Fabricating Fe₃O₄-schwertmannite as a Z-scheme photocatalyst with excellent photocatalysis-Fenton reaction and recyclability

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Here we reported an effective method to solve the rate-limiting steps, such as the reduction of Fe³⁺ to Fe²⁺ and an invalid decomposition of H₂O₂ in a conventional Fenton-like reaction. A magnetic heterogeneous photocatalyst, Fe₃O₄-schwertmannite (Fe₃O₄-sch) was successfully developed by adding Fe₃O₄ in the formation process of schwertmannite. Fe₃O₄-sch shows excellent electrons transfer ability and high utilization efficiency of H₂O₂ (98.5%). The catalytic activity of Fe₃O₄-sch was studied through the degradation of phenol in the heterogeneous photo-Fenton process. Phenol degradation at a wide pH (3 - 9) was up to 98% within 6 min under visible light illumination with the Fe₃O₄-sch as heterogeneous Fenton catalyst, which was higher than that using pure schwertmannite or Fe₃O₄. The excellent photocatalytic performance of Fe₃O₄-sch is ascribed to the effective recycling between =Fe³⁺ and =Fe²⁺ by the photo-generated electron, and also profit from the formation of the “Z-Scheme” system. According to the relevant data, photocatalytic mechanism of Fe₃O₄-sch for degrading phenol was proposed. This study not only provides an efficient way of enhancing heterogeneous Fenton reaction, but also gives potential application for iron oxy-hydroxysulfate mineral.

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I n t r o d u c t i o n

Advanced oxidation processes (AOPs) have been popularly used for removing pollutants in water due to the production of various oxidizers (e.g., -OH, -O·OH and O₂⁻) (Xu and Wang, 2012; Vorontsov, 2015; Hou et al., 2017; Li et al., 2017a; Pouran et al., 2015; Sabaikai et al., 2014). Heterogeneous catalysts using insoluble Fe-containing oxides or compounds instead of soluble Fe²⁺ exhibits potential prospects including expanding the applicable range of pH and preventing from the production of vast iron-containing sludge. However, the long induction period and large consumption of H₂O₂ often restrict heterogeneous catalysts application in practical sewage treatment (Lyu et al., 2017). Fe-based semiconductors show a promising photocatalytic activity in the heterogeneous Fenton process due to the efficient reduction of Fe³⁺ by photo-induced electron (Du et al., 2017; Li et al., 2017b). Among numerous semiconductors, Fe₃O₄ has been largely used in the degradation of organic pollutants due to its fine biocompatibility, unique electric, superparamagnetic, low toxicity, and easy synthesis (Du et al., 2017; Li et al., 2017b; Fenolla et al., 2017; Xie et al., 2012; Wu et al., 2012; Guo et al., 2015; Chen et al., 2017; Vikesland et al., 2007). Nevertheless, Fe₃O₄ as heterogeneous photo-Fenton catalyst has some drawbacks such as the high recombination rate of photo-generated electron-hole pairs, easy agglomeration, and a high concentration of required H₂O₂ (Chen et al., 2017; Vikesland et al., 2007).

Schwertmannite (Sch) is an iron(III)-oxyhydroxysulfate mineral with a variable formula of Fe₈O₈(OH)₈−x(SO₄)ₓ (1 ≤ x ≤ 1.75) (Bigham et al., 1996), which mainly appears in acid mine drainage, acid-sulfate soils or bioleaching environments.
Sch as a heterogeneous catalyst has been studied and used for degrading pollutants in water due to its easy acquisition and low cost (Wang et al., 2013; Yan et al., 2017; Duan et al., 2016; Li et al., 2018b). Likewise, Sch as heterogeneous iron-based catalysts has relative long induction period in the heterogeneous Fenton reaction due to only $\equiv$Fe$^{3+}$ on its surface.

