



Removal and degradation pathway study of sulfasalazine with Fenton-like reaction

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ABSTRACT

The Fenton-like degradation of sulfasalazine solution is studied in this work. The effects of reaction parameters such as Fe^{3+} concentration, initial H_2O_2 dosage and the reaction temperature are evaluated. For sulfasalazine of 100 mg/L, the removal of sulfasalazine, chemical oxygen demand (COD) and total organic carbon (TOC) reached 99.5%, 84.2% and 41% in 60 min with 0.20 mM Fe^{3+} and 16 mM H_2O_2 at 35 °C, respectively. The complexed Fe^{3+} presents a reaction constant of $0.062 \text{ min}^{-1} \text{ mM}^{-1}$ while that of free Fe^{3+} is $2.526 \text{ min}^{-1} \text{ mM}^{-1}$ for sulfasalazine degradation. LC–MS technology was used to analysis the possible degradation intermediates. The degradation of sulfasalazine principally begins with the attack of hydroxyl radical on the azo-group as well as the sulfanilamido group. Both intramolecular rearrangement and bimolecular reaction occur simultaneously after the hydroxyl radical attack. Further attack of the active oxidative species results in the cleavage of the aromatic rings and the production of CO_2 . The degradation of industrial sulfasalazine wastewater with a COD of 3425 mg/L has also been achieved by Fenton reaction with different dosage of H_2O_2 . Relatively better removal efficiency is observed at moderate $\text{Fe}/\text{H}_2\text{O}_2$ molar ratio from 1/5 to 2/5 for industrial sulfasalazine wastewater treatment.

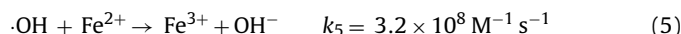
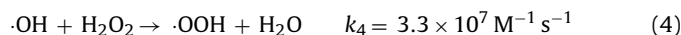
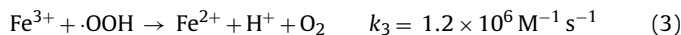
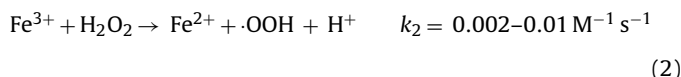
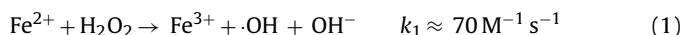
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1. Introduction

Recently, more than 4000 molecules and 10,000 specialized medicines were produced as human and veterinary drugs [1]. The effluents discharged from pharmaceutical industries have complex compositions which are always strongly colored, bio-resistant, toxic and hence harmful to the ecosystem, even at low concentrations [2–5]. Recently, the treatment of pharmaceutical wastewater has raised more and more concern for environmental safety [6–8]. The usual biological technologies such as activated sludge treatment are found not always appropriate for effective treatment of the bio-recalcitrant organics [9–14].

Advanced oxidation processes (AOPs), include heterogeneous and homogeneous photocatalysis, ozonation, Fenton reaction, and wet air oxidation, are well known for their capacity for oxidizing and mineralizing organic contaminants [15]. Fenton reaction is a homogeneous catalytic oxidation reaction which was firstly discovered by Fenton in the 1890s [16]. Fenton and Fenton-like reactions are effective methods to treat the organic pollutants in wastewater, and their mechanism and kinetics have been widely studied

[17–20]. The generally accepted free radical chain mechanism for the Fenton reaction is shown below [21–24].



The hydroxyl radicals generated from the reaction of ferrous ions with hydrogen peroxide are highly reactive species and can attack and mineralize the organic pollutants with non-selectivity. There have been many works done in the pharmaceutical wastewater treatment with Fenton reaction [25–28]. N. Kulik et al. [1] confirmed that pharmaceutical effluents from medical ointment production could be well treated with the Fenton-like reaction. E. Elmolla et al. [25] investigated the degradation of the antibiotics aqueous solution containing a mixture of amoxicillin, ampicillin

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and cloxacillin with Fenton process. It was reported that the chemical oxygen demand (COD) and dissolved organic carbon (DOC) removal reached 81.4% and 54.3% in 60 min, respectively. Further, the biodegradability of the solution was enhanced from 0 to 0.37 in 10 min. C. Sirtori et al. [2,6] decontaminated a real industrial pharmaceutical wastewater with solar photo-Fenton combine with biological treatment. It showed that photo-Fenton process enhanced the biodegradability and over 95% of DOC could be removed. Microwave-assisted Fenton reaction has also been applied in dealing with the pharmaceutical wastewater of high concentration and presented a COD removal of 57% by Y. Yang et al. [26].

About 23,000 tons of antibiotics are used for various purposes every year, leading to large quantities of unmetabolized antibiotics finally entering the aquatic environment. It has been reported that concentrations of sulfamethazine between 1.8 and 7.2 μM pose the greatest risk on growing microorganism resistance [29]. As a typical sulfonamide, sulfasalazine is widely used for the treatment of ulcerative colitis, Crohn's disease, and rheumatoid arthritis [30]. The effluent from the sulfasalazine production is greatly pernicious to the ecosystem, which however cannot be treated well with the biological technologies. Although Fenton (Fenton-like) reaction is confirmed as an effective technique to remove the antibiotics pollutants from the wastewater [25–28], few works have been reported to deal with the sulfasalazine pollutant with Fenton (Fenton-like) process. Hence, degradation of sulfasalazine solution and industrial sulfasalazine wastewater with Fenton (Fenton-like) reaction was investigated in this study. LC–MS technique [31–34] was used to identify the degradation intermediates of sulfasalazine during the reaction, from which a possible Fenton-like degradation pathway for sulfasalazine was proposed.

2. Materials and methods

2.1. Chemicals

Hydrogen peroxide (30%, w/w), sodium dihydrogen phosphate, disodium hydrogen phosphate, sodium hydroxide and sulfuric acid were purchased from Shanghai Lingfeng Chemical Reagents. Ferric nitrate nonahydrate and ferrous sulfate heptahydrate were obtained from Sinopharm Chemical Reagent. Sulfasalazine was obtained from Taizhou Shengyu Dyestuff Chemical. All chemicals were of AR and used without further purification. Doubly distilled water was used throughout the work.

2.2. Degradation procedure of sulfasalazine

The Fenton-like degradation of sulfasalazine was carried out in a 100 mL beaker in a water bath at a fixed temperature. In a typical procedure, sulfasalazine (50 mL, 100 mg/L) and a desired concentration of ferric nitrate were firstly mixed under stirring for 30 min. The pH value of solution was adjusted to 3.0 before reaction. The reaction was timed as soon as the H_2O_2 was added into the solution. At given reaction time intervals, 4.0 mL samples were taken out, and immediately immitted into a 1.0 mL phosphate buffer solution to avoid further reaction (Total phosphate concentration of 0.20 mol L^{-1} , pH 8.0). The residual concentration of sulfasalazine, COD and TOC were then determined, respectively.

The Fenton degradation of the industrial sulfasalazine wastewater was similar to the above procedure. A desired amount of ferrous sulfate heptahydrate was added into 100 mL wastewater and stirred for 30 min in a water bath at a fixed temperature. Calculated amount of H_2O_2 (30%) was then added to start the reaction. The Fenton reaction was stopped after 3 h by the sodium phosphate aqueous solution. The residual COD of the reaction solution was determined immediately without flocculation.

