

Communication

SiO₂@Fe(III)-Based Metal–Organic Framework Core–Shell Microspheres for Water-Purification-Based Photo-Fenton Processes

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Abstract: In this study, SiO₂@MIL-88A(Fe) core–shell microspheres were successfully synthesized through a simple immobilization method for dye degradation via an MIL-88A(Fe)-mediated Fenton-like process. These microspheres were fabricated by in situ immobilizing MIL-88A(Fe) onto mesoporous organosilane spheres functionalized with –COOH groups. Structural analyses and characterizations confirmed the formation of well-defined MOF particles anchored on the silicate microspheres, with electron microscopy verifying their porous core–shell structure. The newly developed core–shell materials achieved a high degree of dye degradation, reaching up to 96% for 10 mg/L dye solutions in neutral aqueous conditions within 30 min at room temperature through the Fenton-like process. Furthermore, SiO₂@MIL-88A(Fe) exhibited excellent stability and recyclability, maintaining its performance over at least seven reuse cycles with minimal loss of activity. This material is easy to synthesize as well as cost-effective and demonstrates significant potential for wastewater purification involving a range of four different dyes.

Keywords: MOFs; core–shell microspheres; photo-Fenton process



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1. Introduction

The urgent need for efficient technologies to address water pollution has become particularly pressing due to severe dye contamination caused by rapidly developing industries and economies [1–5]. As a result, various methods, including biological treatment [6,7], adsorption [8,9], membrane separation [10–12], column separation [13], and advanced oxidation [14,15], have been proposed to alleviate water pollution. Among these methods, the advanced oxidation process (AOP) [16] is widely regarded as an effective approach for tackling toxic, recalcitrant organic pollutants [17]. In particular, Fenton-type processes have garnered significant attention [18] due to their ability to degrade organic pollutants via highly reactive hydroxyl radicals, converting them into environmentally friendly products, such as carbon dioxide and water, using activated H₂O₂ via ferrous ion catalysis [19,20]. The Fenton process is recognized for its high efficiency, simplicity, and suitability for wastewater treatment. However, the key to its successful application in water pollution treatment lies in the use of appropriate, efficient, and highly stable materials [21–23].

Metal–organic frameworks (MOFs) are 3D porous materials consisting of periodically connected organic linkers and inorganic metal ions or clusters [24–28]. They have attracted significant attention as a new type of photocatalyst due to their remarkable ligand–metal

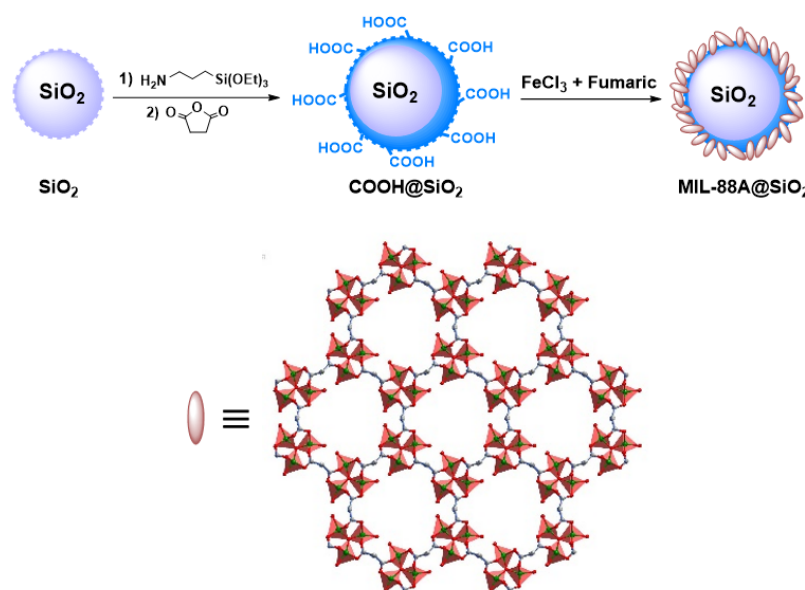
charge transfer (LMCT) properties under light irradiation [29,30]. In particular, Fe-based MOFs show great potential as photocatalysts owing to their $\text{Fe}_3\text{-}\mu_3\text{-oxo}$ clusters and low toxicity, which enable a heterogeneous photo-Fenton-like reaction for wastewater treatment under light irradiation [31–33]. However, the large, tightly packed 3D structure of MOF particles can impede substrate diffusion, sometimes blocking it in the nanosized MOF channels [34,35]. Growing MOFs on larger matrixes can reduce crystal growth due to the matrix's nucleation effect [36], thereby enhancing mass transport speed.

