Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20741

96 (2017) 161–168
November

Degradation of tetracycline by advanced oxidation processes: sono-Fenton and ozonation processes

Chikang Wang*, Bo-Ming Huang

Department of Environmental Engineering and Health, Yuanpei University of Medical Technology, 306 Yuanpei Street, Hsinchu, Taiwan, emails: ckwang@mail.ypu.edu.tw (C. Wang), andy556681@yahoo.com.tw (B.-M. Huang)

Received 5 January 2017; Accepted 20 March 2017

ABSTRACT

In this study, ultrasound, Fenton, ozonation and their combinations were conducted to degrade tetracycline, which is extensively used in humans and animals to treat and prevent bacterial infections and has been proven to be harmful to the environment. Experimental results indicated that the effects of ultrasonic watt and reaction temperatures in sono-Fenton systems were insignificant. However, both the addition of anions and increasing the pH to a basic condition remarkably inhibited the contribution of tetracycline degradation and mineralization. The effects of ozone gas flows and pH levels on the degradation and mineralization of tetracycline were not obvious in ozonation, due to the saturated ozone concentration in solution were close with different ozone gas flows, but they were significantly affected by the change of solution toxicity, as defined by the profiles of cell viability. As the ozonation was combined with ultrasound or/and Fenton, the required treatment durations were shortened, and the mineralization efficiencies were enhanced. Hence, operation costs were also reduced by the combination of ultrasound, Fenton and ozone. The maximum tetracycline degradation efficiency in the ultrasound/Fenton/O_3 process was as high as 99.8%, followed by 65% mineralization, which revealed that the ultrasound/Fenton/O_3 method synergistically increased the mineralization of refractory compounds; additionally, the toxicity of the treated tetracycline solution significantly decreased, whereas the cell viability increased from <50% to 94%.

Keywords: Cell viability; Degradation; Mineralization; Ozonation; Ultrasound/Fenton/O_3 process; Tetracycline

1. Introduction

In recent years, the usage and residues of pharmaceutical and personal care products have gained attention in many countries because of their bio-inhibitory or bio-refractory properties to the natural environment; hence, these organic compounds are named as emerging pollutants and need to be effectively degraded to reduce the health risk to human beings and animals [1]. Tetracycline, which has a four-benzo-ring molecular structure with a formula of $C_{22}H_{24}N_2O_8$, is one of the well-known antibiotics used in many countries to treat human and animal infectious diseases [2]. An increasing amount of research has been carried out to investigate the degradation of tetracycline, at the mg/L level, by chemical and biological treatments, such as photolysis, ozonation and ultrasound [3–6]. In addition, because high concentrations of tetracycline may be present in water and wastewater due to the extensive usage of tetracycline as a medicine and food additive, as such, high concentrations of tetracycline has been detected in municipal and pharmaceutical industrial wastewater [7,8].

Selvam et al. [6] tried to investigate the effect of tetracycline on the continuous thermophilic composting method and found that the tetracycline did not affect the composting process significantly, but did negatively influence the bacterial population. In addition, ~8% of the tetracycline

* Corresponding author.

Presented at the 9th International Conference on Challenges in Environmental Science & Engineering (CESE-2016), 6–10 November 2016, Kaohsiung, Taiwan.

was detected after 42 d of composting, which indicated that the tetracycline might be degraded by thermophilic biological treatments with long treatment durations. Hence, how to effectively degrade tetracycline with a short treatment duration is an important field in recent years, and several advanced oxidation processes (AOPs) have been carried out. Our earlier researches tried to couple the ultrasound and Fenton processes as the sono-Fenton process to degrade pesticides and found that the synergic effect that occurred in the sono-Fenton system was effective in enhancing the degradation of pesticides [9,10]. This fact indicates that the combination of several chemical reagents or processes may be useful to provide a higher oxidation potential to degrade or oxidize the refractory compounds [11,12]. Therefore, combination methods, such as ultrasound/goethite/O_3 [13], ultrasound/O_3 [14] and ultrasound/Fe_3O_4/$Na_2S_2O_8$ [15], have been conducted, and the performances of tetracycline degradation have been investigated. Based on their observations, it was found that the combination of several oxidation processes can produce more •OH radicals that leads to higher oxidation efficiency in tetracycline degradation so that the tetracycline can be readily degraded within 15–20 min of reaction.

Even when the combination of several chemicals or oxidation processes shows excellent performance in the degradation of refractory compounds, an increase in operational costs is anticipated, so finding out the optimal experimental parameters is necessary to achieve better degradation results with lower operational costs. Therefore, in this study, the sono-Fenton process was first discussed with different experimental parameters, based on the observations proposed by Wang and Jian [16], to investigate the applicable treatment conditions. Then, the ozonation and the combination of ultrasound, Fenton and ozone in the degradation of tetracycline were carried out. The objectives of this study were to investigate the effects of reaction parameters on the degradation of tetracycline in sono-Fenton and ozonation experiments and to compare the performance of seven treatment methods based on the results of tetracycline degradation, mineralization and first-order degradation rate constants. This study also employed the cell viability of the tetracycline solution before and after treatment, obtained by cell counting methods as an index to understand the change in toxicity. Moreover, the necessary operational costs of seven treatment methods to degrade and mineralize the tetracycline were calculated, so that the appropriate treatment method could be proposed.