However, we found the drawbacks of Fe$_3$O$_4$ or Sch could be solved effectively when Fe$_3$O$_4$ was imbedded into Sch. Therefore, the purposes of the present study are to investigate the optical property of Sch and develop a magnetic Fe$_3$O$_4$-schwertmannite (Fe$_3$O$_4$-sch) photocatalyst to promote the separation efficiency of photo-generated electron-hole pairs, effectively eliminate the induction period of Sch, and recovery conveniently from treated water. On the one hand, photo-generated electrons ($e^{-}$) from Fe$_3$O$_4$ will easily migrate to Sch due to S=O or S-O groups forming Lewis acid sites, which can accelerate the reduction of $\equiv$Fe$^{3+}$ to $\equiv$Fe$^{2+}$. On the other hand, the formation of Z-scheme system will efficiently improve the separation of photo-generated electron and hole pairs to enhance the photocatalytic performance.

To our knowledge, the optical property of Sch and constructing Fe$_3$O$_4$-sch as Z-scheme photocatalyst for degrading organic compounds have not been reported. In the present study, the photocatalytic activity of Fe$_3$O$_4$-sch was investigated through the degradation of phenol in water with H$_2$O$_2$ under visible light irradiation. Photocatalytic mechanisms of Fe$_3$O$_4$-sch and degradation pathways of phenol were proposed.

1. Materials and methods

1.1. Chemicals and reagents

Hydrogen peroxide (H$_2$O$_2$, 30 wt.%), sulphuric acid (H$_2$SO$_4$, $\geq$ 98 vol.%), sodium hydroxide (NaOH, $\geq$ 96%), ammonium hydroxide (NH$_3$, $\geq$ 25 vol.%), ferric chloride (FeCl$_3$·4H$_2$O, $\geq$ 99%), ferric sulfate (FeSO$_4$·7H$_2$O, $\geq$ 99%), 1,10-phenanthroline hydrate (C$_{12}$H$_8$N$_2$·H$_2$O, $\geq$ 95%), potassium ferricyanide (K$_3$[Fe(CN)$_6$]), $\geq$ 99.5%), methanol (CH$_3$OH, $\geq$ 99%), 4-aminoantipyrine (C$_9$H$_8$N$_3$O, $\geq$ 98.5%), diammonium hydrogen phosphate (NH$_4$H$_2$PO$_4$, $\geq$ 99.5%), ammonia chloride (NH$_3$·HCl, $\geq$ 98.8%), potassium iodide (KI, $\geq$ 99%) and phenol ($\geq$ 98%) were purchased from Sigma-Aldrich (Shanghai, China). Spin trap 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was provided by Sigma Aldrich (St. Louis, USA).

1.2. Synthesis of catalysts

In this study, Fe$_3$O$_4$ was synthesized according to Mondal et al. (2012). Briefly, FeCl$_3$·4H$_2$O (2.0 g) and FeCl$_3$·6H$_2$O (6.0 g) were added into deionized water (200 mL). The reactive mixture was stirred for 30 min. Then, 40 mL NH$_3$·H$_2$O (25 wt.% solution) was slowly added to reaction mixture and stirred for 2 h at 60°C. The black reaction product was washed several times by deionized water until the pH of the suspension was 7 and then dried at 50°C in a vacuum oven to produce Fe$_3$O$_4$, a black solid (3.3 g).

Sch was chemically synthesized according to Regenspurg et al. (2004). FeSO$_4$·7H$_2$O (11.12 g) was dissolved in water (500 mL) by stirring, then H$_2$O$_2$ (30 wt.% 6 mL, 35 mmol/L) was added to react with FeSO$_4$·7H$_2$O in a rotary shaker at 180 r/min and 28°C for 24 h. The ochreous precipitate was harvested by filtering through a Whatman No.4 filter paper and washed with acidified water (600 mL; pH 2.0) three times and deionized water (600 mL) three times to remove soluble impurities. The product was dried at 50°C in a vacuum oven to obtain Sch, an ochreous solid (3.4 g).

