Degradation of Acid Red 73 by Activated Persulfate in a Heat/Fe₃O₄@AC System with Ultrasound Intensification

Liyan Liu, Chao Yang, Wei Tan, and Yang Wang*

ABSTRACT: This work aimed to investigate the degradation efficiency of waste water with an azo dye, Acid Red 73 (AR73), by persulfate/heat/Fe₃O₄@AC/ultrasound (US). The introduction of ultrasound into the persulfate/heat/Fe₃O₄@AC system greatly enhanced the reaction rate because of the physical and chemical effects induced by cavitation. Various parameters such as temperature, initial pH, sodium persulfate dosage, catalyst dosage, initial concentration of AR73, ultrasonic frequency and power, and free-radical quenching agents were investigated. The optimal conditions were determined to be AR73 50 mg/L, PS 7.5 mmol/L, catalyst dosage 2 g/L, ultrasound frequency 80 kHz, acoustic density 5.4 W/L, temperature 50 °C, and pH not adjusted. Nearly 100% decolorization was achieved within 10 min under optimal conditions. Different from some other similar research studies, the reaction did not follow a radical-dominating way but rather had \( \text{1O}_2 \) as the main reactive species. The recycling and reusability test confirmed the superiority of the prepared Fe₃O₄@AC catalyst. The research achieved a rapid decolorization method not only using waste heat of textile water as a persulfate activator but also applicable to a complex environment where common radical scavengers such as ethanol exist.

1. INTRODUCTION

Textile waste water accounts for a large amount of industrial effluent, among which azo dye production makes up 50 to 70 percent of the total output. Because of the presence of such functional groups as aromatic rings and azo bonds in the structure, traditional biochemical treatment exhibits poor performance in the degradation of azo dyes. A trace amount of dyes even as low as 1 mg/L in water is still visible, reducing the transmittance and clarity of water and affecting the photosynthesis of aquatic plants. In addition, printing and dyeing wastewater usually has a high content of organic matter, leading to water eutrophication. Under the potential threat of mutagenicity, carcinogenicity, and genetic toxicity posed by azo dyes and their reaction products, various countries have introduced relevant laws and regulations to prohibit the use of some azo dyes. To meet the increasingly strict discharge requirements, efficient degradation of dyes has become a new challenge for researchers. Presently, the methods used in dyeing wastewater treatment include physical adsorption, biochemical treatment and application of reduction and oxidation. As an important part of oxidation methods, advanced oxidation process (AOP) achieves the degradation of pollutants using free radicals with the merits of being clean and efficient. The common advanced oxidation methods include Fenton method, ultrasonic method, persulfate method, ultraviolet method, and ozone oxidation method. The persulfate \( \text{S}_2\text{O}_8^{2−} \) (\( E_0 = 2.01 \) V), once activated, will produce \( \text{SO}_4^{−} \) (\( E_0 = 2.5−3.1 \) V) with strong oxidation potential, which is close to \( \text{HO}^+ \) (\( E_0 = 2.8 \) V) and has longer survival time than \( \text{HO}^+ \). As described in eqs 1−5, usual persulfate activation methods include transition metals (such as Fe, Mn, and Cu), alkali, ultraviolet, ultrasonic, activated carbon, and thermal activation.

\[
\begin{align*}
\text{S}_2\text{O}_8^{2−} + \text{Fe}^{2+} &\rightarrow \text{SO}_4^{−} + \text{SO}_4^{2−} + \text{Fe}^{3+} \quad (1) \\
2\text{S}_2\text{O}_8^{2−} + 2\text{H}_2\text{O} + \text{OH}− &\rightarrow 3\text{SO}_4^{2−} + \text{SO}_4^{−} + \text{O}_2^{−} + 4\text{H}^+ \quad (2) \\
\text{S}_2\text{O}_8^{2−} &\rightarrow \text{ultraviolet} \rightarrow 2\text{SO}_4^{−} \quad (3) \\
\text{S}_2\text{O}_8^{2−} &\rightarrow \text{ultrasound} \rightarrow 2\text{SO}_4^{−} \quad (4) \\
\text{S}_2\text{O}_8^{2−} &\rightarrow \text{heat} \rightarrow 2\text{SO}_4^{−} \quad (5)
\end{align*}
\]

Researchers have combined various activation methods to activate persulfate, resulting in a considerable synergistic effect. Huang et al. combined heterogeneous Fenton and ultrasound with Fe₃O₄/H₂O₂ and found that ultrasound and Fe₃O₄ had mutually promoting effects. The introduction of ultrasound...
helps to disperse the Fe₃O₄ nanoparticles that were prone to aggregation, thus increasing the surface area of Fe₃O₄. On the other hand, when Fe₃O₄ was added into the system as a solid, the steady cavitation bubbles in the ultrasonic field would explode asymmetrically on its surface, further enhancing the cavitation effect. Weng et al. applied iron aggregates with ultrasonic and heat for persulfate activation.²⁵ The study found that thermal or ultrasonic energy alone does not have significant effect on persulfate activation, and it is difficult to achieve degradation of Direct Red 23. However, when iron aggregates were introduced as another activator, ultrasonic/iron aggregates/persulfate and heat/iron aggregates/persulfate systems both achieved good degradation effect on Direct Red 23. Jafari et al. loaded nano Fe₃O₄ particles on activated carbon and solved the problem of agglomeration of nano Fe₃O₄ particles by using pore structures of activated carbon as support.²⁶ In addition, the presence of Fe₃O₄ particles also contributes to the magnetic recovery performance of activated carbon. The Fe₃O₄@AC catalyst can achieve adsorption of pollutants and activation of persulfate and has excellent durability and reusability. Although researchers have done lots of work on the combination of various activation methods at present, the ultrasonic/thermal activation system for azo dye decolorization has rarely been reported. Moreover, the temperatures of effluents from dyehouse are usually relatively high, which can be of potential use. This contradiction is perhaps due to the negative effect of temperature on cavitation. It is believed that the increase of solution temperature will lead to the increase of water vapor in cavitation bubbles, which will have a buffer effect when cavitation bubbles collapse, weakening the extreme environment in the bubbles during collapse, reducing the HO⁺ and H⁺ produced by the cracking of hydrogen peroxide, and ultimately leading to the weakening of the chemical effect of ultrasound.²⁷ However, the above process is only valid for a single cavitation bubble.²⁷ The increase of temperature will lead to more cavitation bubbles in the solution, which will compensate for the weakening of the cavitation effect of single cavitation bubbles caused by the increase of temperature. In the range of 35⁻⁵⁵ °C, both theoretical calculation and experimental studies prove that increasing temperature will increase the rate and degree of dye degradation.²⁷

