, respectively, when the initial concentration of SO_4^{2-} increased from 0 to 0.5 mol L⁻¹. The removal efficiency of MNZ, TNZ, and DMZ sharply decreased with the increase in the concentration of anions (Cl⁻, HCO_3^-, or SO_4^{2-}), indicating that the presence of anions (Cl⁻, HCO_3^-, or SO_4^{2-}) could inhibit the degradation of nitroimidazole antibiotics. The reaction of anions (Cl⁻, HCO_3^-, or SO_4^{2-}) with hydroxyl radicals could lead to the formation of inorganic radical ions while the oxidation capacity of newly formed free radical is much weaker than that of ozone [45–50]. Besides the reaction of radicals, the anions can also be adsorbed on the catalyst or

contaminate and block the catalyst, thus decreasing reaction sites and leading to the decreased catalytic capability [51].

3.7. Effect of cations on the removal of nitroimidazole antibiotics

The influence of cations (Ca^{2+} and Mg^{2+}) on the removal of antibiotics was also investigated (Fig. 9). The Ca^{2+} and Mg^{2+} exerted a depressing effect on the removal efficiency of all target compounds by catalytic ozonation process with higher concentrations. The removal rate constant of MNZ, TNZ, and DMZ decreased by 63.4%, 57.6%, and 70.3%, respectively, when the initial concentration of Ca^{2+} increased from 0 to 0.5 mol L⁻¹ while that of MNZ, TNZ, and DMZ decreased by 52.4%, 55.9%, and 68.7%, respectively, when the initial concentration of Mg^{2+} increased from 0 to 0.5 mol L⁻¹. One reasonable explanation was that Ca^{2+} and Mg^{2+} belonged to
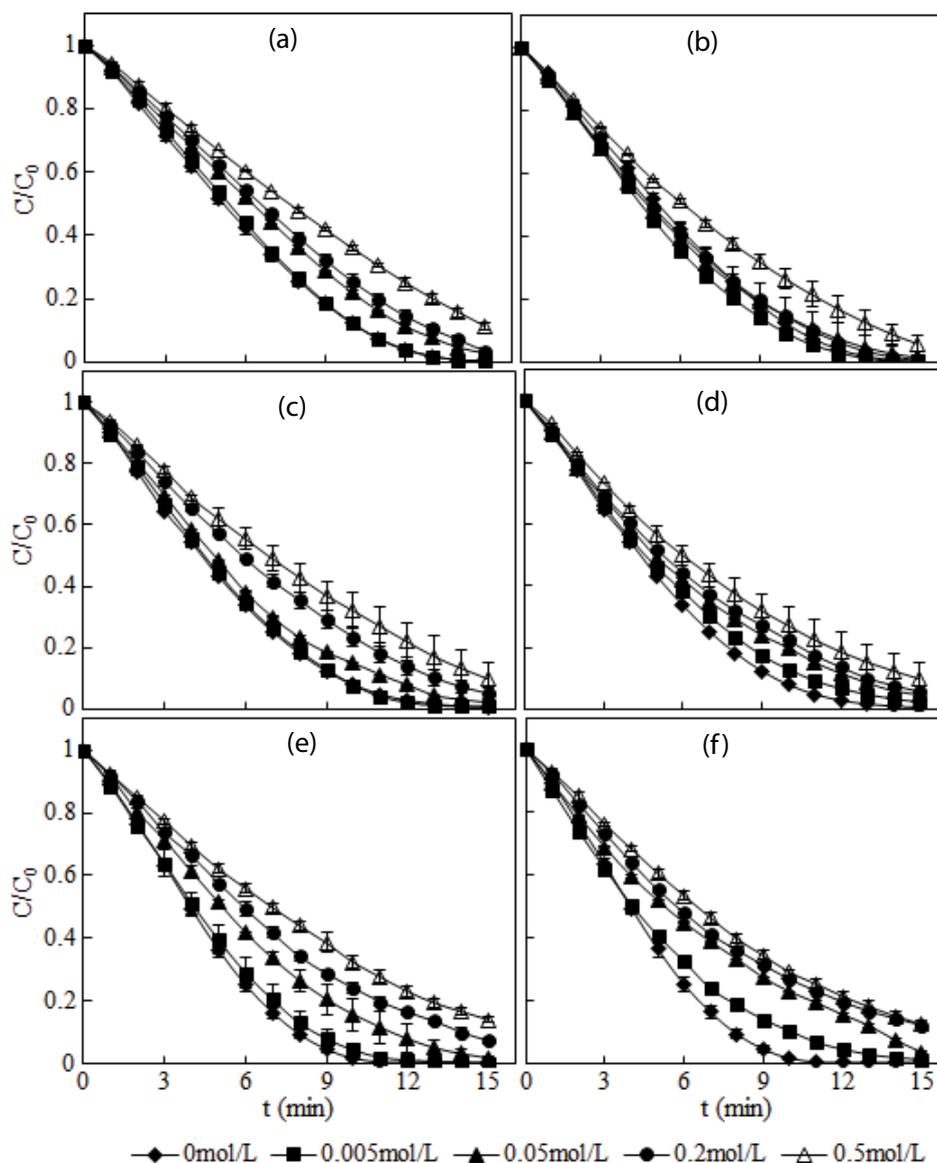