2. Materials and methods

2.1. Standards and reagents

An analytical tetracycline standard ($C_{22}H_{24}N_2O_8$, Sigma-Aldrich, USA) was used as the target compound in this study. The purest grade commercial chemicals, such as sulfuric acid, sodium hydroxide, iron(II) sulfate, calcium chloride dehydrate, sodium carbonate, sodium sulfate, sodium nitrite and sodium hydrogen carbonate, were purchased from Merck (Taiwan) and used without further purification. The aqueous H_2O_2 (30%, w/w in water) was purchased from FERAK (Germany) and stored in dark place to avoid the effect of self-degradation by sunlight.

2.2. Experimental apparatus and treatment designs

Fig. 1 shows the experimental apparatus used in this study, including the sonicator, ozone generator, temperature controller and reactor. The concentration of tetracycline was initiated at 50 mg/L, based on the selected concentrations of tetracycline in references [3,13,14]. In chemically ultrasonic experiments, a 20-kHz sonicator (Microson VCX 750, USA) was used and equipped with a sealed converter (model CV 33; 63.5 mm in diameter and 183 mm in length) and a titanium probe tip (part No. 630-0210; 25 mm in diameter and 122 mm in length) to provide the necessary ultrasonic energy to the reactor. For the ozonation and related experiments, an ozone generator (model LAB2B, Ozonia; maximum output: 4.0–10 g O_3/h; feed gas flow rate: 4–10 L/min air) was attached to the reactor; a flow meter (Bronkhorst, EL-FLOW) with a computer was set up before the ozone generator so that the produced O_3 flow rate was accurately controlled at the required condition.

A Pyrex glass cylinder with a working volume of 1 L was used as the reactor in this study, where a magnetic stirrer with the mixing speed of 100 rpm was equipped to ensure the adequate mixing of all chemicals, and a circulating temperature controller was attached to maintain the necessary reaction temperature. The initial pH of the experiments was adjusted by the addition of 1 N H_2SO_4 or NaOH. In the Fenton, sono-Fenton, O_3/Fenton and ultrasound/Fenton/O_3 processes, the chemicals such as H_2O_2 and Fe^{2+} were pre-adjusted to the desired concentrations and then added dropwise to the reactor in a continuous manner using a micro-pump. The flow rate of each chemical was 0.5 mL/min, and the total added volume of H_2O_2 and Fe^{2+} within a 60-min reaction was 30 mL.

2.3. Tetracycline degradation and mineralization

The concentration of tetracycline was determined with a UV–Vis spectrophotometer (Thermo Scientific GENESYS 10S, USA), where the absorption peak at 357 nm [14] was identified

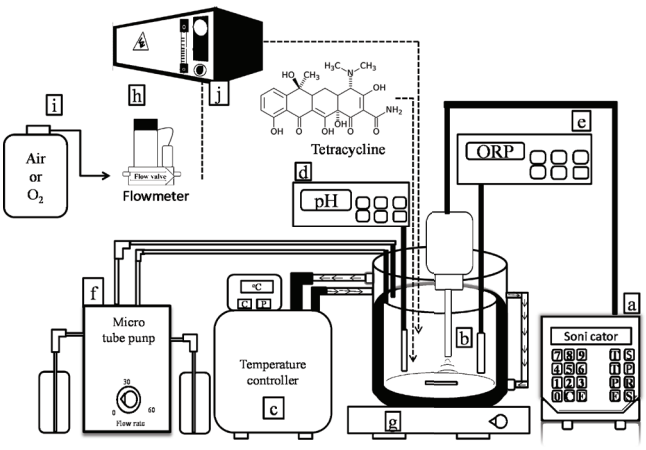

Fig. 1. Experimental apparatus for the sono-Fenton and ozonation experiments (a – sonicator; b – 1 L reactor; c – temperature controller; d – pH meter; e – ORP meter; f – micro-tube pump; g – mixer; h – flow meter; i – gas steel cylinder and j – ozone generator).

as the maximum absorption wavelength. Prior to measuring the tetracycline concentration during the experiments, a calibration curve was generated, and a satisfactory linear regression R^2 value of 0.99998 was acquired. The mineralization of tetracycline was investigated by determining the total organic carbon (TOC) concentration using a TOC analyzer (TOC-500, Shimadzu, Japan). To detect the O_3 concentration in solution, this study used an O_3 concentration analyzer (4-aminoantipyrine absorptiometry with enzyme, KYORITSU WAK-O_3, Japan). As the O_3 was introduced into the deionized water for 10 min, the O_3 concentrations were 2.5 and 3.5 mg O_3/L with flow rates of 0.1 and 0.5 L/min, respectively. When the O_3 aeration time was extended to 60 min, the O_3 concentrations were 3.9 and 4.3 mg O_3/L, respectively. We note that the initial O_3 concentration at differences gas flows (from 0.1 to 0.4 L O_3/min) are remarkable but saturated O_3 concentrations are comparable so that the use of O_3 gas flows as the reaction parameter can help us to understand the rapid profile of refractory compound degradation by ozone. The pH and oxidation-reduction potential (ORP) values were measured using pH and ORP meters (Eutech pH 510, Taiwan).

2.4. Toxicity analysis

Analytical steps of solution toxicity followed our earlier studies [9,10,16] and are shown below. The toxicities of the tetracycline samples before and after treatment were determined based on the rate of liver cell viability, where viability was confirmed by cell counting. In all experiments, cells were treated with tetracycline water samples for 24 h before and after oxidation. Cell viability was determined using a blue formazan assay in which colorless 3-(4,5-dimethyl-thiazol-2-yl)-2,5-diphenyl tetrazolium bromide is metabolized to a blue-colored product by mitochondrial dehydrogenases. Absorbance was recorded at 540 nm using a SpectraMAX 340 reader. The data were expressed as the mean percentages of viable cells compared with the control.

