

The Creation of Sono-Fenton System via Trace Fe²⁺ Addition in Sono-Degradation Dimethoate: Mechanism and Optimization

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Abstract

The mechanism and optimization of a simple sono-Fenton system established by utilizing sono-generated H_2O_2 via trace Fe^{2+} addition were investigated with dimethoate as a target treated pollutant. The results of the Box-Behnken design (BBD) response surface methodology showed that Fe^{2+} dosage, ultrasonic intensity, and initial pH value had significant effects on the pseudo-first-order kinetic rate constant of dimethoate degradation (response variable). The response variable was fitted well by a quadratic polynomial equation. Accordingly, the optimum degradation efficiency (95.3% within 10 minutes) was obtained under the condition of Fe^{2+} dosage = $200\mu\text{M}$, ultrasonic intensity = 0.69 W/cm^2 and the initial pH = 3, which was 38.1% higher than that in single sonication. Of note, the optimal $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio calculated in this sono-Fenton was 25 times higher than that in the conventional Fenton reaction, which indicated that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle was significantly accelerated might due to the $\cdot\text{H}$ produced in the pyrolysis of H_2O and the enhanced mass transfer in sonication. The hydrophilic toxic degradation by-products for dimethoate can be better controlled due to the enhancement of degradation in bulk solution. Considered the acidic condition formed after 5 minutes of sonication, the cost of pH adjustment was reduced by 10% compared with the conventional Fenton system.

Highlights

- A simple sono-Fenton was established by utilizing sono-generated H_2O_2 with trace Fe^{2+} addition
- BBD response surface methodology was used to predict and optimize this sono-Fenton degradation of dimethoate
- The $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle was significantly accelerated in this sono-Fenton system
- The degradation in bulk solution was enhanced in this sono-Fenton system

Introduction

As a promising and environmentally friendly Advanced Oxidation Process(AOPs), sonication has been introduced to eliminate the degradation of organic pollutants with hydrophobicity, volatility, or surface activity(Xiao, He, Diaz-Rivera, Pee, & Weavers, 2014). Sonication induces the formation of cavitation bubbles in water that undergo transient collapse events and yields extremely high temperatures approaching 5,000K and pressures up to 10,000 bar within microseconds for each individual bubble event. In the vapor phase of collapsing cavitation bubbles, water vapor is pyrolytically cleaved to form hydroxyl radicals ($\cdot\text{OH}$) and hydrogen atoms ($\cdot\text{H}$). Locally condensed $\cdot\text{OH}$ is accumulated on the interfaces of the collapsing cavitation bubbles and quickly self-recombines to form hydrogen peroxide (H_2O_2) before reach to the bulk solution (Y. G. Adewuyi, 2005; Hoffmann, Hua, & Höchemer, 1996). Consequently, volatile organic pollutants can enter into the collapsing bubbles and undergo pyrolytic degradation. Hydrophobic pollutants tend to migrate toward the interface of the bubbles and be degraded via condensed $\cdot\text{OH}$ oxidation and pyrolysis. Non-volatile and hydrophilic compounds can stay in the bulk solution and react with $\cdot\text{OH}$ or $\cdot\text{H}$ (G. Y. Adewuyi, 2005; Y. G. Adewuyi, 2005). Studies have shown that the H_2O_2 can be released in the bulk solution under the effect of sonication(Fathinia, Fathinia, Rahmani, & Khataee, 2015). Hua et al further found that the generation rate of

H_2O_2 in the bulk solution is 3 to 5 times faster than that of $\cdot\text{OH}$ under sonication (Hua & Hoffmann, 1997). Unfortunately, H_2O_2 usually does not play an important role in organic pollutants oxidation due to its much lower oxidation activity ($E_{\text{ORP}}=0.68\text{ V}$) compared with $\cdot\text{OH}$ ($E_{\text{ORP}}=2.80\text{ V}$). Therefore, a large number of studies combined sonication with other AOPs to overcome the drawbacks of the poor degradation efficiencies for hydrophilic pollutants in sonication alone (Bolobajev & Goi, 2017; Ghodbane & Hamdaoui, 2009; Li, Lan, Bai, & Song, 2013) and the consequently high energy consumption.

For this purpose, the combinations of sonication with the Fenton reaction have received increasing research interest to compensate for the lower sono-degradation efficiency in bulk solution (Li et al., 2013; Zhu et al., 2019; Zou, Ning, Wang, Sun, & Hong, 2019). In this combined system, all the Fenton reagents (H_2O_2 , Fe^{2+} and acid to keep the $\text{pH} = 2-3$ (de Souza et al., 2006)) are necessary. Sonication can promote the Fenton reaction by accelerating the regeneration of Fe^{2+} via H_2O_2 addition (Zhu et al., 2019). The disturbance caused by the resonances of the cavitation bubble also increases the mass transfer to makes the reaction more sufficient (Ben Abderrazik, Azmani, R'kiek, Song, & O'Shea, 2005; Bolobajev & Goi, 2017; Siddique, Farooq, & Price, 2014). However, the sono-generated H_2O_2 and the acid environment in sonication were neglected. Therefore, in this study, a simple sono-Fenton system was established by utilizing sono-generated H_2O_2 with trace Fe^{2+} addition, and a simple and economic method was explored to enhance the degradation in bulk solution (Pang, Abdullah, & Bhatia, 2011).

Thio-Organophosphates pesticides (Thio-OPs) functioned by non-specific inhibiting enzyme acetylcholinesterase (AChE) (Tarbah, Shaheen, Benomran, Hassan, & Daldrup, 2006) are widely used and frequently detected in surface waters and groundwaters (Gao et al., 2009). The growing public health concerns about Thio-OPs ($\text{P} = \text{S}$) are not only due to their inherent toxicities but also their corresponding O-analogs ($\text{P} = \text{O}$) formed in oxidation processes (Acero, Benitez, Real, & Gonzalez, 2008; Duirk, Desetto, & Davis, 2009; Duirk, Desetto, Davis, Lindell, & Cornelison, 2010). O-analogs are found to have a much higher water-solubility and AChE inhibitory effect (Buratti & Testai, 2007). Our previous research has found that as typically semi-volatile and semi-hydrophobic thio-OPs, dimethoate can be degraded efficiently via $\cdot\text{OH}$ oxidation, hydrolysis, and pyrolysis on collapsing cavitation bubble interfaces under sonication (Yao, Hoffmann, Gao, Zhang, & Li, 2011). However, its O-analog, namely omethoate as main toxic intermediate cannot be secondarily degraded efficiently during the sono-degradation. Omethoate has high solubility (water solubility = 1000g/L) and naturally trends to migrate to the bulk solution and react with $\cdot\text{OH}$ after formation. Therefore, dimethoate is taken as the target pollutant in our study which increases the $\cdot\text{OH}$ content in bulk solution for secondary degradation of hydrophilic and nonvolatile toxic intermediates. Hence, increasing the $\cdot\text{OH}$ in bulk solution is a feasible method for secondary degradation of omethoate.

Given these considerations, we are motivated to establish a simple sono-Fenton system via utilizing sono-generated H_2O_2 and H^+ with trace Fe^{2+} addition and to explore its degradation mechanism and kinetics. BBD response surface methodology was used to predict and optimize this sono-Fenton degradation of dimethoate. All the identified degradation intermediates, especially hydrophilic ones and ions, were also monitored under this optimal sono-Fenton degradation condition to verify the enhancement of degradation efficiency in bulk solution.

Experimental Details

2.1 Chemicals

All the chemical reagents were analytical grade and used without further treatment. Dimethoate (98%, purity) and omethoate (97%, purity) were purchased from Ehrenstorfer GmbH (Germany). N-(methyl) mercaptoacetamide (97%, purity), dichloromethane (PESTANAL®), HCl, NaOH, methanol (PESTANAL®), Supelclean LC-18 cartridge (500 mg / 3 mL) and acetic acid were obtained from Sigma-Aldrich (USA). All the solutions were prepared with water purified with a Milli-Q Gradient water purification system (18.2 MΩ).

2.2 Experiments

All the experiments were operated in the sonochemical reactor as shown in the Ref (Yao et al., 2010). All reactions were performed under atmospheric pressure at a constant temperature of $20.0 \pm 1.0^\circ\text{C}$ with a water bath. In each run, 300 mL of a previously prepared reaction solution was introduced into the reactor and then air saturated. The initial pH of the reaction solutions was adjusted to 7.00 ± 0.05 with 1.0 M HCl and/or 1.0 M NaOH. However, the reaction solutions were not buffered and thus the pH was allowed to vary during the course of sonication. At pre-set time intervals, samples were collected for analysis immediately. All the experiments were carried out in triplicate with standard deviations of less than 10%. Each data point represents the average value.

2.3 Analysis

Simultaneous quantification of dimethoate and omethoate was achieved via Agilent 1100 series LC-ESI-MS as described before without any extraction of the sample. The detection of characteristic fragments m/z of degradation byproducts was carried out by solid-phase extraction-gas chromatography/electron impact mass spectrometry (SPE-GC/EI-MS) as described previously on selective ions mode (SIM) (Yao et al., 2011). The characteristic fragments of degradation byproducts were also confirmed by our previous study (Yao et al., 2011). The ion chromatography (ICS1000, Dionex companies in the US) equipped with an IonPacAS11 anion chromatographic column and a suppressed EDC detector was used in simultaneous quantification of HCOO^- , SO_4^{2-} and PO_4^{3-} . Calorimetry measurements were made to determine the ultrasonic power transferred to the solution. The concentration of H_2O_2 was estimated spectrophotometrically by the molybdate activated iodide method (Beckett & Hua, 2003).

2.4 Experimental design

Response surface methodology (RSM) is a collection of mathematical and statistical techniques a statistical method in which a response of interest is influenced by several variables and the objective is to search the optimum conditions of variables to predict targeted responses. RSM contains an empirical modeling technique devoted to the evaluation of relations existing between experimental factors and the observed results (Bezerra, Santelli, Oliveira, Villar, & Escaleira, 2008). RSM has been widely used for studying the optimization of the treatment process of simulated wastewater (Khayet, Zahrim, & Hilal, 2011; Singh, Gupta, Singh, & Sinha, 2011).

