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Research Paper

Removal of Sulfamethazine by a Fe^0-$Na_2S_2O_8$ System

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Abstract. This study investigates the rapid degradation of sulfamethazine (SM2) in water by adding micron-sized zero-valent iron (Fe^0) to catalyze sodium persulfate (PS) for generating substantial sulfate radicals ($SO_4\bullet^-$). The effects of ZVI particle size, Fe^0 dosage, PS concentration, initial pH, and reaction temperature on SM2 degradation efficiency were examined. Results indicated that within a certain range, the degradation efficiency of SM2 increased with smaller ZVI particle size, higher Fe^0 dosage, and increased PS concentration. In the Fe^0-PS system, complete degradation of SM2 was achieved under conditions of Fe^0 dosage = 0.25 g/L, PS concentration = 7.5 mmol/L, and SM2 concentration = 50 µmol/L. The initial pH and reaction temperature significantly influenced SM2 degradation, with optimal performance observed at pH = 5 and a temperature of 45°C. The Fe^0-PS system not only effectively removed SM2 but also demonstrated good removal efficiency for Chemical Oxygen Demand (COD).

Keywords: *water; advanced oxidation; zero-valent iron; sulfamethazine*

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1 Introduction

Antibiotics are widely used in animal disease treatment. They are continuously and extensively added to feed to prevent diseases and promote animal growth [1]. Among them, sulfonamide antibiotics, known for their broad antibacterial spectrum, stability, and ease of use, are extensively applied in the breeding industry [2]. Antibiotics cannot be completely absorbed by animals; the unabsorbed portion is excreted in feces and enters the environment. These pharmaceuticals have been detected in surface water and groundwater. The increasing use of antibiotics can lead to enhanced bacterial drug resistance, which may spread among bacteria and even to humans, posing a potential threat to human safety [3]. Antibiotics present varying degrees of ecological risk to different aquatic organisms. Research indicates that antibiotics generally pose a low risk to invertebrates, a moderate to high risk to algae, and a moderate risk to fish. Besides, antibiotic residues in the environment endanger microbial communities, prompting the development and spread of Antibiotic Resistance Genes (ARGs). The emergence and dissemination of ARGs represent a potential threat to human health. Urban domestic wastewater collects substantial amounts of ARGs. Even after treatment in wastewater treatment plants, the effluent may still contain varying levels of ARGs. When discharged into the environment, these pose a significant ecological risk to microbial communities. Moreover, due to the continuous and extensive use and discharge of antibiotics, their constant input into the environment creates a state of "pseudo-persistence." As a result, they are frequently detected in various environmental media, such as wastewater treatment plants, rivers, soil, and groundwater.

Current methods for antibiotic removal primarily include filtration, activated carbon adsorption, chemical oxidation, membrane separation, and biological treatment. Among these, filtration, activated carbon adsorption, and membrane separation do not achieve complete degradation of antibiotics in wastewater but merely transfer them. Biological treatment can be effective against antibiotics but requires long processing times, making it challenging to address the increasing pollution caused by antibiotics in the environment. In recent years, advanced oxidation processes (AOPs) based on sulfate radicals ($SO_4{\bullet}^-$) have gained increasing attention. Their high efficiency and selectivity in degrading refractory organic pollutants have developed them into a new technology for treating difficult-to-degrade organic wastewater [4]. Persulfate (PS) can be activated by various methods, including photocatalysis, thermal activation, and transition metal ion catalysis [5-7]. Compared to the high external energy requirements of photocatalysis and the complexity of heating systems in thermal activation, using transition metal ions as catalysts shows good pollutant degradation efficiency. However, some metal ions can cause secondary pollution. While the reaction between metal ions (e.g., Fe^{2+}) and persulfate to generate $SO_4{\bullet}^-$ is rapid, it can conversely lower the utilization efficiency of $SO_4{\bullet}^-$ [8]. Issues such as short catalyst lifespan, low utilization rate, high treatment cost, and long processing time hinder the persistent, efficient, and rapid removal of sulfonamide antibiotics and COD from water.

Utilizing a zero-valent iron (ZVI) - persulfate (PS) system can achieve rapid and efficient removal of organic pollutants from water without causing negative environmental impacts. This study investigates the degradation efficiency of sulfamethazine (SM2) in water by different systems and oxidants and explores the main influencing factors during the reaction process.