3. Results and discussion

3.1. Effect of temperature, ultrasonic watt, pH and anions on sono-Fenton process

To understand the effect of the combinations of ultrasound, transition metals (Fe^{2+}, Ag^+ and Co^{2+}) and oxidizing agents (H_2O_2 and $S_2O_8^{2-}$) on the degradation of tetracycline, Wang and Jian [16] had studied the performance of ten different combinations and found that coupling the ultrasound, Fe^{2+} and H_2O_2 showed better efficiencies of tetracycline degradation and mineralization than others. In addition, the optimal dosages of Fe^{2+} and H_2O_2 were found to be 0.2 and 2 mM, respectively, at pH 3, 0.2 L air/min and a reaction temperature of 25°C by means of a continuous dosing mode; the degradation and mineralization of tetracycline were observed as 91.3% and 26.4%, respectively. However, there were several reaction parameters that needed to be investigated, and the designs of reaction parameters and the results of tetracycline degradation, rate constant, and TOC removal are shown in Table 1.

To further investigate the effect of the initial pH level on tetracycline degradation, experiments were performed that involved changing the pH from 3 to 11 at the optimal experimental conditions shown above. Wang and Jian [16] observed that the effect of initial pH levels between 3 and 6 was insignificant; it is shown in Table 1 that the degradation of tetracycline ranged from 90.5% to 91.3%, and TOC removal was from 25.7% to 28.3%. However, as the pH level increased to 7–11, the ORP values of treated tetracycline solutions decreased in the first 2 min and increased to 409, 364, and 89 mV, respectively, after 60 min (data were not shown), which were remarkably lower than at pH 3–6. Hence, the degradation efficiencies of tetracycline at pH 7–11 were 82.7%, 48.0% and 14.9%, respectively, which were also much lower than pH 3–6. It is understood that acidic pH conditions were found to assist the sono-Fenton process by increasing the formation of •OH radicals to effectively degrade refractory compounds

Table 1
Results of tetracycline degradation, rate constant and TOC removal at different reaction conditions, with designed H_2O_2 and Fe^{2+} dosages by the sono-Fenton process

Factors	Tetracycline degradation		Tetracycline mineralization
	Percentage (%)	Rate constant ($\times10^{-3}$ min^{-1})	TOC removal (%)
pH level			
3[a]	91.3	40.9	26.4
4[a]	90.5	39.9	27.6
5[a]	90.5	39.2	25.7
6[a]	90.9	39.1	28.3
7	82.8	29.3	23.5
9	53.0	12.5	13.7
11	14.9	2.7	9.8
Temperature			
15	85.1	31.7	14.1
25	91.3	40.9	26.4
35	91.9	41.5	27.4
45	93.0	42.7	27.9
55	94.2	43.6	33.2
Ultrasonic watt			
0	60.0	16.0	6.2
25	84.2	30.1	18.4
50	87.0	33.9	20.3
100	91.3	40.9	26.4
200	89.8	38.2	24.8
Anion addition			
SO_3^{2-}	53.4	12.7	14.4
Cl^-	54.4	13.0	15.1
CO_3^{2-}	50.1	11.5	12.3
HCO_3^-	31.5	6.3	7.7
SO_4^{2-}	85.5	32.1	25.1
NO_3^-	67.4	18.7	24.1

[a]Data have been proposed in Wang and Jian [16].

[17,18]. In TOC removal, comparable results found in Table 1 show that the mineralization of tetracycline was 23.5%, 13.7% and 9.8%, respectively, as the pH levels increased from 7 to 11. These results indicate that the degradation and mineralization occur in the cavitation bubbles only, suggesting that the addition of Fenton's reagents does not contribute to the formation of •OH.

In Table 1, it is shown that the degradations of tetracycline slightly increased from 85.1% to 94.2% since the reaction temperature increased from 15°C to 55°C after 60 min of reaction. This result indicates that the degradation of tetracycline is enhanced at higher reaction temperatures with faster reaction rates so that the rate constants of tetracycline increased from 31.7×10^{-3} min^{-1} to 43.6×10^{-3} min^{-1}. In addition, the results of TOC removal were enhanced by the increase of reaction temperatures, which indicates that a higher reaction temperature is effective on the ultrasonic energy transformation, so that the organic compound can be easily destructed to CO_2 [19,20]. However, if the reaction is performed without temperature controls, the solution temperatures increased from room temperature to ~32°C. For this reason, even the results of tetracycline degradation at 55°C were better than other temperatures, and the energy consumption and increase of operational costs by controlling the temperature at very high levels limited the application of ultrasonic processes. Therefore, the subsequent experiments in this study were performed at 25°C.

In sono-chemical processes, adjustment of the ultrasonic watt is an important parameter in the enhancement of the degradation efficiencies of organic compounds. Several authors found that the increase of ultrasonic watt was effective in increasing antibiotics degradation, due to the increase of ultrasonic watt having the potential to introduce more energy into the solution phase and produce more cavitation bubbles, which had been defined as the micro-reactors in sono-chemical systems [15,20,21]. The increase in cavitation bubbles is useful not only in increasing the dissociation of H_2O_2 to produce •OH radicals but also in increasing the amounts of organic compounds transferring into the bubbles so that the refractory compounds can be easily degraded and mineralized by indirect •OH oxidation and direct thermal ultrasonic pyrolysis [22]. Therefore, in Table 1, it is shown that the increase of ultrasonic watt from zero (i.e., the Fenton process) to 100 W leads to the enhancement of tetracycline degradation and mineralization. In addition, the first-order rate constants of tetracycline degradation were increased by the increasing ultrasonic watt. However, as the ultrasonic watt was adjusted to 200 W, the degradation and mineralization of tetracycline were both slightly decreased, which indicated that excess ultrasonic energy introduced into the solution inhibited the production of •OH and the contribution of ultrasonic watt increment was negligible. In addition, the higher energy consumptions and noise produced from the sonicator should be ideally minimized. Accordingly, the subsequent experiments were performed at 100 W.

