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Ultrasonic-assisted ozone oxidation process for sulfamethoxazole removal: impact factors and degradation process

Wan-Qian Guo[a,*], Ren-Li Yin[a], Xian-Jiao Zhou[a], Hai-Ou Cao[a], Jo-Shu Chang[a,b], Nan-Qi Ren[a]

[a] *State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China, Tel./Fax: +86 451 86283008; emails: guowanqian@126.com, guowanqian@hit.edu.cn (W.-Q. Guo), 774858912@qq.com (R.-L. Yin), 491731180@qq.com (X.-J. Zhou), 648942876@qq.com (H.-O. Cao), changjs@mail.ncku.edu.tw (J.-S. Chang), rnq@hit.com (N.-Q. Ren)*

[b] *Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan*

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ABSTRACT

In this study, sulfamethoxazole (SMX) degradation was investigated using an ultrasonic-assisted ozone oxidation process (UAOOP). The influencing factors of ozone concentration, pH, initial SMX concentration, ultrasound power density, and radical scavenger were studied. It was proved that ultrasound application enhanced ozonation function for SMX degradation. Color change of the water during the oxidation process was found to be corresponding to SMX concentration decay in wastewater. The results indicated that SMX degradation followed a pseudo-first-order kinetic model under experimental operating conditions. SMX degradation rate increased with ozone concentration, pH, and ultrasound power density, and was inversely proportional to the initial SMX concentration. Although the direct and indirect oxidation of ozone simultaneously existed in the UAOOP system, the direct oxidation was the predominant way. Meanwhile, the biological toxicity of the solution was weakened and biological oxygen demand/chemical oxygen demand ratio increased from 0 to 0.54. It was indicated that the UAOOP system was efficient to treat SMX wastewater and promote biodegradability for further biological treatment.

Keywords: Sulfamethoxazole; Ozone; Ultrasound; Impact factors; Degradation process

1. Introduction

In recent years, occurrence of antibiotics and antibiotic-resistant genes in aquatic environment has been regarded as an emerging global environmental issue due to the extensive usage of antibiotics, potential growth of resistant bacteria, and adverse health effects on humans. Researchers have reported that antibiotics and antibiotic-resistant genes are found in some sewage treatment effluents plants as well as in surface water and groundwater in the US, the UK, Canada, Germany, and China [1–4]. Moreover, there are significant amounts of pharmaceuticals present in the aquatic environments up to the $\mu g\,L^{-1}$ level. In this work, sulfamethoxazole (SMX), a commonly used sulfonamide antibiotic for bronchitis and urinary tract infections treatment as well as veterinary medicine, was chosen as the target contaminant due to its large

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*Corresponding author.

global consumption in animal food industry [4,5]. Due to the antibacterial nature, SMX shows resistance to traditional biological water treatment methods, which results in an SMX removal efficiency between 20 and 30% during conventional activated sludge processes [6,7]. As a result, SMX residues are usually found with high concentration in wastewater treatment plant effluents, which causes an unrecoverable pollution on the surface water and underground aquifers over years [8–10]. In recent years, SMX has been treated by AOPs [11–14], persulfate technology [15,16] based AOPs, and photolysis [5,17,18]. However, most of these treatment options are expensive (energy demanding, catalyst consuming) and may yield unstable and/or stable metabolites that can be reconverted into more toxic compounds or into original SMX under natural conditions. Accordingly, existing treatment methods have not shown significant advantages for field- or full-scale applications in terms of SMX mineralization extent and residues. It is, therefore, important to develop more efficient treatment techniques to control the presence of SMX and promote its real application and operation in aquatic environments.