For the preparation of complex Fe$_3$O$_4$-sch, Fe$_3$O$_4$ (1.0 g) was added into 500 mL acidified water (pH 2.0) and ultrasonically dispersed by an ultrasonic cleaner (100 W, KQ2200F, Kunshan Ultrasonic Equipment Company, China) for 10 - 15 min to obtain a suspension. Then FeSO$_4$·7H$_2$O (11.12 g) was added into this suspension (500 mL) prior to the addition of H$_2$O$_2$ (30 wt.%, 6 mL). The reaction mixture was then incubated in a rotary shaker at 180 r/min and 28°C for 24 h. The dark brown product was harvested by filtering through a Whatman No.4 filter paper and washed with acidified water (500 mL; pH 2.0) three times and deionized water (500 mL) three times to remove soluble impurities. The crude product was dried to obtain Fe$_3$O$_4$-sch (mass ratio of Fe$_3$O$_4$ to Fe$_3$O$_4$-sch, 0.47), a dark brown solid. The synthesis process of the Fe$_3$O$_4$-sch composite catalyst is depicted in Fig. 1.

1.3. Photocatalytic activity experiments

The pH of 100 mg/L phenol solution was adjusted to 7 via NaOH (0.1 mol/L). Fe$_3$O$_4$, Sch, or Fe$_3$O$_4$-sch (50 mg) was added into the above solution (50 mL), respectively. After adsorbed for 30 min in darkness to achieve adsorption-desorption equilibrium prior to illumination, phenol was measured and taken as the concentration at time zero ($C_0$). H$_2$O$_2$ (30 wt.%, 45 μL) was added in the above treatments (50 mL). The samples were placed in multichannel photocatalytic reaction system (PCX50B Discover, Beijing Perfectlight Technology Co., Ltd, China) and irradiated with visible light, and then withdrawn and determined for phenol using 4-aminoantipyrine method (Federation and Association, 2005) and leached Fe concentration by spectrophotometric procedures according to standard methods made by APHA (1999).

For exploring photocatalytic mechanism of Fe$_3$O$_4$-sch, the controlled photoactivity experiments using different radicals scavengers were also performed with the procedures similar to the above photocatalytic degradation of phenol. Among radicals scavengers, KI (10 mmol/L) as scavenger for photo-generated holes (Guo et al., 2010; Zhao et al., 2013), AgNO$_3$ (0.5 mmol/L) for photo-generated electrons (Chen et al., 2018), p-benzoquinone (BQ) (0.5 mmol/L) for •O$_2^-$ (Zhao et al., 2018) and methanol (20 vol.%) (Xu and Wang, 2012) for •OH.

1.4. Characterization and calculation

The properties of catalysts were characterized by powder X-ray diffraction (XRD-6100, Shimadzu, Japan), Fourier transform infrared (FTIR, Thermo Fisher, USA) spectra, transmission electron microscopy (TEM, FEI-Tecnai G$^2$ F20, 200 kV, USA), energy dispersive spectroscopy (EDS, FEI Tecnai G2 F20, USA), Raman spectra, X-ray photoelectron spectrometer (XPS), and UV-Vis diffuse reflectance spectra (DRS). The photoluminescence (PL) spectra of the catalysts were measured using a fluorescence spectrometer (FLS980, Edinburgh, UK). The transient photocurrent-time curves (t-t curves) of catalysts were tested using the electrochemical workstation (CHI 660E, Shanghai Chenhua, China). The involved active radicals were analyzed by electron paramagnetic resonance (EPR) on a Bruker EMX-10/12 (Bruker, Germany) employing 5,5-dimethyl-1-pyrroline N-oxide (DMPO) (≥ 97.0%, Aldrich) as trapping agent. Fe content in catalyst was measured with inductively coupled plasma atomic emission spectrometry (ICP-AES, ICP-7500, Shimadzu, Japan) after acid digestion. Degradation intermediates of phenol were determined by liquid chromatography-mass spectrometry (LC-MS) (TSQ QUANTUM ACCESS MAX, Thermo Scientific, USA). The detailed test method is shown in Appendix A. Supplementary data.
Conduction band (CB) and valence band (VB) were calculated by following formulas (Mieritz et al., 2016):

\[ E(CB) = X - E^e - 0.5E_g \]  
(1)

\[ E(VB) = E(CB) + E_g \]  
(2)

where \( E(CB) \) is the conduction band edge of a semiconductor at the point of zero charges, \( E(VB) \) is the valence band edge of a semiconductor, \( X \) is the absolute electronegativity of the semiconductor, expressed as the geometric mean of the absolute electronegativity of the constituent atoms, \( E^e \) is the energy of free electrons of the hydrogen scale (4.5 eV), and \( E_g \) is the band gap energy of the semiconductor.