Here, we directly grew MIL-88A(Fe) [37] on silica to produce an MIL-88A(Fe)@SiO₂ core-shell composite material. The MIL-88A(Fe)@SiO₂ was first prepared analogously to MIL-88A(Fe)@SiO₂, except with the addition of a 0.25 weight equivalent of SiO₂. The surface silanol groups on SiO₂ served as nucleation sites for the formation of fusiform-shaped MIL-88A(Fe) particles with an average dimension of $\sim 0.06 \times 0.2 \mu\text{m}$. Due to the enhanced nucleation on the silica surface, the MOF particles in the composite material were smaller than pure MOF particles ($0.3 \times 2 \mu\text{m}$) [37,38] and were homogeneously packed on the silica. The photo-Fenton catalytic activity of MIL-88A(Fe)@SiO₂ in the dye degradation reaction was investigated. In this technique, water was used as a solvent in mild conditions, and the catalyst showed excellent catalytic capacity. Furthermore, MIL-88A(Fe)@SiO₂ showed excellent stability and recyclability and could be reused at least seven times without significant loss of activity. The easy and cost-effective construction of this heterogeneous catalyst, MIL-88A(Fe)@SiO₂, makes it a candidate for applications in high-level environmental engineering.

2. Results and Discussion

2.1. Synthesis and Structural Characterization of the Core-Shell Catalyst

Core-shell-structured MIL-88A@SiO₂ microspheres were synthesized using a simple two-step postgrafting complexation procedure, as illustrated in Scheme 1. In the first step, the co-condensation of tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES), followed by modification with succinic anhydride, resulted in carboxylate-terminated core-shell nanoparticles (COOH@SiO₂), as described in the reported method. In the second step, a postgrafting process was carried out by modifying MIL-88A onto the outer surface of the nanoparticles. The MIL-88A@SiO₂ composite was obtained through a complexation process in water and stirred for 12 h.



Scheme 1. Preparation of the core-shell-structured MIL-88A@SiO₂ microsphere particles.

The microstructure of the core-shell microspheres was observed by SEM (Figure 1). The core-shell microspheres exhibited a rough surface, densely covered with MIL-88A particles. Moreover, the morphology of the MIL-88A particles on the surface was consistent with their original polyhedral structure, confirming the successful preparation of the MIL-88A@SiO₂ core-shell material. The phase purity of MIL-88A@SiO₂ was verified by comparing the observed and simulated powder X-ray diffraction (PXRD) patterns (Figure 2). The thermal gravimetric analysis (TGA) indicated that the MIL-88A loading in the core-shell material was 11.953 mg (0.214 mmol) per gram of catalyst. This result aligns with the Fe loading of 0.198 mmol (11.06 mg) per gram of catalyst, as detected by inductively coupled plasma optical emission spectrometer (ICP-OES) analysis.

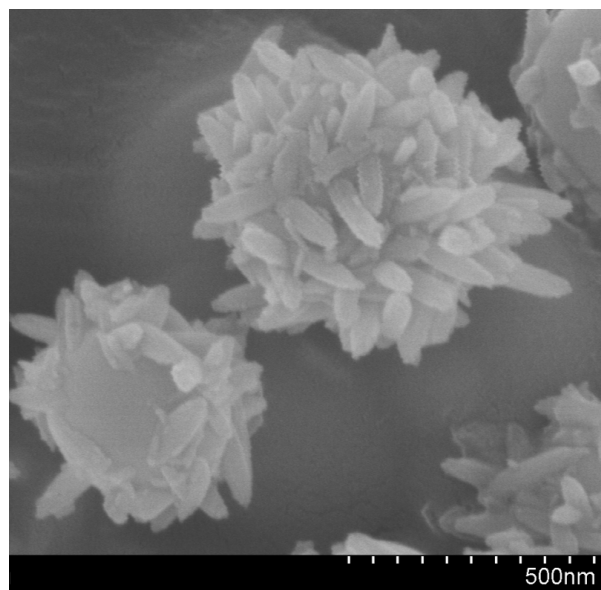


Figure 1. The SEM images of MIL-88A@SiO₂.

