

Degradation of sulphapyridine by Fe-Mn binary oxide-mediated radical reactions

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Abstract—Sewage containing antibiotics is harmful to the water environment. Here, a newly prepared iron manganese binary oxide (FMBO) activated persulfate (PDS) has excellent performance for the degradation of sulfapyridine (SPY) in an aqueous environment. The effects of initial pH, SPY, PDS concentration and FMBO dosage on the degradation ability of SPY were investigated. When the pH of FMBO/PDS was 4.0 and the initial concentration of PDS was 2.0 mmol/L, the degradation ratio of SPY could reach 94.4%. In the system of removing organic pollutants by transition metal activated PDS, $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ radicals are generally generated, and $\cdot\text{OH}$ radical plays a major role. Through the identification of SPY intermediate products by LC/MS, the degradation mechanism was explored. The degradation pathway showed that the strong oxidation of FMBO and the activity of PDS promoted the production of hydroxyl radical and contributed to the degradation and transformation of antibiotics. This study shows that FMBO/PDS has high degradation efficiency in the degradation of SPY.

Keywords: Transition Metal, Antibiotics, $\text{SO}_4^{\cdot-}$ Radicals, Capture Agent, Degradation Mechanism

INTRODUCTION

The content of antibiotics in rivers, lakes and coastal waters is increasing yearly, inducing the development and spread of drug-resistant bacteria, thereby the marine ecological environment and endangering human health. Sulfapyridine (SPY), one of the most widely used sulfonamides, can be found in wastewater from wastewater treatment plants around the world [1]. The highest concentrations of surface waters such as Yangtze Estuary range from 74.6–219 ng/L [2], and it has been reported that the concentration of sulfapyridine in groundwater ranges from 1 ng/L to 1 µg/L [3]. A large amount of water-soluble SP is discharged into water due to the pharmaceutical industry, aquaculture conditioning and other functions, leading to human myalgia, joint aggravation, life-threatening allergies, asthma and so [4]. At present, conventional water disinfection methods such as chlorine oxidation cannot completely mineralize antibiotics in water, and it is difficult to achieve the goal of no antibacterial activity and no negative environmental effects.

Previous scholars have used different ways to activate persulfate to remove organic pollutants in the water environment, such as TiO_2 photocatalytic [5–7], magnetic carbon dry gel (CX/CoFe) [8] and thermally activated [9], and all of them can achieve a good removal effect.

Feng, Sang and others [10,11] selected three transition metal oxides (M_xO_y) of hematite ($\alpha\text{-Fe}_2\text{O}_3$), cobalt oxide (Co_2O_3) and copper oxide (CuO), and took the typical sulfonamide antibiotic sulfamethoxazole (SMZ) as the degradation object to study the enhancement effect and mechanism of hydroxylamine (HA) on the deg-

radation of SMZ by activated persulfate (PDS) of three transition metal oxides.

However, a study on the degradation of SPY (sulfapyridine) in aqueous environment by PDS (persulfate) activated by FMBO (iron manganese binary oxide) has not been reported. Therefore, we selected FMBO activated PDS to degrade SPY in water environment based on previous work, and the effects of initial pH, initial SPY, PDS concentration and FMBO dosage on the degradation ability of SPY were investigated.

The main free radical species in the degradation process of SPY were identified by EPR technology, the intermediate products of SPY degradation were analyzed by LC/MS, and the degradation pathway of SPY was deduced. It was proved that FMBO has a good degradation effect on SPY, which provides a new method, new idea and theoretical basis for the effective degradation of antibiotics in surface water and groundwater.

MATERIALS AND METHODS

1. Chemicals and Reagents

Sulfapyridine (SPY, purity >98%), sulfuric acid and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (purity >99%) were purchased from Aladdin Company in Shanghai, China; ethanol (EtOH) (purity >99.7%) and tert butylalcohol (TBA) (purity >99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd in Shanghai, China; Chromatographic grade acetic acid and acetonitrile were purchased from Tian di Company in the United States; The water used in the experiment is Milli-Q ultrapure water (18.2 Ω).

The preparation process and method of FMBO have been published in the early stage [12].