2.3. Analytical methods

The residual concentration of sulfasalazine was determined by measuring its absorbance at 360 nm on a UV/Vis spectrophotometer (Unico, 4802). All samples were diluted 5 times before measuring, and the very same concentration of Fe^{3+} mixed with phosphate buffer solution was used as the reference solution to minimize the possible measuring interference from the Fe^{3+} . The COD of samples was analyzed according to the dichromate-spectrophotometry method [35]: 2.0 mL of reaction solution was sampled into a Hash COD tube and immediately mixed with a $\text{K}_2\text{Cr}_2\text{O}_7$ standard solution (1 mL, $1/6 \text{K}_2\text{Cr}_2\text{O}_7 = 0.250 \text{ mol/L}$) and a 1% $\text{Ag}_2\text{SO}_4\text{-H}_2\text{SO}_4$ solution (3.0 mL). The Hash COD tube was then sealed, and refluxed at 150 °C for 40 min. The COD value of the reaction solution was calculated from the UV–vis absorbance of the refluxed solution at 605 nm measured with a UV–vis spectrophotometer (Unico, 4802). The TOC Values of samples were analyzed with a TOC analyzer (Shimadzu, TOC-VE).

2.4. LC–MS analyses

The reaction intermediates of sulfasalazine solution were identified with LC–MS technology. The reaction of samples for LC–MS measurement was quenched by adjusting the pH value of the solution to 13 with NaOH aqueous solution (1 mol/L). The obtained solution was then concentrated and filtered through a cellulose membrane (0.2 μm) before use. LC–MS measurements were carried out on a Shimadzu Prominence LCMS-2020 equipped with UFLC_{XR} system (shim-pack XR-ODS II C_{18} column 2.0 \times 150 mm 2.2 μm). The mobile phase was water (A) and acetonitrile (B) mixture with a linear gradient (0–9 min, A/B = 90/10; 10–12 min, A/B = 0/100; 12–16 min, A/B = 90/10). ESI(+) acted as an ion source with a voltage of 4.5 kV. The mass analyzer was single quadrupole with a voltage of 1.10 kV (scanning region: 50–1000 m/z , sampling period: 0.1 s), the temperature of heating module, CDL were 450 °C, 350 °C, respectively.

3. Results and discussion

3.1. Fenton-like degradation of sulfasalazine aqueous solution

It was been reported that Fenton reactions are greatly affected by the reaction parameters [7,11]; Therefore, degradation of sulfasalazine solution under different conditions was investigated in this work.

3.1.1. The effect of Fe^{3+} dosage

The effect of concentration of Fe^{3+} on the Fenton-like oxidation of sulfasalazine was investigated. Fig. 1 presents the degradation of sulfasalazine with various concentration of Fe^{3+} in the presence of 4.0 mM H_2O_2 at 35 °C.

The initial degradation of sulfasalazine increased with the increase in Fe^{3+} concentration in a range of 0.10–0.35 mM. The degradation ratio of sulfasalazine increased from 9.1% to 85.3% in 20 min reaction. However, the relative degradation rate with higher $[\text{Fe}^{3+}]$ decreased quickly. After 30 min reaction, Fenton-like reaction with 0.20 mM $[\text{Fe}^{3+}]$ has the lowest sulfasalazine residue as shown in Fig. 1A. It is known that the degradation efficiency of Fenton process is related closely to the amount of hydroxyl radical produced during the oxidation process [13]. As shown in Eqs. (1) and (2), higher $[\text{Fe}^{3+}]$ would lead to a faster hydroxyl radical generation, which results in a higher initial degradation of sulfasalazine. However, with quicker consumption of H_2O_2 , the degradation rate of sulfasalazine with higher $[\text{Fe}^{3+}]$ quickly decayed and was caught up by that with lower $[\text{Fe}^{3+}]$ (Fig. 1A).

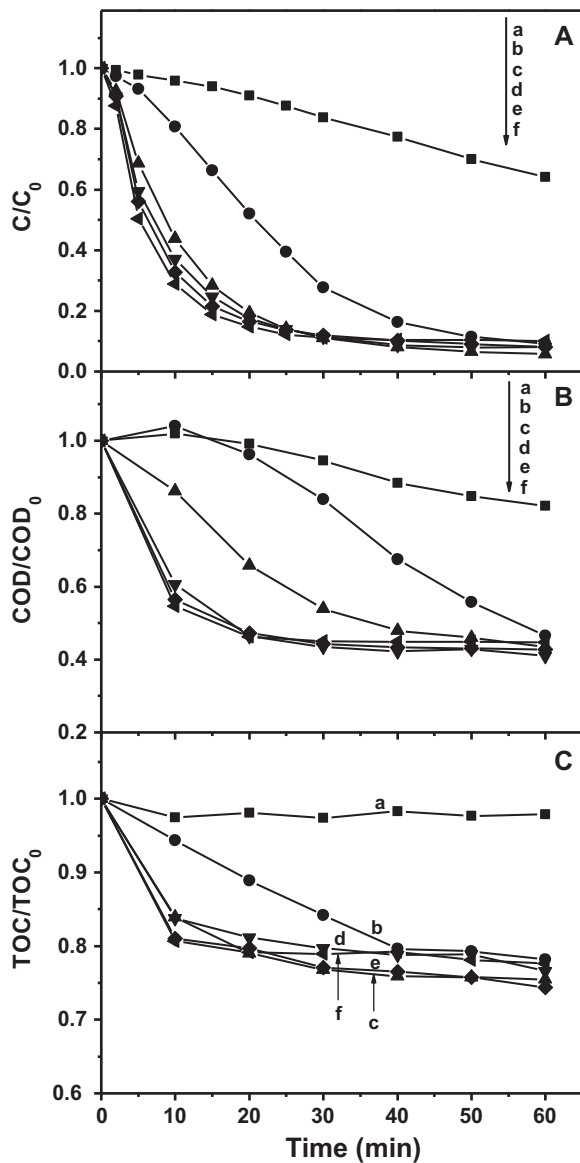


Fig. 1. (A) The degradation of sulfasalazine and removal of (B) COD and (C) TOC with Fenton-like reaction under various concentrations of Fe^{3+} (a) 0.10 mM, (b) 0.15 mM, (c) 0.20 mM, (d) 0.25 mM, (e) 0.30 mM, and (f) 0.35 mM. [sulfasalazine] = 100 mg/L; $[\text{H}_2\text{O}_2]$ = 4.0 mM; $T = 35^\circ\text{C}$.

The COD change of the solution (Fig. 1B) was also recorded to identify the oxidation efficiency of the Fenton-like reaction. Sulfasalazine solution exhibits a COD change of 17.9–59.0% with Fe^{3+} dosage from 0.10 mM to 0.35 mM. Similar with what has happened in UV–vis spectra measurement, the degradation with higher $[\text{Fe}^{3+}]$ shows higher initial COD decrease, which was finally caught up by that with lower $[\text{Fe}^{3+}]$.

