Photodegradation of naphthalene over Fe$_3$O$_4$ under visible light irradiation

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Using FeCl$_3$ and FeSO$_4$ as precursors, Fe$_3$O$_4$ were prepared by co-precipitation method via FeCl$_3$ and FeSO$_4$ aqueous solutions successively added to NaOH solution. The sample was proved by X-ray powder diffraction, transmission electron microscope, ultraviolet–visible spectrophotometry and magnetic measurement. The results showed that the prepared Fe$_3$O$_4$ material was composed of an average diameter of about 15 nm particles and nano rods with well-crystallized magnetite and stronger superparamagnetic, getting a saturation magnetization of 49.5 emu g$^{-1}$. This Fe$_3$O$_4$ material was found to be an effective catalyst for photodegradation of naphthalene with or without H$_2$O$_2$ under visible light irradiation, getting 81.1% and 74.3% degradation rate in these two cases, respectively. The degradation pathway in the absence and presence of H$_2$O$_2$ was analysed via measurement of the distribution of degradation products by GC-MS and adsorption of reactants on the surface of the catalyst by in situ DRIFTS spectra.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) that consist of two or more condensed benzene rings are primarily formed from the incomplete combustion or pyrolysis of organic materials such as petroleum, gas, coal and wood [1]. These compounds have recently attracted a lot of attention in studies on water, soil and air pollution due to their highly carcinogenic, mutagenic and teratogenic potential [2]. The removal of such substances from the environment can be achieved using various methods, including physical, biological and chemical [3–5]. In the case of removing PAHs from aqueous systems, a physical process such as volatilization and adsorption can greatly reduce the amount of PAHs in the aqueous solution. However, this method does
not completely solve the problems of PAHs pollution because of their unavailability for degradation of these pollutants. Besides, the conventionally biological method makes a limited contribution to the removal of PAHs from the aqueous solution due to the biorecalcitrant, toxic nature and low aqueous solubility of PAHs. Therefore, chemical processes have been used as alternatives to physical and biological ones because the former has greater potential for efficient removal of these pollutants from the aqueous system. Among the chemical methods, the removal of PAHs via photodegradation catalysed by heterogeneous semiconductor catalysts has been widely developed. These semiconductor catalysts involving TiO$_2$, ZnO, SnO, WO$_3$, Al$_2$O$_3$ and their modified nanomaterials exhibited efficiently photocatalytic activities for degradation of PAHs [6–9]. In particular, studies on modified or doped TiO$_2$ nanomaterials have been widely conducted due to the pure TiO$_2$ being significantly limited by its wide band gap, low light-application efficiency and high electron-holes recombination [10–12]. In recent years, catalytic and photocatalytic activities of iron oxides have been widely investigated because the iron oxides exhibit good performance, environmentally benign character and low cost. Yang et al. addressed the synthesis of $\alpha$-Fe$_2$O$_3$ nanoparticles using the hydrothermal method and the synthesized $\alpha$-Fe$_2$O$_3$ nanoparticles with smaller crystalline size show higher photocatalytic degradation efficiency than those of $\alpha$-Fe$_2$O$_3$ powders with larger crystalline size [13]. Furthermore, a mixture of $\alpha$-Fe$_2$O$_3$ and Fe$_3$O$_4$ exhibits better photocatalytic activity than that of pure $\alpha$-Fe$_2$O$_3$ [14]. The higher activity of the mixed phase sample was likely attributed to the higher transfer of electrons and holes generated on the surface of $\alpha$-Fe$_2$O$_3$ to the valence band of Fe$_3$O$_4$ which limits the recombination rate of electrons and holes [15]. Besides, Iron oxide nanocrystallites are active and selective catalysts for oxidation of aromatic compounds [16–18]. In the oxidation process using Fe$_3$O$_4$ as a catalyst, Fe$^{3+}$ and Fe$^{2+}$ participate in the catalytic oxidation cycle by interaction with the oxidant and it displays efficient catalytic activity [19–21]. However, few reports on the distribution of degradation products during the degradation of PAHs over iron oxides were found. So far, Fe$_3$O$_4$ nanoparticles are prepared by several methods, such as co-precipitation, precipitation in microemulsions, solvothermal reactions and hydrothermal method etc. [22–26]. Among them, the chemical precipitation is widely used due to its simple and practical nature. Usually, Fe$_3$O$_4$ nanoparticles are prepared by an aging stoichiometric mixture of ferrous [(FeCl$_2$, FeSO$_4$ or Fe(NO$_3$)$_2$] and ferric salts [(FeCl$_3$, Fe$_2$(SO$_4$)$_3$ or Fe(NO$_3$)$_3$] in aqueous medium and this process must have been carried out in a nitrogen atmosphere so as to prevent the Fe$_3$O$_4$ from being oxidized.