2. Apparatus

The main equipment used in this report is as follows: high per-

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formance liquid chromatograph: Agilent 1220 Agilent, Gas bath constant temperature oscillator: QE-3 Tianjin Ono Instrument Co., Ltd, Ultrasonic cleaning machine: SB25-12DTN Ningbo Xinzhi Biotechnology Co., Ltd, PH meter: Leici PHS-3C Shanghai Yidian Scientific Instrument Co., Ltd, Electronic balance: CP114 Shanghai Aohaosi Instrument Co., Ltd, Electric blast drying oven: Shanghai Yiheng Scientific Instrument Co., Ltd, Electron paramagnetic resonance spectrometer (EPR): JES-FA200, JEOL company, Japan.

3. Experimental Method

The kinetic experiment of degradation of SPY by FMBO was carried out in a 500 ml conical flask by batch equilibrium method. First, we added 100 ml of different concentrations of SPY (10.0–100.0 mg/L) solution into the conical flask, then added different concentrations of PDS (0.5–2.5 mmol/L) and different dosage of FMBO (0.5–5.0 g/L), put the conical flask into a 180 r/min gas bath constant temperature oscillator, and carried out all experiments at room temperature ($25 \pm 2^\circ\text{C}$). To investigate the effect of initial pH value, H_2SO_4 with a concentration of 0.1 mol/L was used to adjust the initial pH value. Samples were taken at different time points (2, 4, 6, 8, 10, 20, 30, 40, 50, 60 min). The volume of each sample was 1.0 mL. 1.0 mL salicylic acid (0.72 mmol/L) was added to terminate the reaction and 0.45 min was used μM filter membrane, and then the SPY concentration was determined by high performance liquid chromatography (HPLC). The effects of initial pH, PDS concentration, dosage and repeatability of FMBO on SPY removal were investigated.

To evaluate the types and intensity of free radicals generated in FMBO/PDS System, free radical capture experiment and EPR were used to identify. 5,5-Dimethyl-1-pyrroline-n-oxide (DMPO) was used as the spin trap of $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ free radicals. Finally, the degradation intermediates were identified, and the degradation mechanism and pathway were analyzed.

4. Analysis Method

SPY is determined by Agilent 1220 high performance liquid chromatograph (UV detector), and the chromatographic column is Agilent HC-C18 chromatographic column (4.6×250 mm, 5 μm). The mobile phase was acetonitrile and 0.4% acetic acid solution with a volume ratio of 70:30, Mobile phase flow rate: 1 mL/min, Column temperature: 40°C , Detection wavelength: 270 nm, Injection volume: 20 μL .

The degradation products of SPY were analyzed by liquid chromatography triple four-stage rod tandem mass spectrometry (Agilent 1290+G6460). Use C18 column (2.1×100 mm, 1.7 μm), mobile phase (acetonitrile and 0.4% acetic acid, 30:70) flow rate: 0.2 mL/min, electrospray ionization positive ion mode, capillary voltage: 4 kV, sprayer pressure: 45 psi, gas flow rate: 6 L/min, gas temperature: 325°C .

5. Data Analysis Formula

The degradation ratio of SPY (X%) is calculated by Eq. (1):

$$X\% = (C_0 - C_t) / C_0 \times 100 \quad (1)$$

$$C_t = C_0 + K_{obs} e^{-x/t} \quad (2)$$

where C_0 and C_t are the initial concentration and the concentration at reaction t min (mg/L), respectively. The fitted exponential function equation is shown in Eq. (2) [12].

RESULTS AND DISCUSSION

1. Kinetics of Degradation of SPY by PDS Activated by FMBO

The kinetics of removing SPY by FMBO activated PDS at initial pH 4.0 was investigated. The degradation results of SPY in three methods are shown in Fig. 1. The concentrations of SPY, PDS and FMBO were 10 mg/L, 2.0 mmol/L and 3.0 g/L, respectively. When FMBO and SPY were added alone, 60 min later, the degradation ratio of FMBO to SPY was 9.9%. If adding PDS and SPY alone, the removal rate of SPY was only 3.1% after 60 min of reaction. When FMBO, PDS and SPY were added at the same time, the removal rate of SPY reached 94.4%. Since FMBO was added as an activator, $\text{S}_2\text{O}_8^{2-}$ ($E^0=2.01\text{ V}$) obtained electrons from $\text{Mn}^{2+}/\text{Mn}^{3+}$ ($E^0=1.51\text{ V}$) and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ($E^0=0.77\text{ V}$) through redox to generate $\text{SO}_4^{\bullet-}$ free radical ($E^0=2.60\text{ V}$), which increased the removal efficiency of SPY (As shown in Eqs. (3)–(4)) [7].

