



Cite this: *RSC Adv.*, 2017, 7, 26983

Unveiling the mechanism of electron transfer facilitated regeneration of active Fe²⁺ by nano-dispersed iron/graphene catalyst for phenol removal†

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Nano-dispersed Fe⁰ and Fe₃O₄ on reduced graphene oxide (Fe⁰/Fe₃O₄-RGO) was prepared and characterized. The prepared Fe⁰/Fe₃O₄-RGO was used as a magnetically separable Fenton-like catalyst and showed superior catalytic activity compared to Fe₃O₄-RGO and Fe₃O₄ as well as other Fenton-like catalysts for the removal of phenol. The Fe⁰/Fe₃O₄-RGO achieved 100% removal efficiency for phenol within 30 min. Free radical inhibition experiments and Electron Paramagnetic Resonance (EPR) showed that the main reactive species was ·OH rather than Fe^{IV}. High resolution TEM results revealed that nanoscale Fe⁰ and Fe₃O₄ were uniformly dispersed and distributed on RGO without agglomeration, furnishing more active sites. The catalyst featured a unique mechanism of electron transfer-facilitated regeneration of active Fe²⁺ by nano-dispersed iron/graphene. RGO served as an effective mediator to facilitate the electron transfer from Fe⁰ to ≡Fe³⁺ for the regeneration of ≡Fe²⁺, which was critical in the catalytic process. This electron transfer-facilitated regeneration of active Fe²⁺ resulted in a reusable catalyst with high catalytic activity for the removal of phenol. The nano-dispersed Fe⁰/Fe₃O₄-RGO could be easily separated and recovered by magnetic field. The Fe⁰/Fe₃O₄-RGO catalyst was reusable and the removal efficiency of phenol after 5 catalytic cycles was as high as 93%. The Fe⁰/Fe₃O₄-RGO could be an effective Fenton-like catalyst for the treatment of waste water containing refractory phenol and phenol type pollutants.

Received 17th April 2017
Accepted 7th May 2017

DOI: 10.1039/c7ra04312k

rsc.li/rsc-advances

1. Introduction

The Fenton reaction (Fe²⁺/H₂O₂) is one of most commonly used advanced oxidation processes, which can generate a highly reactive hydroxyl radical (·OH). ·OH is the second strongest oxidizing agent next to fluorine, which can oxidize organic pollutants into H₂O and CO₂ or low molecular weight organic compounds.^{1,2} However, its application for degradation of refractory organic pollutants is limited by difficult separation and low recovery of the catalyst, and further treatments of the dissolved iron and sludge.³ To overcome these limitations, various solid catalysts have been developed, such as supported noble metal nanoparticles (NPs),⁴⁻⁶ iron-based clays, silica and zeolites,⁷⁻¹⁰ and iron-based magnetic NPs,¹¹⁻¹⁵ as heterogeneous

Fenton-like catalysts. Among those, iron-based catalysts have received increasing attention due to their unique advantages including (1) they are inexpensive and relatively non-toxic; (2) the magnetic properties of Fe-based catalysts have the advantage of easy separation by external magnetic field; and (3) desirable catalytic activity in comparison to other catalysts.

Fe₃O₄ was shown to be an efficient catalyst for the heterogeneous Fenton-like reaction due to the presence of Fe^{II} species in the magnetite structure initiating the Fenton reaction.^{11,13,14} The octahedral structure of Fe₃O₄ can accommodate both Fe²⁺ and Fe³⁺, allowing the iron species to be reversibly oxidized and reduced through electron transfer between Fe²⁺ and Fe³⁺. In addition, Fe₃O₄ can be easily separated from the reaction system by an external magnetic field. The mechanism of the heterogeneous Fenton-like reaction was established in the literature.^{11,13,16-18} The process involves the redox recycling of Fe²⁺/Fe³⁺ on the surface of catalysts, analogous to the Haber-Weiss mechanism.² ≡Fe²⁺ can react with H₂O₂ to generate ·OH, as shown in reaction (1) (≡Fe²⁺ stands for Fe²⁺ sites on the catalyst surface). ≡Fe²⁺ can be regenerated through the reaction between ≡Fe³⁺ and H₂O₂/HO₂· as depicted in reaction (2) and (3). However, in most cases, the concentration of HO₂· is