It is well known that the presence of anions influences the degradation or decolorization efficiencies in AOPs [23,24]. Generally, Cl^-, CO_3^{2-} and HCO_3^- are the superior three anions affecting the degradation of organic compounds. When one of these three anions is presented in the solution, the degradation efficiency significantly reduced, which could be explained by the reactions between the anions and •OH [17,22,25], so that the produced •OH was unable to oxidize the organic compounds. In this study, six anions (all concentrations adjusted to 50 mg/L) were individually added to the solution to investigate the effect of each anion on the degradation and mineralization of tetracycline, and the results are shown in Table 1. It was found that the addition of SO_4^{2-} slightly reduced the degradation and mineralization of tetracycline, which was comparable with the results observed by Wang et al. [17]. Further, the addition of CO_3^{2-} and HCO_3^- significantly inhibited the oxidation performance of the sono-Fenton process and led to the remarkable decrease of tetracycline degradation and mineralization. This finding can be understood in terms of the reaction between •OH and CO_3^{2-} or HCO_3^-, where CO_3^{2-} or HCO_3^- easily captures •OH such that •OH does not have the opportunity to react with organic compounds [26]. The presence of all anions inhibited the degradation and mineralization of tetracycline, though to different extents, following the order of $HCO_3^- > CO_3^{2-} > SO_3^{2-} > Cl^- > NO_3^- > SO_4^{2-}$.

Even though we have investigated the effect of different reaction parameters on the degradation and mineralization of tetracycline and shown results above, confirming that the significance of parameters by static method is necessary. In this study, we used the one-way analysis of variance (ANOVA) test with post hoc Tukey honest significant difference (HSD) test to understand, which reaction parameters are significantly affected the degradation of tetracycline. In Table 2, four reaction parameters including pH, temperature, ultrasonic watt, and anion addition were summarized and calculated the sum ($\sum X_i$), mean ($\bar{X}$) and sum of squares (X_i^2), and obtained the necessary statistic factors. Then the results shown in Table 3 indicates that the p value corresponding to

Table 2
Descriptive statistics of four independent parameters

Parameters	pH	Temperature	Watt	Anion	Pooled total
Observations, N	7	5	5	6	23
Sum, $\sum X_i$	513.9000	455.5000	412.3000	342.3000	1,724.0000
Mean, $\bar{X}$	73.4143	91.1000	82.4600	57.0500	74.9565
Sum of squares, $\sum X_i^2$	42,865.8500	41,545.9500	34,658.3700	21,166.1900	140,236.3600
Sample Variance, s^2	856.3748	12.4750	165.0280	327.5950	500.5144
Sample standard deviation, s	29.2639	3.5320	12.8463	18.0996	22.3722
Standard deviation of mean, SE_X	11.0607	1.5796	5.7451	7.3891	4.6649

Table 3
One-way ANOVA of four independent parameters

Source	Sum of squares, SS	Degrees of freedom, v	Mean square, MS	F statistic	p value
Parameters	3,525.0810	3	1,175.0270	2.9822	0.0572
Error	7,486.2356	19	394.0124		
Total	11,011.3165	22			

the F statistic of one-way ANOVA is higher than 0.05, which suggesting that the reaction parameters are not significantly different for that level of significance. In addition, we applied Tukey's HSD test to each of the six pairs to pinpoint which of them exhibits statistically significant difference, and the results are shown in Table 4. It is found that the significance of most parameters pairs are "insignificant" and only the pair of temperature vs. anion addition is significant.

3.2. Effect of pH and ozone gas flow on ozonation

Based on the observations in Table 1, where the optimal operational parameters in the sono-Fenton system have been investigated, it is understood that ~10% of tetracycline was undegraded and more than 70% of organic carbon was still present in the solution after 60 min of treatment. Therefore, in this study, ozonation was conducted to degrade the tetracycline, and the effects of initial pH level and ozone gas flow on the degradation and mineralization of tetracycline were investigated. Fig. 2 shows the results of tetracycline degradation by ozonation with different ozone flow rates (0.1–0.4 L O_3/min) at the initial pH of 5 and 25°C. It was found that the degradation of tetracycline reached ~80% within 10 min of reaction at the ozone flow rate of 0.1 L O_3/min, and then further increased to almost 100% after 60 min of reaction, which was better than the results of the sono-Fenton process shown in Table 1. Additionally, as the ozone flow rate increased to 0.2–0.4 L O_3/min, the degraded tetracycline in solution after 20 min of reaction was close to 100%; this indicated that ozonation was effective in the degradation of tetracycline and the treatment duration could be shortened. However, in Fig. 3, the TOC removal by ozonation with different ozone flow rates was only 17.2% (0.1 L O_3/min), and it increased to 34.5% by increasing the ozone flow rates to 0.2 L O_3/min. As the ozone flow rates increased to 0.3 and 0.4 L O_3/min, mineralization was slightly decreased to 26.9% and 19.7%, respectively. As this result was comparable with the data shown in the sono-Fenton process, which indicated that even when the ozone could easily degrade the tetracycline within a very short treatment duration, more than 65% of TOC was still present in the solution phase and needed to be further mineralized. Therefore, the authors tried to evaluate the profiles of toxicity by the change in cell viability of the tetracycline solution before and after ozonation with different ozone flow rates and combined the data of tetracycline degradation, TOC removal and cell viability in Fig. 4. Before treatment, the cell viability of the original tetracycline solution was ~58% with a standard deviation of 3.8%; after 60 min of treatment, the cell viability increased to 63% with 0.1 L O_3/min and to between 76% and 88% as the ozone flow rates were increased from 0.2 to 0.4 L O_3/min. In earlier researches [9,10], the increase in cell viability obviously