The TOC elimination was lower than that of the COD. As shown in Fig. 1C, the TOC elimination rates are about 20% for sulfasalazine solution with the $[\text{Fe}^{3+}]$ from 0.15 mM to 0.35 mM in 60 min, while that with 0.10 mM $[\text{Fe}^{3+}]$ hardly shows any TOC decrease. The particular low degradation and mineralization of sulfasalazine solution with 0.10 mM can be attributed to the complexation of sulfasalazine with Fe^{3+} . Our previous work showed that organic ligand has a passivation effect towards the Fenton-like reaction in $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system and is harmful for the degradation of the organic pollutants [36]. Sulfasalazine here with an initial concentration of ca. 0.25 mM would complex with the Fe^{3+} at the ratio of 2:1, which retards the Fenton oxidation process [37,38].

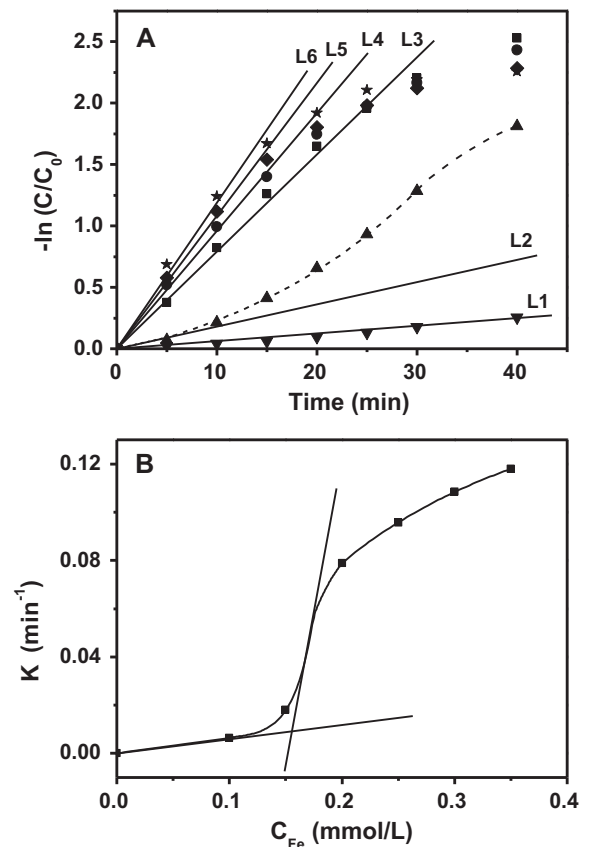


Fig. 2. (A) the relationship of the sulfasalazine concentration with the reaction time during the Fenton-like reaction at various Fe^{3+} concentrations (L1) 0.10 mM, (L2) 0.15 mM, (L3) 0.20 mM, (L4) 0.25 mM, (L5) 0.30 mM, (L6) 0.35 mM and (B) the corresponding pseudo-first order rate constant K vs the Fe^{3+} concentration.

Fenton (Fenton-like) degradation of organics was reported to obey the pseudo-first order reaction kinetics (Eq. (8)) [10,13]. The relationship of the sulfasalazine concentration with the reaction time during the Fenton-like degradation is presented in Fig. 2A according to the Eq. (9).

$$r = kC_{\text{Fe}}C = Kc, \quad (8)$$

in which C_{Fe} means the total Fe^{3+} concentration, C means the sulfasalazine concentration, k is the reaction rate constant and K is the pseudo-first order rate constant containing the factor of Fe^{3+} concentration.

$$-\ln \frac{C}{C_0} = Kt \quad (9)$$

As shown in Fig. 2A, $-\ln(C/C_0)$ of sulfasalazine has a linear relationship against the reaction time at the initial stage. It indicated that the degradation of sulfasalazine in this work also followed the pseudo-first order kinetics. However, the consumption of H_2O_2 during the Fenton-like reaction would decrease the reaction rate in a longer reaction time, which causes the reaction to deviate from the first order kinetics. The rate constants (K) of the sulfasalazine degradation were then obtained from the slope of the linear fit line at Fe^{3+} concentration of 0.10 mM, 0.20 mM, 0.25 mM, 0.30 mM and 0.35 mM, respectively. But for Fe^{3+} concentration of 0.15 mM, a significant variation in kinetics is observed from sulfasalazine degradation in Fig. 2A, which is attributed to the Fe^{3+} release from the Fe^{3+} -containing complex along with reaction time. Therefore, the initial reaction constant (K_2) of the sulfasalazine degradation at Fe^{3+} concentration of 0.15 mM is calculated from the tangent of its fitting curve.

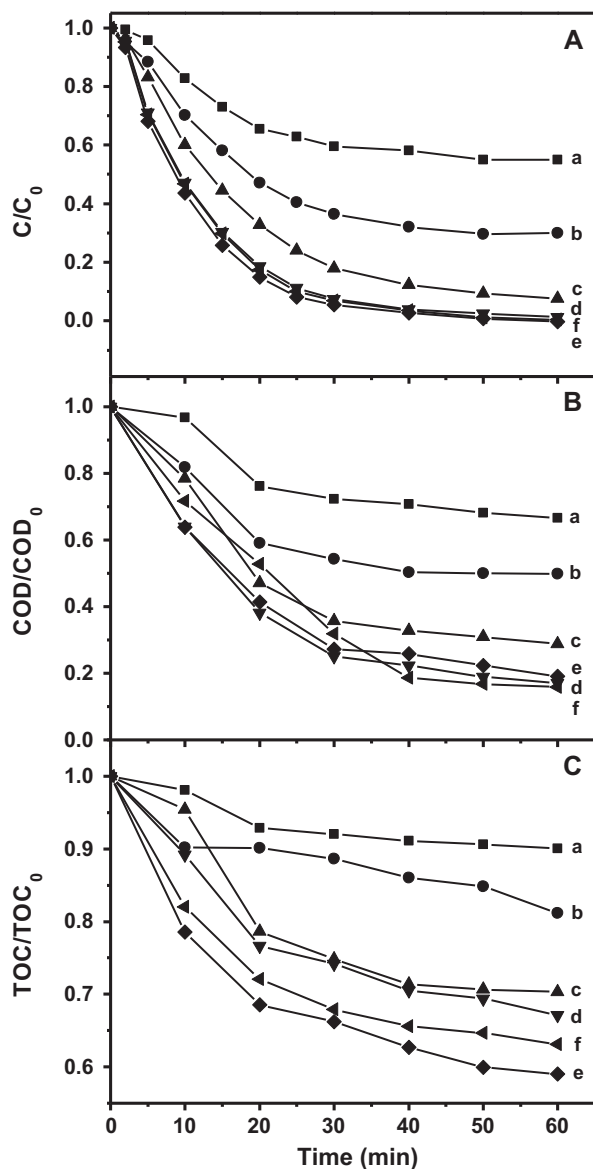


Fig. 3. (A) The degradation of sulfasalazine and removal of (B) COD and (C) TOC with Fenton-like reaction under various H_2O_2 dosages (a) 1 mM, (b) 2 mM, (c) 4 mM, (d) 8 mM, (e) 12 mM, and (f) 16 mM. [sulfasalazine] = 100 mg/L; $[\text{Fe}^{3+}] = 0.2$ mM; $T = 35^\circ\text{C}$.