In this study, the Box-Behnken (BB), a widely used form of RSM, was selected for the optimization of Fe^{2+} enhanced sonication degradation of dimethoate. The BB is one of the ideal design tools for sequential

experimentation and allows testing the lack of fit when an adequate number of experimental values are available. A three-factorial and a three-level BB experimental design, with three replicas at the center point leading to a total number of fifteen experiments, was employed for response surface modeling (Bezerra et al., 2008). The variables used in this study were: the Fe^{2+} dosage (x_1), ultrasonic intensity (x_2), and initial pH value (x_3), while the pseudo-first-order degradation constant of dimethoate (y) was considered as the response.

The data of dimethoate concentration versus ultrasonic irradiation time in the initial 10 minutes were fitted to obtain the pseudo-first-order degradation constant of dimethoate (y) by Origin 8.0 software in each run of the experiment.

For statistical calculations, the variables x_i were coded as X_i according to the following relationship:

$$X_i = (x_i - x_{i,0}) / (x_{i,+} - x_{i,-}) \quad (1)$$

Where X_i are the coded experimental levels of the variables; $x_{i,0}$, $x_{i,+}$ and $x_{i,-}$ represent the actual variable values at the coded level 0, 1 and -1 respectively. The actual values of variables and their variation limits were selected based on the values obtained in Sect. 3.1, 3.2 and 3.3 and coded as shown in Table 1.

Table 1. Level and code of experiment variables

Variables	Unit	Code	Actual values of coded levels		
			-1	0	1
ultrasonic intensity	W/cm ²	X_2	0.24	0.47	0.69
Fe^{2+} dosage	$\mu\text{mol/L}$	X_1	0	150	300
initial pH value	-	X_3	3	6	9

For the analysis of experimental data, the response variable was fitted by a second-order model in the form of the quadratic polynomial equation given below:

2

where Y is the predicted response (Pseudo-first-order degradation kinetics constant of dimethoate); β_i ($i = 0, 1, 2$ and 3) are regression coefficients for linear effects, β_{ii} ($i = 1, 2$ and 3) are the regression coefficients for squared effects and β_{ij} ($i = 1, 2$ and $3; j = 1, 2$ and 3) are the regression coefficients for interaction effects; X_i are coded experimental levels of the variables.

Results And Discussion

3.1 The effect of ultrasonic frequency and intensity on the production of H_2O_2

To figure out whether the amount of sono-generated H_2O_2 is sufficient to create the extra in situ Fenton reaction in sonication, herein, quantification of H_2O_2 was conducted at different ultrasonic frequencies and intensities. The effect of ultrasonic frequency and intensity on the production of H_2O_2 was shown in Fig. 1 (a) and (b). Concentration vs. time profiles were therefore analyzed with a simple pseudo-zero-order equation as follows:

3

Where $k_{\text{app},1}$ is the apparent zero-order rate constant of H_2O_2 formation, t is the irradiation time, and $[\text{H}_2\text{O}_2]_0$ and $[\text{H}_2\text{O}_2]_t$ are the concentrations at time = 0 and time = t , respectively.

As illustrated in Fig. 1 (a) and (b), the formation of H_2O_2 followed pseudo-zero-order kinetics at each ultrasonic frequency and intensity ($R^2 = 0.928$). Meanwhile, the H_2O_2 yields at different frequencies followed the order: 619 > 406 > 226 > 800 > 100 kHz. Of note, the $\cdot\text{OH}$ yields were reported in the order of 354 > 620 > 803 > 206 > 1062 kHz, which is different from that of H_2O_2 herein (Yang, Sostaric, Rathman, & Weavers, 2008). That the H_2O_2 production at 226 kHz is higher than that at 800 kHz can be attributed to more $\cdot\text{OH}$ self-recombination events happening at the water-bubble interface per unit time due to the longer ultrasonic cycle time despite lower $\cdot\text{OH}$ production. However, the self-recombination rate constant of $\cdot\text{OH}$ under ambient condition was measured to be $5.5 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1}$, which indicated that the self-recombination reaction rate was controlled by the mass transfer to some extent. From this viewpoint, an appropriate higher frequency is beneficial to the H_2O_2 production due to greater effects of diffusion from the internal bubble to the water-bubble interface (Campbell, Vecitis, Mader, & Hoffmann, 2009).

The effect of ultrasonic intensity on the production of H_2O_2 with time is shown in Fig. 1(b). $k_{\text{app},1}$ proportionally increases from 0.136 min^{-1} to 2.762 min^{-1} with an increase in lower ultrasonic intensity from 0.20 to 0.69 W/cm^2 ($k_{\text{app},1} = 6.575[\text{ultrasonic intensity}] - 1.34$, $R^2 = 0.973$). These results indicated that H_2O_2 production is strongly dependent on the ultrasonic frequency and intensity under air atmosphere condition. Moreover, compared with ultrasonic frequency, the intensity seems to have a more significant impact on the production of H_2O_2 . The increase in ultrasonic intensity would increase the mixing intensity, in addition to yielding higher numbers of cavitation bubbles (Price & Lenz, 1993) and hence higher yields of $\cdot\text{OH}$. The optimal ultrasonic frequency for dimethoate degradation was found to be 610 kHz, which is almost close to that for H_2O_2 production according to our previous study (Yao et al., 2011). It is proved that the ultrasonic frequency of 610 kHz is beneficial to the degradation of dimethoate and the formation of H_2O_2 in bulk solution.

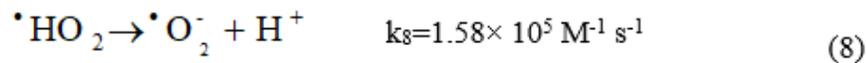
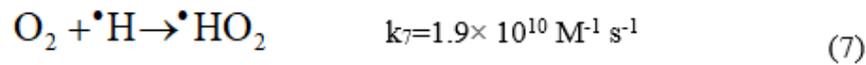
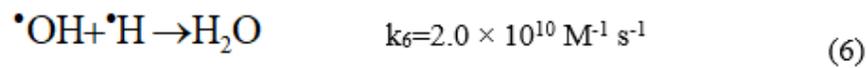
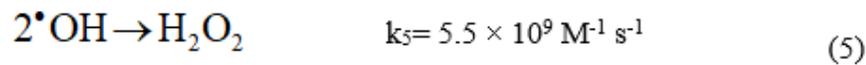
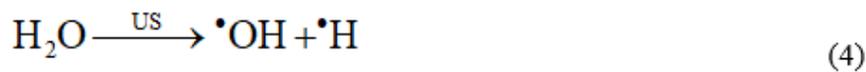
Furthermore, the degradation efficiency of sono-generated H_2O_2 on dimethoate was also verified. Considered totally $160 \mu\text{M}$ H_2O_2 was generated at the ultrasonic frequency of 619 kHz and power density of 0.69 W/cm^2 after 60 minutes, the degradation of dimethoate by $160 \mu\text{M}$ H_2O_2 was conducted. As seen in Fig. 2, only 6.0% was degraded within 120 minutes. Compared with single sonication (Yao et al., 2011), sono-generated H_2O_2 had almost little effect on the degradation of dimethoate, which can be explained by the $\cdot\text{OH}$ produced by sonication plays a major role in the degradation of dimethoate. Therefore, it could be concluded that the sono-generated

H₂O₂ does not play a significant role in the overall sono-degradation of dimethoate. It's more desired to use the sono-generated H₂O₂ from an economic point of view.

3.2 The effect of ultrasonic intensity on the decrease of pH value

Since conventional Fenton reactions are always sensitive to solution pH, different initial pH values and ultrasonic intensities were used to verify whether sonication can produce favorable acidic environmental conditions for the Fenton reaction. The results were shown in Fig. 3. It is observed that the pH value vs. time curves under the different ultrasonic intensities kept a similar decline profile in which the pH value dropped sharply during the initial 5 min and then slightly to 3.5 to 4.1 in the next 25 minutes at the fixed frequency of 600 kHz and same initial pH value of 7.0. Even at a relatively high initial pH value of 9.0, the pH value can still decrease to 4.1 after 30 minutes of sonication with the ultrasonic intensity of 0.69 W/cm².

It was proved that the sonication can create an acid condition which quite approaches the optimal Fenton reaction pH value of 2.8 ~ 3.0 in initial neutral aqueous solutions (Eqs. (4)–(8)) (Brillas, Sirés, & Oturan, 2009).



3.3 The effect of ferrous ions dosage on the consumption of H₂O₂

The variation of H₂O₂ concentrations were monitored to examine the utilization of Fe²⁺ in this sono-Fenton system. It was found that the addition of Fe²⁺ into the bulk solutions would consume the H₂O₂ formed by sonication as shown in Figure 4. Considered the Fenton reaction as follows (Eqs. (9) to (15)), it was obvious that at the beginning of the sonication, the amounts of H₂O₂ was insufficient for the reduction of Fe³⁺ (Eqs. 12). However, the significant enhancement of dimethoate degradation gives evidence that Fenton reaction between Fe²⁺ and H₂O₂ then yields ·OH can keep going, which indicated that the free radicals, and ·H generated in the ultrasonic irradiation, as shown in reaction (4), (7) and (8), should play a significant role in the reduction of Fe³⁺.

$$k_9 = 63 \text{ M}^{-1} \text{ s}^{-1} \quad (9)$$

$$k_{10} = 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \quad (10)$$

$$k_{11} = 4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \quad (11)$$

$$k_{12} \leq 3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \quad (12)$$

$$k_{13} = 1 \times 10^3 \text{ M}^{-1}\text{s}^{-1} \text{ (13)}$$

$$k_{14} = 1.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \text{ (14)}$$



The effect of Fe^{2+} concentration on the amount of H_2O_2 in solution at $\text{pH} = 3.0$ and $\text{pH} = 9.0$ as a function of irradiation time was illustrated in Fig. 4, respectively. When the initial pH value was 3.0, the effect of different iron ion dosages on the net yields of H_2O_2 were obviously different. The concentration of H_2O_2 in solution decreases substantially with increased Fe^{2+} concentration, as expected. The concentration of H_2O_2 is significantly reduced in the presence of relatively low concentrations of Fe^{2+} indicating the conversion of H_2O_2 to $\cdot\text{OH}$ was enhanced with the addition of Fe^{2+} . When the initial pH value is 9.0, the different iron ion dosage does not affect the net yield of H_2O_2 , which may be due to the inhibition of Fenton reaction by the initial alkaline conditions. Furthermore, our previous research has proved that the maximum degradation rate was obtained with the Fe^{2+} concentrations at $100 \mu\text{M}$ in initial neutral condition. A slight decrease in the degradation rates was observed at Fe^{2+} concentrations over $100 \mu\text{M}$ due to the direct scavenging effect of the $\cdot\text{OH}$ by Fe^{2+} . Although it has been proved in the previous discussion that with the progress of the reaction, the pH environment of the optimal reaction conditions will eventually be achieved, the different forms of $\text{Fe}^{2+}/\text{Fe}^{3+}$ at different initial pH values determine the change of the optimal addition dosage of Fe^{2+} for both dimethoate degradation and omethoate controlling. Hence, the dosage of Fe^{2+} less than or equal to $300 \mu\text{M}$ was selected to explore the optimal addition dosage of Fe^{2+} under different initial pH values.