2 Experimental Section

2.1 Reagents and Instruments

Sodium persulfate ($Na_2S_2O_8$, PS), methanol (CH_4O), and acetic acid (CH_3COOH) were chromatographic grade. Calcium peroxide (CaO_2, CP) was chemical pure. Hydrogen peroxide (H_2O_2), peracetic acid ($C_2H_4O_3$, PAA), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), and sodium sulfite (Na_2SO_3) were analytical grade. Sulfamethazine (SM2, $C_{12}H_{14}N_4O_2S$) was used.

2.2 Experimental Methods

At room temperature, a certain amount of water was injected into a 250 mL conical flask. Simultaneously, specific amounts of Fe^0 and PS were added. The conical flask was placed in a water bath shaker for mixing. Finally, a certain amount of SM2 was added to bring the total solution volume to 100 mL, and timing started. Samples were taken at regular intervals, rapidly quenched with an excess of quenching agent Na_2SO_3 to terminate the reaction. The quenched samples were filtered through a 0.22 µm membrane, and the filtrate was collected for subsequent analysis.

2.3 Analytical Methods

An Agilent 1260 high-performance liquid chromatography (HPLC) system was used for detection, equipped with a C18 column (4.6 mm × 150 mm, 5 µm). Chromatographic conditions: column temperature 25°C; mobile phase: methanol and 0.1% (w/w) acetic acid aqueous solution in a volume ratio of 40:60; injection volume 40 µL; detection wavelength 262 nm. COD and NH_3-N content were determined using standard national methods [9].

3 Results and Discussion

3.1 Degradation of SM2 in Different Systems

The degradation trend of SM2 in water under different systems [pH=5, Fe^0 mass concentration 0.25 g/L, PS concentration 7.5 mmol/L, SM2 concentration 50 µmol/L] was studied; results are shown in Figure 1a.

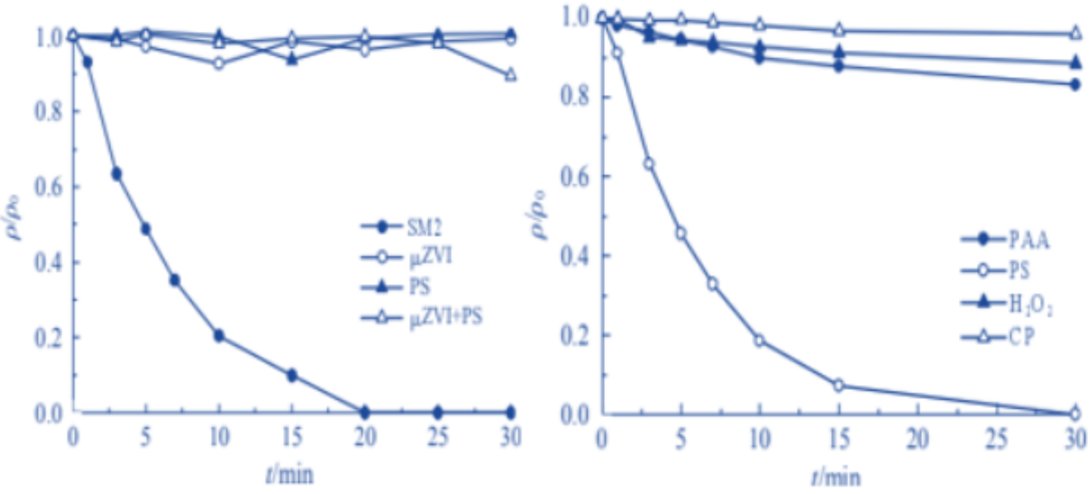

Figure 1 Degradation of SM2 in different systems (a); Degradation of SM2 under different oxidant conditions (b)

From Figure 1a, without any catalyst, the degradation rate of SM2 alone in water within 30 minutes was 0.8%, indicating very low hydrolysis of SM2 in the water body. When Fe^0 was added alone, the SM2 degradation rate fluctuated, but the overall degradation tended towards zero. The main reason is that Fe^0 itself has adsorption capacity; it adsorbed SM2 during the reaction, reaching adsorption-desorption equilibrium as the reaction proceeded. Therefore, the Fe^0-alone system showed no significant degradation effect on SM2 in water. In the PS-alone system, the degradation rate of SM2 in water within 30 minutes was 10.5%, indicating that PS has some degradation effect on SM2. This is likely because both $SO_4{\bullet}^-$ and hydroxyl radicals (•OH) participate in SM2 degradation during the reaction [10]:

