

# Article High-Efficient Elimination of Spiramycin by Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch via Heterogeneous Photo-Fenton Oxidation at Neutral pH

Jiali Yi<sup>1</sup>, Junjun Xu<sup>1,\*</sup>, Jiatong Liu<sup>1</sup>, Yue Zheng<sup>2</sup> and Qiong Wang<sup>1</sup>



<sup>2</sup> School of Chemistry and Environmental Engineering, Liaoning University of Technology, Jinzhou 121001, China

\* Correspondence: xujunjun@bhu.edu.cn; Tel.: +86-152-4164-3885

Abstract: Spiramycin (SPM), a widely employed antibiotic in both clinical therapy and the livestock industry, poses significant challenges in terms of safe and efficacious management. A heterogeneous photo-Fenton system, devised using Schwertmannite (Sch), can effectively degrade contaminants. However, it is accompanied by a relatively low conversion efficiency of  $\equiv$ Fe<sup>3+</sup>/ $\equiv$ Fe<sup>2+</sup> and a significant iron loss. In this study, a catalyst featuring Fe<sub>3</sub>O<sub>4</sub> and ZSM-5 molecular sieve-modified Sch (Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch) was devised to enhance the catalytic activity and stability. The findings revealed that Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch exhibited exceptional catalytic activity, with the reaction first-order kinetic exceeding that of pure Sch. The active species including  $\cdot$ OH, h<sup>+</sup>, e<sup>-</sup>,  $\cdot$ O<sub>2</sub><sup>-</sup> and SO<sub>4</sub><sup>+-</sup> were identified in the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system. The enhanced catalytic activity of Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch could be ascribed to the effective conversion of  $\equiv$ Fe<sup>3+</sup>/ $\equiv$ Fe<sup>2+</sup>. The photogenerated electrons within Fe<sub>3</sub>O<sub>4</sub> were transported to Sch via ZSM-5, which effectually reduced  $\equiv$ Fe<sup>3+</sup>/ $\equiv$ Fe<sup>2</sup>. Moreover, Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch demonstrated outstanding stability; even after six cycles, the degradation efficiency of SPM remained above 86.50%, and the leaching quantity of Fe remained below 0.24 mg/L. This research not only develops an excellent catalyst for the safe treatment of SPM but also proffers innovative perspectives for the future design of efficient iron-based catalysts.

Keywords: schwertmannite; Fe<sub>3</sub>O<sub>4</sub>; ZSM-5; photocatalytic mechanism; stability

# 1. Introduction

Spiramycin (SPM), a broad-spectrum macrolide antibiotic, is extensively employed in the livestock industry and clinical hospital treatments [1,2]. Owing to the incomplete absorption of SPM within the animal's intestinal tract, a substantial quantity of unmetabolized SPM and its metabolites are excreted externally via urine and feces, subsequently entering urban wastewater treatment plants [3]. However, conventional wastewater treatment facilities cannot entirely remove antibiotics, leading to their eventual release into aquatic and terrestrial environments through treated wastewater and sewage sludge [4]. The continuous exposure to residual antibiotics in the environment can enhance bacterial antibiotic resistance, giving rise to multi-drug-resistant strains and even the emergence of superbugs [5]. This poses significant implications for ecosystems and human health. Consequently, the pollution and treatment of SPM in the environment have garnered considerable attention.

Advanced oxidation processes (AOPs) are widely employed in the treatment of organic pollutants in wastewater, utilizing highly oxidative reactive species (such as  $\cdot$ OH,  $\cdot$ OOH and  $O_2^{\cdot-}$ ) generated during the reaction process to effectively oxidize contaminants in water without selectivity, ultimately decomposing them into CO<sub>2</sub> and H<sub>2</sub>O [6]. Compared to traditional homogeneous Fenton processes (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>), heterogeneous Fenton using iron-based solid catalysts offers advantages such as an expanded pH range of applicability



Citation: Yi, J.; Xu, J.; Liu, J.; Zheng, Y.; Wang, Q. High-Efficient Elimination of Spiramycin by  $Fe_3O_4/ZSM$ -5/Sch via Heterogeneous Photo-Fenton Oxidation at Neutral pH. *Sustainability* **2023**, *15*, 12343. https://doi.org/10.3390/su151612343

Academic Editors: Qingjie Hou, Fenwu Liu and Yunxiao Li

Received: 29 June 2023 Revised: 3 August 2023 Accepted: 10 August 2023 Published: 14 August 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and the prevention of generating copious iron-containing sludge [7–9]. Within the heterogeneous Fenton process, the type of iron-based catalyst proves to be a crucial determinant of degradation efficiency.

Schwertmannite (Sch) is a sulfate mineral rich in iron and hydroxide, with a chemical formula of  $Fe_8O_8(OH)_{8-2x}(SO_4)_x \cdot nH_2O$  ( $1 \le x \le 1.75$ ) [10], primarily found in acidic mine waters and acid sulfate soils. As a heterogeneous Fenton catalyst, Sch possesses the ability to activate hydrogen peroxide ( $H_2O_2$ ) to generate hydroxyl radicals ( $\cdot OH$ ,  $E_0 = 2.83 \text{ eV}$ ) for pollutant degradation. Due to its ease of availability and low cost, it has been studied and applied in the degradation of water contaminants [11–13]. The conversion of  $Fe^{3+}$  to  $Fe^{2+}$  is a prerequisite for triggering Fenton reactions. However, as  $Fe^{3+}$  predominantly occupies the Sch surface, Sch-driven heterogeneous Fenton reactions typically experience extended induction periods [14], resulting in reduced catalytic efficiency. Therefore, enhancing catalytic activity by accelerating the conversion of  $Fe^{3+}/Fe^{2+}$  is of great significance. It has been reported that UV can rapidly initiate the redox reactions between  $Fe^{3+}$  and  $Fe^{2+}$ , decomposing  $H_2O_2$  to generate  $\cdot OH$  for pollutant degradation. In addition to constructing photo-driven heterogeneous Fenton processes, another direct approach is to modify Sch with the aid of other catalysts [15].

Magnetite (Fe<sub>3</sub>O<sub>4</sub>), readily obtainable from the natural environment, boasts a unique inverse spinel structure that facilitates electron transfer through the Fe<sub>3</sub>O<sub>4</sub> body itself, accelerating the redox reaction between  $\equiv$ Fe<sup>3+</sup> and  $\equiv$ Fe<sup>2+</sup>. Fe<sub>3</sub>O<sub>4</sub>, as a suitable co-composite catalyst, can enhance the catalytic activity of other iron oxides. However, following the composite formation of Fe<sub>3</sub>O<sub>4</sub>/Sch, agglomeration was still noticeable, and the surface area was not particularly expansive, merely 59.7 m<sup>2</sup>/g [16]. Another drawback of Fe<sub>3</sub>O<sub>4</sub>/Sch is that the iron leaching from the active components is high (2.7 mg/L), exceeding the discharge standard stipulated by the European Union (2 mg/L) [17].

Previous studies have reported that modifying catalysts with carriers can provide a structural framework for the active components of the catalyst, enabling their full distribution on the surface of the composite catalyst [7,18]. This exposes more active sites and simultaneously enhances the mechanical strength of the catalyst, which is beneficial for its stability. Compared to other carriers (clay, bentonite, etc.), synthetic zeolites, with their larger surface area, are more conducive to the adsorption of smaller organic molecules. This adsorption function is believed to be advantageous for the degradation of pollutants, thus offering extensive application prospects. 10-Membered oxygen ring zeolites possess the advantages of high hydrothermal stability, high coke resistance and high activity. Among the family of 10-Membered oxygen ring zeolites, MFI type (ZSM-5) zeolite is a microporous molecular sieve with a shape-selective high silica three-dimensional pore structure. Its unit cell composition is  $Na_nAl_nSi_{96-n}O_{192}$  ·16H<sub>2</sub>O (n  $\leq$  27), where n is the number of aluminum atoms in the unit cell. The ZSM-5 molecular sieve has a large surface area, which can effectively enhance the catalytic activity of the catalyst and boost its stability. For instance, Kasiri et al., using ZSM-5 as a carrier and loading it with Fe<sup>3+</sup>, synthesized the Fe-ZSM5 composite catalyst [19]. In the UV/Fe-ZSM5/ $H_2O_2$  system, under optimal conditions  $(21.4 \text{ mmol/L of } H_2O_2, 0.5 \text{ g/L of catalyst and pH 5}), 51.28\%$  of Acid Blue 74 could be degraded in 120 min, and the iron ion leaching was less than 0.3 mg/L. However, studies on simultaneously modifying Sch with  $Fe_3O_4$  and ZSM-5 have not yet been reported.