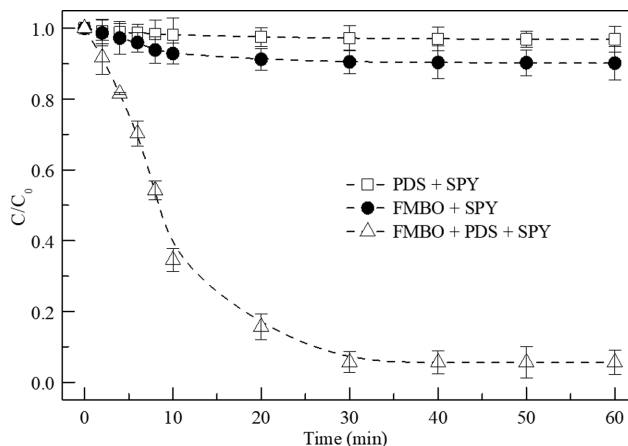
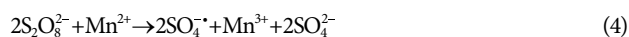
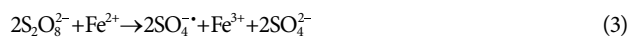


Fig. 1. The kinetic curves of SPY degradation by FMBO.

2. Effect of Initial SPY Concentration on SPY Degradation by FMBO/PDS

The effect of initial SPY concentration on the oxidative removal of that by FMBO/PDS at initial pH 4.0 was studied, and the results are shown in Fig. 2. The concentrations of SPY, PDS and FMBO were 10–100 mg/L, 2.0 mmol/L and 3.0 g/L, respectively. After 30 min, the degradation ratios of different initial SPY concentrations tended to balance. For SPY with an initial concentration of 10 mg/L, the final degradation ratio reached 94.4%. When the concentration increased, the degradation ratio decreased. When the concentration reached 100 mg/L, the degradation efficiency of SPY decreased to 49.3%. It may be attributed to the fact that the concentration of FMBO and PDS initially added in the system was constant, so the concentration of $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ radicals generated after FMBO activated PDS was also constant. Therefore, when the initial concentration of SPY was low, the generated $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ radicals could completely degrade. However, when the concentration of SPY increased, Sufficient $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ radicals could not be generated to degrade SPY in the solution, so the degradation ratio of SPY gradually de-

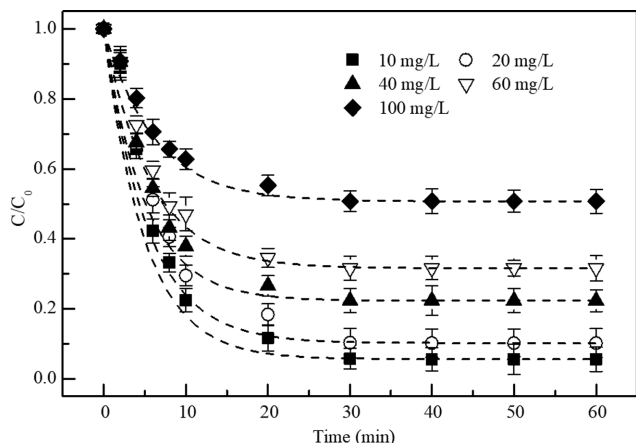


Fig. 2. The effect curves of initial SPY concentration on SPY degradation by FMBO/PDS.