The plot of K against $[\text{Fe}^{3+}]$ shown in Fig. 2B was used to obtain the value of k . Concluded from the foundational mechanism of Fenton reaction (Eqs. (1) and (2)), K should obey a linear relationship with the Fe^{3+} concentration as $K = k C_{\text{Fe}}$. However, no linear relationship but an S-shape curve is observed in Fig. 2B. The complex of organics with the Fe^{3+} here seems reduced by the complexation [36,39] towards the Fe^{3+} , a phenomena termed passivation in our previous work [22,36].

At a very low concentration of Fe^{3+} (i.e., $C_{\text{Fe}} \rightarrow 0$), almost all of the Fe^{3+} got complexed with the ligand sulfasalazine. Therefore, the Fenton-like reaction is carried out with the reaction of complexed Fe^{3+} (FeL) and H_2O_2 . The reaction rate constant here should be k_{FeL} not k_{Fe} (k_{Fe} refers to the reaction rate constant of free Fe^{3+} , and k_{FeL} refers to the reaction rate constant of complexed Fe^{3+}). The value of k_{FeL} in this work can be calculated as below:

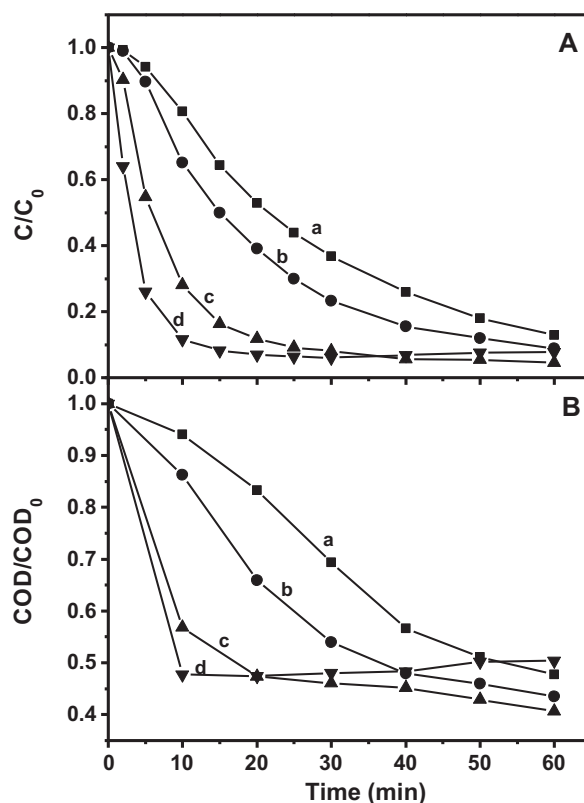


Fig. 4. (A) The degradation of sulfasalazine and (B) removal of COD with Fenton-like reaction at various reaction temperatures (a) 30°C , (b) 35°C , (c) 45°C , (d) 55°C . [sulfasalazine] = 100 mg/L; $[\text{H}_2\text{O}_2] = 4$ mM; $[\text{Fe}^{3+}] = 0.2$ mM.

At a concentration of $C_{\text{Fe}} \rightarrow 0$, for any increment of Fe^{3+} concentration (that is dC_{Fe}), there is

$$dC_{\text{Fe}} \approx d[\text{FeL}] \quad (10)$$

$$d[\text{Fe}] = (dC_{\text{Fe}} - d[\text{FeL}]) = 0 \quad (11)$$

Therefore,

$$dK = k_{\text{FeL}}d[\text{FeL}] + k_{\text{Fe}}d[\text{Fe}^{3+}] \approx k_{\text{FeL}}d[\text{FeL}] \approx k_{\text{FeL}}dC_{\text{Fe}} \quad (12)$$

The value of k_{FeL} thus can be obtained by carefully calculating the slope at low Fe^{3+} concentration, which is $0.062 \text{ min}^{-1} \text{ mM}^{-1}$ as shown in Fig. 2B.

However, at a concentration of Fe^{3+} higher than the ligand (i.e., $C_{\text{Fe}} > L$), further addition of Fe^{3+} in the solution should be considered as the increment of free Fe^{3+} concentration. That is,

$$dC_{\text{Fe}} \approx d[\text{Fe}^{3+}] \quad (13)$$

$$d[\text{FeL}] = (dC_{\text{Fe}} - d[\text{Fe}^{3+}]) = 0 \quad (14)$$

$$dK = k dC_{\text{Fe}} = k_{\text{FeL}}d[\text{FeL}] + k_{\text{Fe}}d[\text{Fe}^{3+}] \approx k_{\text{Fe}}d[\text{Fe}^{3+}] \approx k_{\text{Fe}}dC_{\text{Fe}} \quad (15)$$

Therefore, the slope of K vs C_{Fe} at high Fe^{3+} concentration reveals the reaction rate constant of free Fe^{3+} , k_{Fe} . Unfortunately, high concentration of Fe^{3+} would also induce several by-reactions (Eqs. (3)–(7)), which decrease the Fenton-like degradation of organics. Hence, the value of k_{Fe} is obtained by choosing the maximum slope in Fig. 2B, which is $2.526 \text{ min}^{-1} \text{ mM}^{-1}$.

3.1.2. The effect of H_2O_2 dosage

Since $[\text{Fe}^{3+}]$ with 0.2 mM showed a good Fenton-like degradation and mineralization for sulfasalazine solution. The effect of H_2O_2 dosage on the degradation of sulfasalazine solution by Fenton-like process was investigated with $[\text{Fe}^{3+}]$ of 0.2 mM and

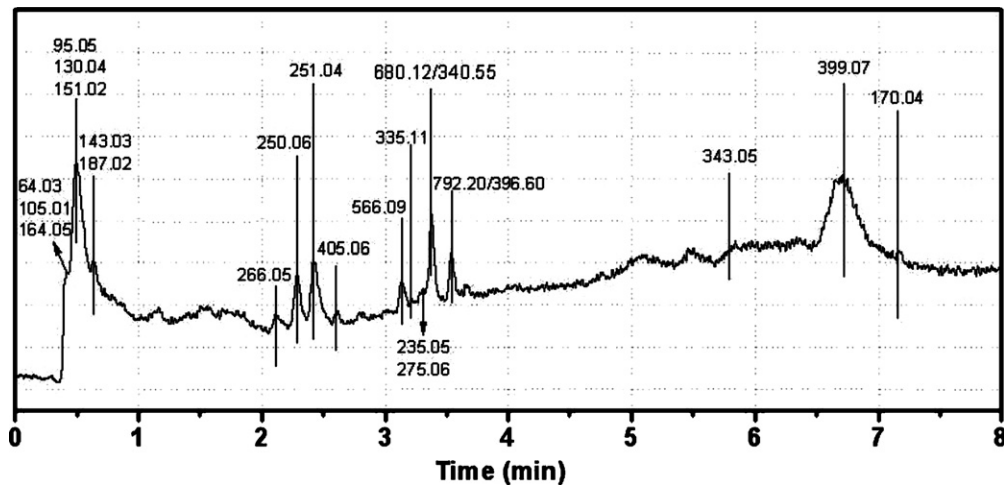


Fig. 5. The LC chromatogram of sulfasalazine reaction solution recorded in total ion mode.