The degradation efficiency (\( \eta \)) was calculated by the following Eq. (3):

\[ \eta = (C_0 - C_t)/C_0 \times 100\% \]  
(3)

where \( C_0 \) is the initial concentration of phenol and \( C_t \) is the concentration of phenol at degradation time \( t \) (min).

All simulation computations were carried out by DFT method using Gaussian09 software at the level of B3LYP/6-31 G basis set (Li et al., 2017a). The highest occupied molecular orbital (HOMO), the natural population analysis (NPA) and Fukui Function representing electrophilic (\( f^+ \)), nucleophilic (\( f^- \)) and radical attack (\( f^0 \)) (Parr and Yang, 1984) are used to evaluate the reactive sites on the phenol molecule. The detailed DFT calculations are shown in Appendix A. Supplementary data.

2. Results and discussion

2.1. Characterization of catalysts

From TEM images, Sch aggregates to spherical particles with approximately 1 \( \mu \)m (Fig. 2a). Fe\(_3\)O\(_4\) exhibits spherical nanoparticles with approximately 10 nm, which is easily aggregated together (Fig. 2b). As expected, Fe\(_3\)O\(_4\) highly dispersed in the bulk and surface of Fe\(_3\)O\(_4\)-sch catalyst after Fe\(_3\)O\(_4\) was added into Sch precursor solution to form Fe\(_3\)O\(_4\)-sch composite (Fig. 2c). This status of Fe\(_3\)O\(_4\) in the composite will be beneficial for electron transfer and surface Fenton reaction. HRTEM result (Fig. 2d) further confirmed the two phases coexistent structure, where lattice fringe of 0.26 nm and 0.21 nm were assigned to Sch (212) and Fe\(_3\)O\(_4\) (400) plane, respectively. In the light of XRD (Fig. 2e), Sch exhibited a typical poorly crystalline structure and diffraction peaks were consistent with the peak position for schwertmannite (ICPDS card No. 47-1775). The diffraction pattern of Fe\(_3\)O\(_4\) showed a typical cubic structure and diffraction peaks well matched those of the standard diffraction data for Fe\(_3\)O\(_4\) (ICPDS card No. 75-0449). Thus, diffraction peaks of Fe\(_3\)O\(_4\)-sch composite mainly showed Fe\(_3\)O\(_4\) diffraction peaks, but the extents of the peaks were much weaker than pure Fe\(_3\)O\(_4\). It means that Fe\(_3\)O\(_4\) mostly appearing in the bulk rather than on the surface. FTIR spectra confirmed the coexistence of Sch and Fe\(_3\)O\(_4\) in Fe\(_3\)O\(_4\)-sch (Fig. 2f). Absorption peaks at 3385 and 980 - 1128 cm\(^{-1}\) are stretching vibration mode of O-H and SO\(_4^{2-}\) (Regenspurg et al., 2004), respectively. Obviously, Fe\(_3\)O\(_4\)-sch contains many -OH and SO\(_4^{2-}\) functional groups. The O-H groups can trap the photo-induced holes, while SO\(_4^{2-}\) groups can attract electrons (Zhong et al., 2015; Kim et al., 2019; Liu et al., 2020), thus electrons/holes on Fe\(_3\)O\(_4\)-sch surface could be efficiently separated.