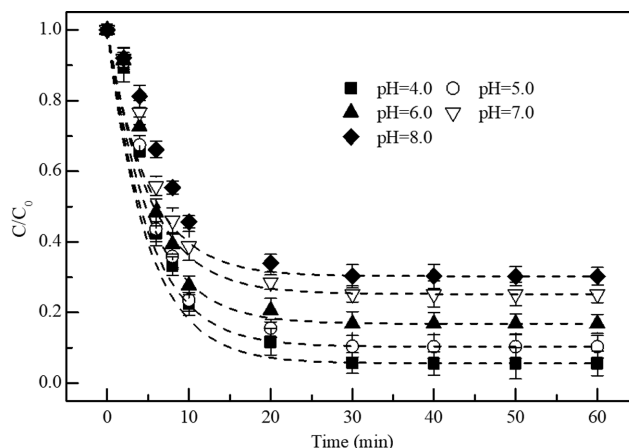


Fig. 3. Effect of initial pH on SPY degradation by FMBO/PDS.

creased with the increase of initial SPY concentration.

3. Effect of Initial pH on SPY Degradation by FMBO/PDS

To investigate the effect of initial pH value on the removal of SPY by FMBO activated PDS, different pH values (pH=3.0, 4.0, 5.0, 6.0, 7.0 and 8.0) were assigned in the experiment. The results are shown in Fig. 3. The concentrations of SPY, PDS and FMBO were 10 mg/L, 2.0 mmol/L and 3.0 g/L, respectively. As shown in the figure, the degradation ratio of SPY gradually decreased with the increase of initial pH value. The maximum degradation efficiency of SMX was 98.1% at the reaction time of 60 min at pH 3.0. After 60 min of reaction, when the initial pH was 4.0, the degradation ratio of SPY was 94.4%, and when the initial pH increased to 8.0, the degradation ratio of SPY decreased to 69.7%. At pH 5.0, 6.0 and 7.0, the degradation ratios were 89.7%, 83.2% and 74.8%, respectively. As the removal was very quick at pH 3.0 and even after 10 min it came into an equilibrium state. Whereas at pH 4.0, the removal gradually increased. From the above results, optimum pH 4.0 was selected for all other experiments.

In acidic solution, the removal rate of SPY is higher than that in neutral and alkaline solution; this may be caused by being more conducive to the release of Fe and Mn ions in FMBO in acidic

solution, so as to promote the formation of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ free radicals. In addition, in neutral and alkaline solutions, Fe^{2+} easily to undergoes hydrolysis reaction and is oxidized to $\text{Fe}(\text{OH})_3$ precipitation, resulting in partial loss of Fe^{2+} [13]. Secondly, under neutral and alkaline conditions, $\text{SO}_4^{\cdot-}$ free radical easily reacts with H_2O , resulting in the loss of $\text{SO}_4^{\cdot-}$ free radical (Eqs. (5)); Finally, when the initial pH value increases, the OH^- concentration in the system also increases, and $\text{SO}_4^{\cdot-}$ radical will react with it to form $\cdot\text{OH}$ radical (Eqs. (6)). However, under alkaline conditions, the redox potential of $\cdot\text{OH}$ radical is lower than that of $\text{SO}_4^{\cdot-}$ radical based on Nernst equation [14]. Theoretically, the redox potential of $\cdot\text{OH}$ radical decreases from 2.63 to 2.15 when pH value increases from 3 to 11 (Eqs. (7)) [15]. Therefore, with the increase of initial pH value, the removal rate of SPY gradually decreases.



