

Degradation of the antibiotic sulfamonomethoxine sodium in aqueous solution by photo-Fenton oxidation

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In this study, photo-Fenton oxidation was applied to degradation of sulfamonomethoxine sodium (SMMS) in aqueous solution. The operation parameters of pH, temperature, and concentrations of H_2O_2 , Fe^{2+} and SMMS were investigated. The optimum conditions for the photo-Fenton process were determined as follows: $[\text{SMMS}] = 4.53 \text{ mg/L}$, $\text{pH} = 4.0$, $[\text{H}_2\text{O}_2] = 0.49 \text{ mmol/L}$, $[\text{Fe}^{2+}] = 19.51 \text{ } \mu\text{mol/L}$ and $T = 25^\circ\text{C}$. Under these conditions 98.5% of the SMMS degraded. The kinetics were also studied, and degradation of SMMS by the photo-Fenton process could be described by first-order kinetics. The apparent activation energy was calculated as 23.95 kJ/mol. Mineralization of the process was investigated by measuring the chemical oxygen demand (COD), and the COD decreased by 99% after 120 min. This process could be used as a pretreatment method for wastewater containing sulfamonomethoxine sodium.

sulfamonomethoxine sodium, degradation, photo-Fenton

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Pharmaceuticals and personal care products (PPCPs) are frequently used in daily life. Recently, they have attracted increasing interest throughout the world because they adversely affect aquatic ecosystems [1–10]. Although their concentrations in the environment are low (ppm or ppb levels), they cause great harm. In fact, most PPCPs and their metabolites are ultimately discharged into wastewater treatment plants (WWTPs), which are typically not designed to remove these specialized organic chemicals. As a result, substantial quantities of these compounds are released into the aquatic environment [11–17].

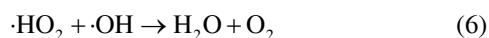
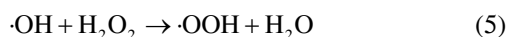
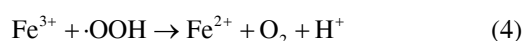
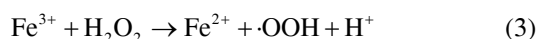
Antibiotics are a class of PPCPs that are used to prevent or treat bacterial infections. Sulfamonomethoxine sodium (SMMS) is a typical antibiotic that is a persistent sulfa veterinary drug. It is widely used because it has the best antibacterial activity among the sulfa drugs. SMMS is active against Gram-negative and Gram-positive bacteria, and has a strong protozoacide function. However, several authors

have reported that only 0–60% of some sulfa drugs are removed from wastewater by traditional methods [8,18,19]. Therefore, alternative technology to remove sulfa drugs from wastewater is required.

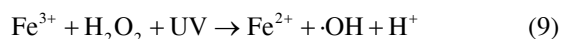
In recent years, advanced oxidation processes (AOPs) have been identified as an attractive option for wastewater treatment, particularly in the case of contaminants that are difficult to remove or eliminate by conventional biological or physicochemical technologies [20–23]. AOPs are based on the generation of highly reactive and nonselective oxidant hydroxyl radicals (OH), which can oxidize a broad range of organic pollutants to CO_2 and H_2O . Among the most promising AOPs, application of Fenton's reagent is noteworthy because of its high oxidation power, rapid oxidation kinetics, relatively low cost, simplicity of equipment and mild operation conditions [24]. Fenton's reactions include the following main steps (eqs. (1)–(7)):



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In the past few years, many studies have shown that degradation of pollutants in water by the Fenton process was greatly enhanced by ultraviolet (UV) irradiation [25–28]. The combination of Fenton's reagent with UV is called the photo-Fenton process. In the photo-Fenton process, the formation of $\cdot\text{OH}$ occurs by the following reactions (eqs. (8) and (9)) in addition to those given above [29].



The addition of UV to the Fenton's process could be useful for degradation of PPCPs because of the direct formation of $\cdot\text{OH}$ radicals. However, many factors will affect the degradation efficiency of organic pollutants in the photo-Fenton system, including pH, temperature, and the concentrations of H_2O_2 , Fe^{2+} , Cl^- , dissolved organic matter (DOM) and contaminations [27,30].