The elements of Fe\(_3\)O\(_4\)-sch were also analyzed by EDS (Appendix A Fig. S1). In Appendix A Table S1, molar ratio of O, S to Fe of Fe\(_3\)O\(_4\)-sch is 20.7:1:6.2, which suggested Fe\(_3\)O\(_4\)-sch containing many OH functional groups and little band water. The results suggest that Fe\(_3\)O\(_4\)-sch surface will be good for producing hydroxyl radicals via a reaction of H\(_2\)O/OH\(^+\) + h\(^+\) \rightarrow \cdot OH + H\(^+\). The effect of SO\(_4^{2-}\) in Fe-O bond length was further analyzed by Raman and XPS spectra (Fig. 3). The bands at 713 and 398 cm\(^{-1}\) are ascribed to SO\(_4^{2-}\) and Fe-O stretching vibration in Sch (Ciobota et al., 2013; Wang et al., 2010) (Fig. 3a). The bands at 712 and 396 cm\(^{-1}\) are the Fe-O bending vibration and the Fe-O stretching vibration in Fe\(_3\)O\(_4\) (Li et al., 2016). The relationship between Raman shift of catalysts and bond length of Fe-O is shown in Eq. (4):

\[ v = a + bR \]  
(4)

where \( v \) is Raman wavenumber, \( a \) (\( a = 6300 \) cm\(^{-1}\)) and \( b \) (\( b = -34.3 \) pm\(^{-1}\)) are simplieremirical correlations between bond lengths and Raman wavenumbers, respectively, and \( R \) (pm) is the Fe-O bond length (Liu et al., 2020). It shows that the Fe-O bond length of Fe\(_3\)O\(_4\)-sch (171.84 pm) is shorter than that of Sch (172.07 pm) or Fe\(_3\)O\(_4\) (172.13 pm). The shortening of the bond length of Fe-O will also be beneficial to electron transfer on the Fe\(_3\)O\(_4\)-sch surface. SO\(_4^{2-}\) was proved to occupy sites both on the surface and within the structure of Sch (Bigham et al., 1996). The XPS spectra of S2p of Fe\(_3\)O\(_4\)-sch are shown in Fig. 3b. Two peaks at 168.7 and 169.8 eV were ascribed to SO\(_4^{2-}\) absorbed on the surface and structural sulfate (Fe-SO\(_4\)), respectively. Therefore, the change in bond length of Fe-O may be caused by forming the bridged bidentate structure between SO\(_4^{2-}\) on Sch surface and Fe atoms of Fe\(_3\)O\(_4\).

The optical absorption property of catalyst is an important factor affecting its photocatalytic performance (Mamba and Mishra, 2016; Song et al., 2017). Sch has a distinct absorption band in the range of 200 - 400 nm and Fe\(_3\)O\(_4\) has strong absorption intensity in the range of 200 - 800 nm (Fig. 4a), which relates to their color. Fe\(_3\)O\(_4\)-sch shows an obviously red shift to larger wavelength regions, which is beneficial to enhance the visible-light catalytic activity. The color change of cata-

![Fig. 1 - Synthesis route of Fe\(_3\)O\(_4\)-schwertmannite (Fe\(_3\)O\(_4\)-sch) composite catalyst.](image-url)
lys from yellow to brown is responsible for the finding. The results indicate that Fe₃O₄ nanoparticles play an important role in enhancing the efficiency of visible-light absorption. The band gap energy (Eₜ) of Fe₃O₄, Sch and Fe₃O₄-sch are 0.37, 2.16 and 1.54 eV, respectively (Fig. 4b). CB of Fe₃O₄ was 0.88 eV lower than that of Sch (1.20 eV) by calculation (Eqs. (1) and (2)). Therefore, the photo-generated electrons from Fe₃O₄ can quickly transfer to the Sch surface, which can also accelerate reduction of Fe³⁺.

Fig. 4c shows PL spectra of Fe₃O₄, Sch and Fe₃O₄-sch to investigate the separation efficiency of the photo-generated electron-hole pairs. In general, the lower PL intensity, the lower recombination rate of photo-induced electron-hole pairs, thus the higher photocatalytic performance. The Fe₃O₄ has the highest fluorescence peak at 500 - 650 nm than others, which indicates the largest recombination rate of photo-generated electron-hole pairs. When loading Fe₃O₄ on the surface of Sch, the fluorescence peak of Fe₃O₄-sch greatly declines. This implies the higher photocatalytic performance of Fe₃O₄-sch than that of pure Fe₃O₄.

