Enhanced Activation of Persulfate by Meso-CoFe₂O₄/SiO₂ with Ultrasonic Treatment for Degradation of Chlorpyrifos

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Supporting Information

ABSTRACT: Magnetic mesoporous CoFe₂O₄/SiO₂ (Meso-CoFe₂O₄/SiO₂) composites were simply synthesized. On the basis of previous studies, optimum preparation conditions of their structure and physical properties can be readily determined. CoFe₂O₄ nanocrystals and their mesoporous structure were authenticated by low-angle and wide-angle X-ray diffraction, high-resolution transmission electron microscopy, scanning electron microscopy, element mapping, X-ray photoelectron spectroscopy, nitrogen adsorption isotherms, and so on. They were applied to degrade chlorpyrifos where Meso-CoFe₂O₄/SiO₂ composites provide a mesoporous microenvironment and combined with ultrasonic treatment can enhance heterogeneous activation of persulfate. Research findings showed that the system can be conducive to remove quickly chlorpyrifos and the removal ratios reached 99.99%. The results provided a strategy for the chlorpyrifos degradation and, similarly, pollution control of pesticide wastewater.

1. INTRODUCTION

Advanced oxidation processes (AOPs) are effective in removal of organophosphorus pesticides. Chlorpyrifos is one of the organophosphorus pesticides around the world with high toxicity, persistence, and refractoriness, causing serious harm to the waterbody environment. Therefore, the use of efficient processes to remove this pesticide from aquatic environments is necessary.

Sulfate-radical-based AOPs (SR-AOP) were considered to possess a similar standard reduction potential (2.5–3.1 V) as the hydroxyl radical (·OH) (2.8 V). Persulfate, with a high oxidative potential and wide adaptability, can overcome the drawbacks of traditional Fenton processes, such as a narrow pH range, excessive iron sludge, and intensive storage and transportation costs. Activation technologies are applied to strengthen the oxidation ability of persulfate, including heating, UV irradiation, transition metal ions, and metal oxides. Major advances and challenges in heterogeneous catalysis have been deeply concerned. The research focus was on utilization of metal, metallic oxide, and biochar to enhance activation of peroxysulfate for PCB degradation. However, many shortcomings of these methods have emerged, such as toxic metal leaching, poor recyclability, and high energy consumption. Therefore, the search for activation methods that are efficient, environmentally friendly, and economical has attracted considerable attention.

Further, ultrasonic treatment, as a clean, safe, and energy-saving technology, has high potential to enhance persulfate activation for the destruction of recalcitrant organic contaminants and enhance the production of free radicals (·OH and SO₄⁻·) by providing ultrasonic cavitation bubbles. Among the transition metals, Co²⁺ is reported to be the most effective in the activation of persulfate to generate SO₄⁻·.

In this study, a mesoporous microenvironment was combined with ultrasonic treatment to enhance chlorpyrifos degradation. Magnetic CoFe₂O₄ nanocrystals embedded in the mesoporous SiO₂ framework were simply synthesized, creating a mesoporous microenvironment to effectively prevent cobalt ion leakage. More specifically, Meso-CoFe₂O₄/SiO₂ composites were considered as promising candidates due to their high...
efficiency, low cobalt leaching, and ferromagnetic nature for convenient separation from aqueous solution. They were applied as activators of persulfate enhanced with ultrasonic treatment for degradation of chlorpyrifos, a typical organophosphorus pesticide. Their key parameters such as catalyst dosage, persulfate concentration, and ultrasonic frequency were studied.