3.4 The interaction effects of ultrasonic intensities, initial pH values, and Fe^{2+} dosages on the Fe^{2+} enhanced sono-degradation of dimethoate

The response surface methodology with the BBD model was utilized to simulate the interaction effects of ultrasonic intensities, initial pH values and Fe^{2+} dosages on the sono-degradation of dimethoate. BBD and its experiment results are shown in Table 2. (Degradation curves of dimethoate under 15 working conditions were shown in figure S1.)

Table 2. BBD and its experiment results

Run order	Code			k _{app} /min ⁻¹		
	X ₁	X ₂	X ₃	Fitted by	Experimental results	R ²
1	0	0	0	0.1786		0.991
2	1	-1	0	0.1291		0.992
3	0	1	-1	0.2713		0.988
4	0	1	1	0.0937		0.982
5	1	1	0	0.2336		0.990
6	-1	0	-1	0.1905		0.990
7	-1	0	1	0.0756		0.995
8	0	-1	-1	0.0976		0.987
9	-1	-1	0	0.0407		0.994
10	-1	1	0	0.0276		0.991
11	0	0	0	0.1766		0.995
12	0	0	0	0.1676		0.989
13	1	0	1	0.2467		0.991
14	0	-1	1	0.1108		0.994
15	1	0	-1	0.3904		0.990

Experimental data were analyzed using Design-Expert program 8.0 trial version including ANOVA to obtain the interaction between the variables and the response. Two-dimensional contour plots and three-dimensional curves of the response surfaces were developed using the Origen 8.0. Optimization of the Y was carried out by the Design-Expert program 8.0 trial version.

An empirical relationship between the response and independent variables (in the term of coded) was attained and expressed by the following second-order polynomial equation:

$$Y_1 = 0.17940 + 0.08317 X_1 + 0.03100 X_2 - 0.05289 X_3 - 0.0753 X_2^2 + 0.0428 X_3^2 + 0.0294 X_1 X_2 - 0.0477 X_2 X_3 \quad (16)$$

Of note, the quadratic terms (X_1^2) and the interaction terms $X_1 X_3$ was found to be not significant by the analysis of variance (ANOVA) and thus be ignored in Eq. (16). Positive and negative signs in front of the terms in Eq. (16) indicated the synergistic effect and antagonistic effect, respectively.

The model F-value of 44.18 implied that the model was significant for the pseudo-first-order degradation constant of dimethoate and there was only a 0.01% chance that a model F-value of this large could occur due to noise. Besides, the model adequate precision of 22.844 (greater than 4 as usually desired) that was greater

indicated that an adequate signal for the model was used to navigate the design space. The "Lack of Fit F-value" of 16.42 implies there is a 5.85% chance that a "Lack of Fit F-value" this large could occur due to noise.

The values of "Prob > F" less than 0.0500 indicate model terms are significant, while the values greater than 0.1000 indicate the model terms are not significant. In this case, the terms of individual variables terms (X_1 , X_2 , and X_3), quadratic terms (X_2^2 and X_3^2), and interaction terms (X_1X_2 and X_2X_3) were confirmed to be significant.

Table 3 summarizes the analysis of variance (ANOVA) results. The Model adjust- R^2 value of 0.956 was relatively high, which indicated that the model obtained was able to give a convincingly good estimate of response in the studied range.

Table 3. The Analysis of variance (ANOVA) for the quadratic model

Source	Freedom degrees	Adjusted Squares sum	Adjusted	F-Value	P-Value	
Model	7	0.127624	0.018232	44.18	0.000	significant
Linear	3	0.085402	0.028467	68.99	0.000	
Ultrasonic intensity	1	0.055341	0.055341	134.12	0.000	
Fe ²⁺ dosage	1	0.007686	0.007686	18.63	0.003	
Initial pH value	1	0.022376	0.022376	54.23	0.000	
Square	2	0.029661	0.014831	35.94	0.000	
Fe ²⁺ dosage* Fe ²⁺ dosage	1	0.020948	0.020948	50.77	0.000	
Initial pH value*Initial pH value	1	0.006851	0.006851	16.60	0.005	
2-Way Interaction	2	0.012561	0.006281	15.22	0.003	
Ultrasonic intensity* Fe ²⁺ dosage	1	0.003453	0.003453	8.37	0.023	
Fe ²⁺ dosage*Initial pH value	1	0.009108	0.009108	22.07	0.002	
Error	7	0.002888	0.000413			
Lack-of-Fit	5	0.002820	0.000564	16.43	0.058	Not significant
Pure Error	2	0.000069	0.000034			
Total	14	0.130513				

R-sq R-sq(adj) R-sq(pred)

97.79% 95.57% 84.25%

Figure 5 shows the actual experimental values versus predicted output values for the pseudo-first-order degradation constant of dimethoate. From Fig. 5, it is noted that a high correlation between the experimental and predicted values, showing that the model was well fitted and had a good prediction ability for the pseudo-first-order degradation constant of dimethoate.

From ANOVA results, significant interaction terms were found to exist between the main factors (X_1X_2 , X_2X_3). Figure 6 shows contour response surface plot of pseudo-first-order degradation constant Y versus Fe^{2+} dosage X_1 and ultrasonic intensity X_2 at initial pH value X_3 of -1, 0 and 1 to investigate the interactive effects. Figure 7 shows contour response surface plot of pseudo-first-order degradation constant Y versus Fe^{2+} dosage X_1 and initial pH value X_3 at ultrasonic intensity X_2 of -1, 0 and 1 to investigate the interactive effects. It was observed that an optimal Fe^{2+} dosage can be found at each ultrasonic intensity and the optimal Fe^{2+} dosage increased with increasing of the ultrasonic intensity, while decreased as the initial pH value increases.

In conclusion, the initial pH = 3, Fe^{2+} dosage = 200 μ M, ultrasound intensity = 0.69 W/cm² were the best reaction condition of the simple sono-Fenton system. The results were shown in Fig. 8 that the optimum degradation efficiency in this sono-Fenton system was 95.3% within 10 minutes, which is 38.1% higher than that of single sonication. It was calculated that 80 μ M H_2O_2 will be produced in bulk solution under 20 min sonication, which was used to figure out the optimal Fe^{2+}/H_2O_2 ratio in the simple sono-Fenton system. Of note, the calculated H_2O_2 concentration was just an approximate steady-state concentration that resulted from a dynamic circulation. The ratio of the optimal Fe^{2+}/H_2O_2 in Fenton system was calculated by the following equation:

17

Where $C_{Fe^{2+}}$ is the concentration of Fe^{2+} in the system at the optimal efficiency, $C_{H_2O_2}$ is the concentration of H_2O_2 in the system at the optimal efficiency, respectively.

The optimal ratio in this simple sono-Fenton system was 25 times higher than that of the conventional Fenton reaction (the optimal Fe^{2+}/H_2O_2 ratio = 0.1) (Chen et al., 2011), which indicated that the Fe^{3+}/Fe^{2+} cycle might significantly be accelerated and the concentration of Fe^{2+} was always sufficient in this simple sono-Fenton system. The accumulation of Fe^{3+} is the rate-limiting step of conventional Fenton reaction (Chen et al., 2011), but it is not suitable for this simple sono-Fenton system. It seems that the sono-generated H_2O_2 contributes to the continuous formation of the oxidizing species ($\cdot H$), which led to accelerating the reduction of Fe^{3+} .

Meanwhile, the mass transfer generated by sonication might also accelerated the Fe^{3+}/Fe^{2+} cycle. In this simple sono-Fenton system, the addition of trace Fe^{2+} could react with the sono-generated H_2O_2 to generate $\cdot OH$ and kept the oxidation reactivity in the bulk solution.

Based on the above findings, with the progress in this simple sono-Fenton system, without adjusting the initial pH value, the reaction can also be carried out at the appropriate pH value. In practical application, the ratio of acid consumption at different initial pH values was calculated by the following equation:

Where a is the initial pH of the real water body, b is the pH value of the simple sono-Fenton system after 5 minutes of sonication, respectively.

When $\text{pH} = 3.0$ was adjusted from the real water body to be treated which the initial $\text{pH} = 7.0$, the H^+ required by conventional Fenton reaction is 1.1 times of this simple sono-Fenton reaction. This proved that the pH adjustment cost of this simple sono-Fenton system is greatly reduced by the acidic condition formed after 5 minutes of sonication.

In the conventional Fenton system, when the initial pH value is neutral or alkaline, Fe^{2+} tends to form amorphous precipitates, which makes the reaction activity in the system decrease and is not conducive to the formation of $\cdot\text{OH}$ (Wang & Liu, 2014). However, an increase in acidity caused by sonication provides an ideal condition for this simple sono-Fenton system, it not only saved the cost of initial pH adjustment but also made the reaction always in high activity. It was proved that the synergistic effect of ultrasound and Fenton reaction can be induced by utilizing sono-generated H_2O_2 with trace Fe^{2+} addition.