In view of these findings, nanosized Fe$_3$O$_4$ crystalline particles were prepared via an alternative method using FeCl$_3$ and FeSO$_4$ solutions successively dropwised in NaOH solution in order to maintain a basic medium for preventing FeO from being oxidized to Fe$_2$O$_3$. The photocatalytic performance of the prepared Fe$_3$O$_4$ nanoparticles for degradation of naphthalene in aqueous solution with or without H$_2$O$_2$ as oxidant were estimated and it displayed highly efficient photocatalytic activity. The results are disclosed in this work.

2. Experimental

2.1. Preparation of the catalysts

Iron oxide was prepared by the following procedure: a three-necked flask filled with 84 g of NaOH aqueous solution (1.25 mol l$^{-1}$) with pH = 13.3 was put in a tank with ultrasonics and 65.4 g of FeCl$_3$ aqueous solution (0.33 mol l$^{-1}$) was dropwise added to the NaOH solution under ultrasonics and stirring. After adding, the reaction mixture was further ultrasonically treated for 40 min, the pH value of the mixture being changed from 13.3 to 12.8. The mixture was then heated in a water bath to 80°C, followed by dropwise addition of 62.8 g of FeSO$_4$ aqueous solution (0.17 mol l$^{-1}$) to this mixture with pH = 12.3, the temperature being changed to about 78°C. The mixture was continuously heated to 80°C and stirred at this temperature for 4 h until its pH value reached 12.1. After cooling down, the sol solution was filtered to remove the filtrate. The obtained gel was washed with anhydrous ethanol and deionized water three times, respectively, until the washing solution reached about pH = 7. Thereafter, it was dried at 50°C to attain Fe$_3$O$_4$.

2.2. Catalyst characterization

The X-ray powder diffraction (XRD) pattern of the sample was performed on a Bruker-D8 advance X-ray diffractometer with Cu K$_\alpha$ radiation (40 kV and 36 mA). The morphology and particle size of the samples
were observed by an FEI Tecnai F20 transmission electron microscope (TEM). The magnetic measurement was performed on a Vibration Sample Magnetometer (Lake Shore 7410). The diffuse reflectance ultraviolet–visible spectrum for the sample was recorded on a CARY 4000 UV–vis spectrometer.

In situ DRIFTS spectra were measured by an FT-IR spectrometer (Brucker TENSOR II) equipped with a diffuse reflectance optics accessory (Harrick Scientific products Inc.). To clean the catalyst surface, the iron oxide sample was thermally pretreated by heating to 50°C for 2 h in vacuo prior to acquisition of DRIFTS spectra. Thereafter, the build-up of naphthalene and/or H2O2 species onto the catalyst surface was performed by taking them along with high pure N2 gas (purity 99.99%) for 2 h, followed by evacuation from the system to about 9.8 × 10⁻⁴ Pa. After that, the DRIFTS spectra of surface species at 50°C were measured half an hour under vacuo conditions.