2. MATERIALS AND METHODS

2.1. Materials. Tetraethoxysilane (TEOS), hydrochloric acid, cobalt(II) nitrate nonahydrate [Co(NO3)2·6H2O], ferric (III) nitrate nonahydrate [Fe(NO3)3·9H2O], ethanol (CH3CH2OH), and sodium persulfate (PDS) were purchased from Southwest Chemical Reagent Co. Ltd., China. All reagents with analytical purity were used as received without further purification. Methanol and dichloromethane were chromatographic purity levels from Southwest Chemical Reagent Co. Ltd., China. A contrastive sample such as the magnetic nanoparticle was marked as Fe3O4.32

2.2. Preparation and Characterization of Meso-CoFe2O4/SiO2: Meso-CoFe2O4/SiO2 composites were in situ synthesized by organic template assembly on the basis of the preliminary research.32 We made use of the following reactants: TEOS as the silica source, Fe(NO3)3·9H2O and Co(NO3)2·6H2O as active components, and F127 and octane as templates. In a typical experiment, first, F127 and octane were dissolved in hydrochloric acid (0.5 M) for 2 h. Second, Fe(NO3)3·9H2O and Co(NO3)2·6H2O were added under stirring for 2 h. Finally, TEOS was added under stirring to get a homogeneous mixture for 24 h at 38 °C. The molar composition of the mixture obtained were 1TEOS:0.83H2O:0.13Octane:0.004F127:0.2Fe(NO3)3·9H2O:0.1Co(NO3)2·6H2O:0.75HCl. The mixture was heated by water for 24 h at 100 °C, evaporated, and dried in a well-ventilated space by heating. The dried powder was heated up to 550 °C at a 10 °C·min⁻¹ heating rate and calcined at this temperature for 6 h. The resulting powder sample was marked as OFE. A contrastive sample such as the magnetic nanoparticle was marked as Fe3O4.32

Transmission electron microscope (TEM) images were taken on a Tecnai F30 TEM (FEI, the Netherlands) at 300 kV working voltage. Nitrogen adsorption–desorption isotherms were measured at 77 K using an AUTOSORB-I analyzer (Contador American). Specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. Pore size distribution was usually calculated from desorption branches of nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) model. X-ray diffraction (XRD) patterns were obtained at room temperature on an XPert MPD pro diffractometer (Panalytical, the Netherlands) using Ni-filtered Cu Kα radiation (λ = 1.5418 nm) at 40 kV and 10 mA. Scanning electron microscopy (SEM) images were taken with a JEOL JSM-6700F field-emission SEM at 20 kV. Magnetic performance was carried out using a vibrating sample magnetometer (VSM, Lakeshore 7407, America) with 20000 Oe fields and at room temperature. X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi) measurements were performed with an Al Kα source. All binding energies were referenced to the C1s peak at 284.6 eV.

2.3. Experimental Process. Catalytic degradation experiments were performed in a chlorpyrifos wastewater treatment process. On the experimental stage, the catalyst was directly added to the reactor filled with chlorpyrifos solution, stirred, and adsorbed for 0.5–1 h. Then a certain amount of persulfate was added to degrade chlorpyrifos. The reactor, such as a beaker, was placed in an ultrasonic cleaner. To study the changes of various parameters, typically, 2 g L⁻¹ catalyst and 4 mM sodium persulfate were added into 200 mL of 100 mg L⁻¹ chlorpyrifos solution. To study the treatment effect of chlorpyrifos wastewater with high concentration, the pH value of the solution was adjusted. After 2.5, 5, 10, 15, 20, 25, 30, and 40 min intervals, 10 mL of sample was taken out. The degradation reaction between free radical and chlorpyrifos was quenched with several drops of methanol. Chlorpyrifos concentration was determined. The changes of various parameters such as catalysts (0.05, 1, 2, 5, 8 g L⁻¹), sodium persulfate (0.5, 2, 4, 8, 14 mM), and ultrasonic frequency (20, 40, 60, 80 kHz) were studied. To study the treatment efficiency of the arbitrary degradation system combined with or without ultrasonic treatment, each experiment was repeated three times. Maximum and minimum values were recorded for each experiment. Its average values were taken. Standard deviation was generally within the allowable range of experimental error.