$$SO_4^{\bullet-} + OH^- \rightarrow HO^{\cdot} + SO_4^{2-} \tag{1}$$

$$SO_4^{\bullet-} + H_2O \rightarrow HO^{\cdot} + SO_4^{2-} + H^+ \tag{2}$$

However, the degradation effect of PS alone on SM2 is relatively small, primarily because the amount of $SO_4{\bullet}^-$ generated by PS itself is low. Increasing the PS dose or adding a catalyst to activate and produce large amounts of $SO_4{\bullet}^-$ is necessary for rapid removal. In contrast, under the Fe^0-PS system, the degradation rate of SM2 reached 100% within 30 minutes. This is because, on one hand, Fe^0 reacts with PS to continuously release Fe^{2+}, effectively activating PS to generate large amounts of $SO_4{\bullet}^-$, promoting SM2 degradation:

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \tag{3}$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4{\bullet}^- + 2SO_4^{2-} + Fe^{3+} \tag{4}$$

On the other hand, Fe^0 can promote the reduction of Fe^{3+} back to Fe^{2+}, continuously catalyzing PS to produce $SO_4{\bullet}^-$:

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \tag{5}$$

Thus achieving rapid oxidative degradation of SM2 [11].

3.2 Degradation of SM2 under Different Oxidants

The effects of different oxidants on SM2 degradation in water were compared; results are shown in Figure 2. Experimental conditions: pH=5, Fe^0 mass concentration 0.25 g/L, concentrations of PS, H_2O_2, CP, PAA all at 7.5 mmol/L, SM2 concentration 50 μmol/L.

From Figure 1b, with the same concentration of PS, H_2O_2, CP, and PAA solutions, the degradation rate of SM2 was relatively slow under the Fe^0/H_2O_2 system within 30 minutes, with a degradation rate of 11.5%. This might be because the soluble iron slowly and continuously dissolved from Fe^0 reacted with H_2O_2, and the generated •OH formed inactive iron hydroxide precipitates, slowing down the SM2 degradation rate. Compared to the Fe^0-H_2O_2 system, the degradation rate of SM2 under the Fe^0-CP system within 30 minutes was even slower, with a degradation rate of only 4.9%. This is mainly because CP dissolution increases the solution pH, resulting in lower dissolved iron levels. Additionally, the increasing H_2O_2 content generated during CP dissolution could quench •OH in the solution:

$$\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O \tag{6}$$

thus slowing the reaction and resulting in low SM2 degradation efficiency.

Compared to the Fe^0-H_2O_2 and Fe^0-CP systems, the degradation rate of SM2 under the PAA system within 30 minutes was 16.9%, showing some improvement but still relatively low. The main reason is that PAA addition can lower the solution pH to some extent, accelerating Fe^0 dissolution and promoting SM2 degradation. However, PAA itself contains a certain amount of H_2O_2. As the reaction proceeds, soluble iron in the solution is rapidly consumed, forming inactive iron hydroxide precipitates, leading to still low degradation efficiency.

Compared to the above oxidants, under the same concentration conditions, the degradation rate of SM2 in the Fe^0-PS system reached 100% within 30 minutes. The main reason is that under the Fe^0-PS system, Fe^0 reacts with PS to continuously release Fe^{2+}, effectively activating PS to produce large amounts of $SO_4\bullet^-$, promoting SM2 degradation, achieving rapid and efficient pollutant removal.

3.3 Effect of Different Iron Particle Sizes

The effect of different iron particle sizes on SM2 degradation in water was studied; results are shown in Figure 3. Experimental conditions: pH=5, Fe^0 mass concentration 0.25 g/L, PS concentration 7.5 mmol/L, SM2 concentration 50 µmol/L.

From Figure 2a, when nano zero-valent iron powder (nZVI), Fe^0, and iron filings were added to water, the degradation rates of SM2 within 30 minutes were 85%, 100%, and 39%, respectively. This indicates that iron particle size significantly affects SM2 degradation. As the particle size decreased to micrometer scale, the SM2 degradation rate accelerated, and the degradation efficiency improved. However, when the particle size reached nanometer scale, the SM2 degradation rate decreased from 100% to 85%. Smaller particle size inhibited SM2 degradation. The main reason is that nano-sized iron powder has a small particle size, increasing the proportion of surface atoms to total atoms, thus increasing the specific surface area and surface energy of ZVI, which can effectively activate PS [12]. However, when nZVI particle size is too small, it tends to agglomerate and easily forms an oxide layer, inhibiting the dissolution of soluble iron, slowing down the reaction rate with PS, and thus reducing the SM2 degradation rate. Therefore, adding Fe^0 showed the best effect, and Fe^0 was selected as the catalyst.