In conclusion, the degradation of AR73 as simulated pollutant by the proposed system ultrasound/heat/transition metal/activated carbon/persulfate was discussed in this paper. Decolorization of AR73 in PS, PS/Fe₃O₄@AC and US/PS/Fe₃O₄@AC systems are compared, and the reaction kinetics and the activation energy were investigated. Various parameters were discussed which could have important effects on AR73 decolorization, including temperature (30⁻⁸⁰ °C), initial pH (3⁻¹¹), sodium persulfate dosage (1⁻30 mmol/L), catalyst dosage (0.25⁻⁴ g/L), initial concentration of AR73 (37.5⁻³⁰⁰ mg/L), ultrasonic frequency (40⁻¹₀₀ kHz), and generator input power (40⁻¹₀₀ W). Reactive species were determined using the method of radical quenching. The reusability and the recyclability tests were performed to ensure the proposed system had both advantages of economy and practicability.

2. RESULTS AND DISCUSSION

2.1. Characterization of Fe₃O₄@AC. The microscopic structure of Fe₃O₄@AC was investigated by SEM analysis. As shown in Figure 1a, obvious pore structures existed in the pristine activated carbon and the surface was rough. Figure 1b,c shows that the pore structures and the surface of activated carbon were filled with particles with size of tens of nanometers. Figure 1d shows the Fe₃O₄@AC micromorphology after 30 min of ultrasound irradiation, and the surface of activated carbon became significantly smooth.

The XRD pattern of the pristine activated carbon (AC), the as-prepared Fe₃O₄@AC catalyst, and the Fe₃O₄@AC catalyst after reaction is shown in Figure 2. The pristine activated carbon without any treatment showed two wide peaks characteristic of amorphous substances at 25° and 44°, and the presence of a highly graphitized fraction is confirmed by the sharp peak at 26.1° representing the (002) plane.²⁸ The XRD pattern of Fe₃O₄@AC showed new peaks at 30.1, 35.4, 43.1, 53.4, 56.9, and 62.5°, which corresponded to the reflection planes of (220), (311), (400), (422), (511), and (440) of magnetite PDF #19-0629 in standard cards, indicating that iron oxides with Fe₃O₄ as the main component were loaded successfully on activated carbon. After 30 min of reaction, the used catalysts were recycled with a magnet,
A pseudo-dye reached nearly 100% decolorization within 40 and 20 min. When the temperature rose to 70 and 80 °C, the reaction rate increased with the temperature. When the temperature was 50 °C, the decolorization reached 58% in 60 min. However, the reaction rate can be rapidly increased by increasing the temperature. When the temperature rose to 60 °C, the decolorization reached 58% in 60 min. When the temperature rose to 70 and 80 °C, respectively, the dye reached nearly 100% decolorization within 40 and 20 min. A pseudo-first-order reaction rate equation was used to investigate the reaction kinetics, and a good fitting degree was found ($R^2 > 0.97$). The reaction constants $k$ at various temperatures are listed in Table 1. For 80 °C, the reaction exhibited a two-stage trend, and the reaction constants were given as $k_1$ and $k_2$ for the two stages. This two-stage phenomenon and the fitting method have been reported in previous research.29,30 As the reaction proceeds, AR73 concentration decreases and intermediates concentration increases, which would compete with AR73 and reduce its decoloration rate, resulting in the second stage of reaction. 80 °C as an activation temperature means not only a very fast AR73 degradation rate but also a considerable intermediate producing rate; this explains why this two-stage phenomenon only happens when the temperature was over 70 °C. According to Arrhenius equation, the reaction activation energy $E_a$ calculated is 140.93 kJ mol$^{-1}$ ($R^2 = 0.9946$), which is similar to the activation energy given in the literature (145.3 kJ mol$^{-1}$).31 2.2. Decolorization in PS, PS/Fe$_3$O$_4$@AC, and US/PS/Fe$_3$O$_4$@AC Systems. Figure 3 shows the degradation effect of sodium persulfate (PS) alone on 50 mg/L AR73 at different temperatures. When the temperature was 50 °C, the degradation degree was very low and the reaction rate was only 16% in 60 min. However, the reaction rate can be rapidly increased by increasing the temperature. When the temperature rose to 60 °C, the decolorization reached 58% in 60 min. When the temperature rose to 70 and 80 °C, respectively, the dye reached nearly 100% decolorization within 40 and 20 min. A pseudo-first-order reaction rate equation was used to investigate the reaction kinetics, and a good fitting degree was found ($R^2 > 0.97$). The reaction constant of PS/Fe$_3$O$_4$@AC system is significantly increased at the different temperatures. Compared with PS system alone, the required activation energy was reduced by around 56%, indicating that the addition of Fe$_3$O$_4$@AC catalyst facilitated the reaction and effectively improved the reaction rate and degree. An interesting phenomenon to be noticed is that at 80 °C, the decolorization increased fast in the beginning 10 min, but a reversed slow decline trend was observed in the following 20 min, which means the degradation reaction was suppressed or new substances which could increase the absorbance was formed. This could result from the possibility that precipitate hard to be degraded was formed. Similar phenomenon was also reported by Zhang et al.32 In their work where metal ions were used to activate persulfate, metal ions reacted with intermediates and formed a kind of complex precipitate consisting of 60–70% metal and 30–40% S, which could not be degraded in the system. Therefore, only the first 10 min data points were used to calculate reaction kinetics, as shown in Figure 4b. Table 1. Degradation Reaction Constant of Sodium Persulfate (PS) Alone to AR73 at Different Temperatures

| $T$ (°C) | $k_1$   | $k_2$   | $R^2$ | $R^2$ |
|----------|---------|---------|-------|-------|
| 50       | 0.0026  | 0.9904  |       |       |
| 60       | 0.0137  | 0.9872  |       |       |
| 70       | 0.0720  | 0.9807  |       |       |
| 80       | 0.2104  | 0.9634  | 0.0397| 0.9872|