Ozone is a powerful oxidant that can directly react with the contaminants or decompose into free radicals, which are even more powerful oxidants [19,20]. With this point of view, ozone and its combined processes were applied to reduce the toxicity of harmful compounds or enhance the biodegradability of organic pollutants, which made the contaminants easily accepted by environment and further mineralized. Many studies have demonstrated that ozonation process was capable of removing refractory organic pollutants with aromaticity, such as dye, disinfection byproducts, and pharmaceuticals and enhancing the wastewater biodegradability [21–24]. These results showed that ozone oxidation was efficient in refractory substances' removal and their biodegradability enhancement. However, with the limitation of selectivity oxidation to organic compounds, high cost of ozone addition, and poor mass transfer rate in aqueous solution, ozonation processes have not been widely used into practical wastewater treatment. As a consequence, ozone was usually combined with other technologies to improve its utilization rate and save the costs, such as ultraviolet/O_3, H_2O_2/O_3, ultrasound/O_3, and catalyst/O_3. Among these combined processes, due to its cavitation and hot spot effects that can accelerate turbulence, reduce the liquid film thickness, promote mass transfer rate, and generate or enhance hydroxyl radical production, ultrasound was usually combined with ozone process in many persistent and refractory pollutants removal [25–31]. In the presence of ultrasonic irradiation, the process of ozone mass transferred to the liquid phase could be enhanced and hydroxyl radicals may be generated by the decomposition of ozone in the gas phase. Hence, combined US and ozone process has been used in the removal of many persistent and refractory pollutants [32–34], which proved that the combined process can improve the biodegradability of wastewater, enhance the dye decolorization, increase chemical oxygen demand (COD) removal efficiency, and reduce biological toxicity. Consequently, the trials on SMX degradation by UAOOP processes will be feasible and promising.

Our previous study has reported the mechanisms and pathways on SMX degradation by UAOOP and also demonstrated the mechanism and degree of ultrasound enhancement on ozonation [19]. However, under different oxidation processes and operation conditions, how the SMX degradation rate changed with the impact factors was also unsure. Therefore, this study aims to investigate the effects of UAOOP-operating parameters, such as ozone concentration, pH, initial SMX concentration, ultrasound power density, and radical scavenger on the SMX removal. Additionally, the acute toxicity and biodegradability variation of the antibiotic solution during UAOOP were also studied to identify the feasibility of UAOOP on SMX removal.

2. Materials and methods

Sulfamethoxazole ($C_{10}H_{11}N_3O_3S$, analytical reagent, 99.0%) was purchased from Sigma and used as received without further purification. The structure and the relevant data of SMX were shown in our previous paper [19]. SMX solutions were buffered by the addition of adequate quantities of Na_2HPO_4, H_3PO_4, and KH_2PO_4, and the initial concentration ($[SMX]_0$) was kept at $100\ mg\ L^{-1}$. Ozonation experiments were carried out in a 1.5-L reactor with a continuous supply of O_3. Ozone was generated using an ozone generator with gaseous flow meter (DHX-SS-1G, Jiujiu ozone, Harbin, China). Ultrasonic was generated by an ultrasonic generator equipped with a titanium probe transducer 8 mm in diameter. The gaseous product from the reactor was led to a terminator, where the remaining ozone was absorbed by KI solution, and the samples were measured by HPLC in 6 h.

SMX concentration was measured using HPLC (Waters), which was equipped with an XBridge C18 HPLC column (150 mm × 2.1 mm × 3.5 μm, Waters). The mobile phase used was a mixture of acetonitrile and 0.2% acetic acid at a 40:60 volume ratio. A 10 μL volume was injected using an auto sampler. To follow the biodegradability of the samples, the biological oxygen demand (BOD_5) (Standard method, 5210 D) and the COD (Standard method, 1250 D) analysis were carried out. The ratio BOD_5/COD has been chosen as biodegradability indicator. The acute toxicity of SMX and its degradation products were tested using 24-h born *Daphnia magna* at different dilutions. These tests were evaluated with the same procedure as Organization for Economic Cooperation and Development Guideline 202.