Thus, the objectives of this study are: (1) to fabricate a highly active catalyst using  $Fe_3O_4$  and ZSM-5-modified Sch, (2) to evaluate the catalytic activity of the  $Fe_3O_4/ZSM-5/Sch$  composite material through the degradation of SPM and explore the mechanism of catalytic activity enhancement and (3) to assess the recyclability and stability of  $Fe_3O_4/ZSM-5/Sch$  during repeated usage. The findings of this study can provide a novel eco-friendly material for the removal of SPM in water.

# 2. Materials and Methods

#### 2.1. Synthesis of the Catalysts

According to the method described in previous studies, Sch was synthesized in the laboratory using chemical methods [20]. Specifically, 11.12 g of FeSO<sub>4</sub>·7H<sub>2</sub>O was weighed and dissolved in 494 mL of deionized water under stirring until fully dissolved. Then, 6 mL of 30% (v/v) H<sub>2</sub>O<sub>2</sub> was added dropwise to the solution within 10 min under magnetic stirring. The resulting mixture was incubated at 180 rpm and 28 °C for 24 h, and the precipitate formed in the system was collected using a 0.45 µm microporous membrane filter. To remove soluble impurities from the precipitate, it was washed three times with 500 mL of acidic water (pH = 2.0) and 500 mL of deionized water, respectively. The collected precipitate was then freeze-dried for 24 h and stored for future use. The sample prepared in this manner was labeled as Sch.

The Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch catalyst was prepared by adding 1 g of Fe<sub>3</sub>O<sub>4</sub> and 6 g of ZSM-5 powder during the synthesis of Sch. In brief, 1.0 g of nano-Fe<sub>3</sub>O<sub>4</sub> was weighed and added to a conical flask containing 494 mL of acidified water (pH = 2.0). The mixture was sonicated for 10 min to obtain a suspension. Then, 11.12 g of FeSO<sub>4</sub>·7H<sub>2</sub>O was added to the suspension and stirred until fully dissolved. Subsequently, 6 g of an H-type ZSM-5 molecular sieve with a silicon-to-aluminum ratio of 110 was added, and the mixture was sonicated for an additional 3–5 min. The subsequent steps were the same as those of the method described earlier for synthesizing Sch. The resulting sample was labeled as Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch.

#### 2.2. Photocatalytic Activity Experiments

The catalyst (30 mg) was added into a 50 mL SPM solution with a concentration of 10 mg/L. After sonication for 2–3 min, the mixture was placed into a multi-channel photoreactor (PCX 50C Discover, Beijing Perfect light Technology Co., Ltd., Beijing, China) and irradiated with UV light (365 nm, 3 W). A given amount of H<sub>2</sub>O<sub>2</sub> (0.5 mmol/L) was added to start the reaction, and the temperature was maintained at  $25 \pm 3$  °C. At 0, 30, 60, 90, 150 and 180 min, 2 mL samples were taken and quenched with 2 mL of methanol. The resulting mixture was filtered through a 0.45 µm filter, and the absorbance was measured at a UV wavelength of 232 nm. Each experiment was performed with three parallel replicates.

The effects of the initial pH values (3, 5, 6.52, 7, 9, 11),  $H_2O_2$  concentrations (0, 0.5, 1, 2, 4, 8 mmol/L) and catalyst loading amounts (0, 0.1, 0.6, 1.2, 2.4 and 4.8 g/L) on the degradation efficiency of SPM were investigated. The impact of free radical scavengers on the reaction system was also studied. Specifically, for the photocatalytic degradation of SPM, 20 vol.% tertbutanol (TBA, to scavenge ·OH), 20 vol.% methanol (to scavenge ·OH and SO<sub>4</sub><sup>--</sup>), 10 mmol/L potassium iodide (KI, to scavenge  $h^+$ ), 0.5 mmol/L AgNO<sub>3</sub> (to scavenge  $e^-$ ) and 0.5 mmol/L p-benzoquinone (BQ, to scavenge  $\cdot O_2^-$ ) were added. The recyclability and stability of the catalyst were evaluated through six continuous degradation experiments. After each experiment, the catalyst was separated by centrifugation and directly reused in the next experiment.

#### 2.3. Analytical Methods

The concentration of SPM was measured using a UV spectrophotometer (752N, Shanghai Jingke, Shanghai, China) at a wavelength of 232 nm. The TOC was measured using a TOC analyzer (TOC-L, Shimadzu, Beijing, China). The active radicals were analyzed using electron paramagnetic resonance (EPR, Bruker EMX-10/12, Karlsruhe, Baden-Württemberg, Germany). The concentrations of Fe<sup>2+</sup>, Fe<sup>3+</sup> and total iron were determined using the 1,10-phenanthroline colorimetric assay at 510 nm on a UV–vis spectrophotometer (752N, Shanghai Jingke, Shanghai, China). The degradation intermediates of SPM were analyzed using liquid chromatography–mass spectrometry (LC–MS, TSQ QUANTUM ACCESS MAX, Thermo Scientific, Waltham, MA, USA).

The morphology and characteristics of the catalyst were analyzed using scanning electron microscopy (SEM, FEI Quanta 400 FEG, Hillsboro, OR, USA), transmission electron

microscopy (TEM, FEI Talos F200x, Hillsboro, OR, USA), energy dispersive spectroscopy (EDS, FEI Talos F200x, Hillsboro, OR, USA), Brunauer–Emmett–Teller (BET, Micromeritics ASAP2460, Norcross, GA, USA), X-ray diffraction (XRD, Rigaku Rotaflex D/max, Akishima, Tokyo, Japan), Fourier transform infrared (FTIR, NEXUS870, Madison, WI, USA) spectra, zeta potential measurements (Malvern Nano-ZS90, Malvern, Worcestershire, UK), UV–vis diffuse reflectance spectra (DRS, PE-Lambda-750, Waltham, MA, USA), X-ray photoelectron spectroscopy (XPS, ESCALAB 25, Waltham, MA, USA), cyclic voltammetry (CV, CHI 660E, Shanghai Chenhua, Shanghai, China), electrochemical impedance spectroscopy (EIS, CHI 660E, Shanghai Chenhua, Shanghai, China), fluorescence spectroscopy analysis (PL, FLS980, Edinburgh, UK) and transient photocurrent response (CHI 660E, Shanghai, China). The detailed test method can be found in the Supplementary Materials.

#### 2.4. Calculation

The conduction band (CB) and valence band (VB) energies were calculated as described in reference [21]. The specific calculation method can be found in the Supplementary Materials.