The transient photocurrent density could directly reflect the separation efficiency of photo-induced electron-hole pairs and the migration rate of the photocatalysts (Wang et al., 2019). As shown in Fig. 4d, Fe₃O₄-sch shows a higher photocurrent density than Fe₃O₄ and Sch, which suggests that the fast charge transfer occurs in the Fe₃O₄-sch. The result further testifies that the Fe₃O₄-sch has great separation ability of photo-induced electron-hole pairs.

2.2. Photocatalytic activity

The degradation efficiency (98%) of phenol at initial pH 7 in the Fe₃O₄-sch+H₂O₂+Vis-light processes are much higher than those in H₂O₂+Vis-light, Sch+H₂O₂+Vis-light, Fe₃O₄+H₂O₂+Vis-light, and Fe₃O₄-sch+H₂O₂ processes (Fig. 5a). Moreover, no induction period occurred in Fe₃O₄-sch catalysis systems. Therefore, Fe₃O₄-sch shows a higher photocatalytic activity in region of visible light than pure Fe₃O₄ and sch. It is ascribed to some reasons including highly dispersion of Fe₃O₄ nanoparticles on the Sch surface, the effective separation of the photo-generated electron-hole pairs and rapid reduction of Fe³⁺, which improves OH· generation. As shown in Fig. 5b, the concentration of leached Fe²⁺ in phenol degradation system with Fe₃O₄-sch as catalyst at pH7 increases with the increase of degradation time. Moreover, the concentration of leached Fe²⁺ in Fe₃O₄-sch system is higher than that in pure Sch or
Fe₃O₄ system. It confirmed that =Fe³⁺ or Fe³⁺ can be rapidly reduced to =Fe²⁺ or Fe²⁺ in the Fe₂O₃-sch+H₂O₂+Vis-light system, which can create a more efficient capacity to decompose H₂O₂ (Fig. 5c). In addition, the concentration of leached iron (1.5 mg/L) at 6 min is very low compared to total Fe content (488 mg/L) in the system containing 1 g/L of Fe₃O₄-sch. The very low iron dissolution (only 0.3%) indicates that the structure of Fe₃O₄-sch is very stable and leached iron don’t play major role in phenol degradation. These results suggest that structure of Fe₃O₄-sch is very stable and iron ions dissolution did not play major role in phenol degradation.

It was further supported by a supplementary homogeneous photo-Fenton experiment with the same concentration of H₂O₂ and 1.5 mg/L, a Fe²⁺ concentration similar to leached total Fe from Fe₃O₄-sch by homogeneous photo-Fenton reaction. Under visible light irradiation, only 18% phenol was degraded after 20 min even at pH = 3.0 (Appendix A Fig. S2).
The utilization efficiency of H$_2$O$_2$ was defined as the ratio of stoichiometric H$_2$O$_2$ consumption for the degradation of phenol to actual H$_2$O$_2$ consumption the reaction (Lyu et al., 2017). Based on TOC removal percentage (64.7%) in Fe$_3$O$_4$-sch+H$_2$O$_2$+Vis-light system (Fig. 5d), Fe$_3$O$_4$-sch exhibited the highest utilization efficiency of H$_2$O$_2$ (98.5%) within the short reaction time than that in the H$_2$O$_2$, Sch and Fe$_3$O$_4$ system.

### 2.3. Factors affecting phenol degradation by using Fe$_3$O$_4$-sch

As shown in Fig. 6a, an increase in the amount of loaded Fe$_3$O$_4$ in Fe$_3$O$_4$-sch composite will enhance the phenol degradation efficiency. The degradation of phenol at 6 min was up to 96% using Fe$_3$O$_4$-sch if Fe$_3$O$_4$ content of Fe$_3$O$_4$-sch exceeded 47.4%. Moreover, the induction period of Sch to initiate phenol degradation was gradually shortened with the increase of loaded Fe$_3$O$_4$.