The aim of this work was to assess the performance of the photo-Fenton process in the treatment of SMMS wastewater, and to investigate the influence of pH, temperature, concentrations of reagents, reaction time and the kinetics. The mineralization of the photo-Fenton process was evaluated by measuring the chemical oxygen demand (COD). Optimum conditions were established for potential application of the photo-Fenton process to treatment of SMMS wastewater. These results provide a basis for the treatment of SMMS wastewater by the photo-Fenton process.

1 Experimental

1.1 Materials

SMMS was obtained from Boyahua Science and Technology Co. Ltd. (Beijing, China) (Table 1). Hydrogen peroxide (H_2O_2) (30%), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), mercury sul-

fate (HgSO_4), dipotassium titanium oxide dioxalate ($\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$), silver sulfate (Ag_2SO_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), and ferrous ammonium sulfate ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$), were all analytical grade. Deionized water was used throughout this study, including to prepare the SMMS solutions.

1.2 Procedures

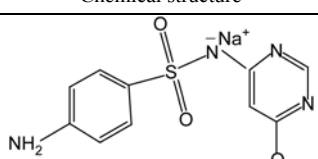
All experiments were carried out in a 200 mL double glass cylindrical jacket reactor (Figure 1), which allowed cycling of water to maintain the temperature of the reaction system. The temperature $(20\text{--}40) \pm 0.5^\circ\text{C}$ was adjusted by a thermostat and a magnetic stirrer was used to mix the reaction solutions at 200 r/min. To start each test, 100 mL of SMMS solution was placed in the double glass cylindrical jacket reactor. The pH of each reaction solution was adjusted to the desired level using 1.0 mol/L sulfuric acid or 1.0 mol/L sodium hydroxide. The required amounts of Fe^{2+} and H_2O_2 were then added to the reactor and the solution was stirred magnetically for the reaction time. In the photo-Fenton process, a 12 W UV lamp (ZF-2, Shanghai AnTing Electron Instrument Factory, China) with an irradiation wavelength of 365 nm was turned on when the H_2O_2 was added. The reaction time was recorded from when the H_2O_2 was added to the solution. Samples were periodically removed from the reactor using a pipette. All samples were filtered through 0.45 μm filter paper before analysis.

1.3 Analysis

The UV spectra of the SMMS aqueous solution was scanned on a Lambda 17 UV-Visible (UV-Vis) spectrophotometer (Lambda 17, Perkin Elmer, USA). No new absorption peaks occurred near the maximum wavelength (260 nm). Thus, the concentration of SMMS in the reaction solutions was obtained by measuring the absorbance at λ_{max} (260 nm).

The mineralization of SMMS was measured by the decrease of COD of the reaction solution. COD was measured according to the standard dichromate titration method. To eliminate interference from H_2O_2 in COD measurement, the H_2O_2 concentration was determined spectrophotometrically using titanium oxalate [31], and then subtracted from the COD calculation. A blank experiment was conducted simultaneously. The mineralization efficiency of SMMS was estimated from the following equation:

Table 1 Chemical characteristics of SMMS

Name	Chemical structure	Molecular formula	Molecular weight (g/mol)	λ_{max} (nm)
SMMS		$\text{C}_{11}\text{H}_{11}\text{N}_4\text{NaO}_3\text{S}$	302.3	260

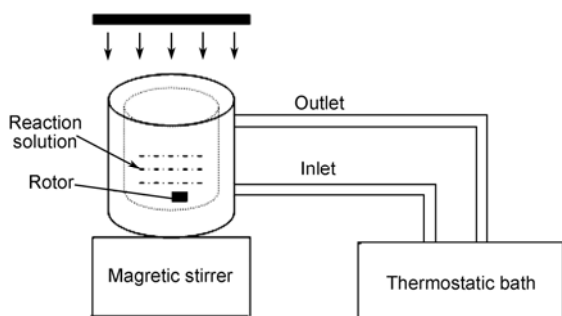


Figure 1 The experimental setup.

$$\text{Mineralization of SMMS}(\%) = \left(1 - \frac{\text{COD}_t}{\text{COD}_0}\right) \times 100\%, \quad (10)$$

where COD_0 and COD_t are the COD concentration at the start of reaction, and at time t (h), respectively.

The pH of each solution was measured by a pHS-3C digital pH meter. Before measurement, the pH meter was calibrated with standard buffers (pH 4.0, 6.86 and 9.18) at 25°C.