Fig. 9. Effect of cations on the degradation of nitroimidazole antibiotics. The a, c, and e refer to the effect of Ca^{2+} on the degradation of metronidazole, tinidazole, and dimetridazole, respectively; while the b, d, and f refer to the effect of Mg^{2+} on the degradation of metronidazole, tinidazole, and dimetridazole, respectively.

alkali metal and their valences were stable so as not to take part in the degradation reaction [52]. On the other hand, when the concentrations of Ca^{2+} and Mg^{2+} were further increased, the content of Cl^- in the system increased exponentially so that the capture of radical increased. Therefore, the catalytic ozonation rates of MNZ, TNZ, and DMZ decreased with the increased concentrations of Ca^{2+} and Mg^{2+}.

3.8. Effect of catalyst dosage on the removal of nitroimidazole antibiotics

The catalytic ozonation of MNZ, TNZ, and DMZ in the presence of nano-$Mg(OH)_2$ (with various concentrations ranging between 0 and 1.0 g L^{-1}) was evaluated (Fig. 10). The increase in catalyst dose led to the increase in the removal rate constant of nitroimidazole antibiotics while further increase in catalyst amount led to the decrease in the removal efficiency. The removal rate constant of MNZ and TNZ increased by 302.2% and 31.2%, respectively to the maximal removal rate constant when the catalyst dosage increased from 0 to 0.15 g L^{-1}. The removal rate constant of DMZ increased by 61.4% to maximal removal rate constant ($k_{DMZ} = 0.515$ min^{-1}) when the catalyst dosage increased from 0 to 0.30 g L^{-1}. The maximal removal rate constant was reached at relatively low dose of catalyst, confirming that the nano-$Mg(OH)_2$ is a promising ozonation catalyst. The increase in catalyst amount could provide larger absolute surface area and more active sites, which enhanced the removal efficiency of antibiotics [53]. However, the removal efficiency decreased when dosage of nano-$Mg(OH)_2$ continued to increase due to the limited amount of ozone in the system [54]. Similar studies have been reported on the catalytic ozonation of metronidazole using nano-MgO catalyst [16]. Considering the treatment cost, 0.15 g L^{-1} was chosen as the optimized catalyst dose for nitroimidazole antibiotics.