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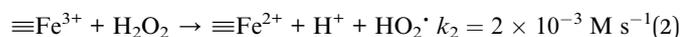
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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra04312k



too low, so the conversion of $\equiv\text{Fe}^{3+}$ to $\equiv\text{Fe}^{2+}$ is a rate-determining step and is quite limited. Therefore, the slow reduction of $\equiv\text{Fe}^{3+}$ to $\equiv\text{Fe}^{2+}$ is critical for the Fenton-like reaction.



Previous reports have shown that Fe^0 as an electrons donor could reduce $\equiv\text{Fe}^{3+}$ into $\equiv\text{Fe}^{2+}$ on the surface of Fe_3O_4 through electron transfer.^{19–21} However, Fe^0 and Fe_3O_4 NPs are prone to aggregate and form large particles due to strong anisotropic dipolar interactions, specifically in the aqueous phase.^{15,22} This dramatically reduced specific surface area and exposed active site, which eventually limited the catalytic activity. Therefore, it is essential to anchor and immobilize Fe^0 and Fe_3O_4 NPs onto supports to prevent aggregation. Furthermore, it would be highly desirable if a support could facilitate rapid interfacial electron transfer between Fe^0 and Fe_3O_4 NPs.

Graphene, a single layer of two-dimensional versatile carbon material with a hexagonal packed lattice, has exhibited promising applications as a 2-D catalyst support^{22–25} due to its high surface area,²⁶ superior mechanical properties,²⁷ and excellent mobility of charge carriers.²⁸ Graphene oxide (GO) consists of abundant oxygenated functional groups, such as hydroxyl and epoxides on the basal plane with carbonyl and carboxyl groups at the edges.²⁹ These oxygenated functional groups can anchor and immobilize metal and metal oxides on its surface and can effectively prevent agglomeration.^{24,30} The combination of graphene-based material and inorganic NPs can also prevent the aggregation of graphene sheets. Furthermore, theoretically, graphene can serve as an effective mediator to facilitate the electron transfer from Fe^0 to $\equiv\text{Fe}^{3+}$ for the regeneration of $\equiv\text{Fe}^{2+}$. In our previous study,³¹ graphene-based material showed excellent absorption ability for bisphenol A owing to the strong π - π interaction between graphene and the aromatic ring of bisphenol A. This significantly promoted the accessibility of active sites, leading to improved mass transfer and catalytic efficiency.

With diminishing fossil fuels such as oil and gas, the coal-based chemical industry is rejuvenating around the world. As a result, increasing amounts of industrial waste water containing refractory phenol and phenol type pollutants has become an intractable environmental concern. Along this line, uniformly dispersed nanoscale Fe^0 NPs and Fe_3O_4 NPs on reduced graphene oxide ($\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO) was designed, prepared and used as a heterogeneous Fenton-like catalyst for enhanced removal of phenol. The catalyst achieved 100% removal efficiency for phenol within 30 min. Nano-dispersed $\text{Fe}^0/\text{Fe}_3\text{O}_4$ on RGO showed superior catalytic activity compared to other Fenton-like catalysts for phenol removal ever reported in the literature. The catalyst featured a unique mechanism of electron transfer-facilitated regeneration of active Fe^{2+} by nano-dispersed iron/grapheme. Moreover, the effects of various

influential parameters, such as the concentration of H_2O_2 and the pH value, on the degradation efficiency of phenol were systematically investigated. The reusability of the catalyst, COD removal, iron leaching and H_2O_2 decomposition are also discussed in detail.