Table 4
Significant of all relevant pairs of parameters evaluation by Tukey HSD test

Parameters Pair	Tukey HSD Q statistic	Tukey HSD p Value	Tukey HSD Inferfence
pH vs. temperature	2.1519	0.446113	Insignificant
pH vs. watt	1.1006	0.852028	Insignificant
pH vs. anion	2.0956	0.468206	Insignificant
Temperature vs. watt	0.9733	0.899995	Insignificant
Temperature vs. anion	4.0063	0.047946	[a]$p < 0.05$
Watt vs. anion	2.9897	0.184423	Insignificant

[a] $Q_{\text{critical}}^{\alpha=0.05,k=4,v=19} = 3.9769$.

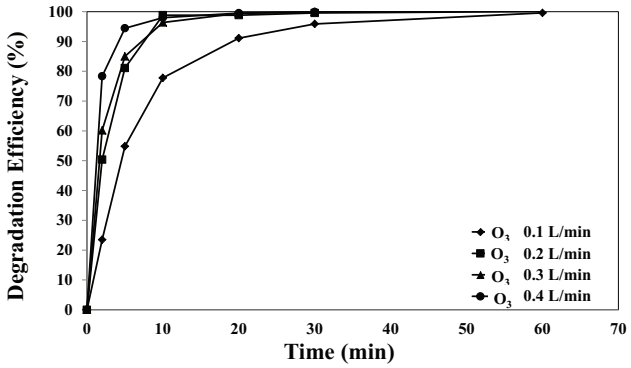

Fig. 2. Degradation of tetracycline by ozonation with different ozone gas flows.

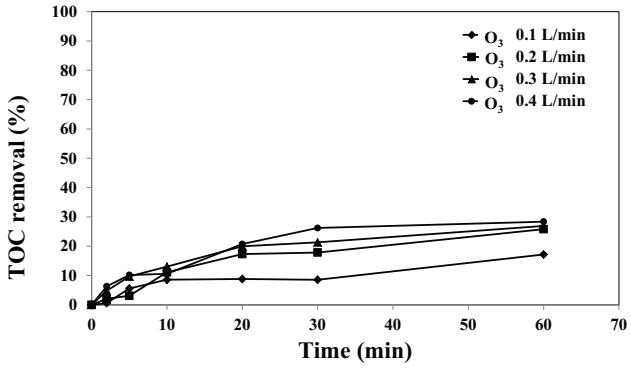

Fig. 3. Mineralization of tetracycline by ozonation with different ozone gas flows.

resulted from the removal of TOC, which indicates that the mineralization of organic compounds is the key step to reducing the toxicity of organic compounds. Therefore, this study also found a comparable result, where the cell viabilities were also decreased to 81% and 76% as the ozone flow rate increased to 0.3 and 0.4 L O_3/min, respectively. This indicated that excessive O_3 introduced into the solution was worthless to enhance the mineralization of organic compounds so that the reduction of toxicity was insignificant.

Fig. 5 shows the results of tetracycline degradation, TOC removal and cell viability by ozonation with different reaction pH levels, where the pH levels were initially from 3 to 10. It was found that the degradation efficiencies of tetracycline at different pH levels all reached almost 100% at 60 min of reaction, which indicated that the tetracycline could be easily degraded by indirect ozonation (•OH produced by ozone and H_2O) and direct ozonation (O_3 molecule) so that the difference of tetracycline degradation with varying pH levels was insignificant [14]. However, the profiles of TOC removal and cell viability with different pH levels were slightly different, where the maximum cell viability (88% ± 1.5%) was observed at pH 3, and gradually decreased to 60% ± 0.7% at pH 10. In addition, the highest TOC removal was found to be 39.4% at pH 10 (the second highest one was 34.5% at pH 3), which indicated that a basic condition was appropriate to mineralize the tetracycline. However, the reduction in solution toxicity was lower than that at acidic conditions, so that the tetracycline degradation by ozonation should be carried out at lower pH levels.

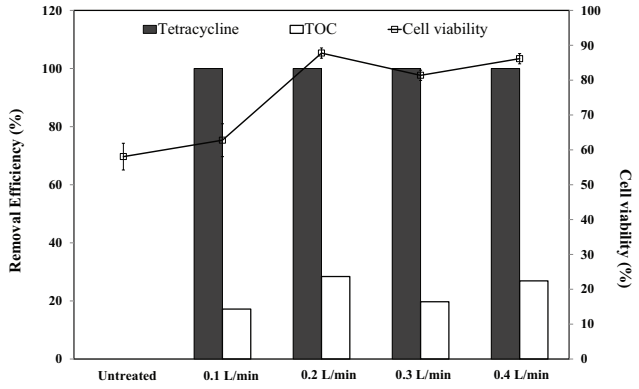

Fig. 4. Profiles of tetracycline degradation, TOC removal and cell viability by ozonation with different ozone gas flows.