3.9. Possible mechanism

It is generally accepted that the catalytic ozonation process can be explained by two possible mechanisms including the direct reaction with ozone molecules and the indirect reaction with free radicals [44,55]. The catalyst $Mg(OH)_2$ showed high catalytic activity based on fast removal of nitroimidazole antibiotics in different processes and little adsorption (around 1%) of nitroimidazole antibiotics on the catalyst. This phenomenon could be explained by the interaction between ozone molecules and increased hydroxyl groups which played a major role in improving transformation of ozone because of the electrophilic properties of ozone [44]. The results of TBA effect showed that indirect reaction with free radicals was an important mechanism for the removal of nitroimidazole antibiotics. However, the inorganic anions strongly affected the removal of antibiotics, indicating that a portion of hydroxyl radicals were released onto the catalyst surface. In summary, both the direct reaction with ozone molecules and the indirect reaction with free radicals could occur in the bulk solution and on the catalyst surface in this study. In the bulk solution, interaction between the ozone and antibiotic molecules caused partial degradation of target antibiotics and the transformation of ozone into hydroxyl radical in
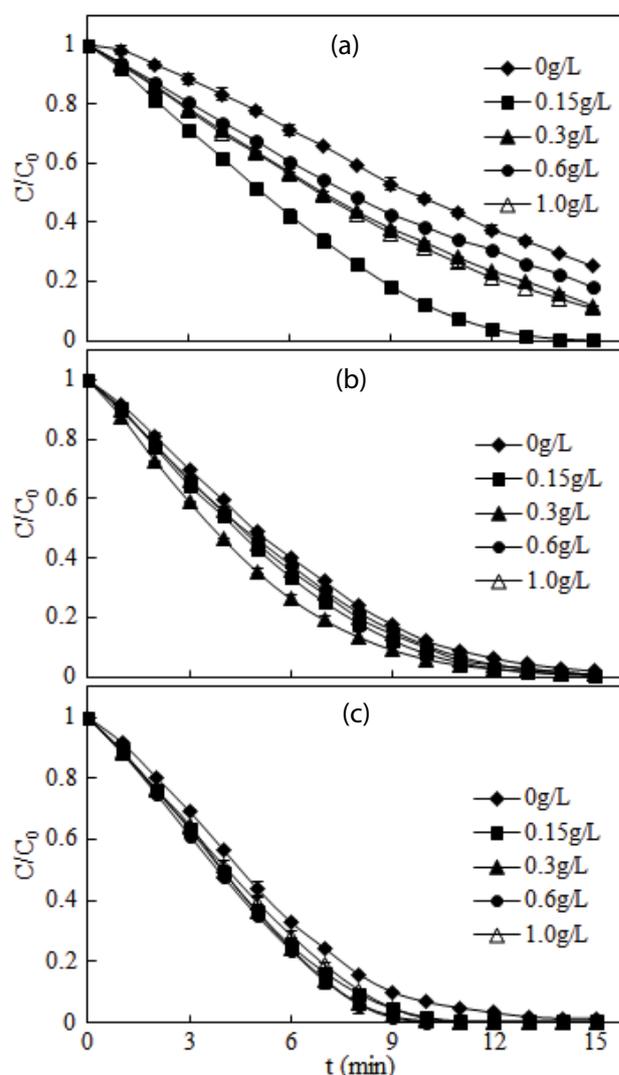

Fig. 10. Effect of catalyst dosage on the degradation of metronidazole (a), tinidazole (b), and dimetridazole (c).

aqueous solution could indirectly degrade the antibiotics. On the surface of nano-$Mg(OH)_2$ catalyst, ozone molecules formed hydrogen bonds with hydroxyl group and then the bounded ozone partially decomposed into atomic oxygen, which accelerated the formation of hydroxyl radicals and indirectly improved the catalytic ozonation of antibiotics. Undissociated ozone combined with nano-$Mg(OH)_2$ could directly oxidize antibiotics.

4. Conclusion

High removal efficiency of nitroimidazole antibiotics and persistent high catalytic activity of the synthesized nano-$Mg(OH)_2$ in the catalytic ozonation were achieved, indicating that the nano-$Mg(OH)_2$ is a promising ozonation catalyst for the removal of antibiotics. The severe inhibition of hydroxyl radical scavenger (TBA) on the catalytic ozonation suggested that hydroxyl radical reaction served as the predominant removal process for nitroimidazole antibiotics, indicating the potential high removal capacity of antibiotics

using nano-Mg(OH)$_2$ as ozonation catalyst. The removal of nitroimidazole antibiotics followed a pseudo-first order kinetic model. The removal of nitroimidazole antibiotics could be greatly influenced by multiple factors such as catalyst dosage, reaction temperature, initial concentration of nitroimidazole antibiotics, anions (Cl$^-$, HCO$_3^-$, and SO$_4^{2-}$), and cations (Ca^{2+} and Mg^{2+}). Increase in the dosage of catalyst and reaction temperature within certain range could enhance the degradation of MNZ, TNZ, and DMZ while increase in the initial concentration of nitroimidazole antibiotics led to the decrease in the removal efficiency. All anions and cations had negative effects on the removal of nitroimidazole antibiotics. Due to the unique features such as low cost, heavy-metals free, high stability in water, more environment-friendly, and less toxicity, the nano-Mg(OH)$_2$ could be a potential green ozonation catalyst for antibiotic removal.