2.4. Analysis Method. Radical types were confirmed by electron paramagnetic resonance (EPR spectrometer, JEFFA200) using 5,5-dimethyl-1-pyrrolidine-N-oxide (DMPO) as a spin-trapping agent. The chlorpyrifos was analyzed by gas chromatograph–mass spectrometry (GC–MS, Agilent 7890A-5975C). A C18 column (30 m × 0.25 × 0.25 μm) was employed. The carrier gas was high-purity helium (99.999%), the flow rate is 1 mL·min⁻¹, and C18 was infiltrated with 1 μL of methanol and eluted with 1 μL of dichloromethane. The elution phase was a mixture of helium/methanol or dichloromethane (20:1, v/v). Under these conditions, the retention time of chlorpyrifos was 3 min. The metal leakage was obtained using inductively coupled plasma mass spectrometry (ICP-MS, Optima 5300DV). The concentrations of persulfate residuals were determined by the spectrophotometric
The ions released from the chlorpyrifos degradation were determined by an ICS-5000 ion chromatograph (Thermo Fisher Scientific, America). A dual-beam ultraviolet visible spectrophotometer (UV-1900PCS, Shanghai Spectrum Co. Ltd., China) was further used to correct the concentration of chlorpyrifos.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of Meso-CoFe₂O₄/SiO₂. HRTEM images of OFE are shown in Figure 1. A mesoporous structure is displayed in Figure 1A,B. As shown in Figure S1, magnetic performance was determined where coercive force was 1358±28 A m⁻¹ of OFE and the saturation magnetization value was 8.58 emu g⁻¹, far below those of Fe₂O₃, Fe₃O₄, γ-Fe₂O₃, and CoFe₂O₄. However, below saturation magnetization will be more favorable for particles uniformly dispersed in the solution. In Figure 2, the SEM micrograph of OFE is shown. The materials exhibited irregular shapes. Moreover, Fe, Co, O, and Si element maps are shown in Figure 2 and Figure S2. The active component was uniformly dispersed and embedded in the mesoporous frameworks. Element percentage contents are shown in Table S1.

In Figure 3, small-angle and wide-angle X-ray diffraction patterns for Meso-CoFe₂O₄/SiO₂ composites are shown. Figure 3A exhibited one broad, relatively weak peak, implying a mesostructured phase, which basically was in good agreement with the three-dimensional channel shown by HRTEM images. The crystalline phase was determined by wide-angle XRD patterns and is displayed in Figure 3B. Eight diffraction peaks were observed at 2θ = 18.31, 30.13, 35.47, 36.87, 43.12, 54.11, 57.00, and 62.59°, which were indexed to the (111), (220), (311), (222), (400), (422), (511), and (440) diffractions consistent with face-centered cubic spinel CoFe₂O₄ nanocrystals (space group: Fd3m, JCPDS card no. 03-0864). Nitrogen adsorption measurements were used to confirm cube-like mesoporous structure characteristics of OFE. It was in good agreement with the results of transmission electron microscopy. As shown in Figure 4, the isotherms of OFE were classified as IV type close to the hysteresis loop between H1 and H2. It is very consistent with Xie and Zhang. The pore system was uniformly distributed with most probable pore size around 7.2 nm. The BET surface area was 331.74 m² g⁻¹, and the pore volume was 0.963 mL g⁻¹. These results manifested that the mesoporous structure could be successfully constructed by this method.

Figure 2. SEM images and element mapping for Meso-CoFe₂O₄/SiO₂.

X-ray photoelectron spectroscopy (XPS) was one of the most powerful tools to confirm the species and valence states of the elements on the catalyst surface in order to understand their catalytic activity. Figure 5 shows XPS full spectra, Fe₂p, Co₂p, and O₁s spectra of OFE before use and after use. Si₂p and O₁s spectra were attributed to the framework of the mesoporous SiO₂ in Figure 5A. Peak positions of Fe₂p₃/2 and Fe₂p₁/2 were 711.6 and 725 eV, respectively, in Figure 5B. Each peak possessed a broadened satellite peak. Relatively weak Co₂p₃/2 and Co₂p₁/2 peaks were observed at 781.9 and 797.7 eV in Figure 5C, respectively. The peak intensity of OFE after use was weaker than that before use in Fe₂p and O₁s XPS spectra, suggesting partial leakage of ferric oxide. The Co₂p XPS spectra implied that the extremely small Co element on the surface was relatively stable and almost no leakage as shown in Figure 5C.