3. Results and discussion

3.1. SMX degradation in different oxidation processes

To understand the roles of ozone and ultrasound in SMX removal, various sets of experiment under different operating parameters were conducted. The experiments were carried out at an ultrasound power density of 600 W L^{-1}, while the initial SMX concentration was 100 mg L^{-1}, pH 7, and ozone dose 5 g h^{-1}. It was found that once the ozone was introduced into the SMX-simulated wastewater, the color of water changed from colorless to orange immediately. With more ozone accessing to the system, the SMX was degraded and the color gradually faded to yellow, and finally to colorless again (Fig. 1). Furthermore, the concentration of SMX was corresponding to the color variation of wastewater, which meant the lighter color of the solution represented the lower concentration of SMX, so we can know the reaction process conveniently and control the ozone input directly to save operation costs.

The SMX removal was negligible in the presence of ultrasound because ultrasound can just produce little ·OH in the solution [19] and the structure of SMX was stable and refractory (Fig. 2). More importantly, it also demonstrated that, when combined with US, the oxidation rate of UAOOP to degrade the SMX was higher than ozonation process. On one hand, in the presence of ultrasound, the cavitation effect may be introduced and an energy gradient in the direction of propagation of the acoustic wave would be formed [35]. The generated free radicals produced in the vapor phase of a cavitation bubble might diffuse into the bulk solution to oxidize the SMX. On the other hand, with the US facilitating, it could lead to the reduction of liquid film thickness of gas bubbles containing ozone, the larger specific surface area between the gas and liquid phases and turbulent flow conditions, which accelerated the mass transfer rate of ozone to improve the reaction velocity with SMX [36]. Overall, ultrasound can simultaneously assist the ·OH production and accelerate the ozone bubble transfer rate to enhance the ozonation for SMX degradation. However, the effect enhanced by ultrasound and the SMX removal rate by UAOOP may be influenced by many factors, like power density, ozone dose, initial SMX concentration, pH, and radical scavenger.

3.2. Effects of power density, ozone dose, and $[SMX]_0$ on SMX degradation

In order to illustrate how these factors impact SMX degradation in the UAOOP system, different sets of experiment under different operation conditions were carried out. The experimental results showed that the SMX removal all followed apparent pseudo-first-order kinetics:

Fig. 1. Color change rule during the oxidation process.

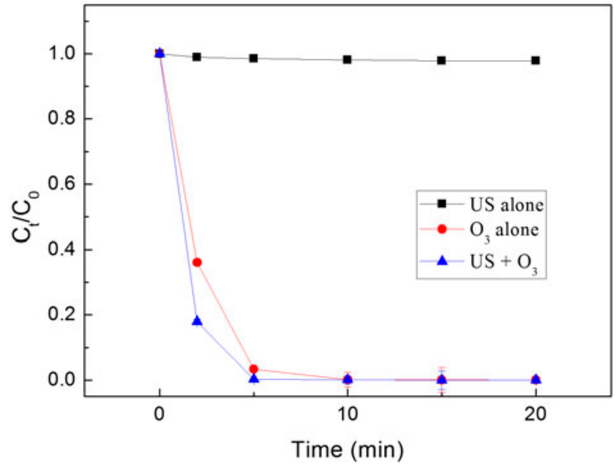

Fig. 2. The effect of US, O_3, and US + O_3 on SMX degradation.

$$\frac{-\mathrm{d}[\mathrm{SMX}]}{\mathrm{d}t} = k[\mathrm{SMX}] \tag{1}$$

where [SMX] is the SMX concentration at time t and k is the pseudo-first-order rate constant, which were verified by very high correlation coefficients R^2 ranged from 0.996 to 0.999 as shown in Table 1.