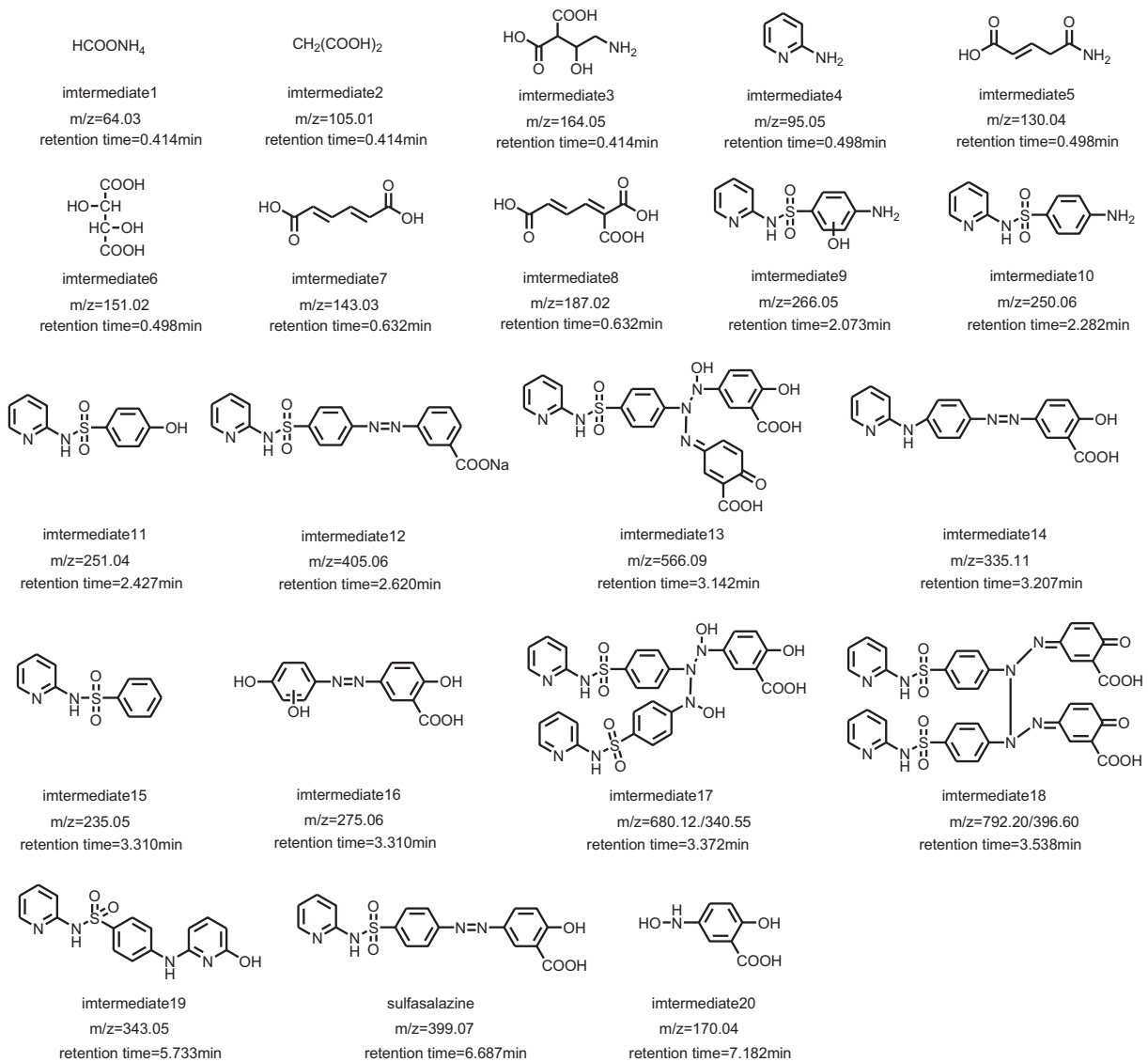


Fig. 6. The m/z values of the LC peaks and their corresponding molecular structures.

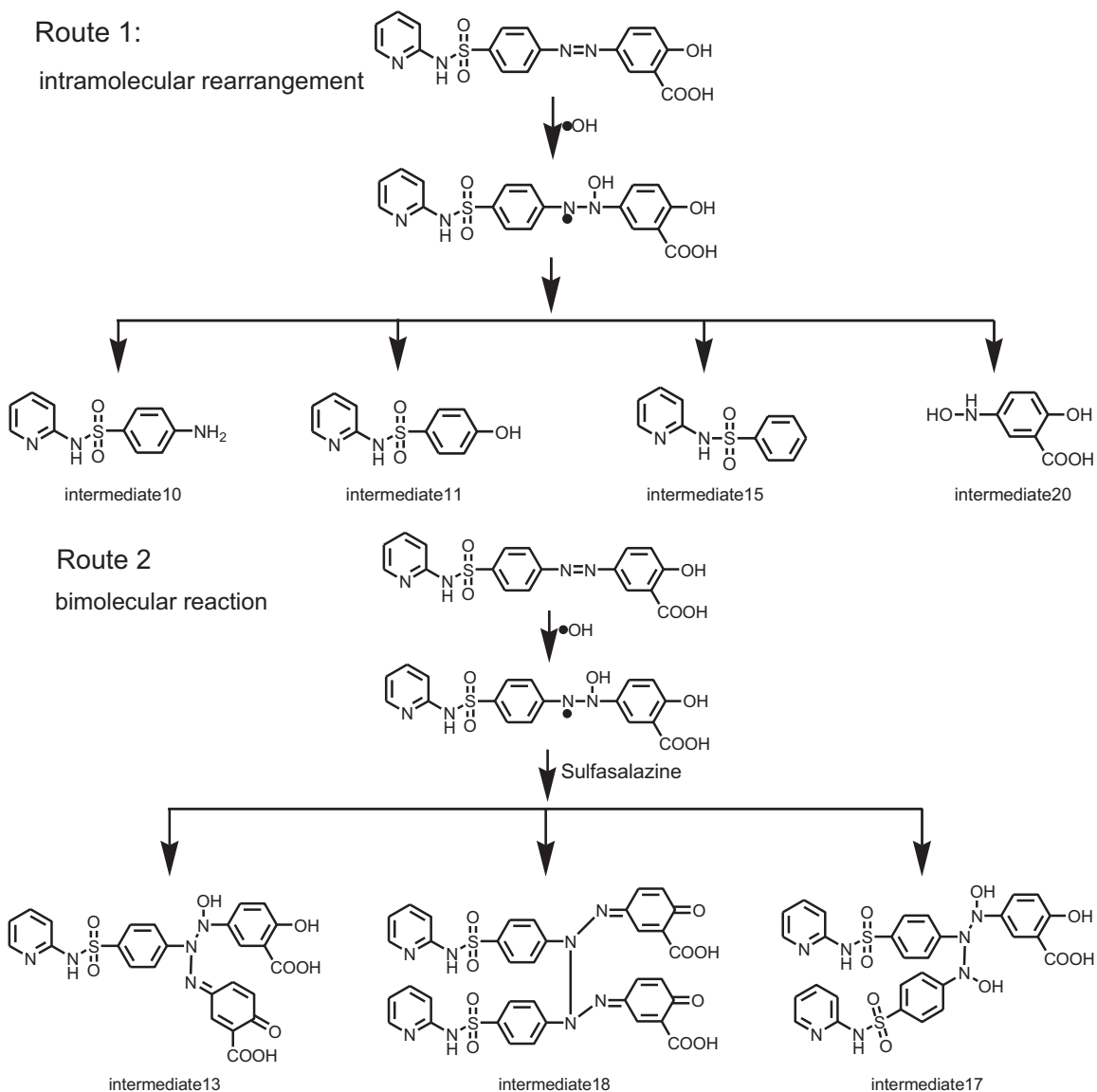


Fig. 7. The degradation pathways of sulfasalazine after be attacked by hydroxyl radical at the azo-group.