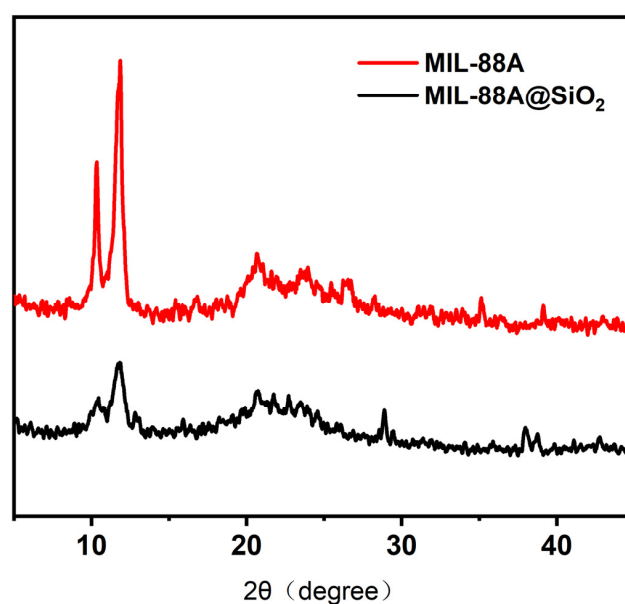


Figure 2. XRD patterns for MIL-88(A) and MIL-88(A)@SiO₂.

The FT-IR spectrum was collected to analyze the molecular structure of the as-synthesized core-shell material (Figure 3). The strong absorption bands corresponding to carboxylate groups were separated into asymmetric ($\nu_{as}\text{COO}$) and symmetric ($\nu_{s}\text{COO}$)

stretching vibrations, appearing at 1607 and 1396 cm^{-1} , respectively. This indicates that the carboxyl groups of fumaric acid linkers were coordinated to the metal centers. The strong peak at 1093 cm^{-1} was attributed to the stretching vibration of the CO-NH bond in the carboxylate-terminated SiO_2 microspheres. XPS spectroscopy of the as-prepared MIL-88A@ SiO_2 was conducted to examine the chemical composition and surface electronic states (Figure 4). The XPS survey spectrum confirmed the presence of C, O, and Fe in MIL-88A@ SiO_2 (Figure S4). The high-resolution XPS spectrum of Fe 2p (Figure 4) shows two peaks at binding energies of 725.47 eV and 712.12 eV, corresponding to Fe 2p_{1/2} and Fe 2p_{3/2}, respectively. These binding energies are consistent with the Fe³⁺ in $\alpha\text{-Fe}_2\text{O}_3$ [20]. Additionally, the satellite peak is a characteristic feature of Fe³⁺. The nitrogen adsorption–desorption isotherm (Figure S3) for MIL-88A@ SiO_2 demonstrates its porous structure, exhibiting a typical type IV isotherm with an H1 hysteresis loop and a distinct step at $P/P_0 = 0.82\text{--}0.95$. The pore size distribution reveals uniform mesopores of approximately 3.8 nm (see Figure S3 in the SI), which is comparable to the pore structure of pure MIL-88A [39,40].

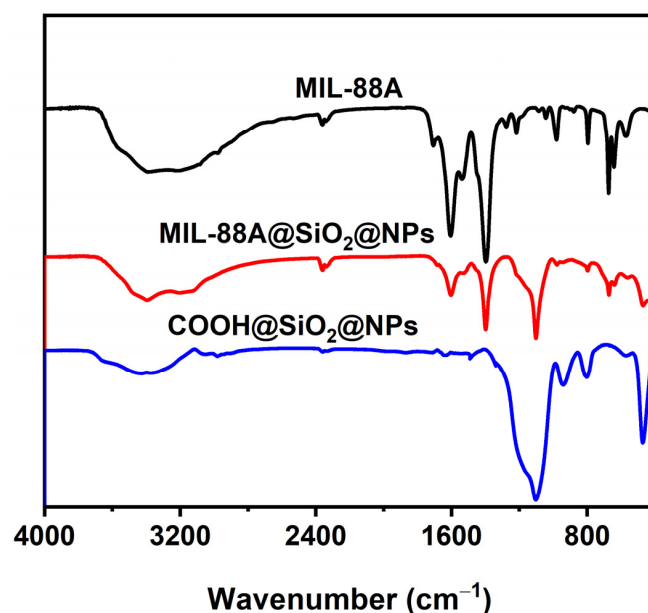


Figure 3. The FT-IR spectrum.

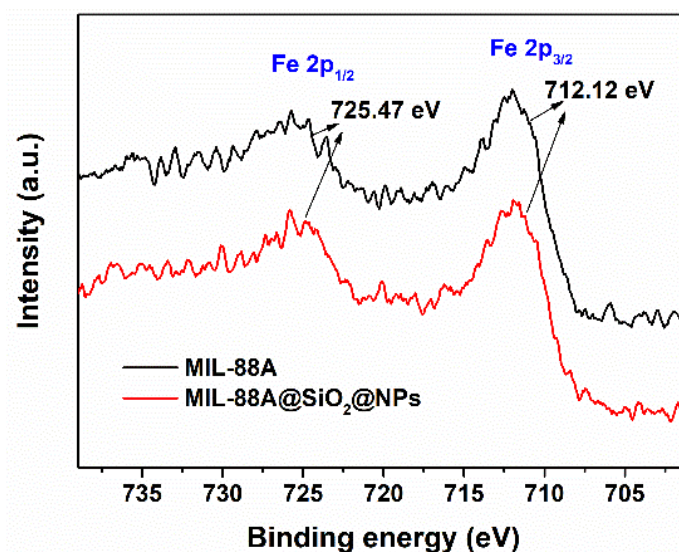


Figure 4. The XPS spectrum.