The degradation rate increased with the increasing power density (seen Fig. 3). The apparent rate constants were 0.25, 0.26, and 0.30 min^{-1}, when power densities were 400, 600, and 800 W L^{-1}, respectively. It can be seen that there is little difference in the rate when power densities were 400 and 600 W L^{-1}. However, when the power density rose from 600 to 800 W L^{-1}, the constant increased about 15%. The results were attributed to these two reasons. On one hand, turbulent condition is in favor of ozone molecules' transfer from gas to liquid. There may be a critical point power to achieve the turbulent atmosphere, when the power was lower than the critical damping. As the liquid was not in turbulence, ozone transfer was corresponding to diffusion theory; while the power was higher than the critical point, more power enhanced the mechanical effects and broke up more ozone gas bubbles to reduce the thickness of liquid film and promote ozone mass transfer rate to strengthen the oxidation ability [37,38]. In this study, the critical point of power was between 600 and 800 W L^{-1}. On the other hand, when ultrasound was introduced into the reaction system, ozone was decomposed and yielded extremely reactive radicals during the thermal process. The more the energy was provided, the more free radicals were generated [35]. As a result, the increasing power density promoted the SMX removal rate.

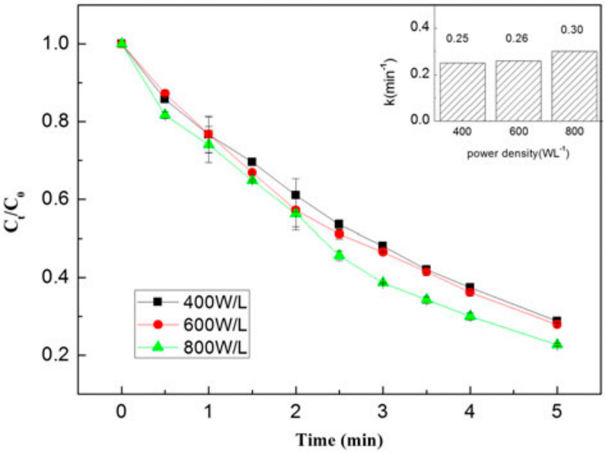

Fig. 3. The effect of power density on SMX degradation.

Higher ozone concentration resulted in higher degradation rate, as shown in Fig. 4. When ozone concentrations rose from 2 to 5 g h^{-1}, the degradation rates of SMX increased by twice, respectively. The increasing ozone concentration would improve the mass transfer driving force, which would increase mass transfer rate of ozone from gas to liquid phase [32,39].

$$J_c = -D_c \frac{\mathrm{d}c}{\mathrm{d}z} \tag{2}$$

Table 1
The pseudo-first-order rate constants under various conditions

No.	$[\mathrm{SMX}]_0$	pH	O_3 (g h^{-1})	P (W L^{-1})	k (min^{-1})	R^2
1	100	7	3	400	0.25	0.999
2	100	7	3	600	0.26	0.997
3	100	7	3	800	0.30	0.996
4	100	7	2	600	0.21	0.994
5	100	7	3	600	0.28	0.999
6	100	7	4	600	0.29	0.998
7	100	7	5	600	0.45	0.990
8	100	3	3	600	0.29	0.985
9	100	5	3	600	0.30	0.999
10	100	7	3	600	0.42	0.988
11	100	9	3	600	0.50	0.987
12	50	7	3	600	0.37	0.999
13	100	7	3	600	0.20	0.999
14	200	7	3	600	0.14	0.999
15	400	7	3	600	0.09	0.999

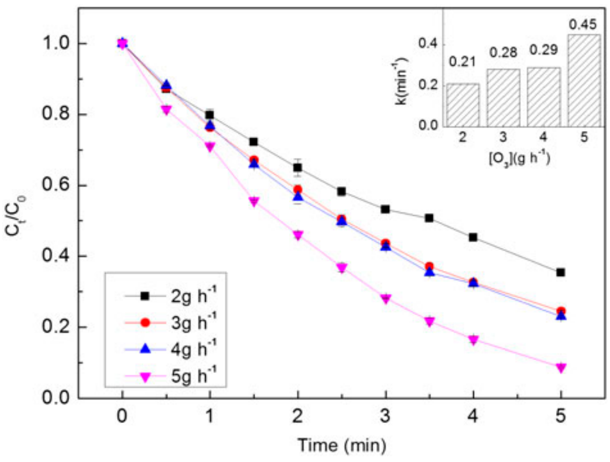

Fig. 4. The effect of ozone dose on SMX degradation.