The reaction constant of US/PS/Fe$_3$O$_4$@AC system on 50 mg/L AR73 at different temperatures is greater than that of PS system alone at the same temperature. According to Arrhenius equation, the reaction activation energy was calculated as 61.41 kJ mol$^{-1}$ ($R^2 = 0.9368$). Figure 4a shows the degradation effect of sodium persulfate and Fe$_3$O$_4$@AC catalyst (PS/Fe$_3$O$_4$@AC) on 50 mg/L AR73 at different temperatures. When the temperature was 30 °C, the decolorization of the target dye reached 34% in 30 min, and the reaction rate increased with the temperature. When the temperature rose to 50 °C, the decolorization reached 49% in 30 min. When the temperature rose to 60 and 70 °C, respectively, the decolorization reaction for 30 min could reach 87 and 96%. The decolorization was 96.7% at 80 °C in 10 min. A good fitting ($R^2 > 0.96$) can be obtained by using the pseudo-first-order reaction rate equation, as shown in Figure 4b. The reaction constants $k$ at various temperatures are listed in Table 2. The reaction constant of PS/Fe$_3$O$_4$@AC system is significantly increased at the different temperatures. Compared with PS system alone, the required activation energy was reduced by around 56%, indicating that the addition of Fe$_3$O$_4$@AC catalyst facilitated the reaction and effectively improved the reaction rate and degree. An interesting phenomenon to be noticed is that at 80 °C, the decolorization increased fast in the beginning 10 min, but a reversed slow decline trend was observed in the following 20 min, which means the degradation reaction was suppressed or new substances which could increase the absorbance was formed. This could result from the possibility that precipitate hard to be degraded was formed. Similar phenomenon was also reported by Zhang et al.32 In their work where metal ions were used to activate persulfate, metal ions reacted with intermediates and formed a kind of complex precipitate consisting of 60–70% metal and 30–40% S, which could not be degraded in the system. Therefore, only the first 10 min data points were used to calculate reaction kinetics, as shown in Figure 4b. Figure 4b shows the degradation effect of US/PS/Fe$_3$O$_4$@AC system on 50 mg/L AR73 at different temperatures. Compared with PS/Fe$_3$O$_4$@AC system and PS system, the reaction rate of US/PS/Fe$_3$O$_4$@AC system was significantly increased at the different temperatures. Compared with PS system alone, the required activation energy was reduced by around 56%, indicating that the addition of Fe$_3$O$_4$@AC catalyst facilitated the reaction and effectively improved the reaction rate and degree. An interesting phenomenon to be noticed is that at 80 °C, the decolorization increased fast in the beginning 10 min, but a reversed slow decline trend was observed in the following 20 min, which means the degradation reaction was suppressed or new substances which could increase the absorbance was formed. This could result from the possibility that precipitate hard to be degraded was formed. Similar phenomenon was also reported by Zhang et al.32 In their work where metal ions were used to activate persulfate, metal ions reacted with intermediates and formed a kind of complex precipitate consisting of 60–70% metal and 30–40% S, which could not be degraded in the system. Therefore, only the first 10 min data points were used to calculate reaction kinetics, as shown in Figure 4b. Figure 5 shows the degradation effect of US/PS/Fe$_3$O$_4$@AC system on 50 mg/L AR73 at different temperatures. Compared with PS/Fe$_3$O$_4$@AC system and PS system, the reaction rate of US/PS/Fe$_3$O$_4$@AC system was significantly increased at the different temperatures.
same temperature after the introduction of ultrasound. When the temperature was 30 °C, the decolorization of the target dye was close to 100% in 30 min, which is more than that of 70 °C in the PS/Fe3O4@AC system (shown in the dashed line). When the temperature rose up to 80 °C, the reaction rate continued increasing to different degrees.

In the research of Chardi et al., 50 °C was reported as the optimal temperature for Toluidine Blue in sonochemical degradation, which was the result of concurrence between the number of bubbles and the single bubble yield. As the discharge temperature of dye wastewater is over 70 °C, 50 °C was selected as the water bath temperature in subsequent experiments.33

The ion concentrations in the PS/Fe3O4@AC and US/PS/Fe3O4@AC systems were determined to further investigate the difference of reaction progress in the two groups. Figure 6 shows the variation of residual concentration of S4O8−2 with time. Compared with the PS/Fe3O4@AC group, the residual concentration of S4O8−2 in the US/PS/Fe3O4@AC group was lower, indicating that S4O8−2 in the ultrasonic group decomposed more rapidly and produced more SO4−2; thus, reaction rate was higher.35 This corresponded to the faster decolorization rate of dyes after the introduction of ultrasonic described in the above experiments. Compared with the PS/Fe3O4@AC, the amount of leaching Fe2+ in the US/PS/Fe3O4@AC group was increased. This may result from the possibility that with the introduction of ultrasound, the microjet and shock wave induced by cavitation continuously hit the surface of the catalyst, accelerating the surface renewal and increasing the mass transfer rate, resulting in an increase in the concentration of leaching Fe2+, which would serve as an activator of persulfate and produce SO4−2, further increasing the reaction rate (eq 1).

SOE represents removed pollutant per oxidant agent, as shown in eq 7.36 For the problem discussed, higher SOE means better utilization of persulfate. The specific oxidation efficiency (SOE) was calculated, respectively, as 0.0299 and 0.0186 for the ultrasonic and stirring group, which means that
the ultrasonic group exhibits better efficiency of persulfate consumption.

$$\text{SOE} = \frac{(\text{Abs}_0 - \text{Abs}_1)}{(\text{PS}_0 - \text{PS}_1)}$$  \hfill (7)

2.3. Effects of Various Parameters on Decolorization in the US/PS/Fe₃O₄@AC System. 2.3.1. Effect of pH on AR73 Decolorization. The pH of the reaction system is an important parameter in the practical application and may have great effects on the reaction; thus, it should be explored to determine the influence on AR73 decolorization. The pH was selected between a relative broad range of 3–11, and the reaction process at various pH values is shown in Figure 7. The pH of the original 50 mg/L AR73 was 6.8 and that of the other two groups were adjusted with alkaline or acid. The reaction rate was relatively fast in an acidic environment when pH was 3, while those of the other two groups were almost the same. This is because that acidic condition could provide high concentration of protons, enhancing the generation of SO₄²⁻ through acid-catalyzing in accordance with eqs 8 and 9.37

$$\text{H}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow \text{HS}_2\text{O}_6^-$$  \hfill (8)

$$\text{HS}_2\text{O}_6^- \rightarrow \text{SO}_4^{*} + \text{H}^+ + \text{SO}_4^{2-}$$  \hfill (9)

For three initial pH values, the decolorization of AR73 in 30 min was almost complete, reaching over 98%. It indicates that the US/PS/Fe₃O₄@AC system can rapidly and effectively degrade 50 mg/L AR73 within a fairly wide pH range. This is because SO₄²⁻ once produced can bring down solution pH by the following reactions (eqs 10 and 11).38 The final pHs were measured to be 2.85, 2.98, and 3.07, which were similar, corresponding to the initial pHs of 3, 6.8, and 11. Besides, the ultrasound increased the reaction rate to the extent that the influence of pH became comparatively negligible.