2.3. Catalytic test and analytic procedure

An amount of 10 ml of naphthalene solution (0.2 mmol of naphthalene dissolved in 100 ml ethanol + 100 ml deionized water), 90 ml of deionized water and 0.3 g of Fe₃O₄ were added to a quartz columnar reactor (placed in a water-bath to maintain the temperature at 23–25°C) fitted with a magnetic stirrer. The reaction mixture with pH = 6.96 was irradiated by λ = 400–780 nm visible light (HSX-F/UV300, using a VISREF780 filter, Beijing NBet science & technology Ltd Co.) under stirring for 8 h (intensity of illumination 2.7 × 10⁵ LX). The light source was close to the wall of the reactor. At the end of the reaction (the mixture solution with pH = 7.22; when using H2O2 oxidant the pH changed from 3.50 initially to 4.50 after the reaction.), the catalyst was separated from the reaction mixture by a magnet. The sample solution was analysed by a Lambda-35 ultraviolet spectrometer (PerkinElmer Company) to determine degradation rate. The sample solution was extracted by 10 ml of CH₂Cl₂ three times and the upper phase was analysed by GC-MS (Agilent GC7890A-MS5975C) using an HP-5 column (30 m × 0.32 mm × 0.25 um) to identify the degradation products. The degradation rate was calculated by the following formula:

$$\text{rate} = \frac{C_0 - C_t}{C_0} \times 100\%,$$

where $C_0$ is the initial concentration of naphthalene, $C_t$ is the concentration of naphthalene at a certain time.

3. Results and discussion

3.1. Preparation and characterization

In our previous work [27], Fe₃O₄ was prepared in an alternative way, using acid pickling waste as a precursor added to the basic solution to ensure the pH ≳ 8 during the preparation process, whereas in this case, Fe³⁺ (FeCl₃) and Fe²⁺ (FeSO₄) solutions were used as precursors in the absence of PEG-400 dispersant and Fe₃O₄ nanoparticles were successfully prepared at pH = 12.1 for precipitation by this simple method.

X-ray powder diffraction of iron oxide sample was recorded in 2θ range of 10–80°. It could be seen from the XRD pattern of the sample shown in figure 1 that typical diffraction peaks at 2θ of 30.1, 35.4, 43.1, 53.4, 57.0 and 62.7° corresponded to (220), (311), (400), (422), (511) and (440) lattice planes, respectively. No peak from other impurities were found in this image, suggesting that close to single phase Fe₃O₄ was successfully prepared and all the diffraction peaks were perfectly indexed, which was in agreement with the data of the cubic phase Fe₃O₄ (magnetite JCPDS 19–0629) [28]. The average crystalline size of the sample was calculated according to the Scherrer equation and the estimated particle size approached 14.4 nm. This estimation was basically in agreement with one observed in the TEM image (figure 2a). As seen from the image, particles of about 15 nm in size and nano rods of about 15 nm in diameter were observed. However, the nanostructured material was further examined with high-resolution TEM. A typical HRTEM image of nanostructured Fe₃O₄ was obtained as shown in figure 2b. The lattice fringes in the image corresponding to a set of atomic planes within the particles were clearly observed. X-ray photoelectron spectroscopy of Fe₃O₄ was shown in figure 3. As seen in the figure, a typical peak corresponding to Fe₃O₄ was observed at 712.2 eV, which was basically in accordance with 711.4 eV for pure Fe₃O₄ in reported literature [29]. Obviously, a set of distinct binding energies were observed for the Fe 2p₁/₂ spectra, one at 725.5 eV and the other at 726.2 eV, which were assigned to
characteristics of FeO and Fe$_2$O$_3$, respectively. The atomic ratio of O to Fe was estimated to be 4:3 by XPS. This also elucidated that pure Fe$_3$O$_4$ was successfully obtained. Besides, the higher visible light absorption of the Fe$_3$O$_4$ sample was found in the range of 400–780 nm, as shown in UV–vis spectrum (figure 4). This indicated that Fe$_3$O$_4$ could be activated by visible light.

The curve of the magnetization versus magnetic field for the prepared sample was shown in figure 5. Because an M-H loop was found in the curve during the external field cycle scanning from −6 kOe to 6 kOe, the hysteresis was observed. The figure shows that the Fe$_3$O$_4$ crystalline was superparamagnetic [30] with the highest magnetization saturation M(s) of 49.5 emu g$^{-1}$, the coercivity

Figure 1. XRD pattern of Fe$_3$O$_4$.

Figure 2. TEM images of Fe$_3$O$_4$ materials.
Figure 3. XPS spectrum of Fe$_3$O$_4$.

Figure 4. Diffuse reflectance UV–vis spectrum of Fe$_3$O$_4$.