#### 3. Results and Discussion

# 3.1. Characterization of Catalysts

The Sch particles appeared as spherical aggregates with an average particle size of around 600-700 nm (Figure 1a). When Fe<sub>3</sub>O<sub>4</sub> and ZSM-5 were added to the Sch precursor solution, the synthesized  $Fe_3O_4/ZSM-5/Sch$  presented an irregular, filamentous spherical appearance with an average particle size of 400-600 nm (Figure 1b). Compared to Sch alone, the  $Fe_3O_4/ZSM-5/Sch$  particles showed a reduction in agglomeration and an increase in dispersion, with more pronounced surface edges and roughness. The specific surface areas of the Sch and Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch catalysts were 20.04 m<sup>2</sup>/g and 205.59 m<sup>2</sup>/g, respectively (Table S1). The surface of the  $Fe_3O_4/ZSM-5/Sch$  catalyst prepared showed an irregular massive structure, indicating that a small number of ZSM-5 particles were embedded in the edge of the Sch structure. Additionally, TEM images of  $Fe_3O_4/ZSM-5/Sch$  catalysts revealed that  $Fe_3O_4$  and ZSM-5 promoted Sch growth on the surface as heterogeneous nuclei (Figure 1c). This finding was supported by high-resolution transmission electron microscopy (HRTEM) results (Figure 1d). The lattice fringe spacings of 0.21 nm and 0.26 nm were characteristic of  $Fe_3O_4$  and Sch, respectively, corresponding to the (400) surface of Fe<sub>3</sub>O<sub>4</sub> and the (212) surface of Sch. Meanwhile, some creases and dislocations could also be observed in the HRTEM diagram of the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch catalyst, indicating that  $Fe_3O_4/ZSM$ -5/Sch possessed structural defects and poor crystallinity. This unique defect structure was beneficial for the activation of  $H_2O_2$  [22]. In addition, the EDS-mapping elemental profiles of Fe, O, S, Si and Al elements recorded on the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch catalyst (Figure 1e–f) further indicated that Fe, O, S, Si and Al elements were uniformly distributed in all regions of the  $Fe_3O_4/ZSM-5/Sch$  composite catalyst.

XRD patterns revealed that the characteristic diffraction peaks of Fe<sub>3</sub>O<sub>4</sub>, Sch and ZSM-5 all appear in the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch structure (Figure 2a). The diffraction angles 20 were 18.45°, 30.36°, 35.76°, 43.47° and 63.16°, which were in good agreement with the standard Fe<sub>3</sub>O<sub>4</sub> diffraction data (JCPDS 75-0449), but the diffraction peak intensity decreased. This suggested that Fe<sub>3</sub>O<sub>4</sub> mainly existed within the composite catalyst rather than on the surface [16]. A diffraction peak with more burrs was observed at 20, which was 35.16°, consistent with the comparison with the standard Sch card (JCPDS 47-1775). However, the intensity of the diffraction peak was stronger than that of pure Sch, and the peak shape also changed, which may be due to the slight alteration of the Sch structure caused by the addition of Fe<sub>3</sub>O<sub>4</sub>. The diffraction peaks in the 20 range of 23°~24° were consistent with those of the ZSM-5 standard (JCPDS 37-0359), whereas the intensity of the ZSM-5 main diffraction peaks decreased, indicating that Fe<sub>3</sub>O<sub>4</sub> and Sch were dispersed on the surface of ZSM-5 molecular sieves, forming a certain degree of crystallization. The infrared spectrum of Fe<sub>3</sub>O<sub>4</sub>, ZSM-5/Sch also revealed the coexistence of Fe<sub>3</sub>O<sub>4</sub>, ZSM-5 and Sch (Figure 2b). The absorption peaks observed at 1250 cm<sup>-1</sup>, 450–790 cm<sup>-1</sup> and 550 cm<sup>-1</sup> were characteristic vibrational peaks of the MFI topology structure of ZSM-5, corresponding to Si-O-Si(Al), Si(Al)-O and the anti-symmetric stretching vibration absorption peak of the double five-membered rings in the ZSM-5 framework [23,24]. These peaks indicated that the framework structure of ZSM-5 remained intact as a carrier for Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch. The absorption peaks at 981–1121 cm<sup>-1</sup> and 3385 cm<sup>-1</sup> corresponded to the stretching vibration absorption peaks of SO<sub>4</sub><sup>2–</sup> and O-H, respectively [20]. This indicated that the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch composite contained numerous -OH and SO<sub>4</sub><sup>2–</sup> functional groups, which could capture holes (h<sup>+</sup>) and electrons (e<sup>-</sup>) [25,26].



**Figure 1.** SEM images of (a) Schwertmannite (Sch) and (b)  $Fe_3O_4/ZSM-5/Sch.$  (c) TEM images of  $Fe_3O_4/ZSM-5/Sch.$  (d) HRTEM of  $Fe_3O_4/ZSM-5/Sch.$  (e–j) EDS elemental-mappings of Fe, O, S, Si and Al elements recorded from the  $Fe_3O_4/ZSM-5/Sch$  catalyst.

The light absorption properties of a catalyst are a crucial factor influencing its photocatalytic performance [27]. Sch exhibited a distinct absorption band in the 200–580 nm range, Fe<sub>3</sub>O<sub>4</sub> demonstrated a strong absorption intensity within the 200–800 nm range, and ZSM-5 possessed a relatively low absorption intensity between 200 and 800 nm (Figure 2c). Compared to pure Sch, Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch displayed a noticeable redshift, presenting an absorption band within the 200–800 nm range, which was advantageous for enhancing photocatalytic activity. The respective bandgap widths (E<sub>g</sub>) of Fe<sub>3</sub>O<sub>4</sub>, Sch and Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch were 0.93, 2.28 and 1.39 eV (Figure 2d). Calculations reveal that the conduction band (CB) of Fe<sub>3</sub>O<sub>4</sub> (0.82 eV) was lower than that of Sch (1.14 eV); thus, upon generating photoelectrons in the composite catalyst, Fe<sub>3</sub>O<sub>4</sub> could rapidly transfer them to the Sch surface, accelerating the reduction in  $\equiv$ Fe<sup>3+</sup>.

#### 3.2. Catalytic Activity for Heterogeneous Fenton

The degradation effect of SPM was evaluated in the UV/Fe<sub>3</sub>O<sub>4</sub>-H<sub>2</sub>O<sub>2</sub>, UV/ZSM-5-H<sub>2</sub>O<sub>2</sub>, UV/Sch-H<sub>2</sub>O<sub>2</sub>, UV/Fe<sub>3</sub>O<sub>4</sub>/Sch-H<sub>2</sub>O<sub>2</sub>, UV/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub>, UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch, UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> systems (Figure 3a). The degradation of SPM was fitted to a pseudo first-order kinetic model (R<sup>2</sup> > 0.96). In the UV/Fe<sub>3</sub>O<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> system, the pseudo first-order rate constant (k) was extremely low (k < 0.0033 min<sup>-1</sup>), indicating that ·OH could not be rapidly and effectively produced in the system. This is primarily due to the agglomeration of Fe<sub>3</sub>O<sub>4</sub>, which reduces the active sites for H<sub>2</sub>O<sub>2</sub> activation [28]. Within the UV/ZSM-5-H<sub>2</sub>O<sub>2</sub> system, the k was 0.0047 min<sup>-1</sup>. Given the large surface area of ZSM-5 (Table S1), its electrostatic adsorption of SPM could be the primary cause for SPM removal [29]. In the UV/Sch-H<sub>2</sub>O<sub>2</sub> system, the k amounted

to 0.0128 min<sup>-1</sup>, indicating that Sch can effectively activate  $H_2O_2$  to generate  $\cdot$ OH. Previous studies demonstrated that  $\equiv$ Fe<sup>3+</sup> within Sch was the predominant iron species, which must first be reduced to  $\equiv$ Fe<sup>2+</sup> and then utilized to activate  $H_2O_2$ , generating  $\cdot$ OH to degrade pollutants, leading to an induction period and rapid degradation stage [30]. However, no induction period appeared in the UV/Sch-H<sub>2</sub>O<sub>2</sub> system, primarily owing to UV's acceleration of the reduction in  $\equiv$ Fe<sup>3+</sup> within Sch. Upon combining ZSM-5 and Sch, within the UV/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system, the k ascended to 0.0139 min<sup>-1</sup>, principally attributed to a greater dispersion of Sch upon loading onto ZSM-5, exposing a larger number of active sites and generating a greater amount of  $\cdot$ OH.



**Figure 2.** (a) XRD, (b) FT–IR, (c) UV–visible diffuses reflectance spectra and (d) relationship of  $(ahv)^2$  versus hv of Fe<sub>3</sub>O<sub>4</sub>, ZSM–5, Sch and Fe<sub>3</sub>O<sub>4</sub>/ZSM–5/Sch.