2 Results and discussion

2.1 Degradation of SMMS wastewater by Fenton and photo-Fenton processes

The degradation of SMMS in aqueous solution by Fenton and photo-Fenton oxidation processes was studied and the results are shown in Figure 2. Both the Fenton and photo-Fenton process degraded SMMS effectively. However, after 120 min, the degradation efficiency of SMMS in the photo-Fenton process (98.5%) was much higher than that in the Fenton process (87.4%). Formation of more hydroxyl radical in the photo-Fenton process may lead to the relatively high degradation efficiency of SMMS compared to the Fenton process. This can be explained by eqs. (8) and (9). Under UV irradiation, H_2O_2 will directly decompose into $\cdot\text{OH}$ in the photo-Fenton process, while OH formation requires Fe^{2+} catalysis in the Fenton process. Additionally, Fe^{3+} in solution could be reduced to Fe^{2+} and simultaneously form $\cdot\text{OH}$ under UV irradiation. Photolysis of SMMS with UV treatment partly accounted for the increase in the degradation efficiency in the photo-Fenton system. Kim et al. [28] reported that more than 90% of SMMS was degraded when UV irradiation was used alone. However, a considerable UV dose would be needed (230 mJ/cm^2 in 10 min) to degrade SMMS in water to a very low concentration regardless of the UV lamp applied. These results indicated that the UV lamp was of importance for degradation of SMMS even though the UV lamp was of low power (12 W). Relatively high degradation efficiency for the treatment of SMMS wastewater was obtained by the photo-Fenton oxidation process, and this was adopted for subsequent reactions.

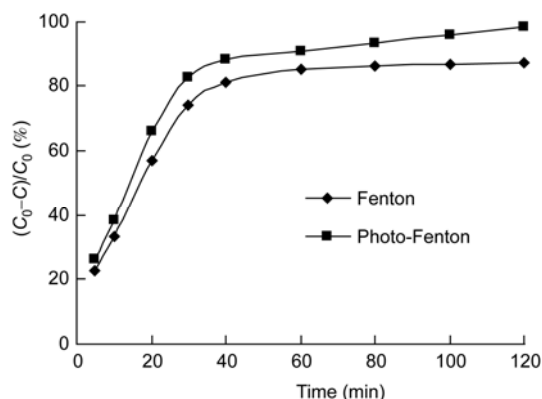


Figure 2 Degradation of SMMS in wastewater by Fenton (◆) and photo-Fenton (■) processes. Experimental conditions: $[\text{SMMS}] = 4.53 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 0.49 \text{ mmol/L}$, $[\text{Fe}^{2+}] = 19.51 \text{ } \mu\text{mol/L}$, pH 4.0 and $T = 25^\circ\text{C}$.

2.2 Optimization of reaction parameters

(1) Effect of pH. The effect of pH on the degradation of SMMS in the photo-Fenton process was evaluated by running the reaction at various pH values while holding the other operating parameters constant. The change in degradation efficiency with the change in pH is presented in Figure 3. The optimum pH for degradation of SMMS in photo-Fenton process was 4.0, and increasing or decreasing the pH decreased the degradation efficiency. At low pH, formation of the oxonium ion (H_3O_2^+) enhanced the stability of H_2O_2 and restricted the generation of $\cdot\text{OH}$ [32]. In addition, H^+ could act as an OH scavenger. At high pH, ferric oxyhydroxides would precipitate and stop the reaction of Fe^{3+} with H_2O_2 to regenerate Fe^{2+} , which would reduce the amount of $\cdot\text{OH}$ [20,29]. Therefore, pH 4.0 was optimum for the photo-Fenton process, and resulted in a maximum degradation of SMMS of 98.5%.

(2) Effect of H_2O_2 concentration. H_2O_2 , which was the source of $\cdot\text{OH}$, played a very important role in the photo-