2.2. Catalytic Performance of the Heterogeneous Catalyst

Using the well-defined $\text{SiO}_2@\text{Fe(III)}$ core-shell microspheres, acid red 18 (AR-18) was selected as a target pollutant due to being a common organic contaminant used in the assessment of various advanced oxidation processes (AOPs). A series of control experiments were conducted to evaluate the degradation of AR-18 under varying amounts of H_2O_2 and catalyst loadings, as shown in Figure 5a. It was observed that approximately 83% of the AR-18 was degraded after 20 min with the addition of 0.5 mL of H_2O_2 . Excessive amounts of H_2O_2 were found to slow the degradation, while no degradation occurred in the absence of H_2O_2 . Catalyst loading was also optimized for AR-18 degradation; without $\text{MIL-88A}@\text{SiO}_2$, degradation did not proceed, and the optimal degradation (up to 84%) was achieved with 20 mg of catalyst loading. These results confirm that $\text{MIL-88A}@\text{SiO}_2$ exhibits catalytic activity for the Fenton-like reaction. Similar findings have been reported by other researchers using different Fe-based MOFs as heterogeneous Fenton catalysts for the degradation of organic contaminants [39,40].

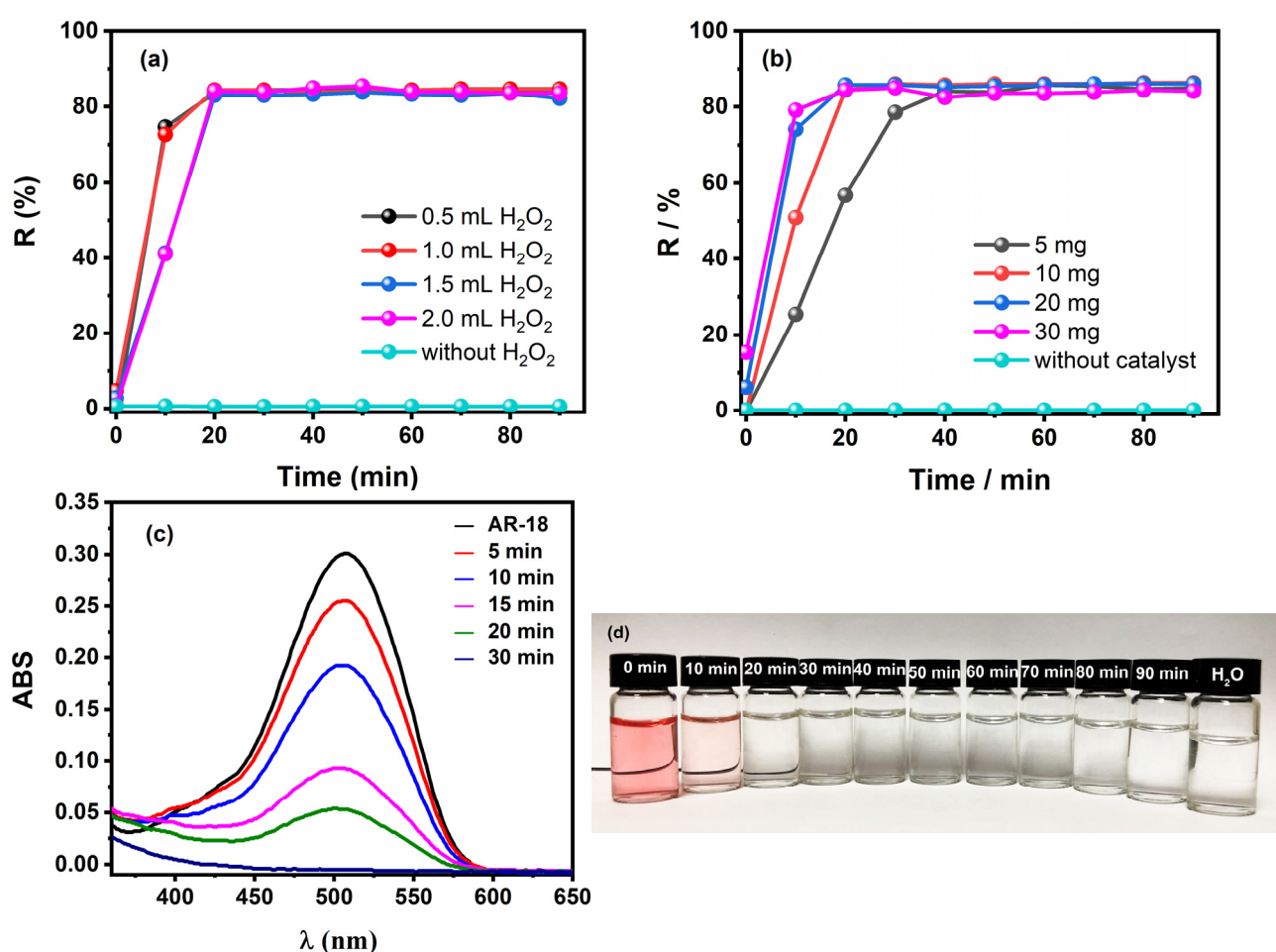


Figure 5. The degree of degradation for AR-18 under different (a) H_2O_2 amounts and (b) catalyst loadings. (c) The UV-visible spectrum and (d) the color change during the degradation of AR-18.

The color changes observed during the degradation of AR-18 in Figure 5d show that the solution became nearly colorless, similar to pure water, after 30 min. Correspondingly, the absorption band at 512 nm in the UV-visible spectrum (Figure 5c) nearly disappeared. Having established the catalytic system described above, the general applicability of the dye degradation process was further investigated using a series of dyes, including methyl orange (MO), methylene blue (MB), and rhodamine B (RHB). As expected, $\text{MIL-88A}@\text{SiO}_2$

effectively degraded these different dyes with degradation rates ranging from 81% to 96%, regardless of whether the dyes were neutral, anionic, or cationic (Figure 6d), consistent with results reported in the literature [14,20].