3.5 Control of dimethoate intermediates by simple sono-Fenton system

In previous studies, the primary degradation pathway of dimethoate under sonication was discussed (Yao et al., 2011). In this study, to verify the control of this simple sono-Fenton system on the intermediate products of dimethoate, and explore whether the degradation of omethoate is effective after adding trace Fe^{2+} , sonication of dimethoate was conducted under the optimal conditions of this simple sono-Fenton system and single sonication. Nine intermediates for dimethoate have been identified using GC-MS detection as shown in Table 4. (The mass spectra of dimethoate (DIM) and its degradation Intermediates (No.1–No.9) formed during the sono-degradation in the presence of Fe^{2+} ($200\mu\text{M}$) was shown in figure S2). As shown in Fig. 9 (a), in this simple sono-Fenton system, dimethoate degradation intermediates mainly were dimethyl phosphite after 45 minutes. And the concentrations of other products were all below the detection line. Compared with the degradation intermediates of sono-degradation alone, Fig. 9 (b), the amount of N-(methyl) mercaptoacetylamide, O, O, S-trimethyl phosphorothioate, 2-(methyl disulfanyl) acetamide, and Omethoate of later decreased obviously in this simple sono-Fenton system. This proves that the system can improve the degradation efficiency of hydrophobic intermediates (The hydrophobic and hydrophilic coefficients of intermediates were shown in Table. S1), and had good control on Omethoate with high toxicity.

In previous studies, it has been known that single sonication on dimethoate mainly depends on $\cdot\text{OH}$ formed by cavitation bubble collapse (Yao et al., 2011). The attack of $\cdot\text{OH}$ on $\text{P} = \text{S}$ resulted in the formation of omethoate and cyclic hexatomic sulfur, but they decreased significantly under this simple sono-Fenton system. Therefore, it can be inferred from the above degradation pathways that $\text{P} - \text{S}$ may be an important attack point for $\cdot\text{OH}$ after the addition of Fe^{2+} . In order to better explore the control effect of this simple sono-Fenton system on toxic by-products, based on the reason that it is difficult to determine TOC at a low concentration of dimethoate, the change of concentration of ionic intermediates (HCOO^- , PO_4^{3-} , SO_4^{2-}) were used for verification. It can be seen from Fig. 10 that the formation rate of the three ions in the solution was doubled after adding a trace Fe^{2+} , which indicated that this simple sono-Fenton system had a great control effect on the dephosphorization and desulfurization of substances. As discussed above, the sonication was more capable to degrade compounds

with higher hydrophobicity so that the degradation intermediates which always showed higher hydrophilicity compared to the parent compound would easily accumulate. However, this simple sono-Fenton system has the advantage to improve the degradation of the accumulated intermediates since the Fenton reaction occurred in the bulk aqueous phase rather than in the interface of cavitation bubbles. The use of sono-generated H_2O_2 solved the secondary increase of omethoate toxicity caused by the accumulation of ineffective H_2O_2 (Inoue, Okada, Sakurai, & Sakakibara, 2006). In addition, the micro-mixing effect by turbulent flow in the reactor during sonication would result in the acceleration of Fenten reaction due to the increase in the mass transfer rate induced from hydrodynamic cavitation. Based on the above findings that this simple sono-Fenton system was more effective to improve the degradation in bulk solution.

Table 4. GC-MS-EI retention times (Rt) and spectral characteristics of dimethoate identified intermediates

No.	Intermediates	Retention times(min)	Similarity (%)	Reference ions	Characteristic ions(m/z)
1	Dimethyl phosphite	4.333	97	109	109,95,80,77,65,51,47,45
2	O, O, O-trimethyl thiophosphate	7.417	90	93	156,126,93,79,63,47
3	N-(methyl) mercaptoacetamide	9.275	80	58	105,78,72,58,48
4	O, O, S-trimethyl phosphorothioate	9.783	93	156	140,110.109,95,79,65,47
5	2-(methyldisulfanyl) acetamide	10.108	80	58	119,73,62,58,47
6	O, O, S-trimethyl phosphorodithioate	11.125	94	125	172,157,141,125,109,93,79,77,63,47
7	O, S, S-trimethyl phosphorodithioate	13.217	86	172	172,157,141,125,94,79,62,47, 45
8	Cyclic hexatomic sulfur	16.858	82	128	206,174,160,142,128,110,96,78,64,45
9	Omethoate	18.142	100	110	156,141,126,110,95,79,58,47,44

3.6 The simple sono-Fenton system in the real water sample

In order to verify the practicability of this simple sono-Fenton system, explore whether the degradation efficiency of it is affected in the real water samples. The removal effect of dimethoate by sonication after adding ferrous ion into pure water, lake water, and tap water were compared (The water quality of real water samples were shown in Table. 1S). It is observed from Fig. 11 that dimethoate concentration vs. time curves under the different water samples kept a similar decline profile, and dimethoate was removed to a lower concentration level within 10 minutes. The experimental results showed that the removal efficiency of dimethoate by this simple sono-Fenton system was not affected by the water environment, and had a wide range of applicability.

Conclusion

In this paper, the degradation in the bulk solution of a simple sono-Fenton system with dimethoate as a target pollutant was studied. Response surface methodology was employed to investigate the interaction effect of ultrasonic intensity, solution initial pH, and Fe^{2+} dosage on sono-degradation with trace Fe^{2+} addition of dimethoate. Analyzing the fitting quadratic response model found that Fe^{2+} dosage, ultrasonic intensity, and initial pH value had significant effects on pseudo-first-order kinetic rate constant; both the ultrasonic intensity and initial pH value had significant interaction with Fe^{2+} dosage. Finally, the initial pH = 3, Fe^{2+} dosage = 200 μM , ultrasound intensity = 0.69 W/cm^2 were the best reaction condition of the simple sono-Fenton system, at this time, the utilization rate of H_2O_2 produced by ultrasound reaches the maximum, and the efficiency of heterogeneous Fenton reaction is also improved. Accordingly, the results showed that the degradation efficiency of dimethoate was 95.3% within 10 minutes under the optimum conditions, which was 38.1% higher than that of single sonication. It is proved that it is feasible to establish a simple sono-Fenton system with sono-generated H_2O_2 with trace Fe^{2+} addition. The $\cdot\text{H}$ produced in the pyrolysis of H_2O and the enhanced mass transfer in sonication may significantly accelerate the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle in this simple sono-Fenton system.

The analysis of dimethoate degradation products showed that the hydrophilic toxic by-products control effect in this simple sono-Fenton system was better than single sonication and confirmed P-S may be an important attack point for $\cdot\text{OH}$ in the degradation path. The addition of trace Fe^{2+} will not only reduce the economic cost of water treatment but also make better use of H_2O_2 with low oxidation performance in bulk solution produced by separate ultrasound. The acid condition formed after 5 minutes of sonication can save 10% of the cost of pH adjustment. In this simple sono-Fenton system, the use time of sonication was reduced by 50%, greatly reducing the cost of sonication. Compared with other advanced oxidation technologies, such as UV/ O_3 , UV/US, this simple sono-Fenton system is more convenient and economical to enhance the degradation of organic pollutants in bulk solution.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

All data generated or analyzed during this study are included in this published article [and its supplementary information files]

Competing interests

The authors declare that they have no competing interests

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Authors' contributions

All authors contributed to the study conception and design. Conceptualization, Resources, Supervision: [Juanjuan Yao], Investigation, Formal analysis, Writing - original draft:[Shiyi Liu], [Yanjuan Fang], Investigation, Methodology:[Naiyun Gao], [Wenchao Jiang], Resources:[Zhi Zhang], Writing – original draft:[Xiangyu Chen]. All authors read and approved the final manuscript.

References

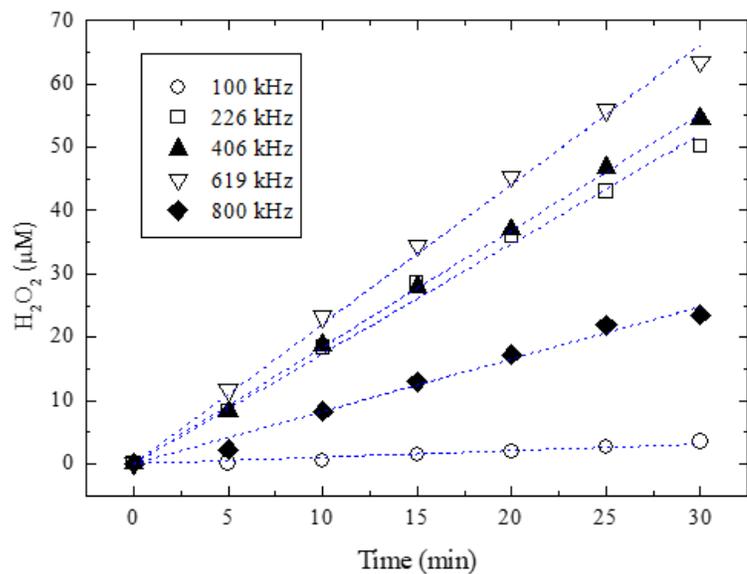
1. Acero, J. L., Benitez, F. J., Real, F. J., & Gonzalez, M. (2008). Chlorination of organophosphorus pesticides in natural waters. *Journal of Hazardous Materials*, *153*(1-2), 320-328. doi:10.1016/j.jhazmat.2007.08.051
2. Adewuyi, G. Y. (2005). Sonochemistry in Environmental Remediation. 2. Heterogeneous Sonophotocatalytic Oxidation Processes for the Treatment of Pollutants in Water. *Environmental Science & Technology*, *39*(22), 8557-8570.
3. Adewuyi, Y. G. (2005). Sonochemistry in Environmental Remediation. 1. Combinative and Hybrid Sonophotochemical Oxidation Processes for the Treatment of Pollutants in Water. *Environmental Science & Technology*, *39*(10), 3409-3420. doi:10.1021/es049138y
4. Beckett, M. A., & Hua, I. (2003). Enhanced sonochemical decomposition of 1,4-dioxane by ferrous iron. *Water Research*, *37*(10), 2372-2376. doi:https://doi.org/10.1016/S0043-1354(03)00005-8
5. Ben Abderrazik, N., Azmani, A., R'kiek, C., Song, W., & O'Shea, K. E. (2005). Iron(II)-catalyzed enhancement of ultrasonic-induced degradation of diethylstilbestrol (DES). *Catalysis Today*, *101*(3), 369-373. doi:https://doi.org/10.1016/j.cattod.2005.03.012
6. Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., & Escalera, L. A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*, *76*(5), 965-977. doi:https://doi.org/10.1016/j.talanta.2008.05.019
7. Bolobajev, J., & Goi, A. (2017). Sonolytic degradation of chlorophene enhanced by Fenton-mediated oxidation and H-scavenging effect. *Chemical Engineering Journal*, *328*, 904-914. doi:https://doi.org/10.1016/j.cej.2017.07.043
8. Brillas, E., Sirés, I., & Oturan, M. A. (2009). Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry. *Chemical Reviews*, *109*(12), 6570-6631. doi:10.1021/cr900136g
9. Buratti, F. A., & Testai, E. (2007). Evidences for CYP3A4 autoactivation in the desulfuration of dimethoate by the human liver. *Toxicology*, *241*(1-2), 33-46. doi:10.1016/j.tox.2007.08.081
10. Campbell, T. Y., Vecitis, C. D., Mader, B. T., & Hoffmann, M. R. (2009). Perfluorinated Surfactant Chain-Length Effects on Sonochemical Kinetics. *The Journal of Physical Chemistry A*, *113*(36), 9834-9842.