Figure 3. Small-angle (A) and wide-angle (B) XRD patterns for Meso-CoFe₂O₄/SiO₂.
ultrasonic irradiation can activate greatly persulfate to promote ·OH and SO$_4^{\cdot-}$ generation based on eqs 1 to 3.\textsuperscript{45,46} Owing to nucleophilic substitution, DMPO-SO$_4$ adducts transformed rapidly into DMPO-OH adducts, with the assistance of ultrasonic treatment.\textsuperscript{47} Therefore, as shown in Figure 6, the dominant radical of this reaction should be the hydroxyl radical. Based on the results obtained and the literature,\textsuperscript{45,48} the mechanism based on enhanced activation of persulfate by Meso-CoFe$_2$O$_4$/SiO$_2$ with ultrasonic treatment to degrade chlorpyrifos was proposed. Chief equations of reaction were as follows:\textsuperscript{46}

$$
\equiv\text{Fe(II)} + S_2O_4^{2-} \rightarrow \equiv\text{Fe(III)} + SO_4^{2-} + SO_4^{\cdot-}
$$

(1)

$$
\equiv\text{Co(II)} + S_2O_8^{2-} \rightarrow \equiv\text{Co(III)} + SO_4^{2-} + SO_4^{\cdot-}
$$

(2)

$$
SO_4^{\cdot-} + OH^- \rightarrow OH + SO_4^{2-} k_1 = 6.5 \times 10^7 \text{M}^{-1}\text{s}^{-1}
$$

(3)

$$
\text{CPs} + SO_4^{\cdot-} / OH \rightarrow \text{CO}_2 + \text{H}_2\text{O} + ... 
$$

(4)

3.3. Chlorpyrifos Degradation Performance. 3.3.1. Preliminary Comparison of Various Systems. The enhanced oxidation was studied through persulfate, Fe$_3$O$_4$/PDS, OFE/PDS, Fe$_3$O$_4$/PDS/US, and OFE/PDS/US systems. Figure 7 illustrates the highest chlorpyrifos removal percentage of pesticide wastewater treated by ultrasonic irradiation as a function of reaction time in the presence of OFE/PDS/US. As
it is noted, without ultrasonic treatment, the removal percentage increased very slowly with increasing reaction time, indicating a slower chlorpyrifos degradation ratio. Obviously, oxidation with only OFE/PDS systems was not qualified as a perfect removal of the chlorpyrifos from water. There was about 55.4% chlorpyrifos removal percentage when the aqueous solution was not exposed to the ultrasonic environment after 40 min of reaction. These results suggest that collaborative ultrasonic application could considerably enhance the removal of chlorpyrifos in a short time.

Further, the role of Meso-CoFe2O4/SiO2 in the acoustic catalysis of ultrasonic irradiation was studied. The following mechanistic steps may describe the interactive reaction between CoFe2O4 nanocrystal and persulfate under the assistance of an ultrasonic field as shown in eqs 1–8. This suggests that the Meso-CoFe2O4/SiO2/PDS/US process combining the synergistic effects of acoustic cavitation and mesoporous structure showed a further enhanced removal activity over any of the other studied AOPs and the chlorpyrifos removal percentage reached 99.99% within 40 min of reaction. However, chlorpyrifos removal percentage was only 55.4% in 40 min of reaction without ultrasonic treatment, while the chlorpyrifos decomposed percentage of the PDS/US process reached 70%. Owing to nucleophilic substitution, DMPO-SO4 adducts transformed rapidly into DMPO-OH adducts in OFE/PDS systems with increasing ultrasonic time based on eq 3.44 As shown in Figure 6, moreover, ultrasonic cavitation bubbles could enhance to generate more free radicals for oxidative cleavage of chlorpyrifos.47,49 In other words, the ultrasonic irradiation could also enhance the oxidation reaction by S2O42− in mesoporous cavitation where the transformation of Co3+ to Co2+ (Fe3+ to Fe2+) (eqs 5 and 6) was increased and consequently the generated Co3+ (Fe3+) catalyzes to produce SO4− radicals on eqs 1 and 2. It is clear from Figure 7 that the approximate complete removal of 100 mg L−1 chlorpyrifos occurred by the synergistic system of ultrasonic treatment and OFE/PDS in 40 min of reaction.