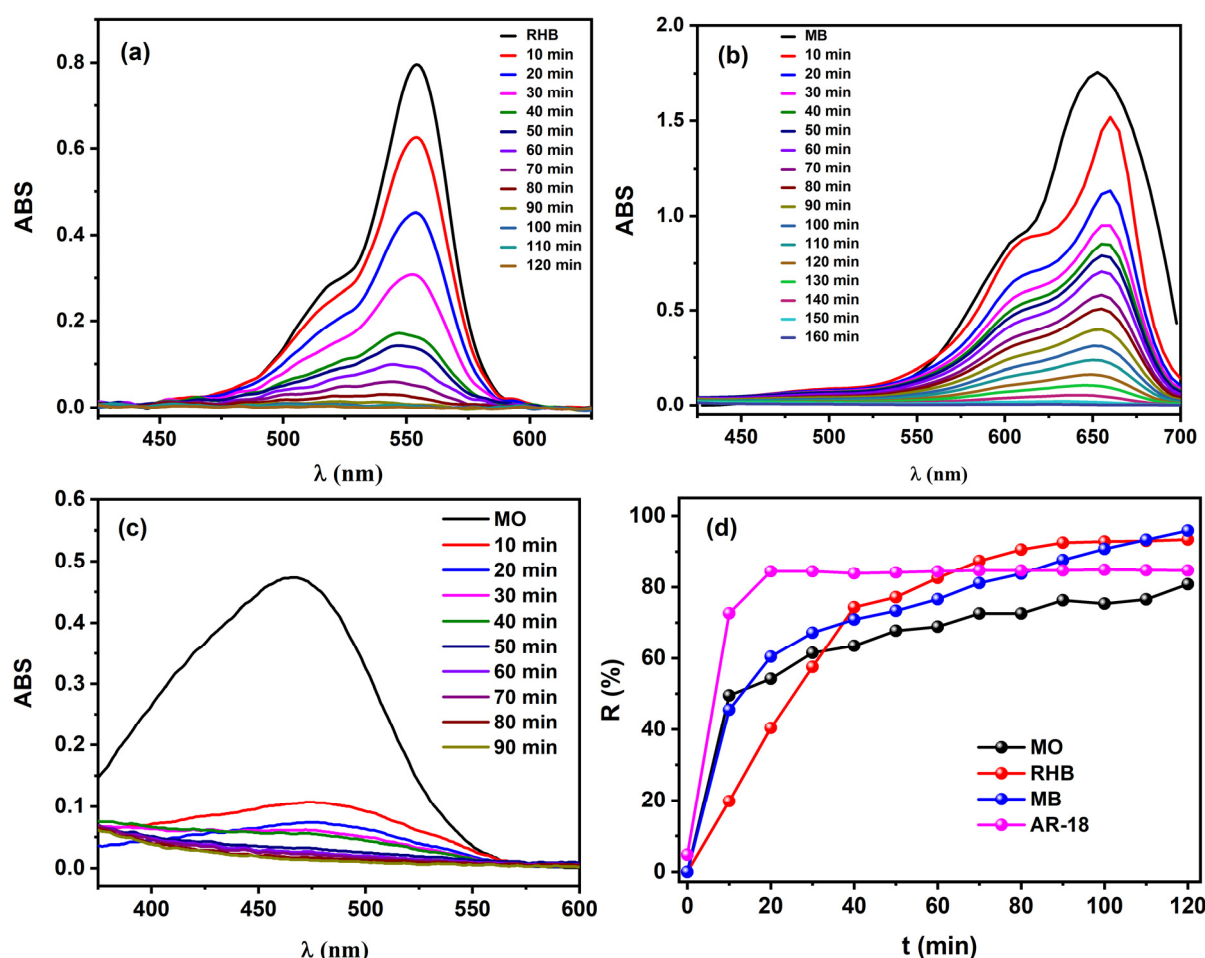


Figure 6. (a–c) The UV–visible spectrum during the degradation. (d) Changes in the degradation amount of four dyes over time.

The photocatalytic mechanism for the Fenton degradation process over $\text{SiO}_2/\text{MIL-88A}(\text{Fe})$ is proposed in Figure 7 based on references [17,18]. Under LED irradiation, the electrons in $\text{MIL-88A}/\text{SiO}_2$ are excited from the valence band (VB) to the conduction band (CB), leaving behind holes in the VB. These photogenerated electrons quickly transfer to the conduction band of MIL-88A, where they react with hydrogen peroxide (H_2O_2) to produce hydroxyl radicals ($\cdot\text{OH}$). Simultaneously, the electrons react with dissolved oxygen (O_2), generating superoxide radicals ($\cdot\text{O}_2^-$). Additionally, the coordinated $\text{Fe}(\text{III})$ within the MIL-88A framework is reduced by H_2O_2 to $\text{Fe}(\text{II})$, which further decomposes H_2O_2 to generate more hydroxyl radicals ($\cdot\text{OH}$). These reactive species, including hydroxyl radicals ($\cdot\text{OH}$) and superoxide radicals ($\cdot\text{O}_2^-$), possess strong oxidative properties, enabling the effective degradation of organic pollutants. Finally, the dyes are oxidized into CO_2 and H_2O , as confirmed by NMR analysis (Figure S8), which show no other organic compounds in the residual solution.