All pHs: \hspace{1cm} SO₄²⁻ + H₂O ↔ HO⁺ + H⁺ + SO₄²⁻ \hfill (10)

Alkaline pHs: \hspace{1cm} SO₄²⁻ + OH⁻ ↔ HO⁺ + SO₄²⁻ \hfill (11)

2.3.2. Effect of Catalyst Dosage on AR73 Decolorization. The effect of catalyst dosage on AR73 decolorization was carried out at 0.25, 0.5, 1, 2, and 4 g/L. Figure 8 shows the reaction process under different catalyst dosage. The reaction rate increased with the increase of catalyst dosage from 0.25 to 4 g/L. This is because of the following two reasons: (1) in this range, the solid surface area of the reaction system increases with the increase of catalytic dose, providing more active sites for AR73 and S₂O₈²⁻. At the same time, more dye molecules react on the catalyst surface, so the initial reaction rate is significantly increased; (2) within a certain range of solid content, the presence of solid phase in the ultrasonic field will provide extra nucleation site for cavitation bubble because of its surface roughness, improving the ultrasonic cavitation intensity, and the cavitation intensity will increase with the increase of solid content.39 As the dosage of catalyst reached 2 g/L, the decolorization in 15 min was up to over 98%. In addition, when the catalytic dose was too large, it will hinder the propagation of ultrasonic wave in the system, thus weakening the reaction intensity. Taking economy and reaction rate comprehensively into consideration, the dosage of catalyst in subsequent experiments was determined to be 2 g/L.

2.3.3. Effect of PS Dosage on AR73 Decolorization. As the main reactive species provider, the PS dosage should have great influence on the decolorization rate. The effect of various PS dosage was explored with concentrations of 1, 3.75, 7.5, 15, and 30 mmol/L and discussed below. Figure 9 shows the reaction process at different Na₂S₂O₈ concentrations. When the dosage of Na₂S₂O₈ increased from 0.5 to 15 mmol/L, the reaction rate showed an obvious growth trend with the increase of dosage of Na₂S₂O₈. When the concentration of Na₂S₂O₈ was 0.5 mmol/L, the decolorization degree was only
about 40% in 5 min, while when the concentration of Na₂S₂O₈ was 7.5 mmol/L, the decolorization degree increased to more than 90% within the same time. This is because the increase of S₂O₈²⁻ increases the amount of SO₄²⁻ by activation, thereby increasing the reaction rate. When Na₂S₂O₈ concentration was further increased to 30 mmol/L, the reaction rate was inhibited. It indicates that the method of increasing the reaction rate by increasing the concentration of Na₂S₂O₈ is only feasible in the lower concentration range. The inhibition of excessive Na₂S₂O₈ is caused by reaction eqs 12 and 13.⁴⁰ On the one hand, SO₄²⁻ with strong oxidation ability is self-consumed into S₂O₄²⁻ with weaker oxidizing potential; on the other hand, excessive S₂O₈²⁻ would consume SO₄²⁻ with a reaction rate of 5.5 × 10⁵ M⁻¹ s⁻¹ and produce S₂O₄²⁻, reducing the oxidizing power and thus the decolorization rate. Considering economy and reaction rate, the Na₂S₂O₈ concentration was determined to be 7.5 mmol/L in subsequent experiments.

\[
\text{SO}_4^{2-} + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} \tag{12}
\]

\[
\text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + 2\text{S}_2\text{O}_4^- \tag{13}
\]

2.3.4. Effect of Initial Concentration of AR73 on Decolorization. In order to explore the influence of different initial concentrations of AR73 on US/PS/Fe₃O₄@AC system, AR73 concentration was set between 37.5 and 300 mg/L for a series of experiments; the result is shown in Figure 10. With the increasing of initial dye concentration, the reaction rate showed a decreasing trend. When the initial concentration of AR73 increased from 37.5 to 300 mg/L, the decolorization rate decreased from 97.3 to 55.4% in 5 min. The decolorization degree increased from 37.5 to 300 mg/L, the decolorization rate showed a decreasing trend. When the initial concentration of reactants reaches a high level, the factor limiting the reaction rate is the mass transfer rate of reactants and intermediate products in the liquid phase and catalyst surface.⁴¹ The introduction of ultrasound greatly accelerated the surface renewal of activated carbon and increased the adsorption rate of dye molecules and the removal rate of intermediate products on the activated carbon surface, which means the transfer rate between the liquid phase and catalyst surface was improved. Therefore, in the US/PS/Fe₃O₄@AC system, fast decolorization can be achieved even if the concentration of AR73 is relatively high.

2.3.5. Effect of Power of US on AR73 Decolorization. Using calorimetric method, the values of acoustic density were measured to be 3.9, 5.4 and 7.7 W/mL, corresponding to the generator input power of 40, 80, and 100 W.⁴² As shown in Figure 11, with the increase of power, the degradation rate first increased and then decreased. The reaction rate was similar at 3.9 and 7.7 W/mL and reached maximum at 5.4 W/mL. With the increase of power, there will be an increase in the number of cavities generated so that the cavitation effect is enhanced, and the micro-jet induced by the cavitation bubble enhances the mass transfer rate in the system, leading to an increase in the reaction rate. When the ultrasonic power continues to increase, the excess cavitation bubbles in the solution close to the transducer will create an acoustic barrier, which will scatter the sound waves to the walls or back to the transducer, hindering the continuous propagation of sound waves and weaken the reaction rate.⁴³ In conclusion, 5.4 W/mL is selected as the appropriate acoustic density (generator input power of 80 W).

2.3.6. Effect of Frequency of US on AR73 Decolorization. The degradation of AR73 is a complex process involving both physical and chemical interactions. Thus, the ultrasonic frequency is discussed below because it is a very important parameter in terms of both physical and chemical effects. The
reaction process at different frequencies of 40, 80, and 100 kHz is shown in Figure 12. It is evidenced that there exists an inverse dependence of mechanical and chemical effects considering frequency, that is, as frequency increases within a range, the chemical effect increases while the physical effect decreases. As described in previous analysis, mass transfer rate is largely accelerated when ultrasound is introduced into the reaction system, and this is mainly due to the physical effect induced by micro-jet and shockwave. Lower frequencies favor the physical effect, which provides a reasonable explanation for the experiment result that groups of 40 and 80 kHz exhibit faster decolorization rates. The 80 kHz group has double the frequency of the 40 kHz group, which means that the pulsation and collapse of the bubbles occur more rapidly and more radicals escape from the bubble, enhancing the chemical effect. In conclusion, compared with the other two frequencies, the 80 kHz group has a relative advantage in both physical and chemical effects, which might explain why the 80 kHz group has the greatest reaction rate.