\[
\begin{align*}
\text{Fe(III)} + S_2O_8^{2−} &\rightarrow \text{Fe(II)} + S_2O_4^{−} \quad (5) \\
\text{Co(III)} + S_2O_8^{2−} &\rightarrow \text{Co(II)} + S_2O_4^{−} \quad (6) \\
S_2O_4^{−} &\rightarrow 2SO_4^{2−} \quad (7) \\
2SO_4^{−} + H_2O &\rightarrow \text{OH}^{-} + HSO_4^{−} \quad (8)
\end{align*}
\]

The persulfate was activated to divide into two circulatory systems. The first was the Fe cycle to generate free radicals on eqs 1 and 5. The second was the Co cycle to produce free radicals for oxidative cleavage of chlorpyrifos.

![Figure 7](image1.png)

**Figure 7.** Removal profiles of chlorpyrifos on different systems enhanced with ultrasonic treatment; [chlorpyrifos]0 = 0.285 mM, C(Fe3O4/OFE) = 2 g L−1, [persulfate]0 = 4 mM, initial T \approx 25 °C, initial pH \approx 7.0, ultrasonic frequency = 40 kHz.

![Figure 8](image2.png)

**Figure 8.** Effect of catalyst dosage (A) and persulfate concentration (C) on chlorpyrifos degradation in OFE/PDS/US systems; relationship between catalyst dosage and reaction ratio constants (B); relationship between persulfate concentration and reaction ratio constants (D); [chlorpyrifos]0 = 0.285 mM, initial T \approx 25 °C, initial pH \approx 7.0, ultrasonic frequency = 40 kHz.
radicals on eqs 2 and 6. Persulfate free radicals were very active and unstable due to their very high oxidation properties. Therefore, it has been speculated that the persulfate radical would decompose into sulfate ions as soon as it was formed on eq 7, with ultrasonic irradiation, so there was no such radical in the EPR spectrum.44

Based on our experimental removal percentages, it can be inferred that the OFE/PDS/US system possesses the best catalytic activity for SO4−−AOPs. Thus, the degradation effect of chlorpyrifos with the OFE system was higher than that with Fe3O4. It might be due to the composition and content in difference on the catalysis surface, also to the mesoporous structure, specific surface area, the dispersity of active components, and so on. Specially, the cobalt active component produced radicals to improve the degradation efficiency of chlorpyrifos. Finally, chlorpyrifos were effectively mineralized on eq 4.

3.3.2. Two Key Parameters and Kinetics for Chlorpyrifos Degradation. Meso-CoFe2O4/SiO2 activated persulfate to remove chlorpyrifos. Removal efficiency of chlorpyrifos in the influences of various parameters was studied. Figure 8A shows the relationship between removal time and chlorpyrifos residual ratio in the condition of various catalysts dosages. It was apparent that higher catalyst dosage was favored to form more radicals in quantity for chlorpyrifos removal.29,30 When the catalyst dosage exceeded 2 g·L−1, there was no significant change in the degradation effect with increasing catalyst dosage. Therefore, the optimum catalyst dosage for degradation was selected as 2 g·L−1. When the catalyst dosage was constant, the reaction system conforms to the first-order kinetic equation: In C/C0 = k·t. K is the ratio constant of chlorpyrifos degradation. As shown in Figure 8B, it was a nearly linear relationship between catalyst dosage and ratio constant Kapp of chlorpyrifos degradation. At the same catalyst dosage, degradation ratio constant Kapp constant of the OFE system was larger than that of the Fe3O4 system. Figure 8C shows that higher persulfate concentration will lead to a lower chlorpyrifos residual ratio. This could be that higher persulfate concentration will produce more reactive oxygen species to remove quickly the chlorpyrifos molecules. However, when the persulfate concentration exceeded 4 mM, the chlorpyrifos removal ratio did not change significantly. Similar to the behavior of catalyst dosage, degradation ratio constant Kapp also linearly increased as persulfate concentration was augmented for 0.5 to 14 mM in Figure 8D. The above conclusion showed that the specific surface area, surface active species, and mesoporous structure of Meso-CoFe2O4/SiO2 and reactive active species were positively correlated with the degradation efficiency of chlorpyrifos.