When Fe<sub>3</sub>O<sub>4</sub> and Sch were combined, within the UV/Fe<sub>3</sub>O<sub>4</sub>/Sch-H<sub>2</sub>O<sub>2</sub> system, the k increased to 0.0158 min-1. Li et al. reported that after Fe<sub>3</sub>O<sub>4</sub> was combined with Sch, the electrons in Fe<sub>3</sub>O<sub>4</sub> readily transfer to Sch, promoting the reduction in Fe<sup>3+</sup> in Sch to Fe<sup>2+</sup>, generating  $\cdot$ OH and improving the degradation rate of pollutants [28]. When Fe<sub>3</sub>O<sub>4</sub> and ZSM-5 were simultaneously combined with Sch, within the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system, the k further increased to 0.0203 min<sup>-1</sup>, indicating that Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch had excellent catalytic performance. Without UV irradiation, the k in the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system was only 0.0063 min<sup>-1</sup>, suggesting that UV irradiation significantly enhanced the catalytic activity of Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch. Moreover, in the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-



5/Sch system, the k was the lowest, only 0.0008 min<sup>-1</sup>, indicating that adsorption was not the main mechanism for the removal of SPM in the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system.

**Figure 3.** (a) SPM degradation efficiency in various reaction systems. Effects of the (b) initial  $pH_r$  (c)  $H_2O_2$  concentration and (d) catalyst dosage on SPM degradation by the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system.

The Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch catalyst exhibited satisfactory performance within a pH range of 3–9 (Figure 3b), suggesting that Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch broadened the applicable pH range for degrading SPM in heterogeneous Fenton systems. Surprisingly, unlike other iron-based catalysts, the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch catalyst exhibited the highest catalytic activity when the initial solution was unadjusted (pH = 6.52). The main reasons were as follows: (1) SPM was a weakly alkaline substance with different acid dissociation constant values (pKa of 7.1 and 8.4), and the amine and hydroxyl groups in its molecular structure were protonated and deprotonated, respectively, depending on pH changes [4]. When the pH was adjusted to 3, SPM assumed a cationic state due to protonation, resulting in a stable structure. The Zeta potential results indicated that the point of zero charge ( $pH_{pzc}$ ) value of Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch was 3.1 (Figure S1). At a pH of 3, the surface of  $Fe_3O_4/ZSM$ -5/Sch also carried a positive charge ( $pH < pH_{pzc}$ ), and the electrostatic force inhibited the adsorption of SPM on the  $Fe_3O_4/ZSM$ -5/Sch surface, ultimately reducing SPM degradation. (2) As the pH increased from 5 to 6.52, SPM became positively charged, while the negative charge on the  $Fe_3O_4/ZSM$ -5/Sch surface increased. This results in enhanced catalytic activity due to electrostatic attraction. (3) When the pH increased from 6.52 to 7, the oxidation potential of ·OH decreased, and iron hydroxide complexes were more likely to form on the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch surface, covering active sites [31] and reducing SPM degradation. (4) When the pH increased from 7 to 9 ( $pH_{pzc} < pK_a < pH$ ), SPM became deprotonated, carrying a negative charge, and the negative charge on the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch surface continued to increase. The enhanced electrostatic repulsion resulted in a slight decrease in SPM degradation. Considering that domestic wastewater or natural water typically had a neutral pH, the subsequent experiments were conducted under natural pH conditions.

This study also explored the influence of the H<sub>2</sub>O<sub>2</sub> concentration (Figure 3c). When the H<sub>2</sub>O<sub>2</sub> concentration increased from 0 to 0.5 mmol/L, the k (R<sup>2</sup> > 0.98) rose from 0.0008 min<sup>-1</sup> to 0.0167 min<sup>-1</sup>. This result was similar to the previous study of Luo et al., who found that trimethoprim degradation increased when the persulfate concentration increased [32]. However, a further increase in H<sub>2</sub>O<sub>2</sub> led to a decrease in the k value. Excess H<sub>2</sub>O<sub>2</sub> reacts with ·OH to produce ·HO<sub>2</sub>, which is less reactive (Equation (1)). This finding was consistent with the results of Su et al. [33]. Meanwhile, the effect of the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch catalyst dosage was investigated (Figure 3d). When the catalyst dosage increased from 0 g/L to 0.6 g/L, the k (R<sup>2</sup> > 0.98) increased from 0.0037 min<sup>-1</sup> to 0.0197 min<sup>-1</sup>. A further increase in the catalyst dosage to 4.8 g/L, however, led to a decrease in the k value to 0.0126 min<sup>-1</sup>. There are mainly two reasons: (1) An excess of the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch catalyst can hinder the propagation of UV light in the system, prevent efficient electron transfer in the catalyst, produce insufficient Fe<sup>2+</sup> and result in an insufficient amount of ·OH generated [34]; (2) A large quantity of the catalyst can easily lead to agglomeration [35], preventing the full exposure of active sites and reducing the removal efficiency of SPM.

$$\cdot OH + H_2O_2 \to H_2O + \cdot HO_2 \tag{1}$$

#### 3.3. Mechanism Consideration of SPM Degradation

# 3.3.1. Identification of Active Species

It is common knowledge that •OH represents the active free radical in Fenton reactions. Upon introducing TBA (a potent scavenger of  $\cdot$ OH) to the reaction system (Figure 4a), the degradation efficiency of SPM declined from 95.21% to 18.17%, indicating that •OH was the primary reactive free radical. When an abundance of •OH formed, it could activate trace-dissolved  $SO_4^{2-}$  in Sch through the reaction  $SO_4^{2-} + OH \rightarrow SO_4^{\cdot-} + OH^-$ , generating  $SO_4$ .<sup>-</sup> (a free radical with a longer lifespan and high redox potential). Methanol was considered a more robust scavenger of both ·OH and SO<sub>4</sub><sup>·-</sup>, further reducing the degradation efficiency to 7.13%. This suggested that the reaction was not entirely inhibited, and other reactive species were involved in the degradation of SPM. In addition to producing ·OH radicals, the photoexcited heterogeneous Fenton system also generates a hole (h<sup>+</sup>) and electron (e<sup>-</sup>), as well as  $\cdot O_2^{-}$ . When KI was introduced to the system, the degradation efficiency of SPM decreased by 40.37%, primarily through the generation of OH via the reaction  $H_2O/OH^- + h^+ \rightarrow OH + H^+$  [36]. Upon adding AgNO<sub>3</sub> to the system, the SPM degradation efficiency dropped to 69.97%, indicating that e<sup>-</sup> played a significant role in accelerating the reduction in  $\equiv$ Fe<sup>3+</sup>. BQ, a scavenger of  $\cdot O_2^-$ , only slightly inhibited the degradation efficiency of SPM. By quantitatively calculating inhibition levels (Figures 4b and S2 and Table S2), the contribution of the five generated reactive species to SPM degradation followed the order:  $\cdot$ OH (93.90%) > h<sup>+</sup> (77.80%) > e<sup>-</sup> (62.11%)  $> \cdot O_2^-$  (16.73%)  $> SO_4^-$  (3.57%). This indicated that  $\cdot OH$  played the dominant role in the degradation of SPM and was the main active species in the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system. Furthermore, EPR analysis delved deeper into the reactive species involved in the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> reaction. In the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch catalyzed photo-Fenton system, a four-line signal peak of DMPO-OH was observed, with a characteristic peak ratio of 1:2:2:1, indicating the production of  $\cdot$ OH (Figure 4c). In addition to the strong DMPO-•OH signal, a faint six-line signal peak with a 1:1:1:1:1:1 ratio was observed, attributable to DMPO-SO<sub>4</sub><sup>.-</sup>. When the reaction solvent was methanol, a weak four-line signal peak was observed (with an intensity ratio of 1:1:1:1), indicating the generation of  $O_2^-$  (Figure 4d). The EPR analysis was consistent with the quenching results in Figure 4a.