Figure 5. Magnetic hysteresis curve for Fe$_3$O$_4$ sample.
value $H(c)$ of 50.1 Oe and the remanence value $M(r)$ of 3.9 emu g$^{-1}$. This suggested that the Fe$_3$O$_4$ particles could act as a magnetically separable catalyst.

### 3.2. Degradation of naphthalene

Table 1 presents the photocatalytic activity of Fe$_3$O$_4$ using various preparation methods. It was clear that Fe$_3$O$_4$ achieved highly photocatalytic activity, exhibiting 74.3% degradation rate in the absence of H$_2$O$_2$. Fe$_3$O$_4$(NH$_3$) prepared by NH$_3$.H$_2$O substituting for NaOH solution displayed lower activity, as did the Fe$_3$O$_4$(7), Fe$_3$O$_4$(c) and $\alpha$-Fe$_2$O$_3$. As a consequence, the Fe$_3$O$_4$ prepared by FeCl$_3$ and FeSO$_4$ aqueous solutions successively added to NaOH solution and reaction at 80°C possessed higher photocatalytic activity, which was applied as a catalyst in the next sections.

Catalytic activity of Fe$_3$O$_4$ without visible light irradiation was analysed in the presence of H$_2$O$_2$. Degradation of naphthalene was performed with 10.0% degradation rate, which could be enhanced under visible light irradiation. The reference experiments in the absence of Fe$_3$O$_4$ under visible light irradiation revealed low rates of 13.6% with H$_2$O$_2$ and 8.3% without H$_2$O$_2$, respectively (figure 6). When using Fe$_3$O$_4$ as a catalyst the photodegradation was greatly promoted. It was therefore evident that Fe$_3$O$_4$ could effectively photocatalyse degradation of naphthalene and the addition of H$_2$O$_2$ into this system indeed enhanced the photocatalytic degradation.

However, the catalytic activity was increased as the amount of the Fe$_3$O$_4$ increased with and/or without H$_2$O$_2$. As the amount of the catalyst approached 0.3 g, the rates reached 74.3% in the absence of H$_2$O$_2$ and 81.1% in the presence of H$_2$O$_2$, respectively. Thereafter, the rates held constant in these two cases as the amount was increased from 0.3 g to 0.5 g.

Besides, increasing the amount of added H$_2$O$_2$ could evidently promote the degradation rate of naphthalene at 0.1 and 0.5 mmol l$^{-1}$ of initial concentrations. As the added amount of H$_2$O$_2$ reached 8 ml, the rates approached 69.5% for 0.5 mmol l$^{-1}$ and 81.1% for 0.1 mmol l$^{-1}$ of initial concentration, respectively; and then continuously increasing the amount of H$_2$O$_2$ led to slight promotion of the degradation rate, as shown in figure 7.

The degradation of naphthalene at initial concentration of 0.1–0.5 mmol l$^{-1}$ was investigated and the results were depicted in figure 8. The rate was increased as the concentration of naphthalene in ethanol–water solution decreased, resulting in 74.3% of degradation rate at a concentration of

### Table 1. Photocatalytic activity of various iron oxides. N-NH$_3$.H$_2$O substituting for NaOH solution during preparation; 7–70°C; c-co-precipitation.

| Fe$_{2-y}$O$_y$ | Fe$_3$O$_4$ | Fe$_3$O$_4$(NH$_3$) | Fe$_3$O$_4$(7) | Fe$_3$O$_4$(c) | $\alpha$-Fe$_2$O$_3$ |
|---------------|-------------|---------------------|----------------|----------------|------------------|
| rate (%)      | 74.3        | 40.4                | 34.2           | 57.3           | 28.2             |

![Figure 6. Effect of catalyst dose on degradation without and with H$_2$O$_2$. Reaction conditions: initial concentration 0.1 mmol l$^{-1}$, time 8 h, H$_2$O$_2$ 8 ml.](image)
0.1 mmol l\(^{-1}\) in the absence of H\(_2\)O\(_2\). Moreover, the addition of H\(_2\)O\(_2\) into this system also enhanced the photocatalytic degradation, the rate was promoted to 81.1\% at the same concentration of naphthalene. The rate of increase for the two cases, photocatalysis and photocatalytic oxidation, were coincident with each other, indicating that the enhancing power of H\(_2\)O\(_2\) was based on the photocatalysis across the entire range of concentrations.