3.4 Effects of Fe^0 and PS Dosage

Under conditions of pH=5 and SM2 concentration of 50 µmol/L, the effect of Fe^0 dosage on SM2 degradation is shown in Figure 2b (PS concentration 7.5 mmol/L). The effect of PS dosage on SM2 degradation is shown in Figure 5 (Fe^0 mass concentration 0.25 g/L).

The dosage of Fe^0 and PS significantly affects SM2 degradation. From Figure 2b, as the Fe^0 dosage increased from 0.10 g/L to 0.25 g/L, the SM2 degradation rate within 20 minutes increased from 87.1% to 100%. Appropriately increasing the Fe^0 dosage can elevate the Fe^{2+} content in the solution, accelerating SM2 degradation. However, when the Fe^0 dosage increased from 0.25 g/L to 0.50 g/L, the SM2 degradation rate within 30 minutes decreased from 100% to 76.8%. The main reason is that excessive Fe^0 leads to excessively high Fe^{2+} content in the solution, and excess Fe^{2+} consumes $SO_4\bullet^-$, reducing the SM2 degradation rate:

$$SO_4\bullet^- + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \tag{7}$$

Thus, within a certain range, the Fe^0 dosage is proportional to the SM2 degradation rate; increasing Fe^0 dosage accelerates SM2 degradation. However, excessively high dosage reduces the degradation effect. Therefore, 0.25 g/L was selected as the optimal Fe^0 dosage for subsequent experiments.