**Figure 4.** (a) Effect of various radical scavengers on SPM degradation efficiency. (b) Free radical contribution in the degradation of SPM. Electron paramagnetic resonance (EPR) spectra of spin-reaction (c) ·OH radicals, SO<sub>4</sub><sup>--</sup> radicals and (d) ·O<sub>2</sub><sup>--</sup> radicals.

### 3.3.2. Enhanced Mechanism for Catalytic Activity

During the heterogeneous Fenton process, some of the active iron species may leach from the catalyst surface and be released into the solution, forming a homogeneous Fenton system with  $H_2O_2$  in the system, thereby contributing to the degradation of pollutants [16]. However, the leached Fe concentration in the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system remained consistently within a low range (Figure S3a), indicating the exceptional stability of the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch structure. An analysis of the degradation efficiency of the UV/Fe<sup>3+</sup>-H<sub>2</sub>O<sub>2</sub> system, constructed by the leached Fe<sup>3+</sup> ions, indicated that it contributed approximately 26.77% to the degradation of SPM (Figure S3b), suggesting that the degradation process was mainly dominated by the heterogeneous Fenton reactions.

XPS analysis was employed to compare the changes in the valence states of Fe  $2p_{3/2}$  on the surface of Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch before and after the reaction (Figure 5a). The Fe  $2p_{3/2}$  peaks located at 710.89 eV and 712.87 eV correspond to  $\equiv$ Fe<sup>2+</sup> and  $\equiv$ Fe<sup>3+</sup>, respectively [37,38]. Prior to the reaction, the molar ratio of  $\equiv$ Fe<sup>2+</sup>/ $\equiv$ Fe<sup>3+</sup> in Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch was 0.50 (Table S3). Upon the reaction completion, a shift in the binding energy of the two individual Fe  $2p_{3/2}$  peaks was observed, moving towards a higher binding energy direction. This suggested that redox reactions occurred between Fe<sup>2+</sup> and Fe<sup>3+</sup> on the catalyst surface during the reaction. After the reaction, the ratio of  $\equiv$ Fe<sup>2+</sup> to  $\equiv$ Fe<sup>3+</sup> in Fe<sub>3</sub>O<sub>4</sub>/Sch/ZSM-5 increased to 1.25, a 2.5-fold increase from its pre-reaction state. This



was greater than the increase factor for both the ratio of  $\equiv Fe^{2+}$  to  $\equiv Fe^{3+}$  in Fe<sub>3</sub>O<sub>4</sub>/Sch (1.25) [28] and the ratio of  $\equiv Fe^{2+}$  to  $\equiv Fe^{3+}$  in Sch (1.67) [17].

**Figure 5.** (a) Fe 2p XPS spectra of Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch before and after the reaction. (b) CV curve, (c) EIS Nyquist plots, (d) PL emission spectra and (e) the transient photocurrent response of Fe<sub>3</sub>O<sub>4</sub>, ZSM-5, Sch and Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch. (f) Proposed mechanism for the high-efficient catalytic activity of the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch catalyst.

It is well known that the reduction of  $\equiv Fe^{3+}$  to  $\equiv Fe^{2+}$  is the rate-limiting step in iron-based catalyst-mediated heterogeneous Fenton reactions, and the efficiency of the conventional H<sub>2</sub>O<sub>2</sub>-induced reduction in  $\equiv$ Fe<sup>3+</sup> is low. Under ultraviolet light irradiation, Fe<sub>3</sub>O<sub>4</sub> and Sch in Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch were excited to generate a photogenerated electron (e<sup>-</sup>)-hole (h<sup>+</sup>) pair, and ZSM-5 acted as an electron transfer carrier to accelerate electron transfer. A photogenerated electron could rapidly reduce  $\equiv Fe^{3+}$  to  $\equiv Fe^{2+}$ . Interestingly, the conduction band edge of  $Fe_3O_4$  (+0.82 eV) and Sch (+1.14 eV) was more positive than the redox potential of  $\equiv Fe^{3+}/\equiv Fe^{2+}$  (+0.77 eV), making them unable to reduce  $\equiv$ Fe<sup>3+</sup>. However, under UV irradiation at an energy of 3.40 eV ( $\lambda$  = 365 nm), e<sup>-</sup> in the valence bands of Fe<sub>3</sub>O<sub>4</sub> and Sch could be excited to higher potential edges (-1.62 eV and 0.02 eV, respectively). In the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch composite catalyst, the modified  $e^-$  reduced  $\equiv$  Fe<sup>3+</sup> to  $\equiv$  Fe<sup>2+</sup>, and the e<sup>-</sup> in Fe<sub>3</sub>O<sub>4</sub> could also reduce O<sub>2</sub> to  $\cdot$ O<sub>2</sub><sup>-</sup> (-0.33 eV). The CV curve further demonstrated that Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch had the highest reduction current (Figure 5b). Additionally, EIS measurements (Figure 5c) revealed that  $Fe_3O_4/ZSM-5/Sch$ had the smallest radius, indicating the lowest charge transfer resistance at the electrolyte interface and a faster electron transfer rate.

Photogenerated  $e^--h^+$  pairs are prone to recombination, leading to a decrease in the oxidation and reduction abilities of photocatalysts. However,  $h^+$  was the main active species involved in the reaction (Figure 4b), indicating the effective separation of  $e^--h^+$  in the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system. The PL spectrum (Figure 5d) showed that Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch had the smallest fluorescence emission peak, indicating a high separation efficiency of photogenerated  $e^--h^+$  pairs in Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch [39]. Furthermore, it was found that the photocurrent density generated by the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch composite catalyst was significantly higher than that of Fe<sub>3</sub>O<sub>4</sub>, Sch and ZSM-5/Sch, which may be due to the electron donor or acceptor characteristics of the ZSM-5 molecular sieve, promoting the separation of charge carriers and hindering  $e^--h^+$  recombination [40,41].

Therefore, Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch could easily be excited by UV irradiation, resulting in the separation of e<sup>-</sup>–h<sup>+</sup> pairs (Equation (2)). The oxidative h<sup>+</sup> reacted with H<sub>2</sub>O<sub>2</sub> to generate ·OH, while e<sup>-</sup> promoted the production of  $\equiv$ Fe<sup>2+</sup> and ·O<sub>2</sub><sup>-</sup> (Equations (3)–(5)). Subsequently, the more efficient conversion of  $\equiv$ Fe<sup>3+</sup>/ $\equiv$ Fe<sup>2+</sup> led to the generation of a large amount of ·OH in the system, enhancing the catalytic activity of Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch (Equations (6)–(9)). In addition, when ·OH was produced in the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system, SO<sub>4</sub><sup>--</sup> was mainly formed through the redox reaction between SO<sub>4</sub><sup>2-</sup> and ·OH (Equation (10)). Finally, SPM adsorbed on the surface of Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch reacted with ·OH, ·O<sub>2</sub><sup>--</sup> and SO<sub>4</sub><sup>--</sup>, degrading into small molecular substances, which were eventually mineralized into H<sub>2</sub>O and CO<sub>2</sub> (Equation (11)). The enhancement mechanism of the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system is shown in Figure 5f.

$$Fe_3O_4/ZSM-5/Sch \rightarrow h^+ + e^-$$
(2)

$$H_2O/OH^- + h^+ \to \cdot OH + H^+$$
(3)

$$O_2 + e^- \to \cdot O_2^- \tag{4}$$

$$\equiv Fe(III) + e^{-} \rightarrow \equiv Fe(II) \tag{5}$$

$$\equiv Fe(II) + H_2O_2 \rightarrow \equiv Fe(III) + \cdot OH + OH^-$$
(6)

$$\equiv Fe(III) + H_2O_2 \rightarrow \equiv Fe(II) + \cdot HO_2 + H^+$$
(7)

$$\equiv Fe(II) + \cdot HO_2 + H^+ \rightarrow \equiv Fe(III) + H_2O_2 \tag{8}$$

$$\equiv Fe(III) + \cdot HO_2 \rightarrow \equiv Fe(II) + H^+ + O_2 \tag{9}$$

$$SO_4^{2-} + \cdot OH \to SO_4^{\cdot-} + OH^-$$
(10)

SPM + 
$$\cdot$$
OH, SO<sub>4</sub><sup>--</sup>,  $\cdot$ O<sub>2</sub><sup>-</sup>  $\rightarrow$  intermediate products  $\rightarrow$  H<sub>2</sub>O + CO<sub>2</sub> (11)

#### 3.4. SPM Degradation Pathways

The main intermediates of SPM during the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> reaction were determined by LC–MS analysis and summarized in Figure S4 and Table S4. Based on the identified intermediates, we proposed the transformation pathway of SPM in this system (Figure 6).