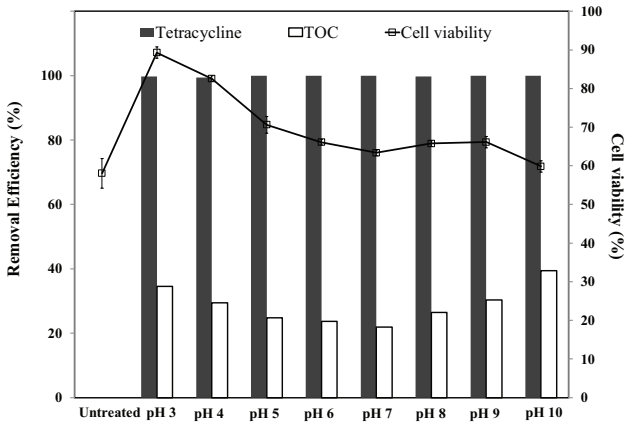

Fig. 5. Profiles of tetracycline degradation, TOC removal and cell viability by ozonation with different reaction pH levels.

3.3. Comparison of different treatment methods

In addition to investigate the degradation of tetracycline by the sono-Fenton process and ozonation at different reaction conditions, this study also compared the performance of seven treatment methods including ultrasound alone, the Fenton process, the sono-Fenton process, ozonation, O_3 + ultrasound, O_3 + Fenton and O_3 + sono-Fenton. There was 8.5% and 5.4% of tetracycline degraded and mineralized by ultrasound alone after 60 min; hence, the cell viability increased slightly from 58% (before treatment) to 62% (after treatment), suggesting that the ultrasound was inappropriate to effectively decrease the toxicity of tetracycline (Fig. 6). As the Fenton and sono-Fenton processes were carried out, the degradation of tetracycline increased to 60% and 94.2%, respectively, which indicates that the addition of Fenton's reagent in the solution is appropriate to provide more •OH to degrade the tetracycline [11,27,28]. In addition, TOC removal by the Fenton and sono-Fenton processes was 16.2% and 33.2%, and the cell viability increased to 62% and 67%, respectively, which indicates that the sono-Fenton process not only increases the production of •OH but also enhances the performance of detoxification for a tetracycline solution, based on the synergetic effect by coupling the ultrasound and Fenton. Even the sono-Fenton process shows a better performance than ultrasound or the Fenton process alone, and ~70% of TOC was still present in the solution; therefore, ozonation and the combination of ultrasound, Fenton and ozone were considered in this study to enhance the degradation and mineralization of tetracycline.

In Fig. 6, it is shown that the degradation of tetracycline by ozone, O_3+ultrasound, O_3+Fenton and O_3+sono-Fenton all reached almost 100% after 60 min of reaction, which indicated that the application of ozone was significantly effective on oxidizing the organic compounds within a short duration. In addition, TOC removals were 34.5%, 40.2%, 48.3% and 65.1%

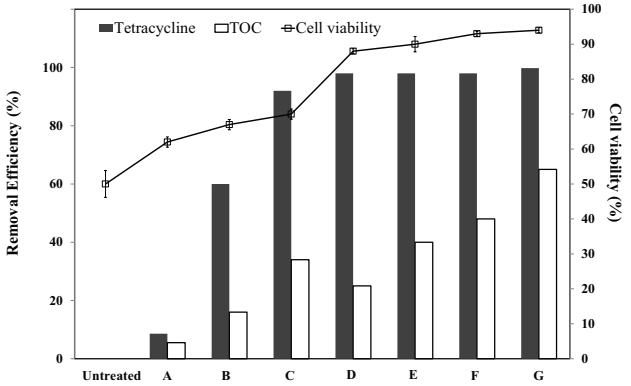

Fig. 6. Profiles of tetracycline degradation, TOC removal and cell viability by ozonation with seven oxidation processes: A – ultrasound; B – Fenton; C – sono-Fenton; D – O_3; E – O_3 + ultrasound; F – O_3 + Fenton and G – O_3 + sono-Fenton.

Table 5
Tetracycline degradation percentage, pseudo-first-order rate constant of tetracycline degradation, TOC removal and operational costs of seven oxidation processes

Methods	Degradation of tetracycline (%)	Degradation rate constant ($\times 10^{-3}$ min^{-1})	TOC removal (%)	Operational cost to degrade 1 kg tetracycline (USD)	Operational cost to remove 1 kg TOC[h] (USD)
US[a]	8.6	1.5	5.5	2,466.53	6,492.84
Fenton[b]	60	16.0	16.2	263.76	1,644.51
Sono-Fenton[c]	94.2	44.3	33.2	393.20	1,833.90
O_3[d]	98	59.5	34.5	330.06	4,592.36
O_3 + US[e]	98	70.4	40.2	405.59	5,018.62
O_3 + Fenton[f]	98	68.9	48.3	193.63	3,993.25
O_3 + sono-Fenton[g]	99.8	71.9	65.1	229.71	3,495.25

[a]100 W, 55°C, pH 3, 60 min.
[b]Fe^{2+} = 0.2 mM, H_2O_2 = 2 mM, 55°C, pH 3, 60 min.
[c]100 W, Fe^{2+} = 0.2 mM, H_2O_2 = 2 mM, 55°C, pH 3, 60 min.
[d]O_3 = 0.2 L/min, 55°C, pH 3, 20 min.
[e]O_3 = 0.2 L/min, 100 W, 55°C, pH 3, 20 min.
[f]O_3 = 0.2 L/min, Fe^{2+} = 0.2 mM, H_2O_2 = 2 mM, 55°C, pH 3, 10 min.
[g]O_3 = 0.2 L/min, Fe^{2+} = 0.2 mM, H_2O_2 = 2 mM, 100 W, 55°C, pH 3, 10 min.
[h]TOC is presented after 60 min.