$$E^0 = E^0_{\cdot\text{OH}/\text{H}_2\text{O}} - 0.059\text{pH} \quad (7)$$

4. Effect of Initial PDS Concentration and FMBO Dosage on SPY Degradation

The effects of initial dosage of PDS and FMBO on the removal

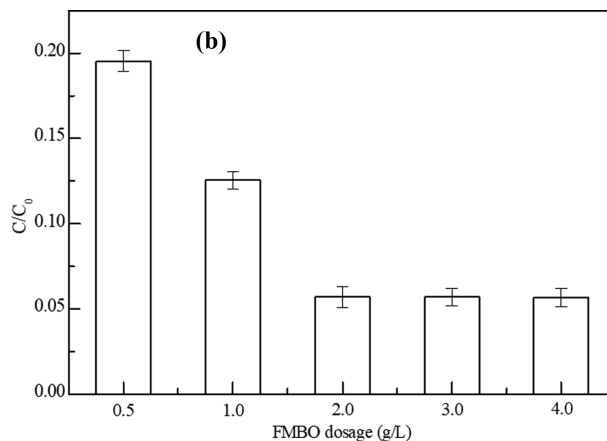
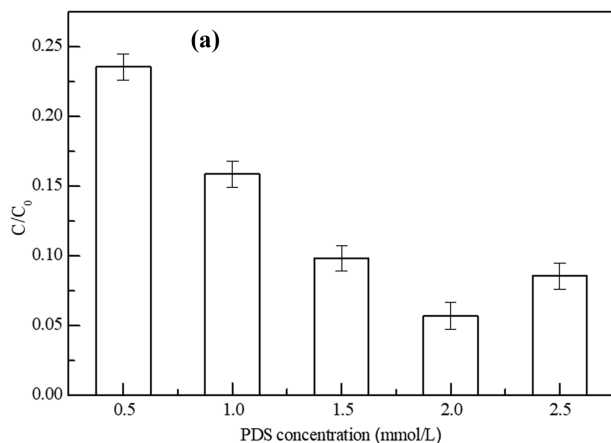


Fig. 4. Effect of (a) initial PDS concentration and (b) initial FMBO dosage on SPY degradation by FMBO/PDS.

of SPY at initial pH 4.0 were studied respectively. The results are shown in Fig. 4. The concentrations of SPY, PDS and FMBO were 10 mg/L, 0.5–2.5 mmol/L and 0.5–4.0 g/L, respectively. As can be seen in Fig. 4(a), when the initial concentration of PDS increased from 0.5 mmol/L to 2.0 mmol/L, the degradation ratio of SPY increased from 76.4% to 94.4% after 60 min of reaction. However, when the initial concentration of PDS increased to 2.5 mmol/L, the degradation ratio of SPY decreased to 91.4%. When the initial concentration of PDS was in the range of 0.5–2.0 mmol/L, with the increase of PDS concentration, the $\text{SO}_4^{\cdot-}$ free radical activated by FMBO in the solution also gradually increased, which increased the degradation ratio of SPY. However, when the initial concentration of PDS was in the range of 2.0–2.5 mmol/L, there was a large number of $\text{SO}_4^{\cdot-}$ free radicals in the solution. $\text{SO}_4^{\cdot-}$ free radicals will react with each other and be quenched under acidic conditions, resulting in low utilization of $\text{SO}_4^{\cdot-}$ free radicals (Eq. (8)) [16]. In addition, $\text{SO}_4^{\cdot-}$ radical ($E^0=2.6$) will also react with $\text{S}_2\text{O}_8^{2-}$ ($E^0=2.0$) (Eq. (9)), consuming $\text{SO}_4^{\cdot-}$ radical generated in the system, but the reaction rate is relatively slow, so the degradation efficiency of SPY does not decrease significantly [17]. As reported by Ghanbari and others, this can be associated with the $\text{SO}_4^{\cdot-}$ radicals scavenging by the Fe^{2+} (Eq. (10)) gathered in the reactor [18].



The effect of the initial dosage of FMBO on the removal of SPY is shown in Fig. 4(b). When the dosage of FMBO increased continuously, the degradation ratio of SPY increased gradually. When the dosage of FMBO was less than 2.0 g/L, the degradation ratio of SPY increased significantly. As shown in Eqs. (3), (4), Fe and Mn ions in FMBO will react with PDS to generate $\text{SO}_4^{\cdot-}$ and $\bullet\text{OH}$ radicals, resulting in the degradation of SPY. When the dosage of FMBO reached 3.0 g/L and 4.0 g/L, the degradation of SPY did not increase; the reason may be that excessive $\text{SO}_4^{\cdot-}$ and $\bullet\text{OH}$ radicals, will react with Me^{n+} according to Eqs. (11), (12), resulting in the decrease of the concentration of the two radicals, so that the oxidation rate of SPY will not increase [19,20].