2.4. Effects of Scavengers on AR73 Decolorization. In order to explore the free radicals that play a role in the reaction process, 10 mL of ethanol (EtOH), 10 mL tert-butyl alcohol (TBA) was added to each reaction system for the free radical inhibition experiment. Figure 13 shows that the reaction rate decreased after the addition of tert-butyl alcohol and ethanol, and compared with the TBA group, the reaction rate decreased more in the system with ethanol. TBA mainly reacts with HO• (3.8 × 10^9 to 7.6 × 10^9 M⁻¹ s⁻¹) produced, while ethanol reacts with both HO• (1.2 × 10^9 to 2.8 × 10^9 M⁻¹ s⁻¹) and SO₄²⁻ (1.6 × 10⁷ to 7.7 × 10⁷ M⁻¹ s⁻¹), so the inhibition degree of the experimental group with ethanol is higher. It should be noted that the decolorization reaction was relatively rapid even with the addition of scavenger doses up to 10 mL, which differs from other studies, in which 0.3 mL of ethanol was able to suppress the reaction by 77.2% when radicals play a main role in dye degradation. This suggests that radical reactions were not the main mechanism for decolorization. As described in other researches, non-radical reactive species such as ¹O₂ are produced when heterogeneous carbon-catalyst is used to activate persulfate. To start with, activated carbon might facilitate the hydrolysis of PS for the production of superoxide radicals, as in eq 2. Thus, a non-radical pathway might reveal the mechanism of the reaction system. In order to further investigate the main active species dominating the reaction, furfuryl alcohol (FFA), which is an effective quencher for ¹O₂ (1.2 × 10⁸ M⁻¹ s⁻¹), was added into the system. As shown in Figure 14, the addition of 10 mL of FFA as an inhibitor obviously suppressed the reaction, validating the assumption that it is the existence of ¹O₂ rather than the radicals that account mainly for the rapid degradation of AR73.

In conclusion, the reactive species in the reaction system are non-radical ¹O₂ accompanied by SO₄²⁻ and HO• radicals, and ¹O₂ is the main reason for rapid AR73 degradation.
scavenger experiment also indicates that free radical scavengers such as ethanol and tert-butyl alcohol in complex liquid environment have little negative effect on the degradation ability of the system, which can be considered as an advantage of the system, extending the application scope and condition of the method. The comparison between this work and relative literatures is listed in Table 3.

2.5. Variation of the UV–Vis Spectrum with Time. The UV–vis spectra of 50 mg/L AR73 in the US/PS/Fe3O4@AC reaction system showed a variation trend over 30 min in Figure 14. At 510 nm, the maximum absorption peak decreased rapidly. This wavelength corresponds to the azo bond of the visible band, indicating that the azo bond is destroyed rapidly at the initial stage of reaction, and the solution color can be observed to fade significantly within 5 min during the experiment. The peaks of bands 220–250 nm correspond to the benzene ring structure, and the peaks of bands 310–360 nm correspond to the naphthalene ring structure. It can be observed that the peaks around 250 and 350 nm decreased gradually with time, indicating that the structures of benzene and naphthalene rings are damaged to some extent but not completely. Another phenomenon worth noticing is that a red shift occurred at the peak corresponding to benzene structure during reaction, which implied that some intermediates of conjugated aromatic structures were formed.

2.6. Recycling and Durability Test of Fe3O4@AC Catalyst. The reusability of catalyst affects the economy of reaction to some extent. In order to test the reusable performance of Fe3O4@AC catalyst, the magnet was used to recover the catalyst in the system after each reaction. The catalyst was washed with deionized water for three times and dried for the next experiment. The figure shows the test results of the reusable performance of Fe3O4@AC catalyst. It can be seen in Figure 15a that the initial decolorization rate showed a decreasing trend as the number of times of use increased. After the reaction, the Fe3O4 particles supported on the surface of the catalyst were peeled off under the mechanical action of ultrasound, resulting in fewer reaction sites, and therefore, the reaction rate decreased. However, in the 5th recycle of catalyst, more than 95% decolorization could still be achieved at 15 min and the decolorization could reach around 99% at 30 min. As shown in Figure 15b, in the third group of experiments, the catalytic dose recovered by magnet was 0.3774 g, only 5.65% less compared with the original dosage, indicating that the synthesized catalyst has good recycling performance. This indicates that although Fe3O4 particles on the surface of activated carbon were peeled off under the action of ultrasound, a large number of Fe3O4 particles were still retained in the huge pore structure of activated carbon.

Table 3. Comparation of Literatures on Wastewater Treatment Employing Ultrasound-Activated Persulfate Oxidation

| analyte | analyte conc. (mmol L−1) | persulfate conc. (mmol L−1) | ctivator | ctivator properties | maximum analyte removal (%) | reaction time (min) | optimization | ref |
|---------|--------------------------|-----------------------------|----------|---------------------|-----------------------------|---------------------|--------------|-----|
| acid orange 7 | 0.060 | 3 | ultrasonication, plus Fe3O4 | 20 kHz, 200 W; 0.4 g L−1 | 90 | 30 | 25 mM tetraborate buffered pH 7.5 | 54 |
| rhodamine B | 0.02 | 0.3 | ultrasonication, plus graphene oxide | 35 kHz, 240 W; 0.25 g L−1 | >99 | 20 | pH > 6.4 (no adjustment) | 55 |
| direct red 23 | 0.100 | 5.00 | ultrasonication plus Fe6 | 106 W cm−2, 60 kHz; 0.5 g L−1 | 95 | 15 | pH = 6 | 25 |
| propranolol | 0.040 | 1.00 | ultrasonication plus Fe6 | 20 kHz, 250 W; 0.15 g L−1 | 94.2 | 30 | pH = 4.5 (no adjustment) | 35 |
| acid orange 7 | 0.086 | 1.26 | ultrasonication plus Fe6 | 20 kHz, 60 W; 0.5 g L−1 | 96.4 | 20 | pH = 5.8 (no adjustment) | 56 |
| tetracycline | 0.225 | 200.00 | ultrasonication plus Fe3O4 | 20 kHz, 80 W; 1 g L−1 | 89 | 90 | pH = 3.7 | 57 |
| sulfadiazine | 0.080 | 1.84 | ultrasonication plus Fe6 | 20 kHz, 40 W; 0.05 g L−1 | 99.1 | 30 | pH = 7.0 | 58 |
| acid orange 7 | 0.143 | 2.10 | ultrasonication plus Fe–Co/GAC | 20 kHz, 100 W; 0.8 g L−1 | 98.3 | 60 | pH = 5.8 (no adjustment) | 59 |
| nitrobenzene | 0.406 | 0.084 | ultrasonication, heat plus ZnO | 20 kHz, 45°C; 3 g L−1 | 96 | 120 | pH = 5 | 60 |
| acid red 17 | 0.020 | 2.00 | ultrasonication plus Fe3O4/coffee waste hydrochar | 300 W/L; 1 g L−1 | 100 | 80 | pH = 6 | 61 |
| AR73 | 0.09 | 7.5 | ultrasonication, heat plus Fe3O4/AC | 80 kHz, 5.4 W/mL; 50°C; 2 g L−1 catalyst | >99 | 10 | pH = 6.8 | this work |
| | 0.54 | 7.5 | ultrasonication, heat plus Fe3O4/AC | 80 kHz, 7.7 W/mL; 50°C; 2 g L−1 catalyst | 100 | 30 | pH = 6.8 | |