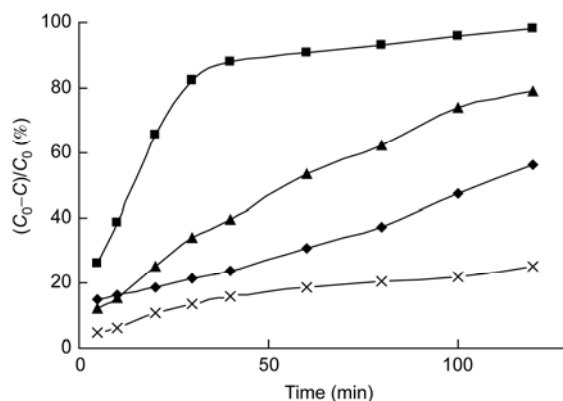


Figure 3 Effect of the pH on the degradation of SMMS in wastewater by the photo-Fenton process. Experimental conditions: $[\text{SMMS}] = 4.53 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 0.49 \text{ mmol/L}$, $[\text{Fe}^{2+}] = 19.51 \text{ } \mu\text{mol/L}$; pH 3.0 (◆), pH 4.0 (■), pH 5.0 (▲), pH 6.0 (×); and $T = 25^\circ\text{C}$.

Fenton process. The effect of H_2O_2 concentration on degradation of SMMS was examined by varying the concentration of H_2O_2 from 0.098–1.92 mmol/L (Figure 4). Increasing $[\text{H}_2\text{O}_2]$ from 0.29 to 0.49 mmol/L generally had a positive effect on the degradation of SMMS because the high H_2O_2 concentration generated more $\cdot\text{OH}$. However, this was not always the case. For example, degradation of SMMS declined from 98.5% to 92.2% when the concentration of H_2O_2 was increased from 0.49 to 1.92 mmol/L in the photo-Fenton process. This phenomenon has been widely reported by many researchers [20,22,27,29]. This could be explained by a critical concentration of H_2O_2 in the Fenton oxidation process. As the concentration of H_2O_2 increased beyond the critical value, it would become a scavenger of $\cdot\text{OH}$ (eqs. (5) and (6)). The optimum concentration of $[\text{H}_2\text{O}_2]$ was 0.49 mmol/L.

(3) Effect of Fe^{2+} concentration. As a catalyst in the Fenton's reagent, Fe^{2+} initiates decomposition of H_2O_2 to generate $\cdot\text{OH}$. Therefore, the initial concentration of Fe^{2+} is an important parameter in the photo-Fenton process. The effect of $[\text{Fe}^{2+}]$ on the degradation of SMMS in photo-Fenton processes was studied. The results (Figure 5) indicated that the extent of SMMS degradation was highly dependent on the $[\text{Fe}^{2+}]$. Degradation of SMMS was low at low $[\text{Fe}^{2+}]$, and increased when the $[\text{Fe}^{2+}]$ was increased. The high degradation efficiency at high $[\text{Fe}^{2+}]$ could be mainly attributed to increased production of $\cdot\text{OH}$ with more Fe^{2+} in the photo-Fenton reaction.

It was important to detect the optimum molar ratio of $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ because this ratio can directly affect the production of $\cdot\text{OH}$ in the Fenton reaction. The effect of high $[\text{Fe}^{2+}]$ (28.99 $\mu\text{mol/L}$) on the photo-Fenton process is plotted in Figure 5. High $[\text{Fe}^{2+}]$ was not good for the degradation efficiency, and only 93.1% of the SMMS degraded in photo-Fenton process at this $[\text{Fe}^{2+}]$. There is currently no agreement in the literature on the optimum molar ratio of $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ for the treatment of various wastewaters by this oxidation process [21,27]. In the present study, experi-

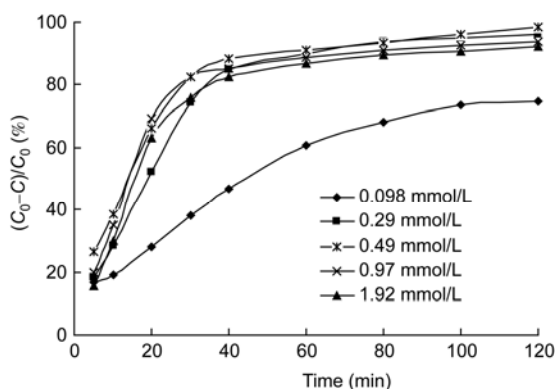


Figure 4 Effect of the $[\text{H}_2\text{O}_2]$ on the degradation of SMMS in wastewater by the photo-Fenton process. Experimental conditions: $[\text{SMMS}] = 4.53 \text{ mg/L}$, $[\text{Fe}^{2+}] = 19.51 \mu\text{mol/L}$, pH 4.0, and $T = 25^\circ\text{C}$.