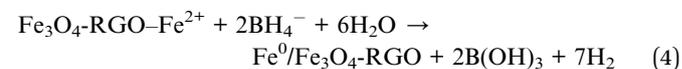
2. Materials and methods

2.1 Materials

Natural graphite powder (200 mesh, 99.9% purity), phenol (99% purity) was purchased from Alfa Aesar Chemical Co., Ltd. All other chemicals were analytical grade and were purchased from Tianjin Zhiyuan Chemical Co., Ltd. All of the chemicals were used without further purification unless notified. Deionized water was used throughout the experiments.

2.2 Preparation of the catalysts

GO was synthesized from graphite powder according to a reported procedure.^{29,31} (For detailed synthesis procedure, see ESI†). The $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO composites were prepared in two steps. Firstly, the nano-dispersed Fe_3O_4 on RGO (Fe_3O_4 -RGO) was prepared by solvothermal method³² as follows: 1.0 g of graphite oxide flakes was exfoliated and dispersed in 200 mL of ethylene glycol (EG)/diethylene glycol (DEG) (EG : DEG = 1 : 19 by volume) through ultrasonic treatment for 1 h. 15 g of sodium acetate, 15 g of sodium acrylate, and 5.4 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, were then added to the suspension of GO under magnetic stirring at 50 °C for 30 min. The resulting homogeneous solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and sealed for solvothermal reaction at 200 °C for 10 h. The product (Fe_3O_4 -RGO) was washed with deionized water and ethanol three times. The obtained Fe_3O_4 -RGO was dispersed in 600 mL of oxygen-free deionized water for further use. Secondly, the $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO was synthesized by *in situ* reduction method. 1.5 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 50 mL of deionized water. The solution was slowly added to the dispersion of Fe_3O_4 -RGO with stirring for 1 h. In the next step, a stoichiometric amount (1.0 g) of NaBH_4 was added dropwise to 50 mL of the solution prepared in the previous step and stirred for 1 h. The ferrous iron was reduced to iron zero according to reaction (4). The product $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO was obtained as black particles and was washed with deionized water and ethanol five times, and was then dried in a vacuum oven at 40 °C for 24 h.



The Fe^0 -RGO was prepared by the following procedure: 0.20 g of graphite oxide flakes was exfoliated and dispersed in 120 mL of deionized water through ultrasonic treatment for 1 h. Then 0.30 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 10 mL of deionized water. The solution was slowly added to the dispersion of GO with stirring for 1 h. Then, a stoichiometric amount (0.20 g) of NaBH_4 was added dropwise to 10 mL of the solution prepared in previous step and stirred for 1 h. The obtained product was washed with deionized water and ethanol five times, and was then dried in a vacuum oven at 40 °C for 24 h.



2.3 Characterization of the catalyst

X-ray diffraction (XRD) spectra were recorded on a Bruker D8 Advance X-ray diffractometer equipped with a diffracted-beam monochromator set for Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra were collected with a Bruker VERTEX-70 spectrometer in the range of 4000–500 cm^{-1} . The morphology and particle size of the prepared catalysts were analyzed using transmission electron microscopy (TEM) (Tecnai G2 F20, FEI, USA). X-ray energy dispersive spectroscopy (EDS) was used to analyze the element composition and distribution. The zeta-potential of the Fe_3O_4 -RGO was measured using a Malvern Zetasizer Ultra ZS90. The Brunauer–Emmett–Teller surface area (S_{BET}) of the catalysts was obtained by N_2 adsorption–desorption using an Automated Gas Sorption Analyzer (Quadrasorb IQ, Quantachrome Instrument Corp). The Raman spectra were recorded from 40 to 4000 cm^{-1} on a micro laser Raman spectrometer (Horiba Scientific, France). The surface element compositions were measured using X-ray photoelectron spectroscopy (XPS) with a Thermo ESCALAB 250XI spectrometer using monochromatic 150 W Al K α radiations. The magnetic properties of the catalysts at room temperature were measured using a vibrating-sample magnetometer (MPMS XL-7, Quantum Design, USA).