is shown in Fig. 3. It is observed that the degradation efficiency of sulfasalazine is obviously enhanced by increasing the amount of H_2O_2 . The degradation rates of sulfasalazine are 45.0%, 70.0%, 92.5%, 98.7%, 99.9% and 99.5% for H_2O_2 dosages of 1 mM, 2 mM, 4 mM, 8 mM, 12 mM and 16 mM in 60 min, respectively. H_2O_2 is the raw material of $\cdot\text{OH}$ and $\text{O}_2\cdot^-$ (Eqs. (1) and (2)) [10]. Increase in the initial concentration of H_2O_2 enhances the generation rate of active oxygen species in Fenton reaction. As shown in Fig. 3, all sulfasalazine disappears with the H_2O_2 dosages higher than 8 mM in 60 min.

Relative higher H_2O_2 dosages also lead to the greater mineralization of sulfasalazine solution, which are shown in Fig. 3B and C. The COD elimination of sulfasalazine solution increases from 33.5% to 84.2% as the H_2O_2 dosage increased from 1 mM to 16 mM in 60 min, while the corresponding TOC elimination increases from 10.0% to 41.0%.

3.1.3. The effect of reaction temperature

The Fenton-like degradation of sulfasalazine solution was also investigated at different temperatures of 30 °C, 35 °C, 45 °C, and 55 °C, as shown in Fig. 4. The degradation reaction kinetics of sul-

fasalazine solution depends greatly on the temperature. In order to achieve ca. 90% of the sulfasalazine removal, about 60 min of reaction time is needed at 35 °C, while that at 55 °C is only 15 min. However, as for the final degradation efficiency and COD removal ($t > 60$ min) of sulfasalazine solution, relative lower temperatures such as 35 °C and 45 °C seem to present better results as shown in Fig. 4.

3.1.4. Degradation intermediates identification and proposed degradation pathway of sulfasalazine

According to the above COD and TOC measurement, various degradation intermediates may remain in the reaction solution even after the complete disappearance of sulfasalazine. Thus, knowledge of the Fenton-like degradation intermediates of sulfasalazine is essential to understand the possible degradation pathway of sulfasalazine and as well as estimation the residual toxicity of the intermediate solution.

LC-MS technology was thus adopted to observe the possible degradation intermediates during the reaction. Fig. 5 presents the LC chromatogram of reaction solution recorded in total ion mode after 60 min Fenton-like degradation. The m/z values of the peaks

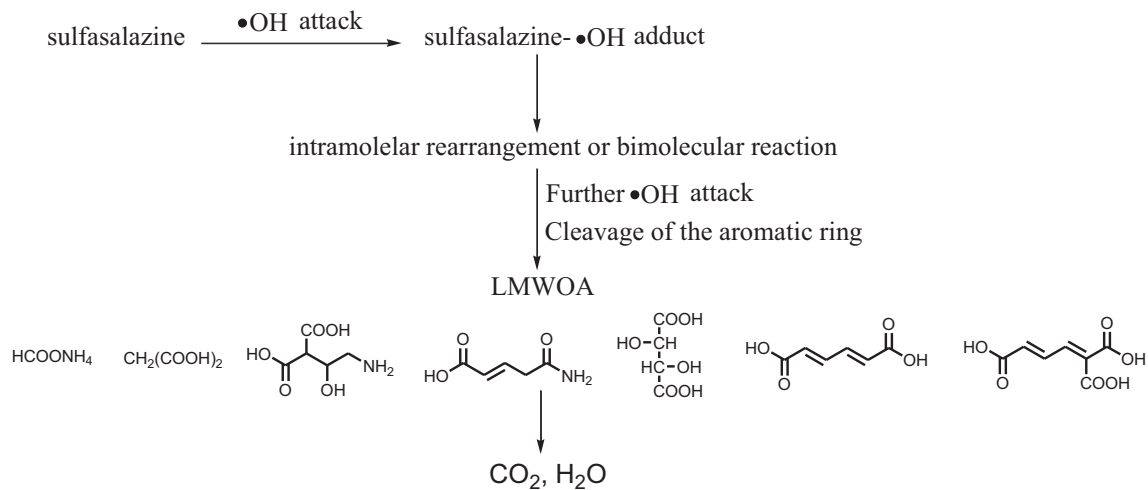


Fig. 8. An oversimplified Fenton-like degradation pathway of sulfasalazine.

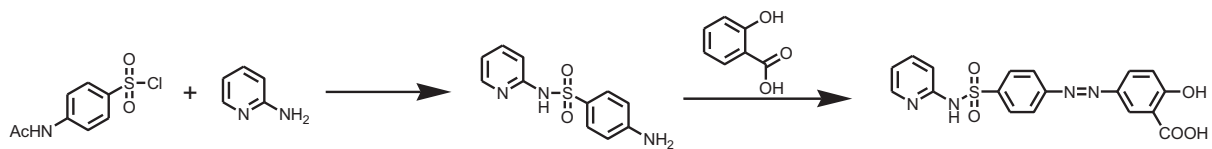


Fig. 9. A simplified synthetic procedure of sulfasalazine in Shanghai Sunve Pharmaceutical.

are directly labeled in Fig. 5 and their corresponding possible molecular structures are listed in the Fig. 6.

Although superoxide radical and oxygen molecule have been suggested as two other main oxidants in the Fenton-like degradation, hydroxyl radical is still the most powerful oxidant in the Fenton-like reaction. The main initial intermediates suggested that the Fenton-like degradation of sulfasalazine principally began with the attack of hydroxyl radical on the azo-group. Several intermediates (intermediate 10, 11, 13, 15, 17, 18, and 20) are produced from the intramolecular rearrangement or bimolecular reaction of sulfasalazine-•OH adduct after hydroxyl radical attack, as shown in Fig. 7. Additionally, the sulfanilamido group is the second choice for hydroxyl radical attack, which can be confirmed from the intermediate 4 ($m/z=95.05$) and intermediate 16 ($m/z 275.06$).

After the initial reaction, hydroxyl radical also attacks some other portions of the intermediates, for example, the reaction of hydroxyl radical with the aromatic rings induces the production of intermediate 16 ($m/z 275.06$) and intermediate 9 ($m/z 266.05$).

Further attack of the active oxidative species results in the cleavage of the aromatic rings. After the 60 min of degradation, a great number of low-molecular-weight organic acids (LMWOA) [40,41] began to appear. The peaks at the beginning of LC chromatogram of reaction solution after 60 min degradation show the presence of intermediates 1–3 and 5–8, while TOC decrease in the Fig. 1 confirms the production of the mineralized carbon, CO_2 . An oversimplified degradation pathway of sulfasalazine is presented in Fig. 8.