where J_c is the mass transfer flux, D_c is the diffusion coefficient, and $\mathrm{d}c/\mathrm{d}z$ represents the concentration gradient in z direction. With more ozone input, the ozone bubble transfer rate was improved, which resulted in the increase in $\mathrm{d}c/\mathrm{d}z$ ratio and also an increment in J_c, so that the oxidation rate was enhanced by more ozone flux into the solution. In addition, the increasing ozone concentration represents that ozone molecules react with SMX more probably, for ·OH as well. Thus, the degradation rate increased with the increasing ozone concentration.

Fig. 5 and Table 1 showed that the apparent rate constants (k) decreased about three times (from 0.37 to 0.09 min^{-1}), while SMX concentration increased from 50 to 400 mg L^{-1}. Except for initial SMX concentration, other operating conditions were kept constant. Then, the available ozone and hydroxyl radicals to oxidize SMX would be nearly the same at different initial SMX concentrations. However, with the increasing initial SMX concentration, the competing reactions between SMX and its degradation products with ozone turned predominant, which decreased the contact probability of SMX with ozone and hydroxyl radicals [35]. As a consequence, the SMX removal rate would decrease with the increasing initial SMX concentration.

3.3. Effects of pH on SMX degradation

It is well known that ozone oxidation pathways include (i) the direct oxidation by ozone bubble that is more selective and predominant under acidic conditions and (ii) the indirect radical oxidation by hydroxyl radicals, which is less selective and predominant under alkaline conditions [22,40]. Knowing the main type in the oxidation system is important to control the reaction process, achieve the optimal operating conditions, and save the operation costs. However, the predominant reaction type during ozonation process varied under different pH conditions. Therefore, the pH is usually considered as an important parameter for ozonation combined ultrasound process.

It was clearly shown in Fig. 6 that the SMX removal rate increased with the increasing in pH, indicating that the increment in pH had a positive influence on the reactivity of ultrasound-enhanced ozonation. SMX has two pK_a values of 1.6 and 5.7, resulting in protonated, non-protonated, and deprotonated forms at different pH values. Considering the structure of SMX, the possible reaction centers that are more susceptible to ozone electrophilic attack can be the amino group. Moreover, the pH of the oxidant

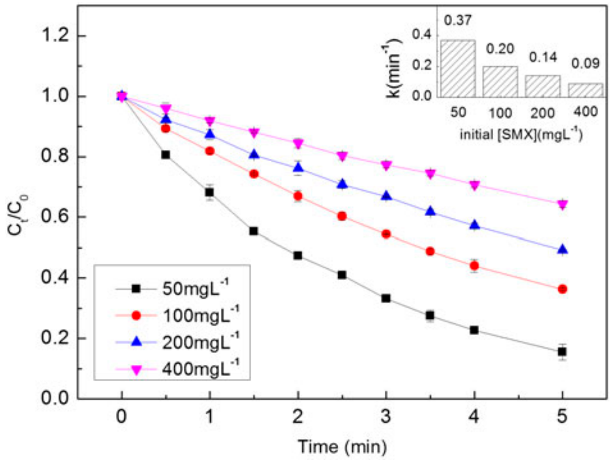

Fig. 5. The effect of initial SMX concentration on SMX degradation.