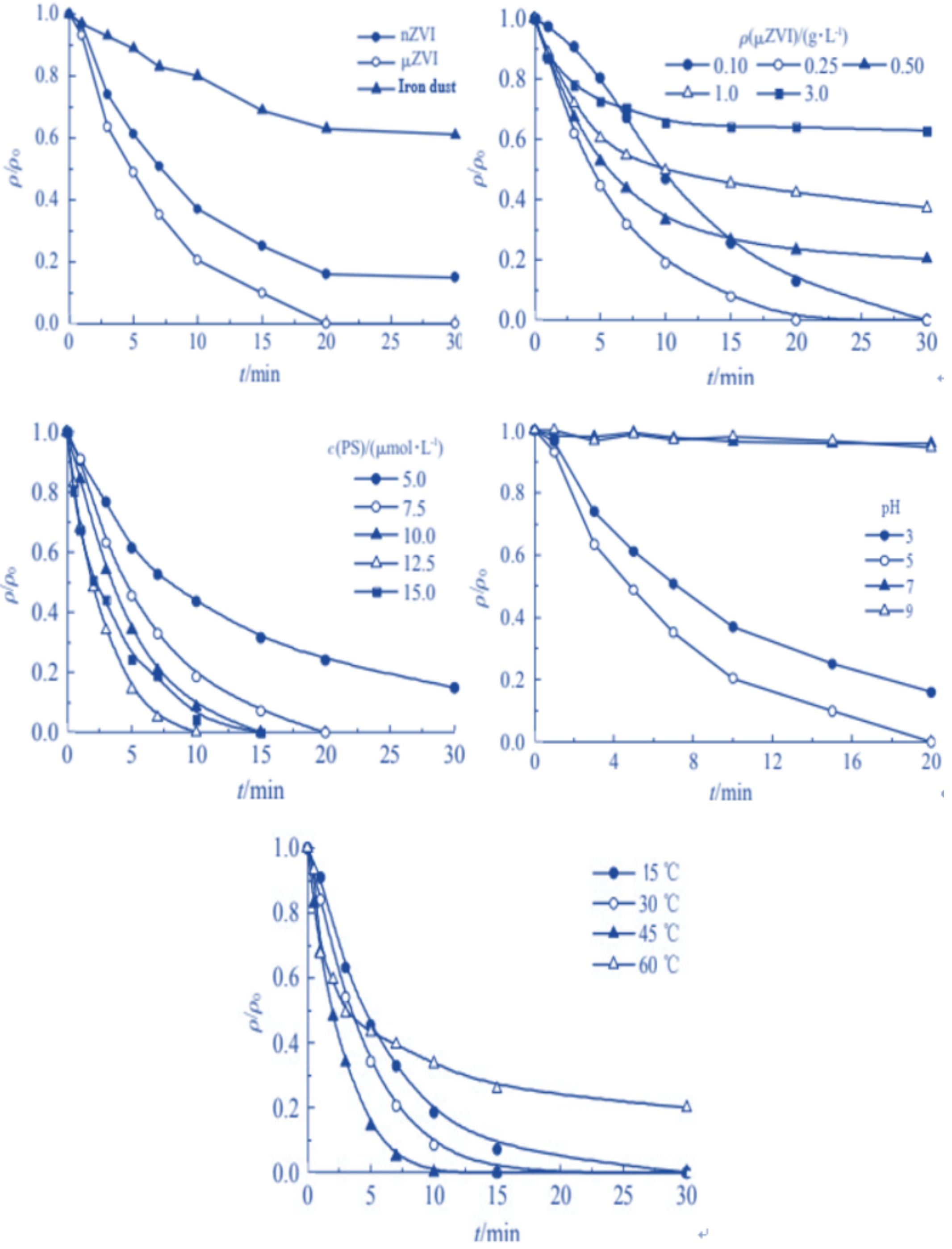

Figure 2 Effect of zero-valent iron with different particle sizes (a); Fe^0 dosage (b); PS dosage (c); initial pH (d); temperature(e) on the degradation of SM2 in the ZVI-PS system

From Figure 2c, as the PS dosage increased from 5 mmol/L to 10 mmol/L, the SM2 degradation rate increased from 85% to 100%. This shows that increasing PS dosage increases the $SO_4\bullet^-$ content in the solution, accelerating the SM2 degradation rate (Equation 1). However, when the PS dosage increased from 10 mmol/L to 15 mmol/L, the SM2 degradation rate showed a slowing trend. One reason is that excess $SO_4\bullet^-$ can quench itself and $S_2O_8^{2-}$:

$$SO_4^{\bullet -} + SO_4^{\bullet -} \rightarrow S_2O_8^{2-} \tag{8}$$

$$SO_4^{\bullet -} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet -} \tag{9}$$

Another reason is that excess PS can rapidly oxidize Fe^{2+} to Fe^{3+}, and the generated Fe^{3+} attaches to the Fe^0 surface, slowing the dissolution of Fe^{2+}, reducing PS activation efficiency, and thus slowing SM2 degradation [13]. Considering these factors, 7.5 mmol/L was selected as the optimal PS dosage for subsequent experiments.

3.5 Effect of Initial pH

The effect of initial solution pH on SM2 degradation in the Fe^0-PS system in water was studied; results are shown in Figure 2d. Experimental conditions: Fe^0 mass concentration 0.25 g/L, PS concentration 7.5 mmol/L, SM2 concentration 50 µmol/L.

From Figure 2d, at initial pH values of 3, 5, 7, and 9, the SM2 degradation rates within 30 minutes were 84%, 100%, 4.2%, and 5.6%, respectively. Under acidic conditions, H^+ can promote the rapid formation of Fe^{2+} from Fe^0 and also catalyze PS, accelerating $SO_4^{\bullet -}$ release, facilitating SM2 degradation:

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{10}$$

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \tag{11}$$

$$HS_2O_8^- \rightarrow SO_4^{\bullet -} + SO_4^{2-} + H^+ \tag{12}$$

However, at initial pH=3, the SM2 degradation rate decreased to 84% within 30 minutes. The main reason might be that while acidic conditions favor $SO_4^{\bullet -}$ generation, excess $SO_4^{\bullet -}$ can quench itself and $S_2O_8^{2-}$ (Equations 5, 6), thus reducing the SM2 degradation rate [14]. Under alkaline conditions, the SM2 degradation rate was only 5.6%. This is primarily because Fe^{2+} and Fe^{3+} are less soluble at higher pH, so iron ions quickly form iron hydroxide and precipitate out of the reaction system, slowing the reaction rate and reducing SM2 degradation efficiency.

3.6 Effect of Temperature

The effect of temperature on SM2 degradation in the Fe^0-PS system was studied; results are shown in Figure 2e. Experimental conditions: pH=5, Fe^0 mass concentration 0.25 g/L, PS concentration 7.5 mmol/L, SM2 concentration 50 µmol/L.