The catalytic degradation-time profile of the degradation reaction of naphthalene using Fe\(_3\)O\(_4\) as a catalyst under visible irradiation in the presence and/or absence of H\(_2\)O\(_2\) was shown in figure 9. The degradation rate was increased in the time range from 2 to 8 h, exhibiting a 74.3\% rate in the absence of H\(_2\)O\(_2\) and a 81.5\% rate in the presence of H\(_2\)O\(_2\) at 8 h. As the reaction proceeded beyond 8 h, the degradation rates of naphthalene basically remained unchangeable with the reaction proceeding from 8 to 12 h in these two cases, implying that the reaction achieved thermodynamic equilibrium at that time. Besides, the photocatalytic degradation of naphthalene was synchronized with the reaction time in the absence or presence of H\(_2\)O\(_2\). As compared with reported works on the photodegradation of naphthalene using TiO\(_2\) supported materials and Ce, N and P tri-doped TiO\(_2\)/AC as catalysts [12,31], the Fe\(_3\)O\(_4\) displayed higher activity than the TiO\(_2\) supported catalyst and almost the same photodegradation efficiency as the doped TiO\(_2\)/AC. In addition, according to the experimental data, as shown in figure 9, a plot of ln (C/C\(_0\)) versus time was obtained (figure 10), where C and C\(_0\) are the concentration of naphthalene at certain time t and the initial one, respectively. These curves for ln (C/C\(_0\)) versus time were linear, suggesting that the photodegradation reaction is clearly quasi-first order in naphthalene whether in the presence or absence of H\(_2\)O\(_2\). The first-order rate constants calculated from the plots are k (H\(_2\)O\(_2\)) = 0.5641 h\(^{-1}\) for photocatalytic oxidation degradation and k (no H\(_2\)O\(_2\)) = 0.4172 h\(^{-1}\) for
photodegradation in the absence of $\text{H}_2\text{O}_2$, respectively. These findings also meant that photogradation of naphthalene with $\text{H}_2\text{O}_2$ is faster than the system without $\text{H}_2\text{O}_2$. Figure 11 displays the effect of pH values of the solution on the degradation without $\text{H}_2\text{O}_2$. It was clear that the pH values did not affect the degradation of naphthalene.

**Figure 9.** Effect of reaction time on the degradation without and with $\text{H}_2\text{O}_2$. Reaction conditions: initial concentration 0.1 mmol l$^{-1}$, amount of catalyst 0.3 g, $\text{H}_2\text{O}_2$ 8 ml.

**Figure 10.** Kinetic curves for photodegradation of naphthalene.

**Figure 11.** Effect of pH value on the degradation without $\text{H}_2\text{O}_2$. Reaction conditions: initial concentration 0.1 mmol l$^{-1}$, amount of catalyst 0.3 g, $\text{H}_2\text{O}_2$ 8 ml.
3.3. In situ DRIFTS spectra and degradation mechanism

In order to explore the degradation mechanism, in situ DRIFTS spectra of the naphthalene and H₂O₂ adsorbed on the catalyst surface were measured at 50°C, as shown in figure 12. The characteristic band of Fe-O bond at 586.7 cm⁻¹, shoulder bands at 659.5 and 726.1 cm⁻¹ in the FT-IR spectrum of Fe₃O₄ catalyst (figure 13) were greatly weakened and it was likely divided into four bands at 613, 637, 650 and 663 cm⁻¹ due to adsorption of the naphthalene and H₂O₂ on the catalyst surface by means of interacting with Fe²⁺ or Fe³⁺ species. The intensity of these bands was markedly increased to the strongest as the adsorption time reached 3.5 h, and it was then decreased from 3.5 to 6.0 h, as shown in figure 12a. This suggested the strong interaction between the reactants and Fe²⁺ or Fe³⁺ active sites on the surface of the catalyst. Synchronously, the characteristic bands around 2800–3000 cm⁻¹ corresponding to C–H stretching vibration in CH₂− or CH₃− groups were enhanced as the time was extended until maximum intensity was achieved at a time 6 h (figure 12b), which
indicated that the aromatic ring open in the naphthalene molecule likely took place on the catalyst surface to generate CH$_3$– or CH$_2$– groups. Besides, abundant free hydroxyl groups at 3500–3800 cm$^{-1}$ and associated hydroxyls at 3100–3500 cm$^{-1}$ such as .OH and .OOH radicals produced by interaction between H$_2$O$_2$ and Fe$^{2+}$ or Fe$^{3+}$ species were found on the catalyst surface. This process for the production of .OH and .OOH radicals proceeded through the following equations [30,32]:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot \text{OH} \tag{3.1}
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{H}^+ + \cdot \text{OOH} \tag{3.2}
\]