Figure 6. The proposed degradation pathways of SPM in the UV/Fe $_3O_4/ZSM-5/Sch-H_2O_2$  system.

(1) Aldoxy oxidation (Pathway 1): The two dimethylamine (DMA) groups at the C5 and C9 positions of SPM were first attacked by ·OH, generating TP859-1 and TP859-2. Upon •OH attack, TP859-1 or TP859-2 underwent oxidation to form TP875. Subsequently, the aldehyde group at the C6 position of TP875 was oxidized by •OH to form a carboxylic acid group, resulting in the formation of TP891. (2) C-O bond cleavage (Pathway 2 and Pathway 3): Under the attack of active radicals ( $\cdot OH$ ,  $\cdot O_2^-$ ,  $SO_4^{\cdot-}$ ,  $e^-$  and  $h^+$ ), the disaccharide (mycaminose and mycarose) linked at the C5 position lost the outermost mycarose, resulting in the formation of TP699. Subsequently, the C-O bond at the C9 position was cleaved, generating TP159 and TP685. Subsequently, the C-O bond at the C5 position of TP685 was cleaved, resulting in the formation of TP352 and TP335. Moreover, because TP159, TP699 and TP335 contain DMA functional groups, these three TPs can generate DMA through the cleavage of N-C bonds. (3) Demethylation (Pathway 4): The N-C bond of forosamine at the C9 position of SPM and the N–C bond at the mycaminose position connected to the C5 position were attacked by active radicals to undergo a demethylation reaction, forming TP814. TP814 was further oxidized to form DMA. Finally, DMA, TP699, TP352, TP335 and TP814 generated in Pathways 2-4 could be further mineralized into CO<sub>2</sub> and H<sub>2</sub>O. In this

process, approximately 23.45% of TOC was mineralized to  $CO_2$  (Figure S5). The proposed SPM degradation pathway in the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system was consistent with the reaction pathways in UV/nano-zerovalent iron/peroxyacetic acid oxidation [42] and visible light/sulfur-doped g-C<sub>3</sub>N<sub>4</sub>/persulfate oxidation [43].

# 3.5. Reusability and Stability of the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch Catalyst

The reusability and stability of catalysts play an important role in practical applications. When the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch composite catalyst was reused for six cycles, the degradation efficiency of SPM remained above 86.50% (Figure 7a), clearly indicating that Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch could be repeatedly used as a heterogeneous Fenton-like catalyst. As seen in Figure S3a, before the recovery of Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch, the leached Fe concentration was 0.24 mg/L, far lower than the iron leaching amount (2.7 mg) in Fe<sub>3</sub>O<sub>4</sub>/Sch [28]. After Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch underwent six cycles, the leaching amount of Fe remained in the range of 0.18–0.23 mg/L (Figure 7b), which is also lower than the dissolution amount of Fe (0.38–0.58 mg/L) after multiple cycles of Sch [17]. According to the European Union emission standards (<2 mg/L) [17], this was acceptable.



**Figure 7.** Changes in (**a**) SPM degradation efficiency and (**b**) dissolution of Total Fe-ion (TFe),  $Fe^{2+}$  and  $Fe^{3+}$  during a multi-cycle experiment with repeated uses of  $Fe_3O_4/ZSM-5/Sch$ .

As shown in Figure 2a,b, the XRD and FT-IR spectra of the reused  $Fe_3O_4/ZSM-5/Sch$  still showed little difference compared to the XRD and FTIR spectra of the newly synthesized  $Fe_3O_4/ZSM-5/Sch$ . These results indicated that the photocatalytic Fenton process did not destroy the structure and functional groups of  $Fe_3O_4/ZSM-5/Sch$ . Additionally, the photocurrent curves of the  $Fe_3O_4/ZSM-5/Sch$  catalyst did not show a decay trend after multiple cycles of light interruption (Figure 5e). These results suggested that  $Fe_3O_4/ZSM-5/Sch$  and  $Fe_3O_4$ 

# 4. Conclusions

The UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system is capable of efficiently removing SPM from water. The composition of Fe<sub>3</sub>O<sub>4</sub> and ZSM-5 reduced the aggregation phenomenon of chemically synthesized Sch, significantly increased the edge-ridged structure on the surface and greatly enlarged the specific surface area. At the same time, compared to the Schmediated Fenton reaction, the degradation efficiency of SPM was substantially improved. Moreover, Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch exhibited broad applicability, with an initial pH range of 3–9, and demonstrated excellent heterogeneous Fenton-like activity for SPM degradation under near-neutral pH conditions. The effective decomposition of H<sub>2</sub>O<sub>2</sub> driven by the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch heterogeneous photocatalytic Fenton catalyst was mainly related to the efficient conversion of  $\equiv$ Fe<sup>3+</sup>/ $\equiv$ Fe<sup>2+</sup>. Before the reaction, the molar ratio of  $\equiv$ Fe<sup>2+</sup>/ $\equiv$ Fe<sup>3+</sup> in

Fe<sub>3</sub>O<sub>4</sub>/Sch/ZSM-5 was 0.50. After the reaction, the molar ratio of  $\equiv$ Fe<sup>2+</sup>/ $\equiv$ Fe<sup>3+</sup> increased to 1.25. Under UV irradiation, Fe<sub>3</sub>O<sub>4</sub> and Sch in Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch generated hole–electron pairs. The photogenerated electrons in Fe<sub>3</sub>O<sub>4</sub> were transferred to Sch via ZSM-5, which effectively reduced the  $\equiv$ Fe<sup>3+</sup> in Sch to  $\equiv$ Fe<sup>2+</sup>, which then reacted with H<sub>2</sub>O<sub>2</sub> to generate  $\cdot$ OH. The photogenerated electrons in Fe<sub>3</sub>O<sub>4</sub> also reacted with O<sub>2</sub> to generate a small amount of  $\cdot$ O<sub>2</sub><sup>-</sup>. Due to the effective transfer of electrons, the holes were allowed to react with surface H<sub>2</sub>O and OH<sup>-</sup>. The abundant  $\cdot$ OH within the system effectively triggers the production of SO<sub>4</sub><sup>--</sup> from SO<sub>4</sub><sup>2-</sup> in Sch. When  $\cdot$ OH,  $\cdot$ O<sub>2</sub><sup>--</sup> and SO<sub>4</sub><sup>--</sup> coexist in the reaction system, the degradation efficiency of organic compounds was significantly enhanced. In the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> reaction, SPM can ultimately be converted into CO<sub>2</sub> and H<sub>2</sub>O. After six cycles of reuse, the Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch as a catalyst in the heterogeneous photo-Fenton process maintained a degradation efficiency for SPM above 86.50%, with iron leaching maintained between 0.18 and 0.24 mg/L, indicating the good stability and reusability of Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch. This research has significant implications for the future design of efficient iron-based catalysts for the degradation of recalcitrant organic pollutants.