3.3.3. Effect of Ultrasonic Frequency on Chlorpyrifos Degradation. The ultrasonic parameters related to the phenomena of cavitation are very important factors to enhance activation systems. Further, ultrasonic frequency is a very important factor. Therefore, it is essential to investigate the effect of various ultrasonic frequencies on the performance of the OFE/PDS/US system. Figure 6 shows that ultrasonic treatment can efficiently promote persulfate activation to generate sulfate radicals and hydroxyl radicals. As discussed in Section 3.3.1, ultrasonic treatment can also promote chlorpyrifos molecular transfer and accelerate chlorpyrifos degradation. Further, it can also be seen that the increase in the degradation ratio from 20 to 40 kHz was more obvious than that from 60 to 80 kHz in a 40 min short time, which could be that too large ultrasonic frequency decreases chemical effects, slowly increases thermal effects, and reduces removal potential of the chlorpyrifos, as shown in Figure 9A. The degradation of chlorpyrifos accorded with the first-order kinetic equation. Based on the experimental results, the ultrasonic frequency was selected as 40 kHz, which was sufficient to remove more than 99% of chlorpyrifos in 40 min. Figure 9B shows the maximum of the degradation ratio constant when ultrasonic frequency was 40 kHz in OFE/PDS systems. This was due to the fact that the cavitation generated by the ultrasonic treatment can be optimized to activate persulfate and the formation and collapse of cavities may generate chemical effects in extremely short timeframes (milliseconds). The reaction ratio constant of the OFE/PDS system was greater than that of Fe3O4/PDS systems due to chemical effects of ultrasonic treatment in mesoporous channels and surface chemical composition.

3.3.4. Study on Mineralization Performance and Degradation Mechanism. Leakage of the active component of the catalyst directly affected the whole treatment process. As shown in Figure 10, the Co3+ leakage concentration was 0.001 mg·L−1 in OFE/PDS/US systems. However, in these systems, the Fe3+ leakage concentration of OFE was far lower than that of Fe3O4, and persulfate displayed higher efficiency utilization. It may be that CoFe2O4 nanocrystals were inlaid or embedded in the framework of mesoporous SiO2 to effectively prevent from metal leakage, in good agreement with those of Figure 5 XPS spectra. Mesoporous channels contributed to persulfate transfer and enhanced oxidation ability. Meso-CoFe2O4/SiO2 composites were reused 10 times, and the removal percentage of chlorpyrifos remained above 90%, as shown in Figure S3. Furthermore, metal leakages were far below the maximum
allowable discharge standard of “integrated wastewater discharge standards” (GB 8978-1996).