\[
\text{Fe}^{3+} + \cdot \text{OOH} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \tag{3.3}
\]

As the adsorption proceeded the intensity of these bands corresponding to free hydroxyls was first increased from 0.5 to 3.5 h and then significantly decreased beyond 3.5 h, implying the .OH and .OOH radicals were generated at the initial stage and consumed to oxidize naphthalene or other intermediates beyond 3.5 h. On the contrary, the intensity of the bands ascribed to associated hydroxyls was increased to the strongest at 6 h, which was likely related to conversion of free hydroxyls into associated ones on the surface. Likewise, the bands at 1000–1200 cm$^{-1}$ attributed to stretching vibration of C–O–O bonds [33] were also increased remarkably (figure 12c). These findings suggested that the decrease in the intensity of free hydroxyls was likely ascribed to conversion of naphthalene interacting with .OOH into hydroperoxy- and/or hydroxy-intermediates, the intermediates further converted into the degradated products.

On the other hand, the distribution of degradated products in the presence or absence of H$_2$O$_2$ were determined by GC-MS. Different degradation products were confirmed due to their different photocatalytic reactions in these two cases. As shown in Scheme 1, the photocatalytic degradation of naphthalene over Fe$_3$O$_4$ was carried out in the absence of H$_2$O$_2$, generating 1,2-diphenyl butadiene (1) or 1,4-diphenyl butadiene (2), 1,3-diphenyl propane (3) and 1,2-diphenyl cyclopropane (4) as the main products (their MS images and data are shown in the electronic supplementary material). This suggested that the degradation process was mainly carried out via aromatic ring-opening reaction in naphthalene molecules and continuous catalytic alkylation, degradation and rearrangement between the ring-opened products to form diphenyl compounds. According to the product distribution and the works reported in the literature, the mechanism for the degradation process was described as shown in scheme 1.

When Fe$_3$O$_4$ was irradiated, a hole and electron were, respectively, generated on its surface. Fe(III) transforms into Fe(II) after receiving an electron, and the oxidation process may proceed by one electron transfer leading to the formation of the naphthalene cation radical [34]. The strong adsorption of naphthalene on the Fe$_3$O$_4$ surface facilitates the electron transfer from the excited Fe(III)-Fe$_3$O$_4$ to organic molecules and such a transfer can initiate the photodegradation of naphthalene. Firstly, adsorbed naphthalene cation opened the aromatic ring to form phenyl butadiene under visible irradiation, then the phenyl butadiene undergoes alkylation with another phenyl butadiene molecule,
followed by degradation catalysed by Lewis acid on the catalyst surface to generate 1, 2 and butadiene; furthermore, the products 1 and 2 continuously perform degradation and/or rearrangement to form 3 and 4 catalysed by Lewis acidity on the catalyst surface.

In the presence of H₂O₂, the transient Fe(II) or Fe(II) in Fe₃O₄ was able to bind and reduce H₂O₂ to produce -OOH and/or -OH radicals with high redox potential, which has been experimentally proven by the reported works [35,36], as well as the above in situ DRIFTS spectra. This strongly suggested that the degradation process was carried out via photocatalysis and oxidative action of -OOH and/or -OH radicals. For this reason, the photocatalytic degradation and oxidation progress of naphthalene took place synchronously in the presence of H₂O₂. As a result, the degradation products were very different from the former due to the oxidizing action. The main products determined by GC-MS included 1,4-diphenylbutene-1 (5), benzyl succinic acid (6), 1,3-diphenyl acrylketone (7), (benzyl methyl ether)-ethyl diacetate (8) and hydroxyethyl methyl ketone (9), a small quantity of 2-ethoxy ethyl ether (10) and ethyl acetate (11) were also found in the reaction mixture as depicted in scheme 2 (Their MS images and data were as shown in the electronic supplementary material). The production of these products in the presence of H₂O₂ revealed that the photocatalytic degradation in this case also initiated from aromatic ring open, and then carried out the oxidation, alkylation and degradation of these ring-open products. Based on the product distribution and the in situ DRIFTS spectra analysis, the reaction mechanism was proposed as well, as shown in scheme 2.