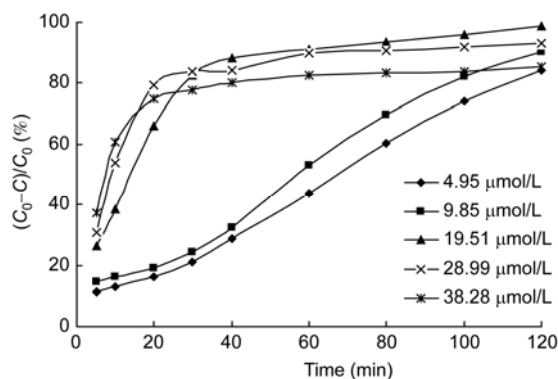


Figure 5 Effect of the $[\text{Fe}^{2+}]$ on the degradation of SMMS in wastewater by the photo-Fenton process. Experimental conditions: $[\text{SMMS}] = 4.53 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 0.49 \text{ mmol/L}$, pH 4.0 and $T = 25^\circ\text{C}$.

ments indicated 25:1 was a suitable $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ molar ratio for degradation of SMMS, and the optimum $[\text{Fe}^{2+}]$ was 19.51 $\mu\text{mol/L}$.

(4) Effect of SMMS concentration. The initial $[\text{SMMS}]$ was another important factor that could affect the oxidation process. Degradation of different concentrations of SMMS was studied and the results are shown in Figure 6. The degradation of SMMS decreased as its initial concentration increased in the photo-Fenton process. This can be explained by generation of a relatively low concentration of $\cdot\text{OH}$ because the concentrations of Fe^{2+} and H_2O_2 were not increased at the same time as the concentration of SMMS. In addition, in the photo-Fenton process, high concentrations of SMMS would hinder entry of the generated photons to the solutions and lower $\cdot\text{OH}$ concentration [29]. However, after a reaction time of 120 min, no big degradation differences were observed among different concentrations of SMMS in the photo-Fenton process (all between 96.6%–98.6%).

(5) Effect of temperature. Figure 7 shows the extent of

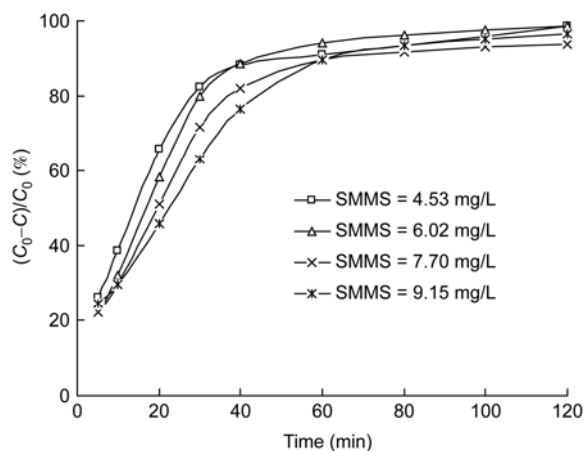


Figure 6 Effect of the $[\text{SMMS}]$ on the degradation of SMMS in wastewater by the photo-Fenton process. Experimental conditions: $[\text{H}_2\text{O}_2] = 0.49 \text{ mmol/L}$, $[\text{Fe}^{2+}] = 19.51 \mu\text{mol/L}$, pH 4.0 and $T = 25^\circ\text{C}$.

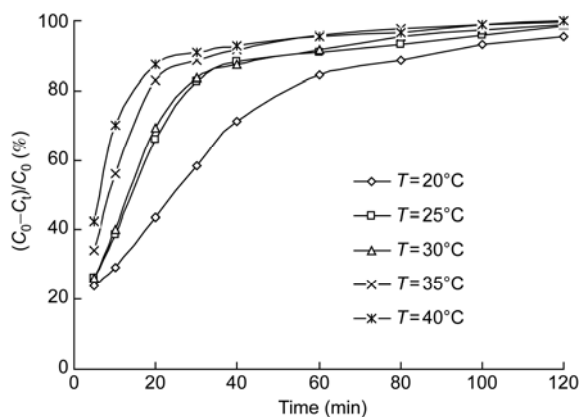


Figure 7 Effect of the temperature on the degradation of SMMS in wastewater by the photo-Fenton process. Experimental conditions: [SMMS]=4.53 mg/L, [H₂O₂]=0.49 mmol/L, [Fe²⁺]=19.51 μmol/L, and pH 4.0.

degradation of SMMS by the photo-Fenton process at different temperatures. In the photo-Fenton process, degradation of SMMS increased obviously with the increase of temperature in the first 30 min. However, after 60 min, degradation of SMMS barely changed. These results could arise from increased generation of ·OH when the temperature was increased, which would enhance the degradation of SMMS. However, H₂O₂ would decompose at high temperature. In the photo-Fenton process, >96.3% of SMMS degraded at all tested temperatures under the optimum experimental conditions. This reached 100% after 140 min in the

photo-Fenton process when temperature was 40°C. In summary, the temperature had a positive effect on the degradation of SMMS in the photo-Fenton process.