3.1.5. Practical application of the Fenton reaction in the industrial sulfasalazine wastewater treatment

Sulfasalazine in Shanghai Sunve Pharmaceutical is produced according to the following procedure (Fig. 9). Hence, the practical effluent contains 2-aminopyridine, 4-amino-N-(pyridin-2-yl)benzenesulfonamide, and salicylic acid as well as some by-products, with an initial COD of 3425 mg/L and pH of 1.12. As Fe^{2+} leads to higher initial degradation rates in the Fenton reaction, Fe^{2+} was used instead of Fe^{3+} for faster removal of the pollutants

with high COD in the industrial sulfasalazine wastewater treatment.

Fig. 10 presents the COD removal of above industrial sulfasalazine wastewater with different amount of H_2O_2 and Fe^{2+} at 30°C for 3 h. The amount of H_2O_2 used was determined from the initial COD of the wastewater. Theoretically, 0.214 mol/L of H_2O_2 contains an $[\text{O}]$ amount of 3425 mg/L, equals the initial COD of the wastewater.

The COD removal results demonstrate that the degradation efficiency increased with increasing the amount of H_2O_2 under every particular $\text{Fe}/\text{H}_2\text{O}_2$ molar ratio. The optimal COD removals are 43%, 72%, 82% under the 0.5, 1 and 2 equivalents H_2O_2 , respectively. Under the equivalent amount of H_2O_2 to COD, the COD removal changes little from $\text{Fe}/\text{H}_2\text{O}_2$ ratio of 1/5 to 1/2 and then decreases at higher $\text{Fe}/\text{H}_2\text{O}_2$ ratios. As for that under the 2 equivalent amount of

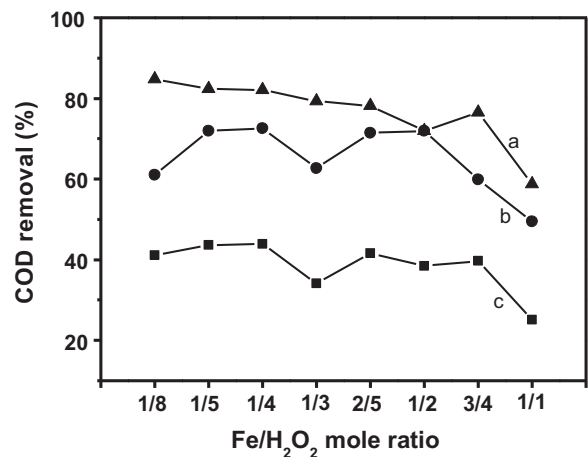


Fig. 10. COD removal of the industrial sulfasalazine wastewater with Fenton reaction in the presence of (a) 0.5, (b) 1, and (c) 2 equivalents amount of H_2O_2 to COD under various $\text{Fe}/\text{H}_2\text{O}_2$ mole ratios.

H₂O₂, the COD removal decreases all along with the enhancement of Fe/H₂O₂ ratios. In the presence of high iron ion, active oxygen species such as hydroxyl radical would bear a high loss from their reaction with iron ion, which impairs the utilization of H₂O₂. It demonstrates that the Fenton reaction would better be carried out at moderate Fe/H₂O₂ molar ratio, from 1/5 to 2/5.

4. Conclusion

The effects of Fe³⁺ concentration, initial H₂O₂ dosage and the reaction temperature were evaluated in the Fenton-like degradation of sulfasalazine solution. These reaction parameters have great effects on the degradation rate and degradation efficiency for the removal of sulfasalazine. The complexation of the sulfasalazine with the Fe³⁺ is important for the reaction kinetics of the Fenton-like degradation. The complexed Fe³⁺ presents a reaction constant of 0.062 min⁻¹ mM⁻¹ while that of free Fe³⁺ is 2.526 min⁻¹ mM⁻¹. Higher H₂O₂ dosage leads to greater mineralization of sulfasalazine solution, while higher reaction temperature results in faster initial degradation but less final degradation efficiency.

A closer view to the degradation intermediates of the sulfasalazine shows that the Fenton degradation of sulfasalazine principally began with the attack of hydroxyl radical towards the azo-group as well as the sulfanilamido group. Both intramolecular rearrangement and bimolecular reactions should occur in sulfasalazine degradation after the hydroxyl radical attack. Further attack of the active oxidative species results in the cleavage of the aromatic rings and the production of CO₂. The degradation of industrial sulfasalazine wastewater has also been achieved with Fenton reaction. Relatively better removal efficiency is observed at moderate Fe/H₂O₂ molar ratio from 1/5 to 2/5 for industrial sulfasalazine wastewater treatment.