Firstly, H₂O₂ and naphthalene were adsorbed on the surface of the catalyst via the interaction of the reactants with the active sites of Fe²⁺ or Fe³⁺ species. The adsorbed H₂O₂ molecule was oxidized by Fe²⁺ to form -OOH and/or -OH radicals on the surface. The surface conversion of adsorbed naphthalene took place to generate adsorbed ring-open product phenyl butadiene; then the ring-opened product carried out alkylation and degradation to form diphenyl butene 5 and butene through interaction with Lewis acids, followed by oxidation and alkylation of phenyl butadiene to generate the compound 6, as well as the compound 8, and oxidation of 5 to produce the product 7. At the same time, the butadiene was degraded and oxidized to the compounds 9, 10 and 11 acting through light irradiation and -OOH or -OH radicals. In addition, a small quantity of the compounds 10 and 11 possibly came from the oxidation and/or reaction between the degraded C1-C2 species or the oxidation and esterification of solvent ethanol.

Scheme 1. The proposed mechanism for degradation without H₂O₂.
3.4. The reusability of the catalyst

In order to further evaluate the photocatalytic performance of Fe₃O₄, recovery and recycling of the Fe₃O₄ were explored. The Fe₃O₄ was recovered by magnetic separation after each run, and then it was reused in the next run under the same reaction conditions. It was clear that the activity of the catalyst was almost unaffected even at the fifth run (figure 14). Moreover, the XRD pattern of the reused catalyst was the same as that of the fresh one four times, as shown in figure 15 (up). Also, the particle size of the reused Fe₃O₄ was almost unchangeable when compared with the fresh one, although slight aggregation was observed in figure 15 (down). These findings showed that the prepared Fe₃O₄ was

Scheme 2. The proposed mechanism of degradation with H₂O₂.

Figure 14. Reusability of Fe₃O₄.
highly stable at least within four repeated runs. The slightly lower activity for the fourth one was likely ascribed to loss of the catalyst amount during the process of recovery.

4. Conclusion

Nanosized Fe₃O₄ material was prepared by using FeCl₃ and FeSO₄ precursor aqueous solution successively dropwised in NaOH solution to maintain the stability of Fe₃O₄ in basic medium. This nanomaterial exhibited high photocatalytic activity for degradation of naphthalene in the absence or presence of H₂O₂, getting 74.3% and 81.5% of degradation rates, respectively, for the two cases. In the process, the photodegradation products involving diphenyl butadiene, diphenyl propane, benzyl succinic acid, 1,3-diphenyl acrylketone, (benzyl methyl ether)-ethyl diacetate and hydroxyethyl methyl ketone etc. were determined by GC-MS. In situ DRIFTS spectra of naphthalene and H₂O₂ adsorbing on the catalyst surface showed that high activity of Fe₃O₄ for photodegradation of naphthalene was ascribed to the production of hole-electron pairs and -OOH radicals on the surface, which preceeded degrading or oxidizing to the adsorbed naphthalene. Based on in situ DRIFTS analysis and distribution of the degradation products, the degradation mechanism involving adsorption of naphthalene and H₂O₂, ring open in naphthalene molecules on the catalyst surface and/or oxidation of ring open intermediates was achieved. Besides, the Fe₃O₄ could be easily recovered and effectively reused.

Data accessibility. The datasets supporting this article have been uploaded as part of the electronic supplementary material.

Authors’ contributions. J.Z. is responsible for the molecular laboratory work and data analysis; S.F. is responsible for the molecular laboratory work; B.L. is responsible for the statistical analysis; Q.C. is responsible for the design of the study and drafting the manuscript; J.Z. helped draft the manuscript; S.Z. is responsible for the design of the study and drafting manuscript.

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