Acknowledgments

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] K. Kümmerer, Antibiotics in the aquatic environment-a review-part II, Chemosphere, 75 (2009) 435–441.
[2] T.P. Van Boeckel, S. Gandra, A. Ashok, Q. Caudron, B.T. Grenfell, S.A. Levin, R. Laxminarayan, Global antibiotic consumption 2000 to 2010: an analysis of national pharmaceutical sales data, Lancet Infect. Dis., 14 (2014) 742–750.
[3] A.K. Sarmah, M.T. Meyer, A.B. Boxall, A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment, Chemosphere, 65 (2006) 725–759.
[4] J.P. Bound, N. Voulvoulis, Pharmaceuticals in the aquatic environment-a comparison of risk assessment strategies, Chemosphere, 56 (2004) 1143–1155.
[5] A. Murata, H. Takada, K. Mutoh, H. Hosoda, A. Harada, N. Nakada, Nationwide monitoring of selected antibiotics: distribution and sources of sulfonamides, trimethoprim, and macrolides in Japanese rivers, Sci. Total Environ., 409 (2011) 5305–5312.
[6] L. Hou, H. Zhang, L. Wang, L. Chen, Y. Xiong, X. Xue, Removal of sulfamethoxazole from aqueous solution by sono-ozonation in the presence of a magnetic catalyst, Sep. Purif. Technol., 117 (2013) 46–52.
[7] Z. Fang, J. Chen, X. Qiu, W. Cheng, L. Zhu, Effective removal of antibiotic metronidazole from water by nanoscale zero-valent iron particles, Desalination, 268 (2011) 60–67.
[8] A.G. Trovó, R.F.P. Nogueira, A. Agüera, A.R. Fernandez-Alba, C. Sirtori, S. Malato, Degradation of sulfamethoxazole in water by solar photo-Fenton. chemical and toxicological evaluation, Water Res., 43 (2009) 3922–3931.
[9] M.L. Richardson, J.M. Bowron, The fate of pharmaceutical chemicals in the aquatic environment, J. Pharm. Pharmacol., 37 (1985) 1–12.
[10] K. Kümmerer, A. Al-Ahmada, V. Mersch-Sundermann, Bio-degradability of some antibiotics, elimination of the genotoxicity and affection of wastewater bacteria in a simple test, Chemosphere, 40 (2000) 701–710.
[11] A. Bendesky, D. Menéndez, P. Ostrosky-Wegman, Is metronidazole carcinogenic?, Mutat. Res., 511 (2002) 133–144.
[12] A. Khataee, M. Kiranşan, S. Karaca, M. Sheydaei, Photocatalytic ozonation of metronidazole by synthesized zinc oxide nanoparticles immobilized on montmorillonite, J. Taiwan Inst. Chem. Eng., 74 (2017) 196–204.
[13] A. Shokri, Investigation of UV/H$_2$O$_2$ process for removal of ortho-toluidine from industrial wastewater by response surface methodology based on the central composite design, Desal. Water Treat., 58 (2017) 258–266.
[14] J. Rivera-Utrilla, M. Sánchez-Polo, G. Prados-Joya, M.A. Ferro-García, I. Bautista-Toledo, Removal of tinidazole from waters by using ozone and activated carbon in dynamic regime, J. Hazard. Mater., 174 (2010) 880–886.
[15] M. Sánchez-Polo, J. Rivera-Utrilla, G. Prados-Joya, M.A. Ferro-García, I. Bautista-Toledo, Removal of pharmaceutical compounds, nitroimidazoles, from waters by using the ozone/carbon system, Water Res., 42 (2008) 4163–4171.
[16] M. Kermani, F.B. Asl, M. Farzadkia, A. Esrafili, S.S. Arian, M. Khazaei, Y.D. Shahamat, D. Zeynalzadeh, Heterogeneous catalytic ozonation by nano-MgO is better than sole ozonation for metronidazole degradation, toxicity reduction, and biodegradability improvement, Desal. Water Treat., 57 (2016) 16435–16444.
[17] Z. Bai, Q. Yang, J. Wang, Catalytic ozonation of sulfamethazine using Ce$_{0.1}$Fe$_{0.9}$OOH as catalyst: mineralization and catalytic mechanisms, Chem. Eng. J., 300 (2016) 169–176.
[18] L. Hou, H. Zhang, L. Wang, L. Chen, Ultrasound-enhanced magnetite catalytic ozonation of tetracycline in water, Chem. Eng. J., 229 (2013) 577–584.
[19] R. Yin, W. Guo, J. Du, X. Zhou, H. Zheng, Q. Wu, J. Chang, N. Ren, Heteroatoms doped graphene for catalytic ozonation of sulfamethoxazole by metal-free catalysis: performances and mechanisms, Chem. Eng. J., 317 (2017) 632–639.
[20] A. Shokri, The treatment of spent caustic in the wastewater of olefin units by ozonation followed by electrocoagulation process, Desal. Water Treat., 111 (2018) 173–182.
[21] A.G. Gonçalves, J.J.M. Órfão, M.F.R. Pereira, Catalytic ozonation of sulphamethoxazole in the presence of carbon materials: catalytic performance and reaction pathways, J. Hazard. Mater., 239–240 (2012) 167–174.
[22] Y. Tian, B. Gao, V.L. Morales, H. Chen, Y. Wang, H. Li, Removal of sulfamethoxazole and sulfapyridine by carbon nanotubes in fixed-bed columns, Chemosphere, 90 (2013) 2597–2605.
[23] J. Akhtar, N.S. Amin, A. Aris, Combined adsorption and catalytic ozonation for removal of sulfamethoxazole using Fe$_2$O$_3$/CeO$_2$ loaded activated carbon, Chem. Eng. J., 170 (2011) 136–144.
[24] Y.-M Dong, K. He, B. Zhao, Y. Yin, L. Yin, A. Zhang, Catalytic ozonation of azo dye active brilliant red X-3B in water with natural mineral brucite, Catal. Commun., 8 (2007) 1599–1603.
[25] K. He, Y.M. Dong, Z. Li, L. Yin, A.M. Zhang, Y.C. Zheng, Catalytic ozonation of phenol in water with natural brucite and magnesia, J. Hazard. Mater., 159 (2008) 587–592.
[26] Y. Dong, K. He, L. Yin, A. Zhang, Catalytic degradation of nitrobenzene and aniline in presence of ozone by magnesia from natural mineral, Catal. Lett., 119 (2007) 222–227.
[27] A. Shokri, Degradation of 4-nitrophenol from industrial wastewater by nano catalytic ozonation, Int. J. Nano Dimens., 7 (2016) 160–167.
[28] A. Shokri, F. Rabiee, K. Mahanpoor, Employing a novel nanocatalyst (Mn/Iranian hematite) for oxidation of SO$_2$ pollutant in aqueous environment, Int. J. Environ. Sci. Technol., 14 (2017) 2485–2494.
[29] W. Wang, X. Qiao, J. Chen, H. Li, Facile synthesis of magnesium oxide nanoplates via chemical precipitation, Mater. Lett., 61 (2007) 3218–3220.
[30] D.L. Flamm, Analysis of ozone at low concentrations with boric acid buffered KI, Environ. Sci. Technol., 11 (1977) 978–983.
[31] A. Shokri, Degradation of 2-nitrophenol from petrochemical wastewater by ozone, Russ. J. Appl. Chem., 88 (2015) 2038–2043.