doi:10.1021/jp903003w

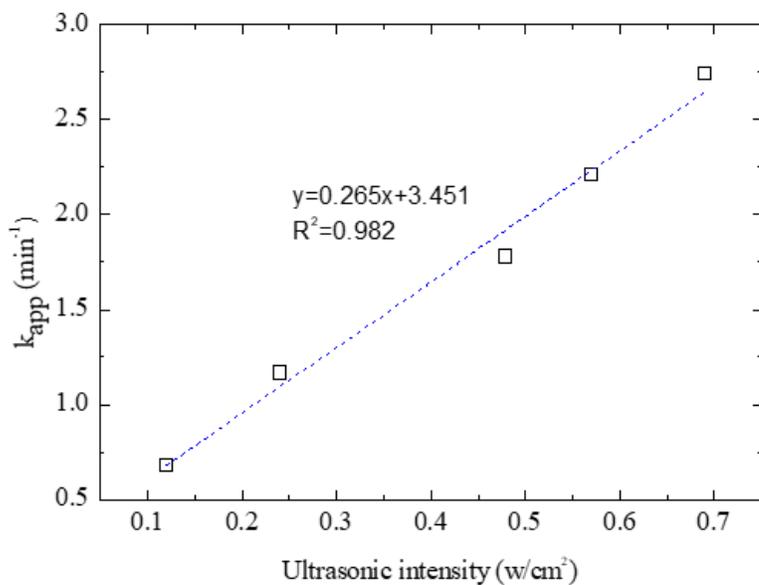
11. Chen, L., Ma, J., Li, X., Zhang, J., Fang, J., Guan, Y., & Xie, P. (2011). Strong Enhancement on Fenton Oxidation by Addition of Hydroxylamine to Accelerate the Ferric and Ferrous Iron Cycles. *Environmental Science & Technology*, *45*(9), 3925-3930. doi:10.1021/es2002748
12. de Souza, D. R., Duarte, E. T. F. M., de Souza Girardi, G., Velani, V., da Hora Machado, A. E., Sattler, C., . . . de Miranda, J. A. (2006). Study of kinetic parameters related to the degradation of an industrial effluent using Fenton-like reactions. *Journal of Photochemistry and Photobiology A: Chemistry*, *179*(3), 269-275. doi:https://doi.org/10.1016/j.jphotochem.2005.08.025
13. Duirk, S. E., Desetto, L. M., & Davis, G. M. (2009). Transformation of Organophosphorus Pesticides in the Presence of Aqueous Chlorine: Kinetics, Pathways, and Structure-Activity Relationships. *Environmental Science & Technology*, *43*(7), 2335-2340. doi:10.1021/es802868y
14. Duirk, S. E., Desetto, L. M., Davis, G. M., Lindell, C., & Cornelison, C. T. (2010). Chloramination of organophosphorus pesticides found in drinking water sources. *Water Research*, *44*(3), 761-768. doi:10.1016/j.watres.2009.10.012
15. Fathinia, S., Fathinia, M., Rahmani, A. A., & Khataee, A. (2015). Preparation of natural pyrite nanoparticles by high energy planetary ball milling as a nanocatalyst for heterogeneous Fenton process. *Applied Surface Science*, *327*, 190-200. doi:https://doi.org/10.1016/j.apsusc.2014.11.157
16. Gao, J. J., Liu, L. H., Liu, X. R., Zhou, H. D., Lu, J., Huang, S. B., & Wang, Z. J. (2009). The Occurrence and Spatial Distribution of Organophosphorous Pesticides in Chinese Surface Water. *Bulletin of Environmental Contamination and Toxicology*, *82*(2), 223-229. doi:10.1007/s00128-008-9618-z
17. Ghodbane, H., & Hamdaoui, O. (2009). Degradation of Acid Blue 25 in aqueous media using 1700kHz ultrasonic irradiation: ultrasound/Fe(II) and ultrasound/H₂O₂ combinations. *Ultrasonics Sonochemistry*, *16*(5), 593-598. doi:https://doi.org/10.1016/j.ultsonch.2008.11.006
18. Hoffmann, M. R., Hua, I., & Höchemer, R. (1996). Application of ultrasonic irradiation for the degradation of chemical contaminants in water. *Ultrasonics Sonochemistry*, *3*(3), S163-S172. doi:https://doi.org/10.1016/S1350-4177(96)00022-3
19. Hua, I., & Hoffmann, M. R. (1997). Optimization of ultrasonic irradiation as an advanced oxidation technology. *Environmental Science & Technology*, *31*(8), 2237-2243.
20. Inoue, M., Okada, F., Sakurai, A., & Sakakibara, M. (2006). A new development of dyestuffs degradation system using ultrasound. *Ultrasonics Sonochemistry*, *13*(4), 313-320. doi:https://doi.org/10.1016/j.ultsonch.2005.05.003
21. Khayet, M., Zahrim, A. Y., & Hilal, N. (2011). Modelling and optimization of coagulation of highly concentrated industrial grade leather dye by response surface methodology. *Chemical Engineering Journal*, *167*(1), 77-83. doi:https://doi.org/10.1016/j.cej.2010.11.108
22. Li, J.-T., Lan, R. J., Bai, B., & Song, Y. L. (2013). Ultrasound-Promoted Degradation of Acid Brown 348 by Fenton-Like Processes. *Asian Journal of Chemistry*, *25*, 2246-2250.
23. Pang, Y. L., Abdullah, A. Z., & Bhatia, S. (2011). Review on sonochemical methods in the presence of catalysts and chemical additives for treatment of organic pollutants in wastewater. *Desalination*, *277*(1), 1-14. doi:https://doi.org/10.1016/j.desal.2011.04.049

24. Price, G. J., & Lenz, E. J. (1993). The use of dosimeters to measure radical production in aqueous sonochemical systems. *Ultrasonics*, 31(6), 451-456. doi:[https://doi.org/10.1016/0041-624X\(93\)90055-5](https://doi.org/10.1016/0041-624X(93)90055-5)
25. Siddique, M., Farooq, R., & Price, G. J. (2014). Synergistic effects of combining ultrasound with the Fenton process in the degradation of Reactive Blue 19. *Ultrasonics Sonochemistry*, 21(3), 1206-1212. doi:<https://doi.org/10.1016/j.ultsonch.2013.12.016>
26. Singh, K. P., Gupta, S., Singh, A. K., & Sinha, S. (2011). Optimizing adsorption of crystal violet dye from water by magnetic nanocomposite using response surface modeling approach. *Journal of Hazardous Materials*, 186(2), 1462-1473. doi:<https://doi.org/10.1016/j.jhazmat.2010.12.032>
27. Tarbah, F. A., Shaheen, A. M., Benomran, F. A., Hassan, A. I., & Daldrup, T. (2006, Aug 27-Sep 01
28. Aug 6). *Distribution of dimethoate in the body after a fatal organophosphate intoxication*. Paper presented at the 44th Annual Meeting of the International-Association-of-Forensic-Toxicologists (TIAFT), Ljubljana, SLOVENIA.
29. Wang, C., & Liu, C. (2014). Decontamination of alachlor herbicide wastewater by a continuous dosing mode ultrasound/Fe²⁺/H₂O₂ process. *Journal of Environmental Sciences*, 26(6), 1332-1339. doi:[https://doi.org/10.1016/S1001-0742\(13\)60608-7](https://doi.org/10.1016/S1001-0742(13)60608-7)
30. Xiao, R., He, Z., Diaz-Rivera, D., Pee, G. Y., & Weavers, L. K. (2014). Sonochemical degradation of ciprofloxacin and ibuprofen in the presence of matrix organic compounds. *Ultrasonics Sonochemistry*, 21(1), 428-435. doi:<https://doi.org/10.1016/j.ultsonch.2013.06.012>
31. Yang, L., Sostaric, J. Z., Rathman, J. F., & Weavers, L. K. (2008). Effect of Ultrasound Frequency on Pulsed Sonolytic Degradation of Octylbenzene Sulfonic Acid. *The Journal of Physical Chemistry B*, 112(3), 852-858. doi:10.1021/jp077482m
32. Yao, J.-J., Gao, N.-Y., Deng, Y., Ma, Y., Li, H.-J., Xu, B., & Li, L. (2010). Sonolytic degradation of parathion and the formation of byproducts. *Ultrasonics Sonochemistry*, 17(5), 802-809. doi:<https://doi.org/10.1016/j.ultsonch.2010.01.016>
33. Yao, J.-J., Hoffmann, M. R., Gao, N.-Y., Zhang, Z., & Li, L. (2011). Sonolytic degradation of dimethoate: Kinetics, mechanisms and toxic intermediates controlling. *Water Research*, 45(18), 5886-5894. doi:<https://doi.org/10.1016/j.watres.2011.08.042>
34. Zhu, Y., Zhu, R., Xi, Y., Zhu, J., Zhu, G., & He, H. (2019). Strategies for enhancing the heterogeneous Fenton catalytic reactivity: A review. *Applied Catalysis B: Environmental*, 255, 117739. doi:<https://doi.org/10.1016/j.apcatb.2019.05.041>
35. Zou, H., Ning, X.-a., Wang, Y., Sun, J., & Hong, Y. (2019). Sono-advanced Fenton-like degradation of aromatic amines in textile dyeing sludge: efficiency and mechanisms. *Environmental Science and Pollution Research*, 26. doi:10.1007/s11356-019-04147-9

Figures



(a)



(b)