2.3 Kinetic study

The AOPs can be represented by the following *n*-th-order reaction kinetics:

$$\frac{dC}{dt} = -kC^n, \quad (11)$$

where *C* is the concentration of SMMS, *n* is the order of the reaction, *k* is the reaction rate constant, and *t* is the time. For zero-, first- and second-order reactions (eqs. (12), (13), and (14), respectively), the kinetic expression can be presented as follows:

$$C_t = C_0 - k_0 t, \quad (12)$$

$$\ln\left(\frac{C_0}{C_t}\right) = k_1 t, \quad (13)$$

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t. \quad (14)$$

Regression analysis based on the zero-, first- and second-order reaction kinetics for the degradation of SMMS in the photo-Fenton processes was studied and the results are shown in Figure 8(a), (b), and (c). The correlation

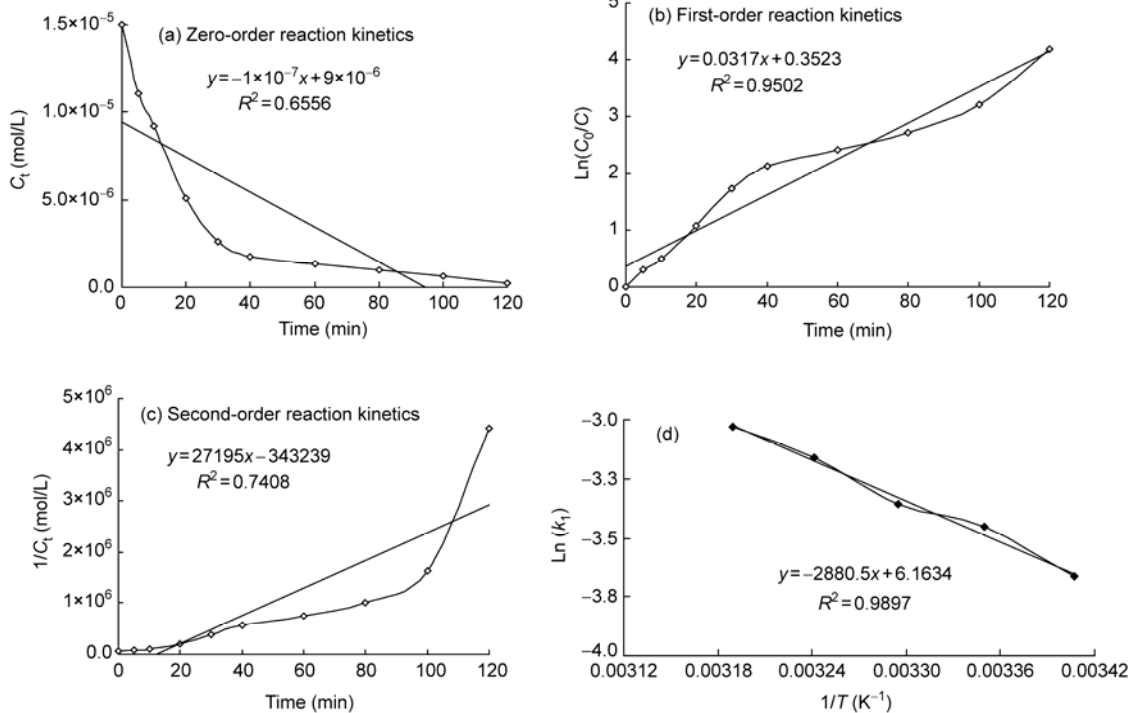


Figure 8 The *n*th-order kinetics of the degradation of SMMS in wastewater by the photo-Fenton process. Experimental conditions: [SMMS]=4.53 mg/L, [H₂O₂]=0.49 mmol/L, [Fe²⁺]=19.51 μmol/L, pH 4.0 and *T*=25°C.

between $\ln(C_0/C)$ and reaction time t was linear ($R^2 = 0.9502$), which is typical of a pseudo-first-order reaction. Therefore, degradation of SMMS in the photo-Fenton process follows pseudo-first-order kinetics. From Figure 8, we could obtain the rate constant (0.0317/min) for degradation of SMMS in the photo-Fenton processes.