https://dx.doi.org/10.1021/acsomega.0c00903
ACS Omega 2020, 5, 13739–13750
endowing the catalyst with considerable magnetic recycling property. In general, the synthesized Fe₃O₄@AC catalyst has not only good magnetic recycling potential but also excellent reusability in catalytic capacity.

2.7. Economic Analysis of the US/Heat/PS/Fe₃O₄@AC System.

The cost analysis with ultrasound is usually of great concern. The current electricity bill in Tianjin is 0.092USD/kWh. Taking the cost of the raw materials of FeSO₄·7H₂O (28.58 USD/t), FeCl₃·6H₂O (500 USD/t) and granular activated carbon (428 USD/t) into consideration, and based on the assumption that the catalyst is disposable, the cost of the Fe₃O₄/AC catalyst is calculated to be 1.2 USD/m³. The cost of Na₂S₂O₈ is 929 USD/t, that is, 1.66 USD per cubic meter waste water, for the proposed method. The heat cost of the proposed method is considered 0 USD/t because it is obtained directly from the waste heat of the dye effluents. As derived from Table 4, the electricity consumption of ultrasound accounts for around 10–33% of the total cost, which is acceptable compared with the positive acceleration effect it brings.

It should be noted that the catalyst cost of 1.2 USD/m³ is overestimated on the assumption that the catalyst is disposable, considering the recyclability and reusability of the catalyst for at least five repeated use, and the total cost could be further decreased.

3. CONCLUSIONS

PS activated by heat (50 °C) was able to degrade AR73 with a relative slow speed. When Fe₃O₄@AC was added into the system, the degradation was accelerated with double efficiency and the reaction activation energy Eₐ calculated was 61.41 kJ·mol⁻¹, reduced by around 56% compared with PS alone. The decolorization process was further enhanced with the physical and chemical effects induced by US. When the temperature was 30 °C, the decolorization of AR73 in the US/PS/Fe₃O₄@AC system was close to 100% in 30 min, which is more than that of 70 °C in the PS/Fe₃O₄@AC system. The optimal conditions were determined to be AR73 50 mg/L, PS 7.5 mmol/L, catalyst dosage 2 g/L, ultrasound frequency 80 kHz, acoustic density 5.4 W/L, temperature 50 °C, and pH not adjusted. The dominating reactive species was non-radical ¹O₂ rather than radicals such as SO₄· and HO·; thus, the reaction system was applicable in a complex environment. The prepared catalyst had good magnetic recycling ability and excellent reusability in catalytic capacity.

4. MATERIALS AND METHODS

4.1. Materials.

Granular activated carbon was obtained from Calgon carbon (Suzhou) co. LTD. FeCl₃·6H₂O, FeSO₄·7H₂O, and persulfate sodium (Na₂S₂O₈) were obtained from Yuanli Chemical co. LTD (Tianjin). AR73 (C₂₂H₁₄N₄Na₂O₇S₂) was purchased from Macklin Inc. (Shanghai). All other reagents were of analytical grade. Figure 16 shows the chemical structure of AR73.

4.2. Preparation of Fe₃O₄@AC.

The Fe₃O₄@AC catalyst was prepared using in situ chemical co-precipitation method, as reported by Kakavandi et al. with some modification. First of all, 200 mL of deionized water was purged with nitrogen in a 250 mL beaker for 20 min to remove the extra oxygen. FeSO₄·7H₂O (2.224 g) and 3.244 g FeCl₃·6H₂O were then dissolved.
in the degassed water, and the mixture was placed in 70 °C water bath and constantly stirred with a speed of 400 rpm for 45 min. Next, 10 g of activated carbon (35–45 mesh) was added into the mixture, after which 28% ammonia solution was added drop by drop to the mixture till the pH of the final solution reached the range of 10–10.5. The solution was stirred vigorously for 1 h at a speed of 600 rpm in the water bath at 80 °C. Finally, the beaker was taken out and cooled down to the room temperature. The solution was washed 3 times with DI-water until the pH reached neutral. The magnetic catalyst was separated using an external magnet and dried in oven at 70 °C overnight.

4.3. Batch Experiments. During each experiment, 200 mL of AR73 solution was put into a 250 mL beaker. The beaker was placed 1 cm above the transducer of the ultrasonic bath, and the reaction temperature was kept constant by the circulating water bath system. Exact amounts of Fe3O4@AC catalyst and sodium persulfate were added in turn, and the ultrasonic was immediately turned on. Sample (3 mL) was taken out from the solution at pre-set time intervals and filtered with 0.45 μm needle filter, and the absorbance at 510 nm was quickly measured. Each degradation test was repeated three times, and the data were averaged. The effects of temperature, initial pH, sodium persulfate dosage, catalyst dosage, initial concentration of AR73, ultrasonic frequency and power, and free-radical quenching agent on the reaction were investigated. Unless otherwise stated, the experiments without ultrasonic were all stirred at a speed of 200rpm as control experiments.

The required instruments in the experiment are KQ-100VDB, KQ-100VDE dual-frequency numerical control ultrasonic cleaner (Kunshan Ultrasound Instrument Co., Ltd.), ultraviolet–visible spectrophotometer (Shanghai Mapada Instruments Co., Ltd.), and acidity meter (Sartorius AG).