5. Identification of Free Radicals in FMBO/PDS System

$\text{SO}_4^{\cdot-}$ and $\bullet\text{OH}$ free radicals are generally generated in the system of transition metal activated PDS to remove organic pollutants [21]. Therefore, this paper verifies the types of free radicals that play a major role in the degradation of SPY in the system of FMBO activated PDS by adding ethanol (EtOH) and tert butyl alcohol (TBA) as free radical capture agents. EtOH is mainly used to capture $\text{SO}_4^{\cdot-}$ and $\bullet\text{OH}$ radicals, and the reaction rate constants of EtOH and $\bullet\text{OH}$ are similar and rapid, $k_{\text{OH}}=1.2 \times 10^9$ – 2.8×10^9 L/(mol·s), $k_{\text{SO}_4^{\cdot-}}=1.6 \times 10^7$ – 7.7×10^9 L/(mol·s). TBA is mainly used to capture $\bullet\text{OH}$ radical, mainly because TBA and $\bullet\text{OH}$ radical ($k_{\text{OH}}=3.8 \times 10^8$ – 7.6×10^8 L/(mol·s)) are much higher than that of $\text{SO}_4^{\cdot-}$ radical ($k_{\text{SO}_4^{\cdot-}}=4.0 \times 10^5$ – 9.1×10^5 L/(mol·s)) [21].

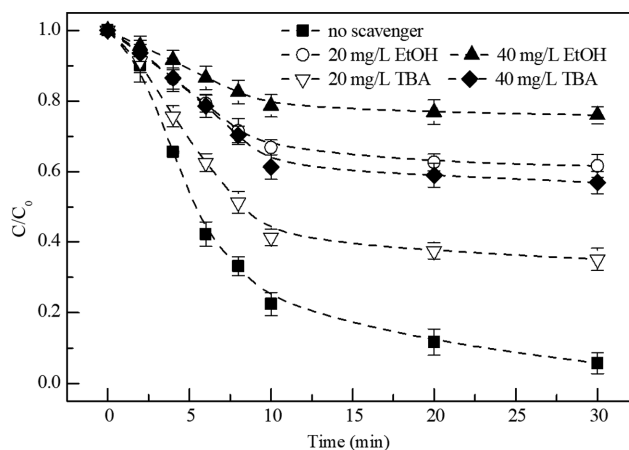


Fig. 5. Effect of radical scavengers on the degradation of SPY.

The effect of adding capture agent on the removal efficiency of SPY is shown in Fig. 5. When EtOH and TBA are added, the removal rate of SPY decreases, and when the concentration of capture agent increases, the removal rate of SPY also decreases. After 30 min of reaction without capture agent added, the removal rate of SPY was 94.4%, while 20 mg/L EtOH and TBA were added, the degradation ratios of SPY were 38.4% and 64.9%, respectively. When the concentration of EtOH and TBA increased to 40 mg/L, the degradation ratio of SPY decreased to 24.0% and 43.1%, respectively. The results show that the inhibition effect of EtOH on the degradation of SPY is higher than that of TBA, which shows that $\text{SO}_4^{\cdot-}$ and $\bullet\text{OH}$ free radicals contribute to the degradation of SPY; with the increase of the concentration of capture agent, the inhibition ratio of TBA is higher than that of EtOH. Instead, $\bullet\text{OH}$ radical plays a major role in the degradation of SPY.

The intensity of free radicals generated by FMBO activated PDS under different pH conditions (pH=4.0, 5.0, 6.0, 7.0 and 8.0) was further verified by EPR analysis. The results are shown in Fig. 6. Because the free radicals generated in FMBO/PDS system are unstable, especially $\text{SO}_4^{\cdot-}$ free radicals, which are not easy to be detected directly, DMPO was selected as the capture agent, and DMPO will form products DMPO- SO_4 and DMPO-OH with $\text{SO}_4^{\cdot-}$ and $\bullet\text{OH}$. As shown in Fig. 6, the four DMPO-OH characteristic peaks (intensity ratio 1:2:2:1) are particularly obvious, and when the pH value rises, the intensity of characteristic peak decreases continuously. In addition, although the characteristic peak of DMPO- SO_4 is not obvious under different pH conditions, it can also be clearly observed in the figure, and the intensity decreases gradually with the increase of pH. This is consistent with the detection results of free radicals in FeS_2/PS system by Fang et al. [22].