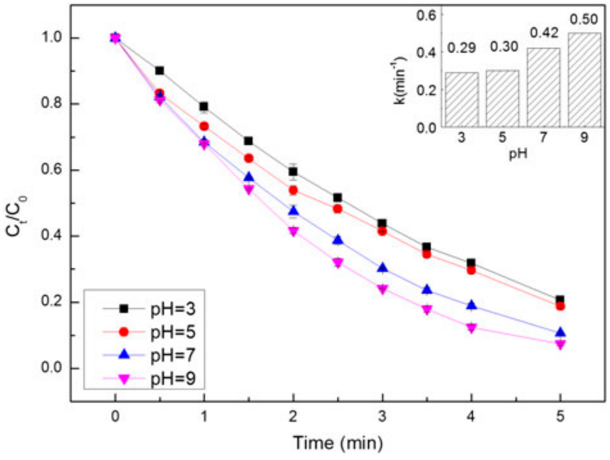

Fig. 6. The effect of pH on SMX degradation.

played an important role in the reaction. When the pH was lower than 7, the ozonation depended on the ozone direct oxidation and the ozone selected to break down the double bone in SMX. At the same time, the non-protonated form was the predominant form, which was less susceptible to ozone attack than that of the deprotonated form. So, the reaction rates were lower under the acidic condition (0.29 min^{-1}, pH 3; 0.30 min^{-1}, pH 5). It can be seen from the results that the ozone direct oxidation plays an important role in the SMX degradation by UAOOP. Further increasing pH to 7, all the SMX molecules were present in a completely deprotonated form, which received a higher reactivity toward ozone. Under basic conditions, most of the ozone oxidation reactions mainly generated hydroxyl radicals, whose oxidation abilities were stronger than ozone (0.42 min^{-1}, pH 7; 0.50 min^{-1}, pH 9). Consequently, the degradation rate under basic condition was higher than that under acidic condition. However, higher pH needs too much of chemical reagents to be economical. Better operating pH in practice was chosen as 7–9 for SMX degradation by UAOOP. Furthermore, it also indicated that the UAOOP generated hydroxyl radicals in degrading SMX. So, the direct and indirect oxidation type of ozone simultaneously existed in the UAOOP system.

3.4. Effect of radical scavenger tert-butanol on SMX degradation

In order to further confirm which oxidation-type SMX removal complied was predominant in the UAOOP system, the radical scavenger tert-butanol (TBA) with concentration 10 mM was added during ultrasonic-assisted and ozonation process. Fig. 7 showed that the presence of TBA accelerates the SMX degradation, indicating the TBA favors the reaction between SMX and ozone, which is more effective than radicals for the degradation. The results are also corresponding to Goncalves' research results [41]. TBA, which contains hydrophilic and hydrophobic groups, changed the surface characteristics by reducing the surface tension of aqueous solution, and increasing the contacting areas between gaseous ozone and aqueous solution by accumulating at gas–liquid interface as conventional surfactants did. Meanwhile, in the presence of TBA, the ozone bubble size was reduced and the bubbles became more spherical and uniform in size [42]. Therefore, the addition of TBA improves the ozone mass transfer; consequently, the amount of available ozone in water phase was enhanced, which reinforced the direct ozonation pathway. It was inferred from the above results that the direct ozonation was the predominant pathway of SMX degradation by UAOOP; otherwise, the addictive of TBA could have limited the oxidation rates.

3.5. Mineralization, biodegradability, and acute toxicity tests

To reveal the mineralization of SMX in the UAOOP system, experiments were carried out when the SMX concentration was 100 mg L^{-1}, pH was 7.0, ozone dose was 3 g h^{-1}, and ultrasonic power density was 600 W L^{-1}. In Fig. 8, 49.1% COD was removed after a 30-min reaction time, compared with almost complete removal of SMX. At the beginning of the process, the COD was found to increase with the SMX removal, and when the SMX nearly decomposed completely, the COD dropped with the extension of the reaction time. The reason was that the COD standard method is using $K_2Cr_2O_7$ to oxidize the targets. SMX

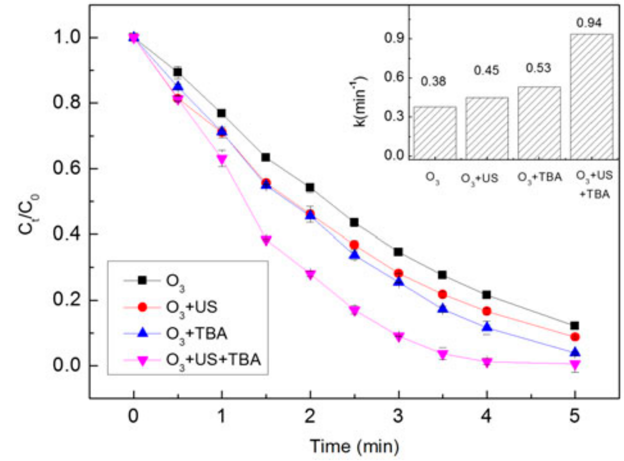

Fig. 7. The effect of TBA on SMX degradation.