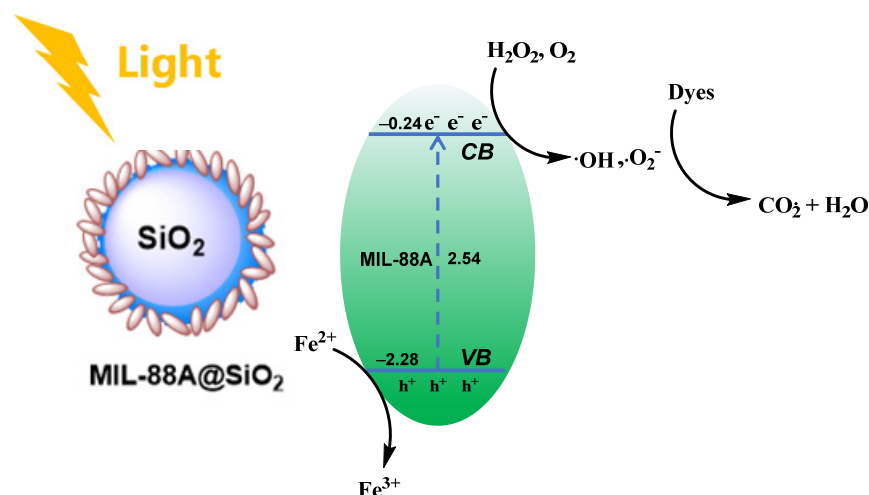


Figure 7. Schematic illustration of the proposed mechanism for photo-Fenton degradation of dyes over SiO_2 @MIL-88A(Fe).

In addition to the goal of developing a modified hollow-shell Fenton-like catalyst for dye degradation, another key consideration in the design of SiO_2 -based MIL-88A materials is the ease of separation via simple centrifugation and the ability to maintain catalytic activity after multiple recycling cycles. It was found that MIL-88A@ SiO_2 could be easily recovered by centrifugation at 10,000 rpm for 5 min. The MIL-88A@ SiO_2 was then Soxhlet-extracted with ethanol and water until no organic compounds were detected in the eluent. The recovered MIL-88A@ SiO_2 was reactivated at 80 °C under a vacuum overnight and reused for subsequent reactions. Notably, after seven consecutive degradation cycles, the recycled MIL-88A@ SiO_2 still achieved at least 79.3% degradation (Figure 8). Moreover, the recovered MIL-88A@ SiO_2 remained structurally intact, as confirmed by XRD analysis (Figure S2).