6. Insights into the Mechanism of Degradation of SPY by FMBO/PDS System

Under the good synergistic effect between Fe and Mn ions in catalyst FMBO, the activation effect of PDS is significantly improved, so as to enhance the degradation effect of SPY in aqueous environment. Through experimental observation, it was found that the degradation pathway of SPY activated by FMBO is as follows: first, $\text{Fe}^{2+}/\text{Mn}^{2+}$ catalyzes PDS to generate $\text{SO}_4^{\cdot-}$ (Eqs. (3), (4)). Second, $\text{SO}_4^{\cdot-}$ may undergo hydrolysis reaction or react with OH^-

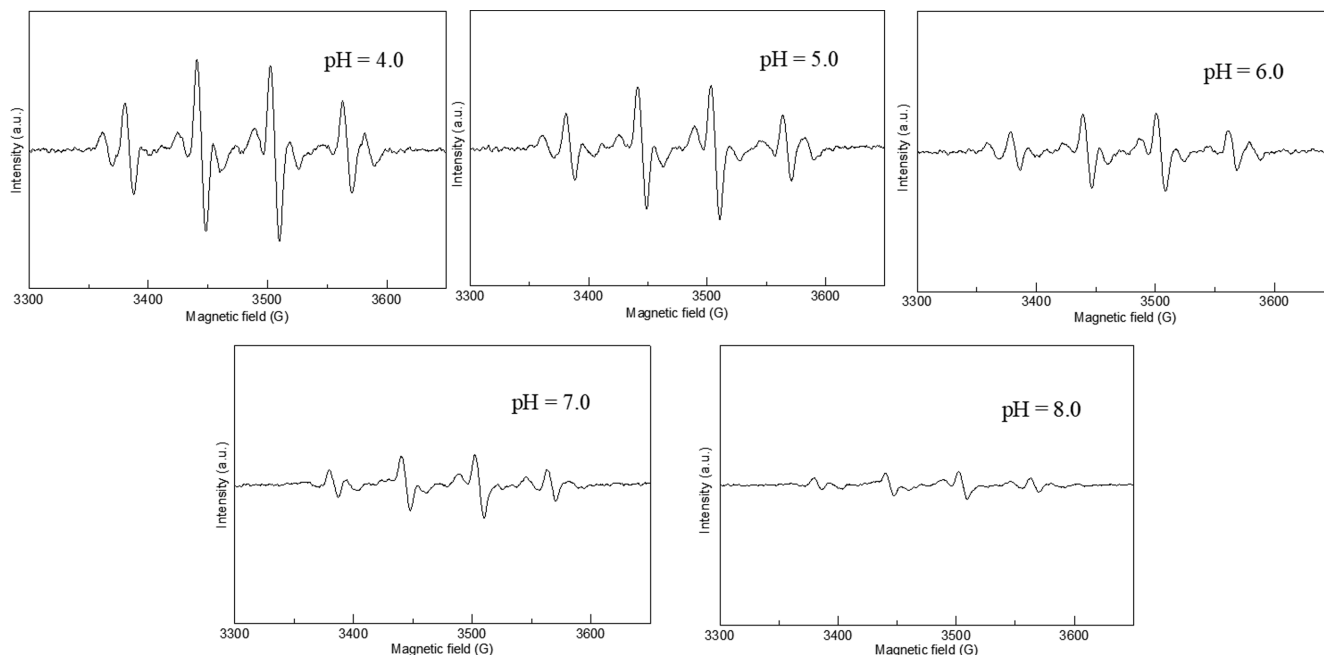


Fig. 6. The EPR spectra of FMBO collected at different pH values.

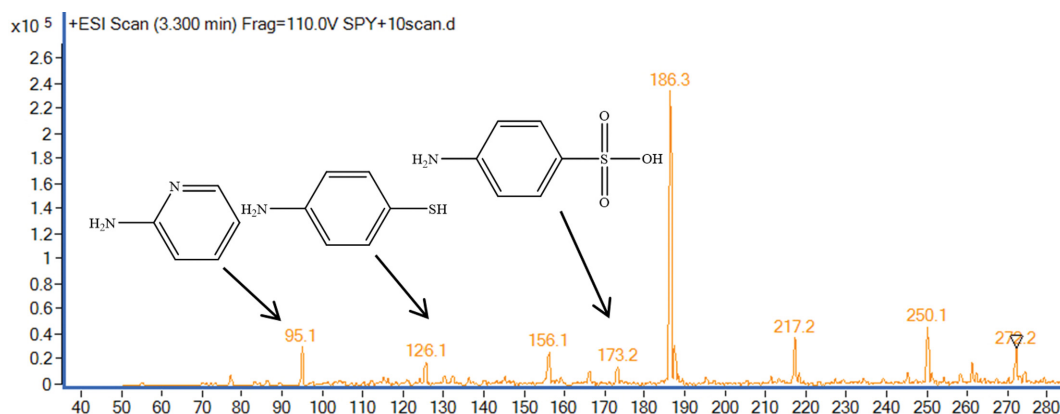


Fig. 7. Total ion chromatograph (TIC) of degradation intermediates of SPY detected by LC/MS.