The goal of the chlorpyrifos degradation would complete mineralization and nontoxicity. That was thoroughly mineralized into CO₂, H₂O, and inorganic ions. Chemical oxygen demand (COD) and various ion concentrations in the OFE/PDS/US system are displayed in Figure 11. Further, only 92.4% COD removal ratios in the OFE/PDS/US system was higher than 65% in the MMS/PS system. The active component, mesoporous structure, and ultrasonic cavitation improved more effectively the surface reaction to mineralize the chlorpyrifos. The concentration of various ions in the solution was determined by ion chromatography. The results showed that organic chlorine of chlorpyrifos was almost thoroughly transformed into chlorides and a small amount of organic nitrogen was completely converted into ammonia nitrogen or nitrate nitrogen. Taking predominant hydroxyl radicals as an example, the possible degradation mechanism was elucidated. In the OFE/PDS/US systems, the removal mechanism of chlorpyrifos might be separated into two possible degradation pathways, as shown in Scheme 1. The first possible degradation pathway of chlorpyrifos was α-site dechlorination of three chlorines: the pyridine molecular fragment, attacked by hydroxyl radicals. The diethyl thiophosphate molecular fragment, attacked by hydroxyl radicals, was converted into the thiophosphate molecular fragment. The second possible degradation pathway was the breakdown of oxygen and phosphorus bonds, attacked with hydroxyl radicals, on the pyridine ring to form three chloropyridines and diethyl thiophosphate, which further oxidizes into sulfur phosphoric acid. The intermediates of these two possible degradation routes were in good agreement with the molecular fragments of chlorpyrifos in Figure S4. That is, the chemical bond that was most likely to break has a certain correlation with the molecular fragment in the mass spectrometry analysis of chlorpyrifos. As shown in Scheme 1, chemical bond fission was initiated by OH or SO₄⁻; chlorpyrifos would be decomposed into these intermediates, further mineralizing into CO₂, H₂O and inorganic ions, confirmed indirectly by the COD removal ratio and inorganic ions generated. Especially, it was pointed out that CO can easily react with two hydroxyl radicals to form carbonic acid, which overflows from the system in the form of carbon oxide when carbonic acid was in excess in the reaction system.

3.4. Discussion. From dispersity of the active component and ordering of the mesoporous structure, magnetic mesoporous composite materials were prepared. First, F127, octane, TEOS, [Fe(OH)₃]ₙ, and [Co(OH)₃]ₙ were dispersed in hydrochloric acid (0.5 M). Second, during the hydrophilic and hydrophobic colloidization, a large amount of surface OH⁻ group induced [Fe(OH)₃]ₙ and [Co(OH)₃]ₙ clusters "adsorbed" on the silicon polymer chains, which then assembled with the micelles made of F127 and octane. Finally, the [Fe(OH)₃]ₙ and [Co(OH)₃]ₙ clusters and silicon polymer chain were oxidized when mixed surfactant micelles were removed by calcination. Most cobalt iron oxide was dispersedly embedded or inlaid in the silica framework of the cubic mesoporous structure, which enhanced to activate persulfate in ultrasonic cavitation. At the same time, the OFE/PDS/US system could prevent metal leakage and generate a lot of SO₄⁻ and OH to mineralize completely chlorpyrifos.

4. CONCLUSIONS

In summary, Meso-CoFe₂O₄/SiO₂ composites have been successfully synthesized for heterogeneous activation of persulfate enhanced with ultrasonic treatment for chlorpyrifos degradation. Meso-CoFe₂O₄/SiO₂ displayed excellent activation performance of persulfate. The chlorpyrifos degradation ratio in the OFE/PDS/UV system was up to 99.99%. According to the results of EPR analysis, the introduction of ultrasonic treatment can activate persulfate to generate more free radicals than that without ultrasonic treatment in this
paper. The degradation efficiency of chlorpyrifos was dependent on ultrasonic frequency, catalyst dosage, and persulfate concentration. Using an ultrasonic frequency of 40 kHz, catalyst dosage of 2 g/L, and persulfate concentration of 4 mM, the removal ratio of chlorpyrifos was optimized to be 99.99%. Meso-CoFe2O4/SiO2 combined with ultrasonic treatment showed favorable chlorpyrifos removal performance. CoFe2O4 nanocrystals were inlaid or embedded in the mesoporous framework to leak lower in the OFE/PDS/US system. As shown in Figure 5 XPS, its catalytic performance improved.

**ASSOCIATED CONTENT**

**Supporting Information**
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Magnetization hysteresis loop, EDS, element percentages, reusability and MS data (PDF)

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**Notes**
The authors declare no competing financial interest.

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