Figure 1

The effect of ultrasonic frequency and intensity on the production of H_2O_2 (Experimental conditions: (a) ultrasonic intensity = $0.60 W/cm^2$, (b) ultrasonic frequency = $600 kHz$)

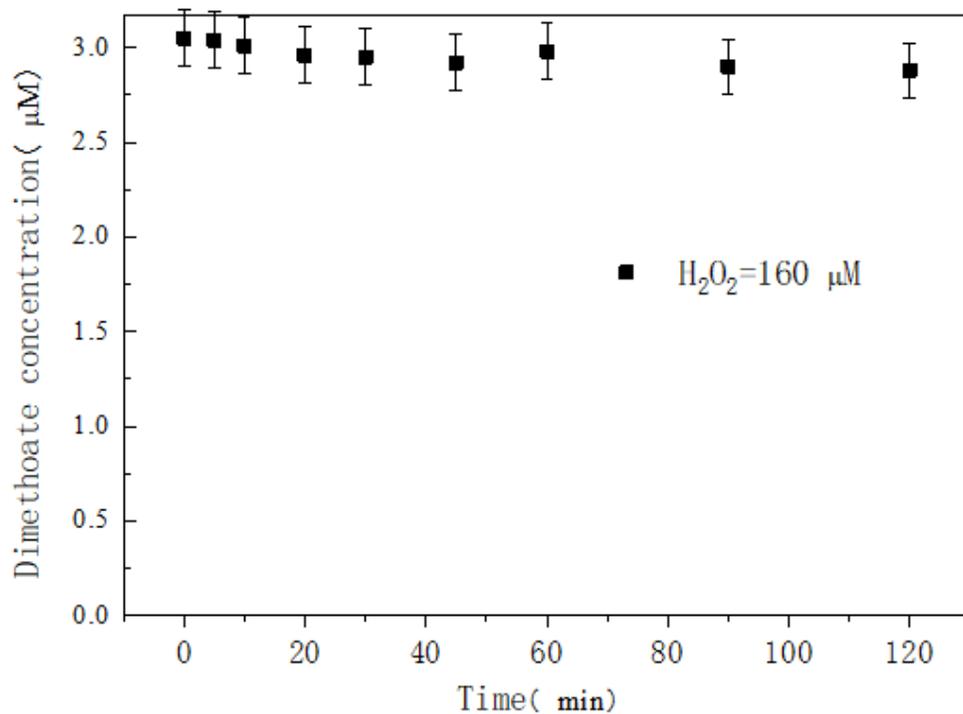


Figure 2

The degradation of dimethoate by trace H_2O_2

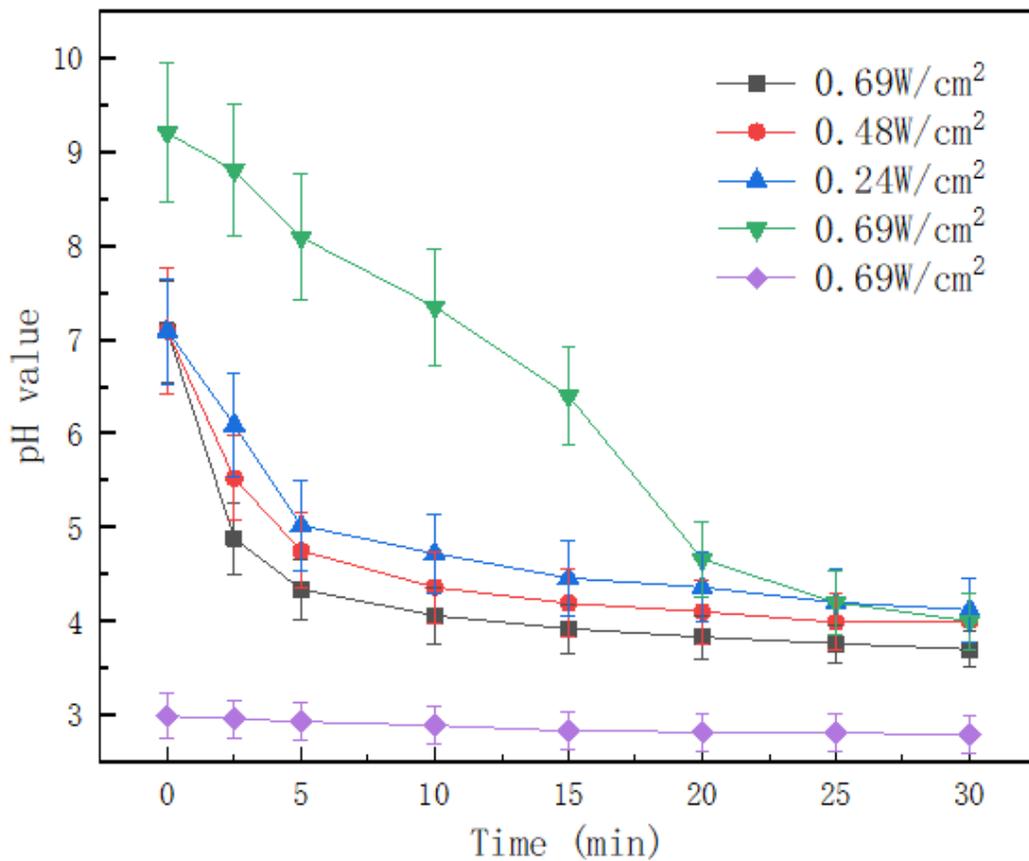
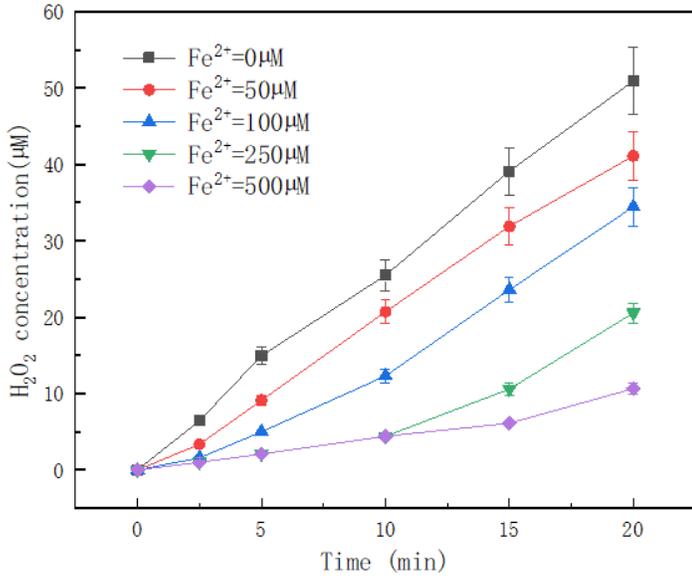
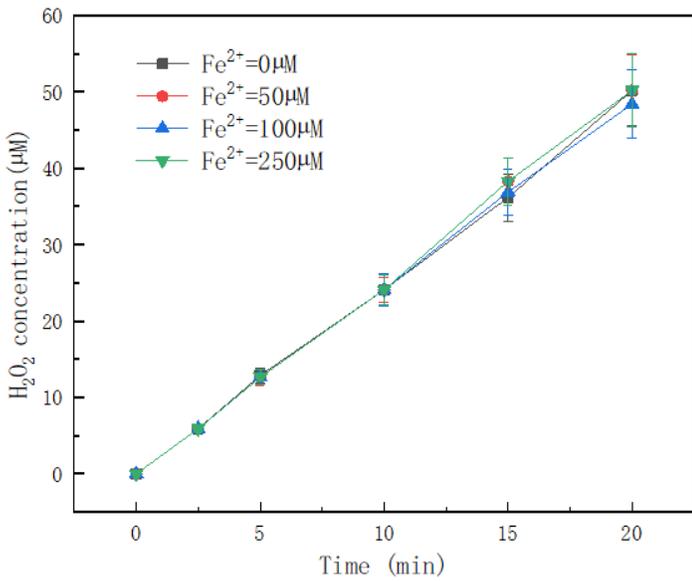


Figure 3

The effect of ultrasonic intensity on the decrease of pH value (Experimental conditions: ultrasonic frequency=600 kHz)



(a)



(b)

Figure 4

The effect of Fe²⁺ dosage on the net production of H₂O₂ Experimental conditions: ultrasonic frequency=600 kHz, ultrasonic intensity:=0.69 W/cm², (a).initial pH=3.0;(b).initial pH=9.0