In the photo-Fenton process, we also validated the rate constant (k_1) by the Arrhenius equation (eq. (15)):

$$\ln k_1 = \ln A - \frac{Ea}{RT}, \quad (15)$$

where A is the pre-exponential factor, E is the apparent activation energy (J/mol), R is the ideal gas constant (8.314 J/mol K), and T is the absolute temperature (K). The plot of $\ln k_1$ versus $1/T$ is shown in Figure 8(d). There was a good linear relationship between $\ln k_1$ and $1/T$ ($R^2 = 0.9897$). The apparent activation energy $E = 23.95$ kJ/mol was obtained from the slope of the plot, and the pre-exponential factor $A = 170.80/\text{min}$ was obtained from the y -intercept. Typical thermal reactions usually have reaction activation energies between 60 and 250 kJ/mol [23]. The apparent activation energy in this study implied that the degradation of SMMS in aqueous solution by the photo-Fenton oxidation process required much lower activation energy and could be easily achieved.

2.4 Mineralization study

During the SMMS degradation, some aromatic intermediates will be form. These new compounds may be more difficult to degrade and more toxic than the parent compounds. The COD is related to the total concentration of organic compounds in the solution. Therefore, the reduction in COD can reflect the degree of mineralization. To quantify the degree of mineralization of SMMS in the photo-Fenton processes, COD was measured and the results are shown in Figure 9. The COD decreased by 99% after 120 min of

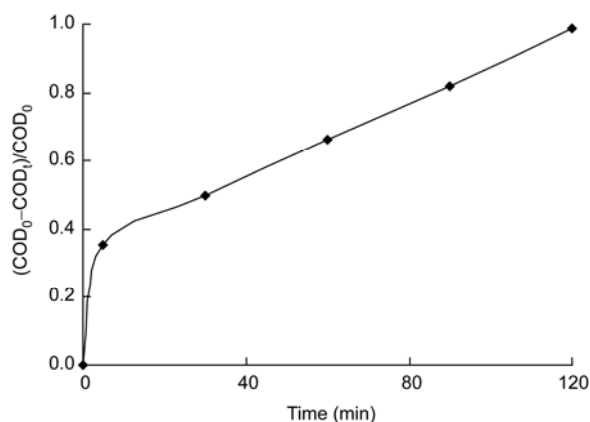


Figure 9 COD reduction during the degradation of SMMS in wastewater by the photo-Fenton process. Experimental conditions: [SMMS]=4.53 mg/L, [H₂O₂]=0.49 mmol/L, [Fe²⁺]=19.51 μmol/L, pH 4.0 and T=25°C.

reaction, which suggests that nearly all of intermediates were mineralized at this stage. After this time it is likely the wastewater will not be toxic, with respect to its SMMS content, to the environment. It is worth noting that in the first 5 min degradation of SMMS was much faster than at later stages, and the COD decreased by 36% in this time. This indicates that most of the compounds begin to decompose in the first 5 min. These results show that the photo-Fenton process is promising for treatment of this kind of wastewater, even though the UV lamp is low power (12 W).

3 Conclusions

In this paper, the degradation of SMMS by the photo-Fenton process was investigated. The optimum degradation conditions for SMMS in the photo-Fenton process were determined as follows: [SMMS]=4.53 mg/L, pH 4.0, [H₂O₂]=0.49 mmol/L, [Fe²⁺]=19.51 μmol/L and T=25°C. Under the optimum conditions, 98.5% of the SMMS was degraded after 120 min. Degradation of SMMS in photo-Fenton process was described by first-order kinetics, and the apparent activation energy was determined to be 23.95 kJ/mol. Mineralization of the process was studied by measuring the chemical oxygen demand (COD), and the COD decreased by 99% after 120 min, which suggests that nearly all of intermediates are mineralized at this stage of the reaction. These results provide a basis for the treatment of wastewater containing SMMS by AOPs.

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