[32] A. Ikhlaq, B. Kasprzyk-Hordern, Catalytic ozonation of chlorinated VOCs on ZSM-5 zeolites and alumina: formation of chlorides, Appl. Catal. B: Environ., 200 (2017) 274–282.

[33] A. Shokri, K. Mahanpoor, D. Soodbar, Degradation of ortho-toluidine in petrochemical wastewater by ozonation, UV/O_3, O_3/H_2O_2 and UV/O_3/H_2O_2 processes, Desal. Water Treat., 57 (2015) 16473–16482.

[34] Z. Honrmandrad, A. Asadipour, M. Malakootian, Investigating the use of ozonation process with calcium peroxide for the removal of metronidazole antibiotic from aqueous solutions, Desal. Water Treat., 77 (2017) 315–320.

[35] S.A. Snyder, E.C. Wert, D.J. Rexing, R.E. Zegers, D.D. Drury, Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater, Ozone Sci. Eng., 28 (2006) 445–460.

[36] J.L. Wang, L.J. Xu, Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application, Crit. Rev. Env. Sci. Technol., 42 (2012) 251–325.

[37] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot$OH/$\cdot$O$^-$) in aqueous solution, J. Phys. Chem. Ref. Data, 17 (1988) 513–886.

[38] J. Hoigné, H. Bader, Rate constants of reactions of ozone with organic and inorganic compounds in water-I: non-dissociating organic compounds, Water Res., 17 (1983) 173–183.