4.4. Analysis. The absorption at 510 nm was measured using a UV–vis spectrophotometer to determine the concentration of AR73. The decolorization degree is defined by the pseudo-first-order equation

\[ -\ln(C/C_0) = kt \]  

(16)

The residual concentration of persulfate was determined with KI method. Briefly 5 mL of residual was sampled into a 50 mL vessel, quenched with EtOH and then mixed with NaHCO3 and KI. The residual concentration of persulfate can be indirectly obtained by measuring the absorbance of the generated I2, at 352 nm. The leaching Fe3+ was measured with the method of 1,10-phenanthroline spectrophotometry. The morphological and surface characteristics of the prepared catalysts were studied using field emission scanning electron microscopy (HITACHI-S4800) at 5 keV. After the catalyst was grounded to 320 mesh, an X-ray diffractometer (Panalytical, X’Pert Pro) with CuKα radiation (\( \lambda = 1.54 \text{ Å} \), 40 kV and 40 mA) was used to determine the crystal structure of the catalyst in the 2θ scanning range of 20–80°, with a scanning rate of 2°(2θ) min⁻¹.

AUTHOR INFORMATION

Corresponding Author

Yang Wang – School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, PR China; Tianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin 300072, PR China; orcid.org/0000-0003-1928-2506; Email: yangwang2017@tju.edu.cn

Authors

Liyan Liu – School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, PR China; orcid.org/0000-0003-1941-1689

Chao Yang – School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, PR China

Wei Tan – School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, PR China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00903

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors want to acknowledge the financial support from the National Natural Science Foundation of China (no. 21808160).

REFERENCES

[1] Konstantinou, I. K.; Albanis, T. A. TiO2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. Appl. Catal., B 2004, 49, 1–14.
[2] Hassani, A.; Çelikdağ, G.; Eghbali, P.; Sevim, M.; Karaca, S.; Metin, Ö. Heterogeneous sono-Fenton-like process using magnetic cobalt ferrite-reduced graphene oxide (CoFe2O4-rGO) nanocomposite for the removal of organic dyes from aqueous solution. Ultrason. Sonochem. 2018, 40, 841–852.
[3] Modirshahla, N.; Behnajady, M. A.; Rahbarfam, R.; Hassani, A. Effects of Operational Parameters on Decolorization of C. I. Acid Red 88 by UV/H2O2 Process: Evaluation of Electrical Energy Consumption. Clean: Soil, Air, Water 2012, 40, 298–302.
[4] Khataee, A.; Eghbali, P.; Irani-Nezhad, M. H.; Hassani, A. Sonochemical synthesis of WS2 nanosheets and its application in sonocatalytic removal of organic dyes from water solution. Ultrason. Sonochem. 2018, 48, 329–339.
[5] Agency for Environmental Protection (EPA). Clean Water Act; United States of America: 1977.
[6] European Commission. Water Framework Directive, 2000.
[7] Lei, C.; Pi, M.; Xu, D.; Jiang, C.; Cheng, B. Fabrication of hierarchical porous ZnO-Al2O3 microspheres with enhanced adsorption performance. Appl. Surf. Sci. 2017, 426, 360–368.
[8] Thung, W.-E.; Ong, S.-A.; Ho, L.-N.; Wong, Y.-S.; Ridwan, F.; Lehl, H. K.; Oon, Y.-L.; Oon, Y.-S. Biodegradation of Acid Orange 7 in a combined anaerobic-aerobic up-flow membrane-less microbial fuel cell: Mechanism of biodegradation and electron transfer. Chem. Eng. J. 2018, 336, 397–405.
[9] Zhang, H.; Duan, L.; Zhang, Y.; Wu, F. The use of ultrasound to enhance the decolorization of the C.I. Acid Orange 7 by zero-valent iron. Dyes Pigm. 2005, 65, 39–43.
[10] Hamdaoui, O.; Meroouni, S. Improvement of sonochemical degradation of Brilliant blue R in water using periodate ions: Implication of iodine radicals in the oxidation process. Ultrasound Sonochem. 2017, 37, 344–350.
[11] Wang, N.; Zheng, T.; Zhang, G.; Wang, P. A review on Fenton-like processes for organic wastewater treatment. J. Environ. Chem. Eng. 2016, 4, 762–787.
[12] Liu, L.; Wen, J.; Yang, Y.; Tan, W. Ultrasound field distribution and ultrasonic oxidation desulfurization efficiency. Ultrason. Sonochem. 2013, 20, 696–702.
[13] Fang, G.; Liu, C.; Gao, J.; Dionysiou, D. D.; Zhou, D. Manipulation of Persistent Free Radicals in Biochar to Activate Persulfate for Contaminant Degradation. Environ. Sci. Technol. 2015, 49, 5645–5653.
(14) Gupta, V. K.; Jain, R.; Mittal, A.; Saleh, T. A.; Nayak, A.; Agarwal, S.; et al. Photo-catalytic degradation of toxic dye amaranth on TiO2/UV in aqueous suspensions. *Mater. Sci. Eng., C* 2012, 32, 12–17.

(15) Holkar, C. R.; Jadhav, A. J.; Pinjari, D. V.; Mahamuni, N. M.; Pandit, A. B. A critical review on textile wastewater treatments: Possible approaches. *J. Environ. Manage*. 2016, 182, 351–366.

(16) Matzek, L. W.; Carter, K. E. Activated persulfate for organic chemical degradation: A review. *Chemosphere* 2016, 151, 178–188.

(17) Montagueo, J. M.; El-taliawy, H.; Durán, A.; Caro, G.; Bester, K. Sono-activated persulfate oxidation of diclofenac: Degradation, kinetics, pathway and contribution of the different radicals involved. *J. Hazard. Mater*. 2018, 357, 457–465.

(18) Ji, Q.; Li, J.; Xiong, Z.; Lai, B. Enhanced reactivity of microscale Fe/Cu bimetallic particles mFe/Cu with persulfate PS for p-nitrophenol PNP removal in aqueous solution. *Chemosphere* 2017, 172, 10–20.

(19) Tan, C.; Gao, N.; Fu, D.; Deng, J.; Deng, L. Efficient degradation of paracetamol with nanoscaled magnetic CoFe2O4 and MnFe2O4 as a heterogeneous catalyst of peroxymonosulfate. *Sep. Purif. Technol.* 2017, 175, 47–57.

(20) Bozckaj, G.; Fernandes, A. Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review. *Chem. Eng. J.* 2017, 320, 608–633.

(21) Wang, Z.; Shao, Y.; Gao, N.; Lu, X.; An, N. Deposition of diethyl phthalate DEP by UV/persulfate: An experiment and simulation study of contributions by hydroxyl and sulfate radicals. *Chemosphere* 2018, 193, 602–610.