**Supplementary Materials:** The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/su151612343/s1, Table S1: Specific surface area, pore volume and pore size of various catalysts; Figure S1: Zeta potential of Fe<sub>3</sub>O<sub>4</sub>, ZSM-5, Sch and Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch; Figure S2: Effect of various radical scavengers on SPM degradation kinetics; Table S2: Pseudo firstorder rate constant for the effect of radical quenching agents; Figure S3: (a) Changes in Total Fe-ion (TFe), Fe<sup>2+</sup> and Fe<sup>3+</sup> concentration in the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system, (b) comparison of homogeneous and heterogeneous photo-Fenton; Table S3: Binding energy of iron ions on the surface of Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch before and after the reaction; Figure S4: Mass spectra of the degradation intermediates detected using LC–MS during the degradation of SPM in the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system; Table S4: Retention time, chemical formula, mass charge ratio and proposed molecular structure of the detected degradation intermediates of SPM; Figure S5: Changes in TOC in the UV/Fe<sub>3</sub>O<sub>4</sub>/ZSM-5/Sch-H<sub>2</sub>O<sub>2</sub> system.

**Author Contributions:** Investigation, data curation, formal analysis, writing—original draft preparation, J.Y.; Formal analysis, methodology, data curation, investigation, conceptualization, project administration, supervision, writing—review and editing, funding acquisition, J.X.; Validation, J.L.; Validation, writing—review and editing, Y.Z.; Methodology, funding acquisition, Q.W. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Natural Science Foundation of China (No. 21607012 and No. 22205027).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

**Data Availability Statement:** All data included in this study are available upon request by contact with the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

#### References

- 1. Calcagnile, M.; Jeguirim, I.; Tredici, S.M.; Damiano, F.; Alifano, P. Spiramycin Disarms *Pseudomonas aeruginosa* without Inhibiting Growth. *Antibiotics* **2023**, *12*, 499. [CrossRef]
- Nasiri, A.; Mokhtari, S.; Jahani, R.; Daraie, B.; Yazdanpanah, H.; Faizi, M.; Kobarfard, F. Challenges for the determination of spiramycin in aqueous matrices using LC-MS/MS: Evidence for t-he solvent intrusion on the molecule integrity. *RSC Adv.* 2022, 12, 17096–17103. [CrossRef] [PubMed]
- Boti, V.; Toli, V.; Efthymiou, C.; Albanis, T. Screening of Commonly Used Antibiotics in Fresh and Saltwater Samples Impacted by Aquacultures: Analytical Methodology, Occurrence and Environmental Risk Assessment. Sustainability 2023, 15, 9199. [CrossRef]
- 4. Wang, G.; Liu, H.; Wang, J.; Gong, P.; Cai, C.; Dai, X.; Wang, P. Pretreatment of spiramycin fermentation residue by thermally activated peroxydisulfate for improving biodegradability: Insights into matrix disintegration and antibiotics degradation. *Chem. Eng.* J. **2022**, 427, 130973. [CrossRef]

- Xexaki, A.; Papadopoulos, D.K.; Alvanou, M.V.; Giantsis, I.A.; Papageorgiou, K.V.; Delis, G.A.; Petridou, E. Prevalence of Antibiotic Resistant *E. coli* Strains Isolated from Farmed Broilers and Hens in Greece, Based on Phenotypic and Molecular Analyses. *Sustainability* 2023, 15, 9421. [CrossRef]
- 6. Kanjal, M.I.; Muneer, M.; Jamal, M.A.; Bokhari, T.H.; Wahid, A.; Ullah, S.; Mouni, L. A Study of Treatment of Reactive Red 45 Dye by Advanced Oxidation Processes and Toxicity Evaluation Using Bioassays. *Sustainability* **2023**, *15*, 7256. [CrossRef]
- Ren, Y.; Shi, M.; Zhang, W.; Dionysiou, D.D.; Lu, J.; Shan, C.; Pan, B. Enhancing the Fenton-like catalytic activity of nFe<sub>2</sub>O<sub>3</sub> by MIL-53 (Cu) support: A mechanistic investigation. *Environ. Sci. Technol.* 2020, *54*, 5258–5267. [CrossRef] [PubMed]
- Zhu, Y.; Zhu, R.; Xi, Y.; Zhu, J.; He, H. Strategies for Enhancing the Heterogeneous Fenton Cat-alytic Reactivity: A review. *Appl. Catal. B Environ.* 2019, 255, 117739. [CrossRef]
- 9. Montoya-Bautista, C.V.; Avella, E.; Ramírez-Zamora, R.M.; Schouwenaars, R. Metallurgical wastes employed as catalysts and photocatalysts for water treatment: A review. *Sustainability* **2019**, *11*, 2470. [CrossRef]
- Bigham, J.M.; Schwertmann, U.; Traina, S.J.; Winland, R.L.; Wolf, M. Schwertmannite and the chemical modeling of iron in acid sulfate waters. *Geochim. Cosmochim. Acta* 1996, 60, 2111–2121. [CrossRef]
- Yan, S.; Zheng, G.; Meng, X.; Zhou, L. Assessment of catalytic activities of selected iron hydroxysulphates biosynthesized using *Acidithiobacillus ferrooxidans* for the degradation of phenol in heterogeneous Fenton-like reactions. *Sep. Purif. Technol.* 2017, 185, 83–93. [CrossRef]
- 12. Zhang, Z.; Wang, L.; Zhou, B.; Wang, S.; Fan, L.; Hu, S.; Wu, Y. Adsorption performance and mechanism of synthetic schwertmannite to remove low-concentration fluorine in water. *Bull. Environ. Contam. Toxicol.* **2021**, *107*, 1191–1201. [CrossRef] [PubMed]
- 13. Wang, X.; Ying, H.; Zhao, W.; Feng, X.; Tan, W.; Beyer, K.A.; Zhu, M. Molecular-scale understanding of sulfate exchange from schwertmannite by chromate versus arsenate. *Environ. Sci. Technol.* **2021**, *55*, 5857–5867. [CrossRef] [PubMed]
- Ma, S.; Jing, J.; Liu, P.; Li, Z.; Jin, W.; Xie, B.; Zhao, Y. High selectivity and effectiveness for removal of tetracycline and its related drug resistance in food wastewater through schwertmannite/graphene oxide catalyzed photo-Fenton-like oxidation. *J. Hazard. Mater.* 2020, 392, 122437. [CrossRef] [PubMed]
- Wang, X.; Chen, Y.; Li, T.; Liang, J.; Zhou, L. High-efficient elimination of roxarsone by MoS<sub>2</sub>@ Schwertmannite via heterogeneous photo-Fenton oxidation and simultaneous arsenic immobilization. *Chem. Eng. J.* 2021, 405, 126952. [CrossRef]
- 16. Li, T.; Wang, X.; Chen, Y.; Liang, J.; Zhou, L. Producing ·OH, SO<sub>4</sub> <sup>--</sup> and ·O<sub>2</sub><sup>--</sup> in heterogeneous Fenton reaction induced by Fe<sub>3</sub>O<sub>4</sub>-modified schwertmannite. *Chem. Eng. J.* **2020**, *393*, 124735. [CrossRef]
- 17. Meng, X.; Yan, S.; Wu, W.; Zheng, G.; Zhou, L. Heterogeneous Fenton-like degradation of phenanthrene catalyzed by schwertmannite biosynthesized using acidithiobacillus ferrooxidans. *RSC Adv.* **2017**, *7*, 21638–21648. [CrossRef]
- Su, R.; Xie, C.; Sikpaam, I.; Huang, S.; Chen, R.; Xiang, S.; Wang, Z.; Hang, L. Oxygen Reduction Reaction in the Field of Water Environment for Application of Nanomaterials. *Nanomaterials* 2020, 10, 1719. [CrossRef]
- 19. Kasiri, M.B.; Aleboyeh, H.; Aleboyeh, A. Degradation of Acid Blue 74 using Fe-ZSM5 zeolite as a heterogeneous photo-Fenton catalyst. *Appl. Catal. B Environ.* 2008, *84*, 9–15. [CrossRef]
- Regenspurg, S.; Brand, A.; Peiffer, S. Formation and stability of schwertmannite in acidic mining lakes. *Geochim. Cosmochim. Acta* 2004, 68, 1185–1197. [CrossRef]
- Mieritz, D.G.; Renaud, A.; Seo, D.K. Unusual Changes in Electronic Band-Edge Energies of the Nanostructured Transparent n-Type Semiconductor Zr-Doped Anatase TiO<sub>2</sub> (Ti<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>; x<0.3). *Inorg. Chem.* 2016, 55, 6574–6578. [CrossRef] [PubMed]
- 22. Xia, H.; Zhang, Z.; Liu, J.; Deng, Y.; Zhang, D.; Du, P.; Zhang, S.; Lu, X. Novel Fe-Mn-O nanosheets/wood carbon hybrid with tunable surface properties as a superior catalyst for Fenton-like oxidation. *Appl. Catal. B Environ.* **2019**, 259, 118058. [CrossRef]
- Yang, X.; Wang, F.; Wei, R.; Li, S.; Wu, Y.; Shen, P.; Wang, H.; Gao, L.; Xiao, G. Synergy effect between hierarchical structured and Sn-modified H [Sn, Al] ZSM-5 zeolites on the catalysts for glycerol aromatization. *Microporous Mesoporous Mater.* 2018, 257, 154–161. [CrossRef]
- Inagaki, S.; Shinoda, S.; Hayashi, S.; Wakihara, T.; Yamazaki, H.; Kondo, J.N.; Kubota, Y. Improvement in the catalytic properties of ZSM-5 zeolite nanoparticles via mechanochemical and chemical modifications. *Catal. Sci. Technol.* 2016, 6, 2598–2604. [CrossRef]
- Kim, J.; Choe, Y.J.; Kim, S.H.; Jeong, K. Enhancing the decomposition of refractory contaminants on SO<sub>4</sub><sup>2-</sup>-functionalized iron oxide to accommodate surface SO<sub>4</sub><sup>--</sup> generated via radical transfer from •OH. *Appl. Catal. B Environ.* 2019, 252, 62–76. [CrossRef]
- Liu, Z.; Tian, J.; Yu, C.; Fan, Q.; Liu, X.; Yang, K.; Zeng, J.; Ji, H. Ultrasonic fabrication of SO<sub>4</sub><sup>2-</sup> doped g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite applied for effective removal of dyestuffs and antibiotics. *Mater. Chem. Phys.* 2020, 240, 122206. [CrossRef]
- 27. Mamba, G.; Mishra, A.K. Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) nanocomposites: A new and exciting generation of visible light driven photocatalysts for environmental pollution remediation. *Appl. Catal. B Environ.* **2016**, *198*, 347–377. [CrossRef]
- 28. Li, T.; Liang, J.; Zhou, L. Fabricating Fe<sub>3</sub>O<sub>4</sub>-schwertmannite as a Z-scheme photocatalyst with excellent photocatalysis-Fenton reaction and recyclability. *J. Environ. Sci.* **2020**, *98*, 186–195. [CrossRef]
- Yao, L.; Zhou, Y.; Guo, S.; Ma, Y.; Liu, D.; Jin, Z. Comparison of VOCs adsorption performance between Y and ZSM-5 zeolite. *Chin. J. Environ. Eng.* 2022, 16, 182–189. [CrossRef]
- Li, T.; Chen, Y.; Wang, X.; Liang, J.; Zhou, L. Modifying organic carbon in Fe<sub>3</sub>O<sub>4</sub>-loaded schwertmannite to improve heterogeneous Fenton activity through accelerating Fe(II) generation. *Appl. Catal. B Environ.* 2020, 285, 119830. [CrossRef]