[39] B. Lan, R. Huang, L. Li, H. Yan, G. Liao, X. Wang, Q. Zhang, Catalytic ozonation of p-chlorobenzoic acid in aqueous solution using Fe-MCM-41 as catalyst, Chem. Eng. J., 219 (2013) 346–354.

[40] F. Qi, Z. Chen, B. Xu, J. Shen, J. Ma, C. Joll, A. Heitz, Influence of surface texture and acid-base properties on ozone decomposition catalyzed by aluminum (hydroxyl) oxides, Appl. Catal. B Environ., 84 (2008) 684–690.

[41] C.Y. Kwan, W. Chu, A study of the reaction mechanisms of the degradation of 2,4-dichlorophenoxyacetic acid by oxalate-mediated photooxidation, Water Res., 38 (2004) 4213–4221.

[42] R.R. Giri, H. Ozaki, S. Taniguchi, R. Takanami, Photocatalytic ozonation of 2, 4-dichlorophenoxyacetic acid in water with a new TiO_2 fiber, Int. J. Environ. Sci. Technol., 5 (2008) 17–26.

[43] Z. Ma, L. Zhu, X. Lu, S. Xing, Y. Wu, Y. Gao, Catalytic ozonation of p-nitrophenol over mesoporous Mn-Co-Fe oxide, Sep. Purif. Technol., 133 (2014) 357–364.

[44] G. Moussavi, M. Mahmoudi, Degradation and biodegradability improvement of the reactive red 198 azo dye using catalytic ozonation with MgO nanocrystals, Chem. Eng. J., 152 (2009) 1–7.

[45] M.A. Fard, B. Aminzadeh, H. Vahidi, Degradation of petroleum aromatic hydrocarbons using TiO_2 nanopowder film, Environ. Technol., 34 (2013) 1183–1190.

[46] A. Khataee, T.S. Rad, M. Fathinia, The role of clinoptilolite nanosheets in catalytic ozonation process: insights into the degradation mechanism, kinetics and the toxicity, J. Taiwan Inst. Chem. Eng., 77 (2017) 205–215.

[47] G.V. Buxton, A.J. Elliot, Rate constant for reaction of hydroxyl radicals with bicarbonate ions, Int. J. Radiat. Appl. Instrum. Part C., 27 (1986) 241–243.

[48] J. Hoigné, H. Bader, W.R. Haag, J. Staehelin, Rate constants of reactions of ozone with organic and inorganic compounds in water-III inorganic compounds and radicals, Water Res., 19 (1985) 993–1004.

[49] R.A. Burns, J.C. Crittenden, D.W. Hand, V.H. Selzer, L.L. Sutter, S.R. Salman, Effect of inorganic ions in heterogeneous photocatalysis of TCE, J. Environ. Eng., 125 (1999) 77–85.

[50] K.-H. Wang, Y.-H. Hsieh, C.-H. Wu, C.-Y. Chang, The pH and anion effects on the heterogeneous photocatalytic degradation of o-methylbenzoic acid in TiO_2 aqueous suspension, Chemosphere, 40 (2000) 389–394.

[51] R. Yuan, B. Zhou, D. Hua, C. Shi, Enhanced photocatalytic degradation of humic acids using Al and Fe co-doped TiO_2 nanotubes under UV/ozonation for drinking water purification, J. Hazard. Mater., 262 (2013) 527–538.

[52] C. Song, L. Wang, J. Ren, B. Lv, Z. Sun, J. Yan, X. Li, J. Liu, Comparative study of diethyl phthalate degradation by UV/H_2O_2 and UV/TiO_2: kinetics, mechanism, and effects of operational parameters, Environ. Sci. Pollut. Res. Int., 23 (2016) 2640–2650.

[53] A. Shokri, A.H. Joshagani, Using microwave along with TiO_2 for degradation of 4-chloro-2-nitro phenol in aqueous environment, Russ. J. Appl. Chem., 89 (2016) 1985–1990.

[54] G. Li, Y. Lu, C. Lu, M. Zhu, C. Zhai, Y. Du, P. Yang, Efficient catalytic ozonation of bisphenol-A over reduced grapheme oxide modified sea urchin-like α-MnO$_2$ architectures, J. Hazard. Mater., 294 (2015) 201–208.

[55] A. Shokri, K. Mahanpoor, Degradation of ortho-toluidine from aqueous solution by the TiO_2/O_3 process, Int. J. Ind. Chem., 8 (2017) 101–108.