The degradation efficiency of phenol is up to 98% at a wide pH range from 3 to 9 with exceptions for pH 2 or 10 (Fig. 6b). The effect of Fe$_3$O$_4$-sch catalyst dosage was also explored in this study (Fig. 6c). Phenol can be completely degraded within 10 min when catalyst dosage was up to 1.0 g/L. Meanwhile, the effect of H$_2$O$_2$ concentration was investigated at catalyst concentration 1.0 g/L (Fig. 6d). Degradation percentage of phenol reaches 97% when H$_2$O$_2$ concentration exceeds 160 mg/L. These results indicate that Fe$_3$O$_4$-sch has excellent catalytic activity and high utilization efficiency of H$_2$O$_2$ at a wide pH range.

### 2.4. Magnetism and reusability of Fe$_3$O$_4$-sch

Nonmagnetic Sch in water can’t be adsorbed on the magnet and thus is hardly separated from solution after degradation of phenol (Fig. 7a). Magnetic Fe$_3$O$_4$ and Fe$_3$O$_4$-sch can be easily adsorbed on the magnet and recovered easily from solution when applied in water treatment. Fig. 7b showed a good reusability of Fe$_3$O$_4$-sch, as exhibiting that more than 97% of degradation efficiencies of phenol using Fe$_3$O$_4$-sch in successive five cycles could still achieved for 10 min reaction. The XRD and FTIR spectra of the Fe$_3$O$_4$-sch before and after degradation reaction did not show significant changes, which proves that its structure has good stability (Fig. 7c and d).

### 2.5. Mechanism consideration

#### 2.5.1. Roles of radical species

The EPR technology was used to detect the radical species in the phenol degradation reaction system. As expected, strong four-line EPR spectra with relative intensities of 1:2:2:1 corresponding to DMPO–OH adduct were observed in the Fe$_3$O$_4$-sch suspension (Fig. 8a). It is obvious that H$_2$O$_2$ can produce more ·OH in the Fe$_3$O$_4$-sch system than that in Fe$_3$O$_4$ and Sch.

To further determine the main reactive species for degrading phenol by Fe$_3$O$_4$-sch, a series of quenchers were employed to scavenge the relevant reactive species (Fig. 8b). After adding 20% (V/V) methanol, the pseudo-first-order rate constants (k) of phenol dramatically decreased from 0.4919 to 0.0188 min$^{-1}$, indicating ·OH played a key role in the degradation of phenol. With the addition of KI, k value decreased from 0.4919 to

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Fig. 5 - (a) Degradation of phenol using Fe$_3$O$_4$, Sch and Fe$_3$O$_4$-sch, (b) concentration of iron leaching, (c) consumption of H$_2$O$_2$ and (d) total organic carbon (TOC) removal in the degradation process. Reaction conditions: Initial pH 7, H$_2$O$_2$ 300 mg/L, catalyst 1 g/L, and phenol 100 mg/L.
Fig. 6 – Effects of (a) different amount of loaded Fe$_2$O$_4$ in Fe$_3$O$_4$-sch, (b) pH, (c) catalyst dosage and (d) H$_2$O$_2$ concentration in the degradation of phenol. Reaction conditions for (a): Initial pH 7, H$_2$O$_2$ 300 mg/L, catalyst 1 g/L, and phenol 100 mg/L.

Fig. 7 – (a) Magnetic separation of different catalysts, (b) reusability of Fe$_3$O$_4$-sch, (c) XRD and (d) FTIR spectra of Fe$_3$O$_4$-sch before and after degradation reaction.
was the important trons, 2019 0.0624 band; degrading Fig. 8 – (a) Electron paramagnetic resonance (EPR) spectra of spin-reaction •OH radicals and (b) effect of radical quenching agents in the phenol degradation. $k$: the first-order rate constant; BQ: benzoquinone.

Fig. 9 – Photocatalytic mechanism of Fe₃O₄-sch for degrading phenol. $E_g$: band gap energy; CB: conduction band; VB: valence band; $h^+$: hole; $e^-$: electron.