in the system to form $\bullet\text{OH}$ (Eqs. (5), (6)). After that, SPY would be attacked by $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ and generate small molecular organics (Eqs. (13), (14)). Then, similar to the Fenton mechanism of FMBO catalysis, the presence of Mn ions can improve the catalytic capacity of the system, facilitate the conversion of Fe^{3+} to Fe^{2+} , and reduce the catalyst loss caused by precipitation (Eq. (10)). Therefore, in FMBO/PDS System, the cyclic reaction between $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$ enhances the electron transfer between FMBO and PDS, and promotes the generation of more $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ in the system, so as to improve the degradation efficiency of SPY.



The degradation intermediate product of SPY produced by free radical action in FMBO/PDS System was investigated, which was identified the intermediate product of SPY by LC/MS (as shown

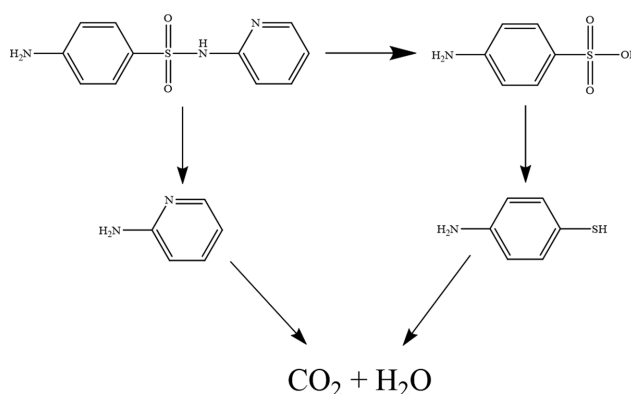


Fig. 8. Proposed reaction pathways of SPY in the FMBO/PDS system.

in Fig. 7), and its degradation pathway deduced (as shown in Fig. 8).

According to the results of LC/MS spectrum, there are three

main intermediates of degradation of SPY: 2-aminopyridine, 4-aminobenzene sulfonic acid and 4-aminophenylthiophenol. In FMBO/PDS System, the degradation process of SPY is roughly three steps. First, different sites on SPY react with active radicals dominated by $\bullet\text{OH}$ to form hydroxylated derivatives. Second, as shown in Fig. 8, $\bullet\text{OH}$ attacks the sulfonyl group connected to the benzene ring, breaking the S-N bond to form the intermediate products, 2-aminopyridine ($m/z=95$) and 4-aminobenzenesulfonic acid ($m/z=173$). Finally, due to the strong oxidation of FMBO and the activity of PDS, sufficient $\bullet\text{OH}$ are generated to continue the oxidation of the intermediate product, so that the sulfonyl group on 4-aminobenzene sulfonic acid is oxidized to thiophenol group to form the intermediate product 4-aminobenzene thiophenol ($m/z=126$) [23].

CONCLUSIONS

FMBO was used to activate PDS to generate $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$, and a new advanced oxidation technology was established to degrade SPY efficiently. The results show that initial pH, SPY concentration, PDS concentration and FMBO dosage can affect the removal efficiency of SPY significantly. The degradation mechanism of SPY by FMBO/PDS oxidation technology was verified by free radical capture experiment and EPR analysis of the strength of free radicals generated in the solution. The results of this study are of great significance for the further design and use of FMBO for advanced oxidation reaction. This study also shows the feasibility for FMBO as a promising SPY degradation material, and FMBO also has potential high degradation efficiency for SPY removal in actual wastewater.

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DATA AVAILABILITY

All data generated or analyzed during this study are included in this published article.

DECLARATIONS

Conflict of interest The authors declare no competing interests.

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