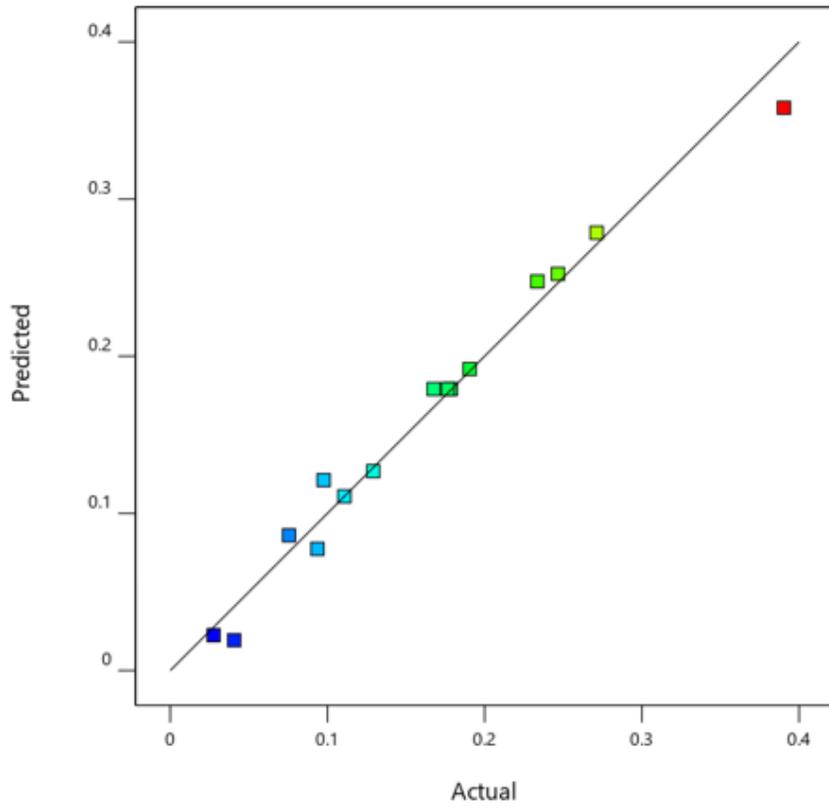
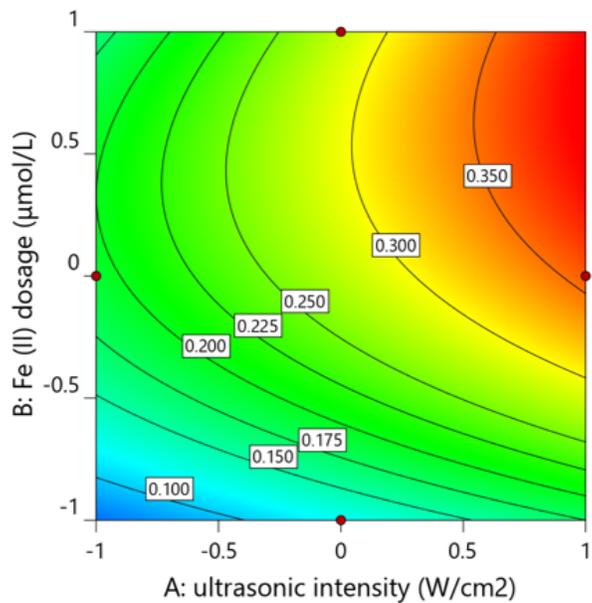
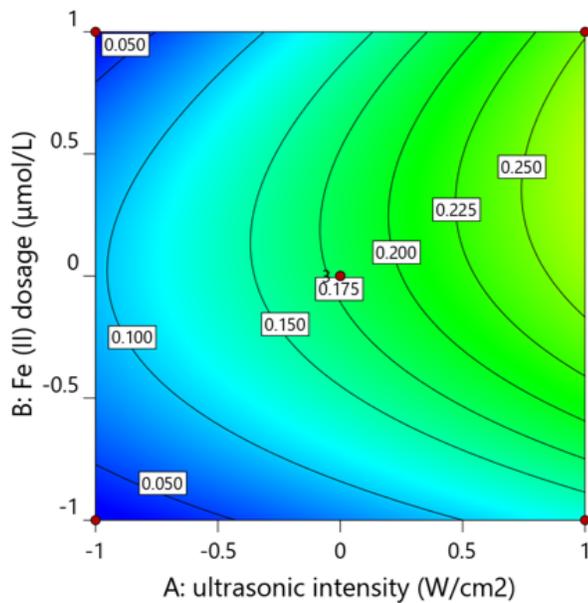


Figure 5

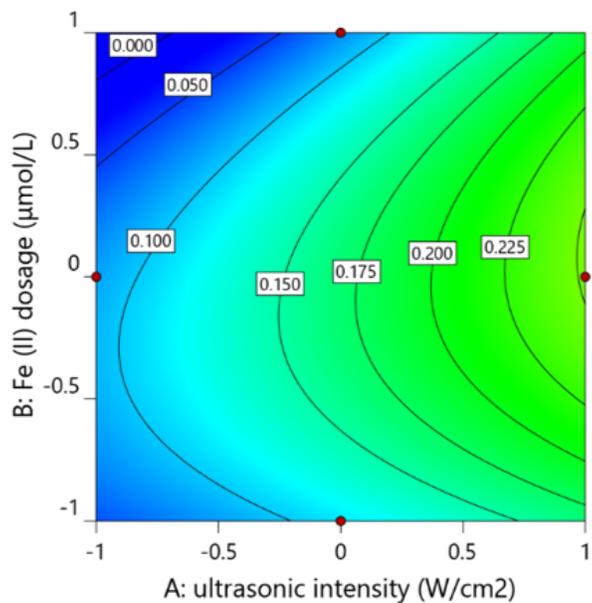
Experimental and predicted values of sono-degradation of dimethoate



(a)



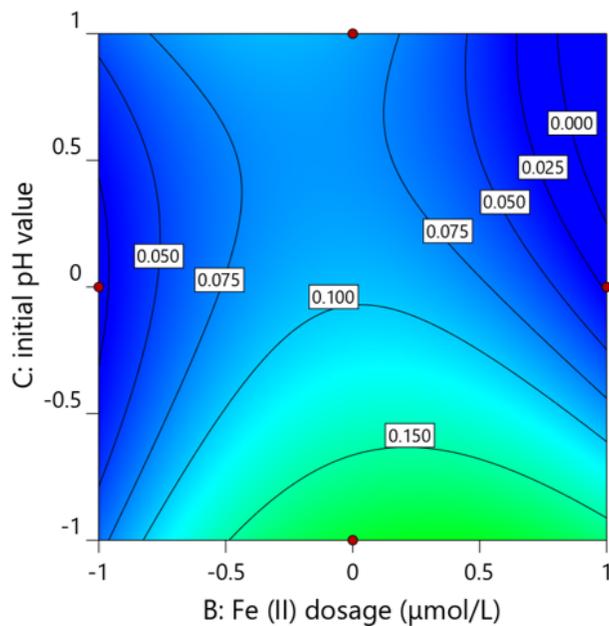
(b)



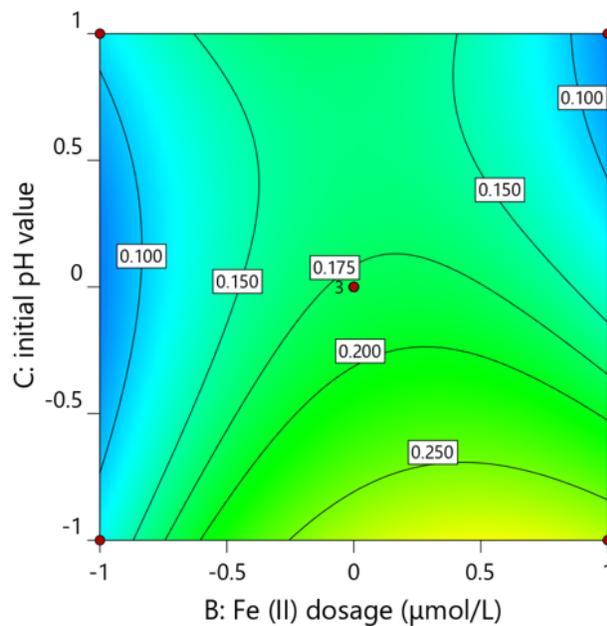
(c)

Figure 6

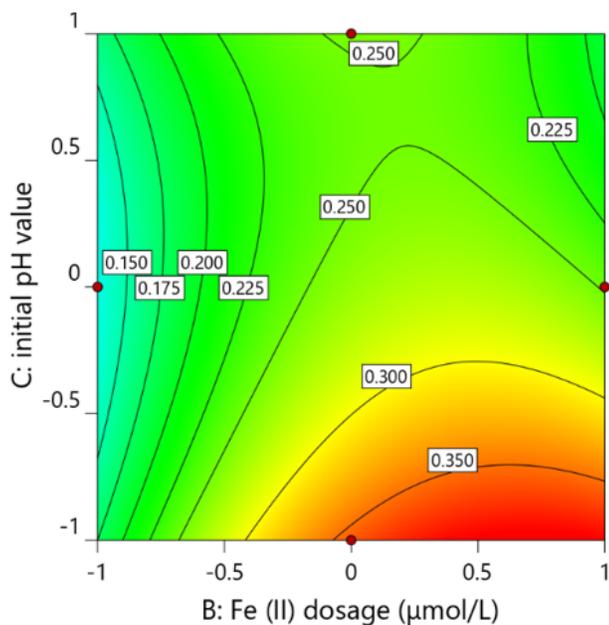
The contour response surface plot of pseudo-first-order degradation constant Y versus Fe^{2+} dosage X_1 and initial pH value X_3 at an ultrasonic intensity of 0.24W/cm^2



(a)



(b)



(c)

Figure 7

The contour response surface plot of pseudo-first-order degradation constant Y versus ultrasonic intensity X_2 and initial pH value X_3 at a Fe^{2+} dosage of $200\mu mol/L$