0.0624 min⁻¹, indicating that $h^+$ is highly related to generate •OH via a reaction of H₂O/OH− + $h^+$ → •OH + H⁺ (Baran et al., 2019). When AgNO₃, a scavenger for photo-generated electrons, was added to the reaction system, an inhibition for degrading phenol was also observed. It suggests that $e^-$ pays an important role in the reduction of Fe³⁺⁺ (or Fe³⁺). However, BQ has a slight effect on the degradation rate, suggesting that •O₂− does not dominate phenol degradation. By calculating the kinetic constants with addition of different scavengers, the contributions of •OH, $e^-$, $h^+$ and •O₂− to phenol degradation were 96.2%, 77.3%, 87.3% and 10%, respectively. Therefore, •OH, $h^+$ and $e^-$ play a pivotal role in degradation of phenol.

2.5.2. Photocatalytic mechanism of Fe₃O₄-sch
Photocatalytic mechanism of Fe₃O₄-sch for degrading phenol was proposed based on the above results and depicted in Fig. 9. Under visible light irradiation, both Fe₃O₄ and Sch can be ex-
2.5.3. Degradation pathways of phenol and DFT calculation

LC-MS and theoretical DFT method could be used to deduce possible degradation pathways of phenol in the Fe$_3$O$_4$-sch photocatalytic system although there was the lack of more detection including GC–MS for intermediate. The detected intermediates by LC-MS were shown in Appendix A Fig. S3. The chemical structure and HOMO of phenol, NPA and Fukui index representing $\rho^0$ of atoms are demonstrated in Fig. 10. The optimized structure of phenol is shown in Fig. 10a. The HOMO of phenol is mainly located on the benzene ring, which can be more likely to be attacked by -OH (Fig. 10b) (Liu et al., 2019; Zhao et al., 2018). The red color degree in Fig. 10c shows different levels of $\rho^0$, and it demonstrates that the carbon atoms (C2, C4, C5 and C6) in phenol ring with relative larger values (Fig. 10c) are more vulnerable to radical attacks. According to the identified intermediates and DFT results, hydroxylation of phenol is the major degradation pathway in this system (Fig. 10d). Firstly, the C2 and C4 atoms with the highest $\rho^0$ (0.207629 and 0.20249) are the most susceptible to be attacked by -OH, resulting in the formation of intermediate with mass to charge ratio (m/z) 109.8 (hydroquinone or catechol). The finding is consistent with those from the already-published literatures (Gao et al., 2018; Li et al., 2018; Wei et al., 2017). Subsequently, C6 and C5 with relatively higher $\rho^0$ (0.195512 and 0.162116) are further attacked by -OH to produce a trihydroxyl derivative (m/z 130.1). The hydroxylation of aromatic ring by -OH can lead to the ring cleavage. Ultimately, these ring-opened products were further oxidized to form CO$_2$ and H$_2$O, which is agreement with TOC results (Fig. 5d).

3. Conclusions

In summary, a magnetic heterogeneous photocatalyst, Fe$_3$O$_4$-sch was synthesized by adding Fe$_3$O$_4$ in the growth process of Sch, which improves the separation efficiency of electron and hole, effectively eliminates the induction period of Sch and agglomeration of Fe$_3$O$_4$. Fe$_3$O$_4$-sch shows high utilization efficiency of H$_2$O, and much higher photocatalytic activity for degrading phenol than pure Fe$_3$O$_4$ or Sch at a wide pH range. This is attributed to SO$_4^{2–}$ species on the Fe$_3$O$_4$-sch surface. The formation of Z-scheme system plays a significant role in separating the electron-hole and improvement of redox ability. Besides, the Fe$_3$O$_4$-sch was easily separated from treated water due to its magnetic properties. At last, the photocatalytic mechanism of Fe$_3$O$_4$-sch for degrading phenol was proposed. The outcome of this study provides a new insight into improving the activities of photocatalysts for removing refractory pollutants in water.

Declaration of competing interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, and there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in this manuscript.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jes.2020.06.005.

REFERENCES