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References

- [1] N. Kulik, M. Trapido, A. Goi, Y. Veressina, R. Munter, Combined chemical treatment of pharmaceutical effluents from medical ointment production, *Chemosphere* 70 (2008) 1525–1531.
- [2] C. Sirtori, A. Zapata, I. Oller, W. Gernjak, A. Agüera, S. Malato, Solar photo-Fenton as finishing step for biological treatment of a pharmaceutical wastewater, *Environ. Sci. Technol.* 43 (2009) 1185–1191.
- [3] J. Radjenović, M. Godehard, M. Petrović, A. Hein, M. Farré, M. Jekel, D. Barceló, Evidencing generation of persistent ozonation products of antibiotics roxithromycin and trimethoprim, *Environ. Sci. Technol.* 43 (2009) 6808–6815.
- [4] B.L. Edlund, W.A. Arnold, K. McNeill, Aquatic photochemistry of nitrofurantoin antibiotics, *Environ. Sci. Technol.* 40 (2006) 5422–5427.
- [5] S.K. Khanal, B. Xie, M.L. Thompson, S. Sung, S.-K. Ong, J. van Leeuwen, Fate, transport, and biodegradation of natural estrogens in the environment and engineered systems, *Environ. Sci. Technol.* 40 (2006) 6537–6546.
- [6] C. Sirtori, A. Zapata, I. Oller, W. Gernjak, A. Agüera, S. Malato, Decoloration industrial pharmaceutical wastewater by combining solar photo-Fenton and biological treatment, *Water Res.* 43 (2009) 661–668.
- [7] H. Tekin, O. Bilkay, S.S. Ataberk, T.H. Balta, I.H. Ceribasi, F.D. Sanin, F.B. Dilek, U. Yetis, Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater, *J. Hazard. Mater.* 136 (2006) 258–265.
- [8] I.A. Balcıoğlu, M. Ötör, Treatment of pharmaceutical wastewater containing antibiotics by O₂ and O₃/H₂O₂ process, *Chemosphere* 50 (2003) 85–95.
- [9] K. Kent, A.A. Weston, D. Caminada, Ecotoxicology of human pharmaceutical, *Aquat. Toxicol.* 76 (2006) 122–159.
- [10] S.-P. Sun, C.-J. Li, J.-H. Sun, S.-H. Shi, M.-H. Fan, Q. Zhou, Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: Effect of system parameters and kinetic study, *J. Hazard. Mater.* 161 (2009) 1052–1057.
- [11] D.R. de Souza, E.T.F.M. Duarte, G. de Souza Girardi, V. Velani, A.E. da Hora Machado, C. Sattler, L. de Oliveira, J.A. de Miranda, Study of kinetic parameters related to the degradation of an industrial effluent using Fenton-like reactions, *J. Photochem. Photobiol. A: Chem.* 179 (2006) 269–275.
- [12] D. Kassinos, N. Varnava, C. Michael, P. Piera, Homogeneous oxidation of aqueous solutions of atrazine and fenitrothion through dark and photo-Fenton reactions, *Chemosphere* 74 (2009) 866–872.
- [13] M. Fares Al, S. Mo'ayyad, S. Ahmad, A.-S. Mohammad, Impact of Fenton and ozone on oxidation of wastewater containing nitroaromatic compounds, *J. Environ. Sci.* 20 (2008) 675–682.
- [14] L.A. Pérez-Estrada, S. Malato, A. Agüera, A.R. Fernández-Alba, Degradation of dipyrone and its main intermediates by solar AOPs: identification of intermediate products and toxicity assessment, *Catal. Today* 129 (2007) 207–214.
- [15] C. Cominellis, A. Kapalka, S. Malato, S.A. Parsons, I. Poullos, D. Mantzavinos, Advanced oxidation processes for water treatment: advances and trends for R&D, *J. Chem. Technol. Biotechnol.* 83 (2008) 769–776.
- [16] H.J.H. Fenton, Oxidation of tartaric acid in the presence of iron, *J. Chem. Soc.* 65 (1894) 899–910.
- [17] W. Gernjak, T. Krutzler, A. Glaser, S. Malato, J. Caceres, R. Bauer, A.R. Fernández-Alba, Photo-Fenton treatment of water containing natural phenolic pollutants, *Chemosphere* 50 (2003) 71–78.
- [18] H.-J. Hsing, P.-C. Chiang, E.-E. Chang, M.-Y. Chen, The decolorization and mineralization of Acid Orange 6 azo dye in aqueous solution by advanced oxidation processes: a comparative study, *J. Hazard. Mater.* 141 (2007) 8–16.
- [19] Y. Xie, F. Chen, J. He, J. Zhao, H. Wang, Photoassisted degradation of dyes in the presence of Fe³⁺ and H₂O₂ under visible irradiation, *J. Photochem. Photobiol. A: Chem.* 136 (2000) 235–240.
- [20] R.G. Zepp, B.C. Faust, J. Hoigne, Hydroxy radical formation in aqueous reactions (pH 3–8) of Iron(II) with hydrogen peroxide: The photo-Fenton reaction, *Environ. Sci. Technol.* 26 (1992) 313–319.
- [21] J.J. Plgnatello, Dark and photoassisted iron(3+)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, *Environ. Sci. Technol.* 26 (1992) 944–951.
- [22] F. Chen, W. Ma, J. He, J. Zhao, Fenton degradation of malachite green catalyzed by aromatic additives, *J. Phys. Chem. A* 106 (2002) 9485–9490.
- [23] F. Chen, J. He, J.C. Zhao, C.Y. Jimmy, Photo-Fenton degradation of malachite green catalyzed by aromatic compounds under visible light irradiation, *New J. Chem.* 26 (2002) 336–341.
- [24] Y. Deng, J.D. Englehardt, Treatment of landfill leachate by the Fenton process, *Water Res.* 40 (2006) 3683–3694.
- [25] E. Elmolla, M. Chaudhuri, Optimization of Fenton process for treatment of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution, *J. Hazard. Mater.* 170 (2009) 666–672.
- [26] Y. Yang, P. Wang, S. Shi, Y. Liu, Microwave enhanced Fenton-like process for the treatment of high concentration pharmaceutical wastewater, *J. Hazard. Mater.* 168 (2009) 238–245.
- [27] M.I. Badawy, R.A. Wahaab, A.S. El-Kalliny, Fenton-biological treatment processes for the removal of some pharmaceuticals from industrial wastewater, *J. Hazard. Mater.* 167 (2009) 567–574.
- [28] Z.-P. Xing, D.-Z. Sun, Treatment of antibiotic fermentation wastewater by combined polyferric sulfate coagulation, Fenton and sedimentation process, *J. Hazard. Mater.* 168 (2009) 1264–1268.
- [29] K. Neafsey, X. Zeng, A.T. Lemley, Degradation of sulfonamides in aqueous solution by membrane anodic Fenton treatment, *J. Agric. Food Chem.* 58 (2010) 1068–1076.
- [30] H. Zaher, A.A. Khan, J. Palandra, T.G. Brayman, L. Yu, J.A. Ware, Breast cancer resistance protein (Bcrp/abcg2) is a major determinant of sulfasalazine absorption and elimination in the mouse, *Mol. Pharmaceut.* 3 (2006) 55–61.
- [31] H.-J. Fan, S.-T. Huang, W.-H. Chung, J.-L. Jan, Degradation pathways of crystal violet by Fenton and Fenton-like systems: condition optimization and intermediate separation and identification, *J. Hazard. Mater.* 171 (2009) 1032–1044.
- [32] J. Poerschmann, U. Trommler, T. Görecki, F.-D. Kopinke, Formation of chlorinated biphenyls, diphenyl ethers and benzofurans as a result of Fenton-driven oxidation of 2-chlorophenol, *Chemosphere* 75 (2009) 772–780.
- [33] M. Petrovic, D. Barceló, LC-MS for identifying photodegradation products of pharmaceuticals in the environment, *Trend. Anal. Chem.* 26 (2007) 486–493.
- [34] M.J. Lovdahl, S.R. Priebe, Characterization of clinafloxacin photodegradation products by LC-MS/MS and NMR, *J. Pharm. Biomed. Anal.* 23 (2000) 521–534.
- [35] National Occupation Standard for Environment Protection of the People's Republic of China HJ/T 399-2007, Water quality-determination of the chemical oxygen demand-fast digestion-spectrophotometric method.
- [36] F. Chen, Y. Li, L. Guo, J. Zhang, Strategies comparison of eliminating the passivation of non-aromatic intermediates in degradation of Orange II by Fe³⁺/H₂O₂, *J. Hazard. Mater.* 169 (2009) 711–718.
- [37] C. Walling, Fenton's reagent revisited, *Acc. Chem. Res.* 8 (1975) 125–131.
- [38] B. Siegel, J. Lanphear, Iron-catalyzed oxidative decarboxylation of benzoic formic acid, *J. Am. Chem. Soc.* 101 (1979) 2221–2222.
- [39] K. Pirkanniemi, S. Metsarinne, M. Sillanpää, Degradation of EDTA and novel complexing agents in pulp and paper mill process and waste water by Fenton's reagent, *J. Hazard. Mater.* 147 (2007) 556–561.
- [40] T. Brinkmann, P. Hörsch, D. Sartorius, F.H. Frimmel, Photoformation of low-molecular-weight organic acids from brown water dissolved organic water, *Environ. Sci. Technol.* 37 (2003) 4190–4198.
- [41] J.H. Ma, W.H. Ma, W.J. Song, C.C. Chen, Y.L. Tang, J.C. Zhao, Fenton degradation of organic pollutants in the presence of low-molecular-weight organic acids: cooperation effect of quinone and visible light, *Environ. Sci. Technol.* 40 (2006) 618–624.