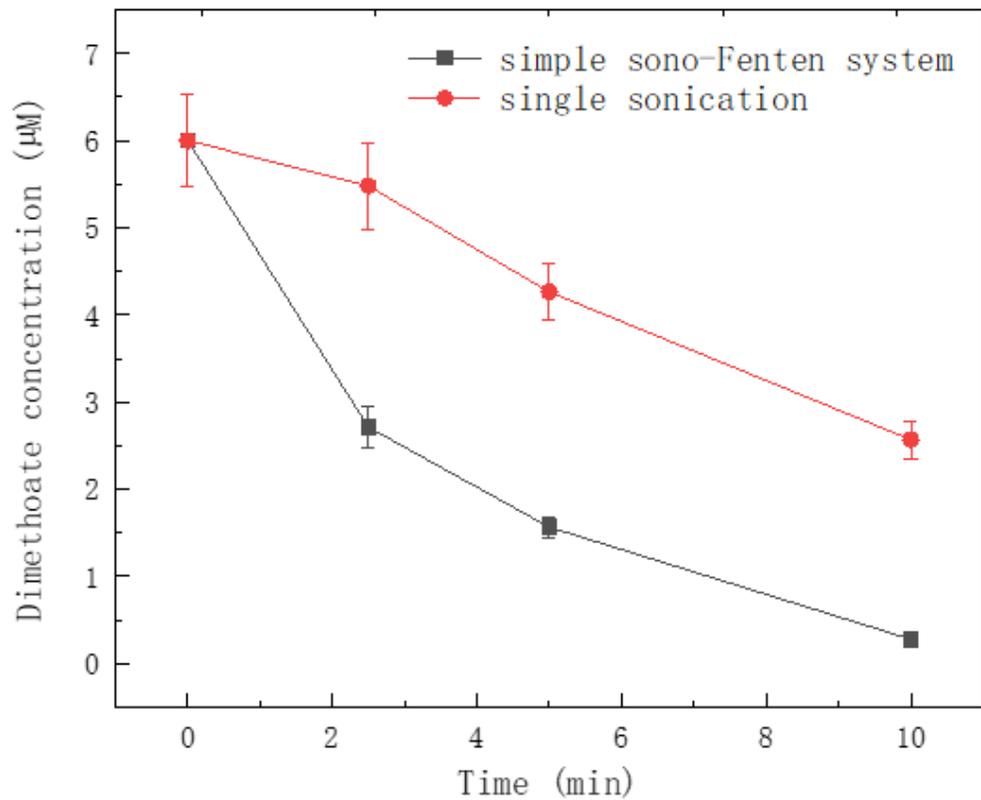
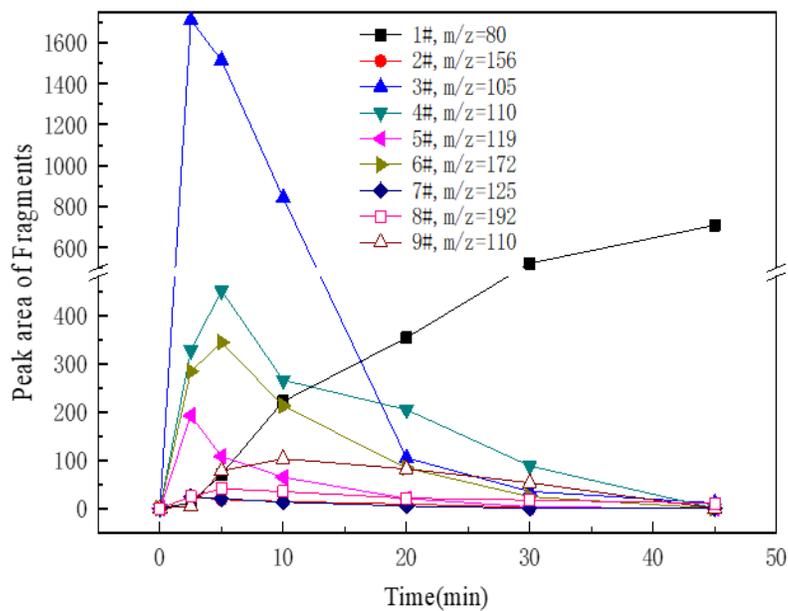
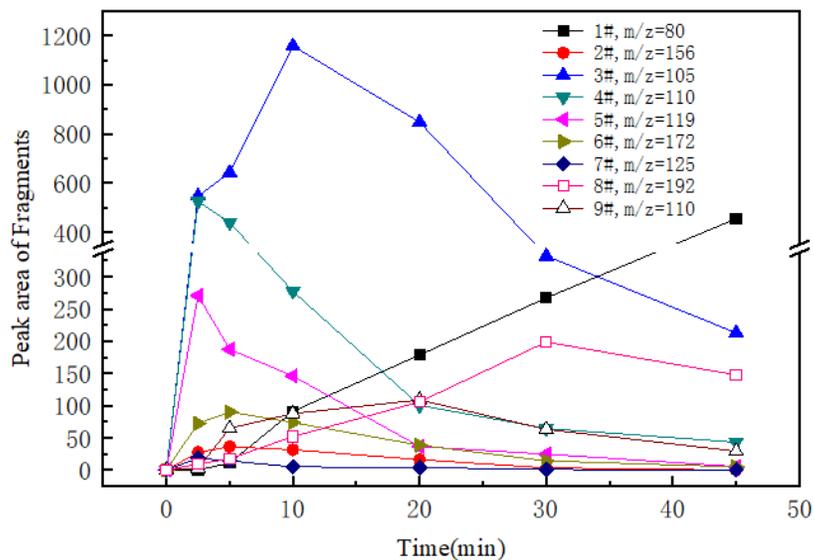


Figure 8

Concentration of dimethoate in simple sono-Fenton system and single sonication Experimental conditions: simple sono-Fenton system:ultrasound frequency=619kHz, ultrasound intensity=0.69 W/cm², the initial pH value=3, dimethoate=6 μM , Fe²⁺ dosage=200 μM ; single sonication: ultrasound frequency=619kHz; ultrasound intensity=0.69 W/cm²; the initial pH value=7 (dimethoate=6 μM)



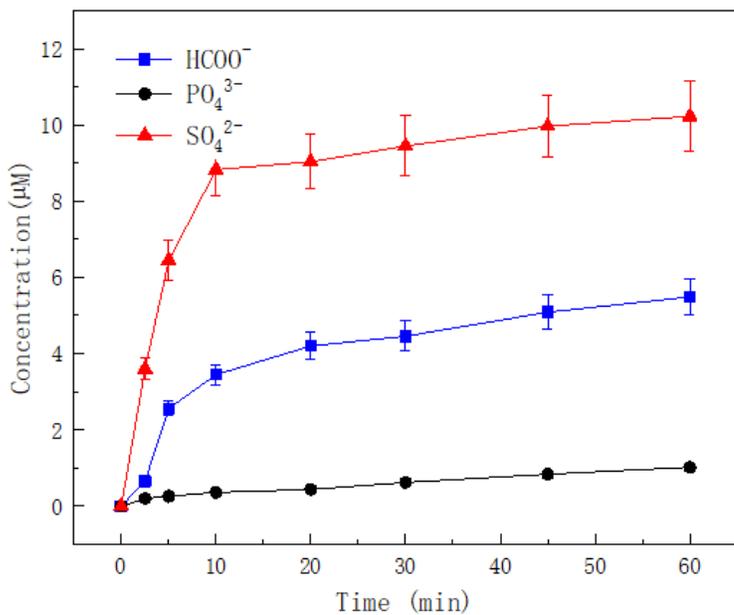
(a)



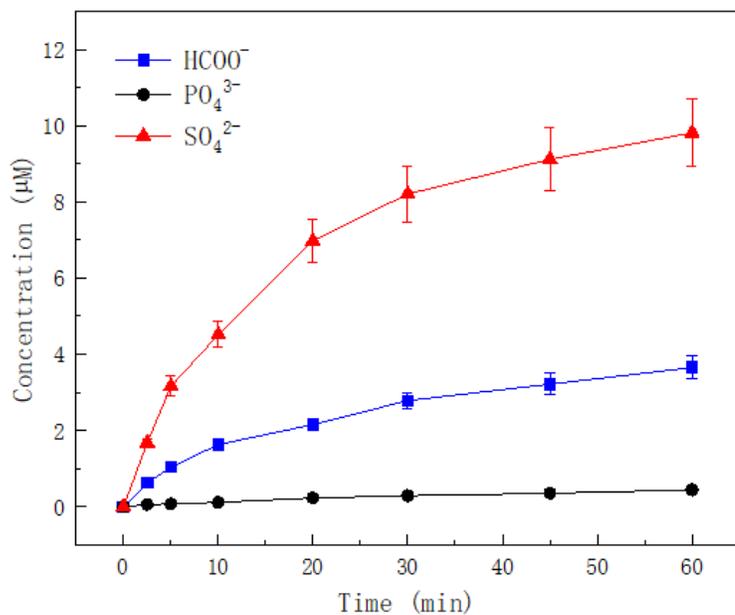
(b)

Figure 9

the comparison of the intermediate yields between US/ Fe²⁺ and US degradation of dimethoate ((a) US/ Fe²⁺: Fe²⁺ dosage=200μM; ultrasonic frequency=619 kHz; ultrasound intensity= 0.69 W/cm²; the initial pH value=3; dimethoate=3 μM; (b). US: ultrasound frequency=619kHz; ultrasound intensity=0.69 W/cm²; the initial pH value=7; dimethoate=3μM)



(a)



(b)

Figure 10

Concentration changes of ionic intermediates during dimethoate degradation((a) US/ Fe²⁺; (b). US ; Experimental conditions: ultrasonic frequency=619 kHz, ultrasonic intensity=0.69 W/cm²; concentration=6.34 μM)

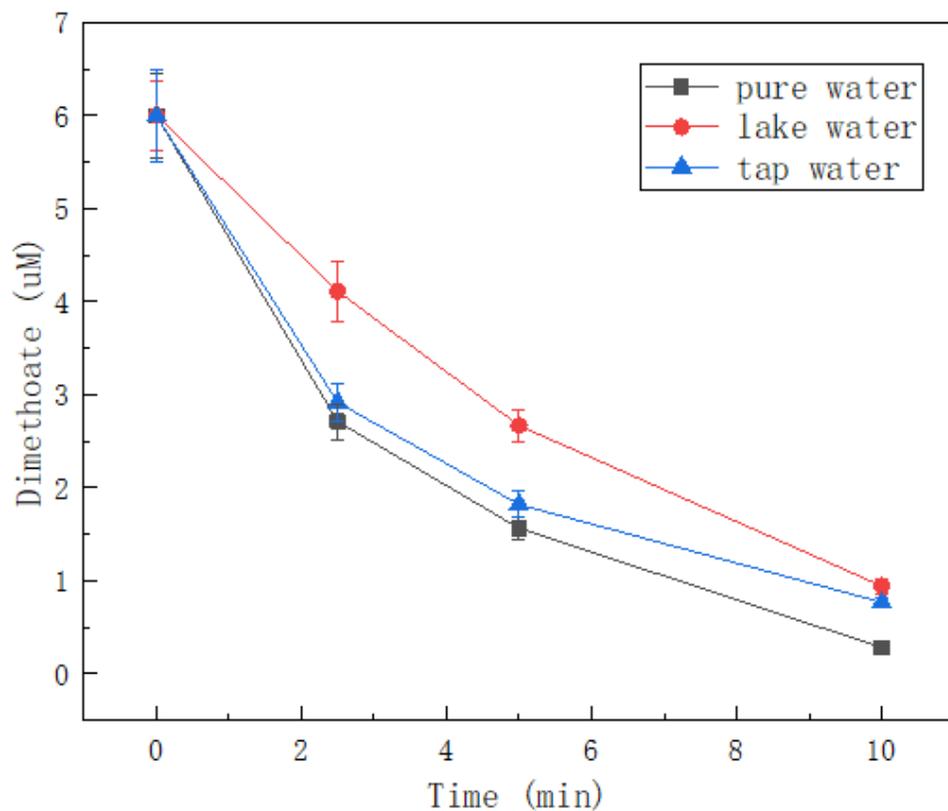


Figure 11

Concentration of dimethoate in different water environment (Experimental conditions: ultrasound frequency=619kHz; ultrasound intensity=0.69 W/cm²; the initial pH value=3 (dimethoate=6 μM))

Supplementary Files

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