(22) Ferrous, H.; Merouani, S.; Hamdaoui, O.; Pétrie, C. Persulfate-enhanced sonochemical degradation of naphtol blue black in water: Evidence of sulfate radical formation. *Ultrason. Sonochem.* 2017, 44, 580–587.

(23) Forouzesh, M.; Ebadi, A.; Aghaeinejad-Meybodi, A. Degradation of metronidazole antibiotic in aqueous medium using activated carbon as a persulfate activator. *Sep. Purif. Technol.* 2019, 210, 145–151.

(24) Huang, R.; Fang, Z.; Yan, X.; Cheng, W. Heterogeneous sono-Fenton catalytic degradation of bisphenol A by Fe3O4 magnetic nanoparticles under neutral condition. *Chem. Eng. J.* 2012, 197, 242–249.

(25) Weng, C.-H.; Tsai, K.-L. Ultrasound and heat enhanced persulfate oxidation activated with Fe0 aggregate for the decolorization of C.I. Direct Red 23. *Ultrason. Sonochem.* 2016, 29, 11–18.

(26) Jonidi Jafari, A.; Kakavandi, B.; Jaafarzadeh, N.; Rezaei, N.; et al. Ultrasound-assisted heterogeneous activation of persulfate by nano zero-valent iron nZVI for the propranolol degradation in water. *Ultrason. Sonochem.* 2018, 49, 33–40.

(27) Cheng, X.; Guo, H.; Zhang, Y.; et al. Non-photocatalytic production of singlet oxygen via activation of persulfate by carbon nanotubes: Oxidation of organic compounds by nonradical mechanism. *Chem. Eng. J.* 2015, 266, 28–33.

(28) Meng, Y.; Wu, S.; Jiang, Y.; et al. Photo-catalytic degradation of organic dyes in aqueous solution by zerovalent iron/Copper Fe/Cu Bimetallic Particles. *Ind. Eng. Chem. Res.* 2014, 53, 3665–3673.

(29) Rezaei, N.; et al. Fenton-like catalytic degradation of bisphenol A by Fe3O4 magnetic nanoparticles under neutral condition. *Chem. Eng. J.* 2012, 197, 242–249.

(30) Yuan, Y.; Li, H.; Lai, B.; Yang, P.; Gou, M.; Zhou, Y.; et al. Removal of High-Concentration C.I. Acid Orange 7 from Aqueous Solution by Zerovalent Iron/Copper Fe/Cu Bimetallic Particles. *Ind. Eng. Chem. Res.* 2014, 53, 2605–2613.

(31) Yuan, Y.; Li, H.; Lai, B.; Yang, P.; Gou, M.; Zhou, Y.; et al. Ultrasonic-assisted heterogeneous activation of persulfate by nano zero-valent iron nZVI for the propranolol degradation in water. *Ultrason. Sonochem.* 2018, 49, 33–40.

(32) Pandit, A. B. A critical review on textile wastewater treatments: Evidence of sulfate radical formation. *Porif. Technol.* 2017, 259, 320–417.
(53) Cheng, X.; Guo, H.; Zhang, Y.; Wu, X.; Liu, Y. Non-photochemical production of singlet oxygen via activation of persulfate by carbon nanotubes. Water Res. 2017, 113, 80–88.
(54) Liu, J.; Zhou, J.; Ding, Z.; Zhao, Z.; Xu, X.; Fang, Z. Ultrasound irritation enhanced heterogeneous activation of peroxymonosulfate with Fe₃O₄ for degradation of azo dye. Ultrason. Sonochem. 2017, 34, 953–959.
(55) Cherifi, Y.; Addad, A.; Vezin, H.; Barras, A.; Ouddane, B.; et al. PMS activation using reduced graphene oxide under sonication: Efficient metal-free catalytic system for the degradation of rhodamine B, bisphenol A, and tetracycline. Ultrason. Sonochem. 2019, 52, 164–175.
(56) Wang, X.; Wang, L.; Li, J.; Qiu, J.; Cai, C.; et al. Degradation of Acid Orange 7 by persulfate activated with zero valent iron in the presence of ultrasonic irradiation. Sep. Purif. Technol. 2014, 122, 41–46.
(57) Hou, L.; Zhang, H.; Xue, X. Ultrasound enhanced heterogeneous activation of peroxydisulfate by magnetite catalyst for the degradation of tetracycline in water. Sep. Purif. Technol. 2012, 84, 147–152.
(58) Zou, X.; Zhou, T.; Mao, J.; Wu, X. Synergistic degradation of antibiotic sulfadiazine in a heterogeneous ultrasound-enhanced Fe²⁺/persulfate Fenton-like system. Chem. Eng. J. 2014, 257, 36–44.
(59) Cai, C.; Wang, L.; Gao, H.; Hou, L.; Zhang, H. Ultrasound enhanced heterogeneous activation of peroxydisulfate by bimetallic Fe-Co/GAC catalyst for the degradation of Acid Orange 7 in water. J. Environ. Sci. 2014, 26, 1267–1273.
(60) Guo, J.; Zhu, L.; Sun, N.; Lan, Y. Degradation of nitrobenzene by sodium persulfate activated with zero-valent zinc in the presence of low frequency ultrasound. J. Taiwan Inst. Chem. Eng. 2017, 78, 137–143.
(61) Khataei, A.; Kayan, B.; Kalderis, D.; Karimi, A.; Akay, S.; et al. Ultrasound-assisted removal of Acid Red 17 using nanosized Fe₃O₄-loaded coffee waste hydrochar. Ultrason. Sonochem. 2017, 35, 72–80.
(62) Wang, C.; Yang, Q.; Li, Z.; Lin, K.-Y. A.; Tong, S. A novel carbon-coated Fe-C/N composite as a highly active heterogeneous catalyst for the degradation of Acid Red 73 by persulfate. Sep. Purif. Technol. 2019, 213, 447–455.
(63) Kakavandi, B.; Jahangiri-rad, M.; Rafiee, M.; Esfahani, A. R.; Babaei, A. A. Development of response surface methodology for optimization of phenol and p-chlorophenol adsorption on magnetic recoverable carbon. Microporous Mesoporous Mater. 2016, 231, 192–206.
(64) Liang, C.; Huang, C.-F.; Mohanty, N.; Kurakalva, R. M. A rapid spectrophotometric determination of persulfate anion in ISCO. Chemosphere 2008, 73, 1540–1543.
(65) Tian, K.; Yang, C.; Xiao, Q.; Fu, X.; Huang, Y. Degradation of 2,4,6-TCP in an ultrasound-enhanced zero-valent iron/potassium persulfate system. China Environ. Sci. 2017, 37, 3729.