- Gong, C.; Chen, F.; Yang, Q.; Luo, K.; Yao, F.; Wang, S.; Wang, X.; Wu, J.; Li, X.; Wang, D. Heterogeneous activation of peroxymonosulfate by Fe-Co layered doubled hydroxide for efficient catalytic degradation of Rhoadmine B. *Chem. Eng. J.* 2017, 321, 222–232. [CrossRef]
- Luo, Y.; Su, R.; Yao, H.; Zhang, A.; Xiang, S.; Huang, L. Degradation of trimethoprim by sulfate radical-based advanced oxidation processes: Kinetics, mechanisms, and effects of natural water matrices. *Environ. Sci. Pollut. Res.* 2021, 28, 62572–62582. [CrossRef]
- 33. Su, R.; Chai, L.; Tang, C.; Li, B.; Yang, Z. Comparison of the degradation of molecular and ionic ibuprofen in a UV/H<sub>2</sub>O<sub>2</sub> system. *Water Sci. Technol.* **2018**, *77*, 2174–2183. [CrossRef] [PubMed]
- Yan, S.; Zhan, L.; Meng, X.; Wang, D.; Wang, X.; Zheng, G.; Lu, J.; Zhou, L. Role of schwertmannite or jarosite in photocatalytic degradation of sulfamethoxazole in ultraviolet/peroxydisulfate system. *Sep. Purif. Technol.* 2021, 274, 118991. [CrossRef]
- 35. Kader, S.; Al-Mamun, M.R.; Suhan, M.B.K.; Shuchi, S.B.; Islam, M.S. Enhanced photodegradation of methyl orange dye under UV irradiation using MoO<sub>3</sub> and Ag doped TiO<sub>2</sub> photocatalysts. *Environ. Technol. Innov.* **2022**, *27*, 102476. [CrossRef]
- 36. Hao, H.; Lu, D.; Wang, Q. Photoelectrochemical study on charge separation mechanisms of Bi<sub>2</sub>WO<sub>6</sub> quantum dots decorated g-C<sub>3</sub>N<sub>4</sub>. *Int. J. Hydrogen Energy* **2018**, *43*, 8824–8834. [CrossRef]
- Ye, Q.; Huang, Z.; Wu, P.; Wu, J.; Dang, Z. Promoting the photogeneration of hydrochar reactive oxygen species based on Fe-Al layered double hydroxide for diethyl phthalate degradation. *J. Hazard. Mater.* 2020, 388, 122120. [CrossRef] [PubMed]
- 38. Xu, S.; Wang, M.; Saranya, G.; Chen, N.; Zhang, L.; He, Y.; Wu, L.; Gong, Y.; Yao, Z. Pressure-driven catalyst synthesis of Co-doped Fe3C@Carbon nano-onions for efficient oxygen evolution reaction. *Appl. Catal. B Environ.* **2020**, *268*, 118385. [CrossRef]
- Yu, J.; Ma, T.; Liu, S. Enhanced Photocatalytic Activity of Mesoporous TiO<sub>2</sub> Aggregates by Embedding Carbon Nanotubes as Electron-Transfer Channel. *Phys. Chem. Chem. Phys.* 2011, 13, 3491–3501. [CrossRef] [PubMed]
- Chang, C.; Kan, L.; Mu, W.; Wang, Q.; Lu, S. Tetragonal/orthorhombic-bismuth tungstate homojunction formed through in situ bismuth induced phase transformation as highly efficient photocatalyst for pollutant degradation. *J. Colloid Interface Sci.* 2022, 607, 269–280. [CrossRef]
- Rayalu, S.S.; Dubey, N.; Labhsetwar, N.K.; Kagne, S.; Devotta, S. UV and visibly active photocatalysts for water splitting reaction. *Int. J. Hydrogen Energy* 2007, 32, 2776–2783. [CrossRef]
- Wang, L.; Yan, T.; Tang, R.; Ping, Q.; Li, Y.; Wang, J. Motivation of reactive oxidation species in peracetic acid by adding nanoscale zero-valent iron to synergic removal of spiramycin under ultraviolet irradiation: Mechanism and n-nitrosodimethylamine formation potential assessment. *Water Res.* 2021, 205, 117684. [CrossRef] [PubMed]
- Dou, Y.; Yan, T.; Zhang, Z.; Sun, Q.; Wang, L.; Li, Y. Heterogeneous activation of peroxydisulfate by sulfur-doped g-C<sub>3</sub>N<sub>4</sub> under visible-light irradiation: Implications for the degradation of SPM and an assessment of N-nitrosodimethylamine formation potential. *J. Hazard. Mater.* 2021, 406, 124328. [CrossRef] [PubMed]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.