(Table 5), respectively, which reveals that the combination of ozone with ultrasound or Fenton was profitable for increasing the performance of tetracycline mineralization [29]. It is also shown in Table 5 that the first-order degradation rate constant increased from 1.5×10^{-3} min^{-1} (ultrasound only) to 71.9×10^{-3} min^{-1} (O_3 + sono-Fenton), which is evident that the combination of several AOPs was useful to rapidly degrade the organic compounds. Due to the increase in TOC removal, it is shown in Fig. 6 that the cell viability increased to as high as 94%, which indicated that the detoxification of a tetracycline solution by O_3 + sono-Fenton process was much higher than other processes. Not only the tetracycline degradation and mineralization or the profiles of toxicity but also the operational costs by seven treatment methods are summarized in Table 5. As only ultrasound was applied in tetracycline degradation, it is found that 2,466.53 USD were needed to remove 1 kg tetracycline from solution (i.e., if the tetracycline concentration is 50 mg/L, removal of 1 kg tetracycline equates to treating 20 m^3 wastewater); additionally, 6,492.84 USD was needed to totally mineralize the tetracycline and transfer it into CO_2. As the Fenton process was carried out, the removal of 1 kg tetracycline and 1 kg TOC needed 263.76 and 1,644.51 USD, respectively, which was much lower than ultrasound alone. In the sono-Fenton system, the cost, including the chemical reagents (Fenton) and electric charge (sonicator), was calculated so that the operational cost for removing 1 kg tetracycline and 1 kg TOC slightly increased to 393.20 and 1,833.90 USD, respectively. When the ozone was used in the treatment processes, the operational costs to remove 1 kg tetracycline were 330.06, 405.59, 193.63 and 229.71 USD for O_3, O_3 + US, O_3 + Fenton and O_3 + sono-Fenton, respectively, which indicated that the operational costs for O_3 + Fenton and O_3 + sono-Fenton processes were lower than the Fenton process alone. It is important that the necessary treatment duration was only 10 min to remove the 50 mg/L tetracycline by O_3 + Fenton and O_3 + sono-Fenton process, so that the charge of electrical power (ozone generator and sonication) and usage of chemicals (Fe^{2+}, H_2O_2, pure O_2 gas) could be reduced, and thus, operational costs were saved. However, considering TOC removal, the highest result in Table 5 was 65.1% within 60 min of reaction, which indicated that the treatment duration could not be saved even when coupling O_3 and the sono-Fenton process for tetracycline degradation. Hence, the necessary operational costs for removing 1 kg TOC by four ozone-related processes were among 3,495.25 and 5,018.62 USD, which were much higher than the Fenton and sono-Fenton processes.

4. Conclusions

This study investigated the performance of seven treatment methods: ultrasound, the Fenton process, the sono-Fenton process, ozonation, O_3 + Fenton, O_3 + ultrasound and O_3 + sono-Fenton process on the degradation of tetracycline, by systematically varying certain reaction parameters, including pH, temperature, ultrasonic watt, ozone gas flows and adding specific anions to the reaction solution. It was observed that the degradation and mineralization of tetracycline at pH 3–6 are comparable but was significantly decreased as the pH level increased to >7. Increasing reaction temperatures and ultrasonic watts were appropriate to the increase of tetracycline degradation and mineralization; as the ultrasonic watt was adjusted to 200 W, the performance was slightly lower than that at 100 W. Therefore, 25°C and 100 W are suggested to be the optimal reaction conditions. Six anions in the solution lead to the decrease of tetracycline degradation, where the HCO_3^- and CO_3^{2-} were the two dominate anions inhibiting the oxidation performance. Ozonation and

ozone-related processes demonstrated superior performance in the degradation and detoxification of tetracycline, where the O_3 + sono-Fenton process shows the optimal result in tetracycline degradation, TOC removal and decrease in toxicity. However, if the objective is to achieve the rapid degradation of tetracycline, the O_3 + sono-Fenton process should be considered as the optimal method based on the higher tetracycline degradation and mineralization results; otherwise, if the objective is to treat the tetracycline wastewater economically, the Fenton and sono-Fenton processes should be considered as the priority ones.

Acknowledgments

Financial support from the National Science Council, Republic of China (grant No. 101-2221-E-264-005) and the Ministry of Science and Technology, Republic of China (grant No. 103-2221-E-264-001-MY2) is gratefully acknowledged.