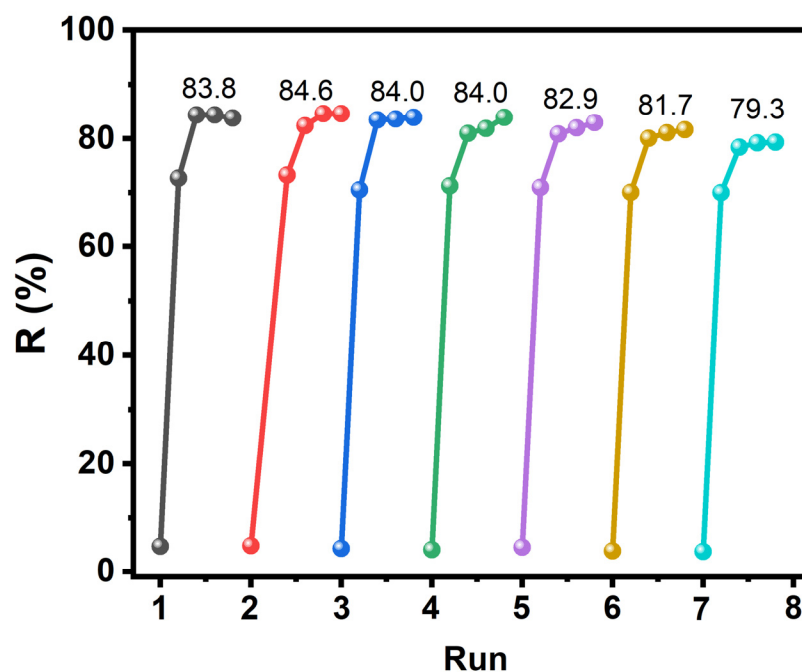


Figure 8. The degradation recycles for MO.

3. Experimental Section

3.1. Characterization

Fourier-transform infrared (FT-IR) spectra were collected using a Nicolet Magna 550 (Madison, WI, USA) spectrometer by the KBr pellet method. Scanning electron microscopy (SEM) images were acquired on a JEOL JSM-6380LV microscope (Akishima, Japan) operating at 29 kV. Nitrogen adsorption isotherms were measured at 77 K with a Quantachrome Nova 4000 analyzer (Graz, Austria), with the samples degassed overnight at 423 K. Pore size distributions were calculated using the BJH model, while specific surface areas (S_{BET}) were determined from the linear portions of BET plots ($P/P_0 = 0.05\text{--}0.3$). Powder X-ray diffraction (XRD) patterns were recorded on a RINT2000 vertical goniometer (Rigaku, Akishima, Japan) over a 2θ range of $5\text{--}50^\circ$. The concentrations of MO, AR18, RhB, and MB were determined using the external standard method on a UV-Vis spectrophotometer (Hitachi U-3900, Tokyo, Japan) based on their absorbance at peak wavelengths of 465, 507, 554, and 664 nm, respectively. Fe loading in the catalysts was analyzed with an inductively coupled plasma optical emission spectrometer (ICP-OES, Varian VISTA-MPX, Palo Alto, CA, USA).

3.2. Synthesis of Carboxylate-Terminated SiO_2 Microspheres

The first step was the synthesis of the silicate yolk according to the literature [41]; 10 mL of 1-propanol, 1.04 mL of deionized water, and 0.95 mL of ammonium hydroxide (25%) were added into a round-bottomed flask. Then, the mixture was stirred at 10°C , and a propanol solution of tetraethoxysilane (2.6 mL, 0.23 mol/L) was dropped into the above mixture under vigorous stirring. After 30 min, 75 mL of 1-propanol, 17.1 mL of deionized water, and 12 mL of ammonium hydroxide (25%) were added, and the mixture was stirred under 450 rpm at 25°C for 10 min. Subsequently, 48 mL of ammonium hydroxide (25%) and propanol solution of tetraethoxysilane (177 mL, 0.23 mol/L) was dropped into the mixture over a period of 15 min under vigorous stirring. The mixture continued to be stirred for 8 h, and the milky silicate yolk (SiO_2) was obtained after being filtered and washed with excess ethanol and dried at 60°C under vacuum for 8 h.