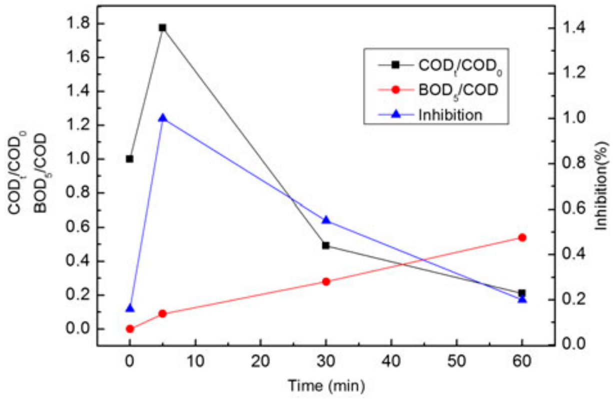

Fig. 8. Variation of COD, BOD_5/COD, and toxicity with *D. magna*.

cannot be oxidized completely by $K_2Cr_2O_7$, but the intermediates can be efficiently oxidized compared to their parent. So, the COD removal tendency increased firstly for the occurrences of its products, and then decreased with the SMX and its products degradation by UAOOP.

The biodegradability and the toxicity of the effluent in the UAOOP were also evaluated in this study. The BOD_5/COD ratio of the initial solution was 0, indicating that SMX was hardly biodegraded. After a 60-min treatment, the value of BOD_5/COD was increased to 0.54. Compared with Dantas' [22] research (BOD_5/COD ratio: 0–0.28), this study showed about a twofold higher increment in the BOD_5/COD ratio during the same period. It showed that the effluent after UAOOP treatment was much more easily biodegradable than the influent. Furthermore, the results also demonstrated that combined US and O_3 was an efficient pretreatment for biological treatments of SMX wastewater.

To evaluate the potential environmental impact of SMX and its byproducts, the variation of acute toxicity during UAOOP before and after the reaction was examined by a 24-h immobilization test with *D. magna*. As shown in Fig. 8, the initial solution of SMX led to 16% death of the crustacean. The acute toxicity increased significantly after a 5-min reaction, and 100% death of *D. magna* was observed, because more toxic immediate products were generated. With the further progress of reaction, the acute toxicity reduced gradually, indicating the toxic structures were destructed and the immediate products were degraded into the less toxic products. In conclusion, combined ozone and ultrasound process is efficient in eliminating the environmental risks of SMX and reducing the reaction time of the process to save operation costs.

4. Conclusions

SMX could be effectively degraded, mineralized, and detoxified in the UAOOP. The removal rate of SMX increased with the increasing ozone concentration, power density, and pH value but decreased with the increasing initial SMX concentration. Addition of radical scavenger tert-butanol could accelerate SMX degradation rate. SMX could quickly react with ozone and the hydroxyl radicals that were generated from ozone. Though the direct and indirect oxidation of ozone simultaneously existed in the UAOOP system, the direct oxidation type was also the predominant way of ozonation. The acute toxicity of the solution quickly reached the maximum in 5 min. The increment of BOD_5/COD ratio from 0 to 0.54 made it suitable to apply biological technology to treat the SMX effluent from UAOOP, which lowers the cost of the antibiotic wastewater treatment. These findings suggested that UAOOP was an alternative method for enhanced SMX degradation and similar structure refractory organic (antibiotics) pollutants.

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