References

[1] A. Kładna, I. Kruk, T. Michalska, P. Berczyński, H.Y. Aboul-Enein, Characterization of the superoxide anion radical scavenging activity by tetracycline antibiotics in aprotic media, Luminescence, 26 (2011) 611–615.
[2] K. Kümmerer, Significance of antibiotics in the environment, J. Antimicrob. Chemother., 52 (2003) 5–7.
[3] S. Yahiat, F. Fourcade, S. Brosillon, A. Amrane, Removal of antibiotics by an integrated process coupling photocatalysis and biological treatment – case of tetracycline and tylosin, Int. Biodeterior. Biodegrad., 65 (2011) 997–1003.
[4] Y. Kitazono, I. Ihara, G. Yoshida, K. Toyoda, K. Umetsu, Selective degradation of tetracycline antibiotics present in raw milk by electrochemical method, J. Hazard. Mater., 243 (2012) 112–116.
[5] L. Hou, H. Zhang, X. Xue, Ultrasound enhanced heterogeneous activation of peroxydisulfate by magnetite catalyst for the degradation of tetracycline in water, Sep. Purif. Technol., 84 (2012) 147–152.
[6] A. Selvam, Z. Zhao, Y. Li, Y. Chen, K. Leung, J. Wong, Degradation of tetracycline and sulfadiazine during continuous thermophilic composting of pig manure and sawdust, Environ. Technol., 34 (2013) 2433–2441.
[7] S.C. Kim, K. Carlson, LC-MS2 for quantifying trace amounts of pharmaceutical compounds in soil and sediment matrices, TrAC, Trends Anal. Chem., 24 (2005) 635–644.
[8] K.G. Karthikeyan, M.T. Meyer, Occurrence of antibiotics in wastewater treatment facilities in Wisconsin, USA, Sci. Total Environ., 361 (2006) 196–207.
[9] C.K. Wang, Z.H. Liu, Decontamination of alachlor herbicide wastewater by a continuous dosing mode ultrasound/Fe^{2+}/H_2O_2 process, J. Environ. Sci., 26 (2014) 1332–1339.
[10] C.K. Wang, Y.H. Shih, Degradation and detoxicity of diazinon by sono-Fenton and sono-Fenton-like processes, Sep. Purif. Technol., 140 (2015) 6–12.
[11] Z. Zeng, H. Zou, X. Li, M. Arowo, B. Sun, J. Chen, G. Chu, L. Shao, Degradation of phenol by ozone in the presence of Fenton reagent in a rotating packed bed, Chem. Eng. J., 229 (2013) 404–411.
[12] L. Zhao, W. Ma, J. Ma, G. Wen, Q. Liu, Relationship between acceleration of hydroxyl radical initiation and increase of multiple-ultrasonic field amount in the process of ultrasound catalytic ozonation for degradation of nitrobenzene in aqueous solution, Ultrason. Sonochem., 22 (2015) 198–204.
[13] Y. Wang, H. Zhang, J. Zhang, C. Lu, Q. Huang, J. Wu, F. Liu, Degradation of tetracycline in aqueous media by ozonation in an internal loop-lift reactor, J. Hazard. Mater., 192 (2011) 35–43.
[14] Y. Wang, H. Zhang, L. Chen, Ultrasound enhanced catalytic ozonation of tetracycline in a rectangular air-lift reactor, Catal. Today, 175 (2011) 283–292.
[15] L. Hou, H. Zhang, L. Wang, L. Chen, Ultrasound-enhanced magnetite catalytic ozonation of tetracycline in water, J. Chem. Eng., 229 (2013) 577–584.
[16] C.K. Wang, J.J. Jian, Feasibility of tetracycline wastewater degradation by an enhanced sonolysis, J. Adv. Oxid. Technol., 18 (2015) 39–46.
[17] C.K. Wang, C.W. Hou, Y.X. Wei, Degradation and detoxicity of ethylenediamine wastewater by a continuous dosing mode sono-Fenton process, Sustain. Environ. Res., 23 (2013) 413–420.
[18] M.H. Sheydaei, A.R. Khataee, Sonocatalytic decolorization of textile wastewater using synthesized r-FeOOH nanoparticles, Ultrason. Sonochem., 27 (2015) 616–622.
[19] I. Yahiaoui, F. Aissani-Benissad, F. Fourcade, A. Amrane, Removal of tetracycline hydrochloride from water based on direct anodic oxidation (Pb/PbO_2 electrode) coupled to activated sludge culture, J. Chem. Eng., 221 (2013) 418–425.
[20] L. Hou, L. Wang, S. Royer, H. Zhang, Ultrasound-assisted heterogeneous Fenton-like degradation of tetracycline over a magnetite catalyst, J. Hazard. Mater., 302 (2016) 458–467.
[21] P. Villegas-Guzman, J. Silva-Agredo, A.L. Giraldo-Aguirre, O. Flórez-Acosta, C. Petrier, R.A. Torres-Palma, Enhancement and inhibition effects of water matrices during the sonochemical degradation of the antibiotic dicloxacillin, Ultrason. Sonochem., 22 (2015) 211–219.
[22] Y.S. Ma, Short review: current trends and future challenges in the application of sono-Fenton oxidation for wastewater treatment, Sustain. Environ. Res., 22 (2012) 271–278.
[23] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, Photocatalytic degradation for environmental applications – a review, J. Chem. Technol. Biotechnol., 77 (2002) 102–116.
[24] C.K. Wang, C.W. Hou, Z.H. Liu, Decontamination of alachlor by continuously dosed sono-Fenton process: effects of system parameters, Mod. Environ. Sci. Eng., 2 (2016) 1–10.
[25] J.H. Sun, S.P. Sun, J.Y. Sun, R.X. Sun, L.P. Qiao, H.Q. Guo, M.H. Fan, Degradation of azo dye Acid black 1 using low concentration iron of Fenton process facilitated by ultrasonic irradiation, Ultrason. Sonochem., 14 (2007) 761–766.
[26] Z. Qiang, C. Liu, B. Dong, Y. Zhang, Degradation mechanism of alachlor during direct ozonation and O_3/H_2O_2 advanced oxidation process, Chemosphere, 78 (2010) 517–526.
[27] I. Grčić, M. Obradović, D. Vujević, N. Koprivanac, Sono-Fenton oxidation of formic acid/formate ions in an aqueous solution: from an experimental design to the mechanistic modeling, Chem. Eng. J., 164 (2009) 196–207.
[28] K. Ninomiya, H. Takamatsu, A. Onishi, K. Takahashi, N. Shimizu, Sonocatalytic-Fenton reaction for enhanced OH radical generation and its application to lignin degradation, Ultrason. Sonochem., 20 (2013) 1092–1097.
[29] Z.R. Hopkins, L. Blaney, A novel approach to modeling the reaction kinetics of tetracycline antibiotics with aqueous ozone, Sci. Total Environ., 468–469 (2014) 337–344.