The second step was for the coating above the yolk. In a 100 mL round-bottomed flask, 500 mg of silicate yolk was dispersed into 50 mL of ethanol. The mixture was stirred at 80°C under 800 rpm, and 3-aminopropyltriethoxysilane (APTES, 2 mL) was added dropwise. The mixture was stirred for 6 h, and, after cooling the mixture down to room temperature, the solid was filtered and washed with ethanol and dried at 60°C for 8 h to produce $\text{NH}_2@\text{SiO}_2$. Subsequently, the $\text{NH}_2@\text{SiO}_2$ (500 mg) was dispersed into 30 mL *N,N*-dimethylformamide (DMF) under stirring at 500 rpm. Then, succinic anhydride (1.2 g) was added, and the mixture was refluxed at 85°C for 8 h. After cooling the reactant to room temperature, the $\text{COOH}@\text{SiO}_2$ was obtained as white powder by filtering and washing with deionized water and drying at 60°C under a vacuum for 8 h. IR (KBr, cm^{-1}): 3742–3115 (w), 3070 (s), 2975(s), 2348 (s), 1648(s), 1494(s), 1331 (s), 1099(m), 947 (m), 800 (m), 579 (m), 474 (m).

3.3. Preparation of the Core-Shell MIL-88A@ SiO_2

First, the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.338 g) was completely dissolved in 10.0 mL of deionized water in a 25 mL sealed tube; then, 10 mg $\text{COOH}@\text{SiO}_2$ was added to the mixture and stirred (150 rpm) at 65°C for 12 h. Third, 0.0725 g fumaric acid was added, and the mixture stirred slowly for 12 h at 65°C after being subject to ultrasonication for 30 min. After cooling the above mixture to room temperature, the target MIL-88A@ SiO_2 (Catalyst 1) was filtered and washed with excess water and ethanol, then dried overnight under a vacuum. The ICP analysis indicated that the content of Fe was 11.953 mg (0.214 mmol) per gram of

heterogeneous catalyst. IR (KBr, cm^{-1}): 3680–2895 (w), 2358 (s), 1675 (s), 1607 (m), 1529 (s), 1396 (m), 1093 (m), 975 (s), 795 (s) 670 (m), 642 (s), 557 (s), 467 (s).

3.4. General Procedure for the Photo-Fenton Processes

The photo-Fenton processes were conducted under a 65 W LED lamp. Catalyst **1** (20.0 mg, 0.358 mmol of Fe based on the ICP analysis) was added into 50 mL of dye solution (10 mg/L) containing H_2O_2 (10 mmol/L). Then, we turned on the LED irradiation, and 2 mL of solution was collected at regular time intervals (10 min). During the degradation process, the catalyst was uniformly dispersed within the solution via vigorous magnetic stirring at about 500 rpm to avoid concentration gradients, ensuring the catalyst contacted the reactants, thereby enhancing the reaction efficiency.

The concentration of contaminants was measured by UV–Vis spectra. The separation or degree of degradation was calculated via the following equation:

$$R = \left(1 - \frac{C_f}{C_0}\right) \times 100\%$$

where C_f and C_0 are the contaminant concentration of the original and reaction solutions, respectively.

After completion of the reaction determined by the UV–Vis spectra, the mixture was centrifuged at 10,000 rpm for 5 min, and the precipitate was Soxhlet extracted with ethanol and H_2O until no organic compounds were detected in the eluent. The recovered solid was reactivated at 80 °C under vacuum overnight and then reused for the next runs directly.

4. Conclusions

In conclusion, $\text{SiO}_2@\text{MIL-88A}(\text{Fe})$ core–shell-structured microspheres were successfully synthesized. The structure of $\text{SiO}_2@\text{MIL-88A}(\text{Fe})$ was characterized using XRD, BET, FT-IR, ICP, XPS, and electron microscopy. As demonstrated in this study, $\text{SiO}_2@\text{MIL-88A}(\text{Fe})$ enables an efficient Fenton-like degradation of dyes, achieving up to 96% degradation. Moreover, $\text{SiO}_2@\text{MIL-88A}(\text{Fe})$ can be easily recovered by filtration and washing, maintaining its high catalytic activity over six consecutive cycles in the Fenton process. This work provides a promising approach for designing heterogeneous catalysts with both high catalytic efficiency and cost-effectiveness.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal15010023/s1>, Figure S1: FT-IR spectra; Figure S2: XRD patterns; Figure S3: The N_2 adsorption-desorption isotherm; Figure S4: XPS spectra; Figure S5: SEM image; Figure S6: TGA curve; Figure S7: UV-vis spectra; Table S1: The heterojunctions constructed with Fe-MOFs for the degradation of organic pollutants in the photo-Fenton system; Figure S8: NMR.

Author Contributions: Conceptualization and methodology, C.T.; formal analysis, investigation, and data curation, K.L. and Y.Z. writing—original draft preparation, K.L.; writing—review and editing, T.C. and G.L.; visualization, supervision, and project administration, C.T.; funding acquisition, C.T. and G.L. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data is contained within the article.

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

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