From Figure 2e, as the temperature increased from room temperature to 45°C, the SM2 degradation rate significantly improved. Thus, increasing temperature promotes SM2 degradation to some extent. One reason is that elevated temperature can activate PS, generating large amounts of $SO_4^{\bullet -}$, thereby accelerating SM2 degradation [15]:

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{\bullet -} \tag{13}$$

Another reason might be that higher temperature promotes the hydrolysis of SM2 itself, achieving accelerated pollutant removal. However, when the temperature increased from 45°C to 60°C, the SM2 degradation rate decreased from 100% to 79.9%. The reason is that increasing temperature accelerates the formation of iron hydroxide precipitates, slowing the reaction rate and reducing SM2 degradation [16]. Therefore, temperature significantly impacts the Fe^0-PS system and is a major factor influencing the catalytic generation of ROS and promoting SM2 hydrolysis.

3.7 Removal of COD and NH_3-N

Addressing the high levels of COD and NH_3-N in water, besides studying the degradation of antibiotics by the Fe^0-PS system, its removal effects on COD and NH_3-N were also investigated; results are shown in Figure 8. Experimental conditions: pH=5, Fe^0 mass concentration 0.25 g/L, SM2 concentration 50 µmol/L.

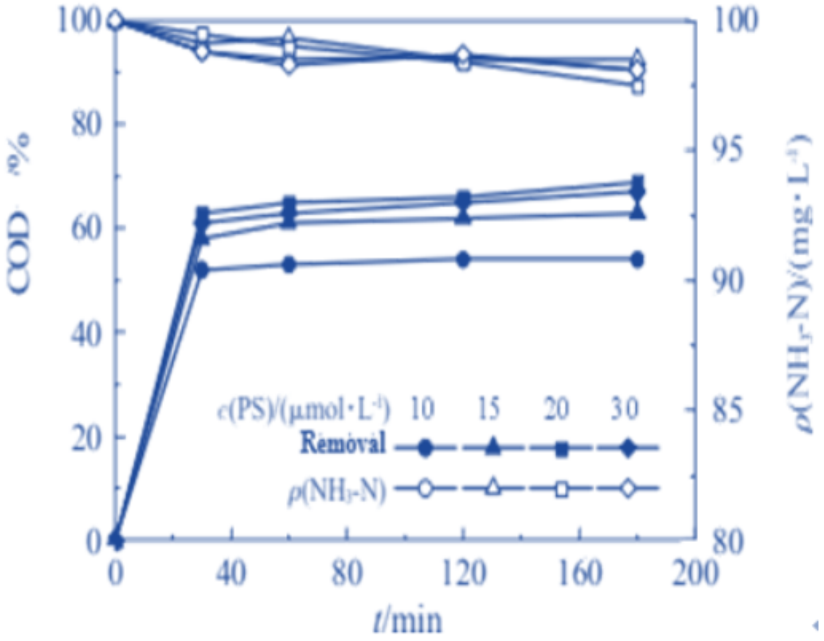

Figure 3 Removal of COD and NH3-N by Fe^0-PS system

From Figure 3, as the PS concentration increased from 10 mmol/L to 20 mmol/L, the COD removal rate increased from 54% to 69%. However, when the PS concentration increased from 20 mmol/L to 30 mmol/L, the COD removal rate decreased from 69% to 67%. The main reason is that excessively high PS content leads to consumption of $SO_4{\bullet}^-$, reducing COD removal efficiency. The PS content had little effect on NH_3-N removal in the Fe^0-PS system, and the effect was minimal. When the PS concentration increased from 10 mmol/L to 30 mmol/L, the highest NH_3-N removal rate was only around 2.5%.

4 Conclusion

Through comparison of different systems and oxidants, the Fe^0-PS system effectively degraded SM2 in the water matrix while improving the utilization efficiency of $SO_4{\bullet}^-$ to some extent.

The degradation effect of SM2 was proportional to the dosage of Fe^0 and PS within a certain range; excessive Fe^0 inhibited SM2 degradation. The optimal degradation effect was observed at pH=5; both strongly acidic and alkaline conditions were unfavorable for the reaction.

Excessively large or small ZVI particle sizes were detrimental to SM2 degradation. SM2 degradation was proportional to temperature to some extent, with optimal performance at 45°C; temperatures too high or too low were unfavorable for SM2 degradation.

The Fe^0-PS system not only degraded SM2 in water but also exhibited certain COD removal efficiency. However, it had no significant effect on NH_3-N removal.

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