2.4 Degradation experiments

The phenol degradation experiments were carried out in a 50 mL conical flask placed in a rotary shaker in the dark. The rotate speed was set at 150 rpm. Typically, 25 mg of catalyst was added to 25 mL of 50 mg L^{-1} phenol solution whose pH value was adjusted by addition of H_2SO_4 or NaOH . H_2O_2 was added to the solution to initiate the reaction. Then, 1.0 mL of the suspension was taken at given time intervals using a syringe, separated and quenched with an excessive amount of methanol. To test the stability of catalyst, the catalyst was collected, washed, dried under vacuum, and reused in a fresh solution of phenol and H_2O_2 for multiple catalytic cycles.

2.5 Sample analysis

The concentrations of phenol were analyzed *via* high-performance liquid chromatography (Ultimate 3000, Dionex) equipped with UV absorbance detector and C18 column (4.6 $\text{mm} \times 250 \text{ mm}$). The H_2O_2 concentration was analyzed by iodometric method.³³ Chemical Oxygen Demand (COD) was determined by a known procedure.³³ The concentration of total dissolved iron was measured with 1,10-phenanthroline after adding hydroxylamine hydrochloride at 510 nm on a UV/Vis spectrophotometer.^{34,35} (For detailed procedure, see ESI†).

2.6 Electron paramagnetic resonance (EPR) studies

The EPR spectra were obtained on a Bruker E500 spectrometer with a microwave bridge at room temperature. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was used as spin-trapping agent (for detailed procedure, see ESI†).

3. Results and discussion

3.1 Synthesis methods and characterization

The typical synthesis of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO is depicted in Fig. 1. Firstly, the pre-synthesized graphite oxide was transformed to exfoliated graphene oxide sheets *via* ultrasonic dispersion. Then, the nano-dispersed Fe_3O_4 on RGO composite was prepared by solvothermal method followed by reduction to RGO. Zeta potential analysis (Fig. S1†) illustrated that the surface of Fe_3O_4 -RGO was electronegative. The Fe_3O_4 -RGO captured Fe^{2+} ions in ferrous sulfate solution. Finally the Fe^{2+} ions captured on the Fe_3O_4 -RGO surface were reduced to Fe^0 NPs by NaBH_4 and were deposited on the Fe_3O_4 -RGO surface.

The transmission electron microscope (TEM) images of the Fe_3O_4 -RGO composites revealed that the nanoscale Fe_3O_4 NPs with a size of 8–15 nm were uniformly anchored on the surface of the graphene sheets (Fig. 2a and b). As shown in Fig. 2c, the high-resolution TEM (HRTEM) image of Fe_3O_4 -RGO showed the presence of crystal lattices of Fe_3O_4 . The lattice fringes of Fe_3O_4 -RGO were observed clearly with interlayer spacing of 0.25 nm, which matched well with the (311) lattice planes of Fe_3O_4 . The TEM images of the $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO displayed distinctive differences compared to that of Fe_3O_4 -RGO. As shown in Fig. 2d and e, more iron NPs were evenly deposited on the graphene sheet, which was ascribed to the formation of Fe^0 NPs on Fe_3O_4 -RGO. HRTEM revealed that one could even distinguish the two different iron phases (Fe^0 and Fe_3O_4). The HRTEM image of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO (Fig. 2f) explicitly showed lattice fringes with interlayer spacing of 0.25 nm and 0.21 nm, which were ascribed to the (311) lattice plane of Fe_3O_4 and the (110) lattice plane of Fe^0 , respectively.

XPS measurements were conducted to analyze the surface element composition and chemical states of Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO. The XPS survey spectra of Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO are shown in Fig. 3a. The peaks at 285 eV, 531 eV, 711 eV and 725 eV were assigned to C 1s, O 1s, Fe 2p $_{3/2}$ and Fe 2p $_{1/2}$, respectively. The survey spectra revealed the presence of

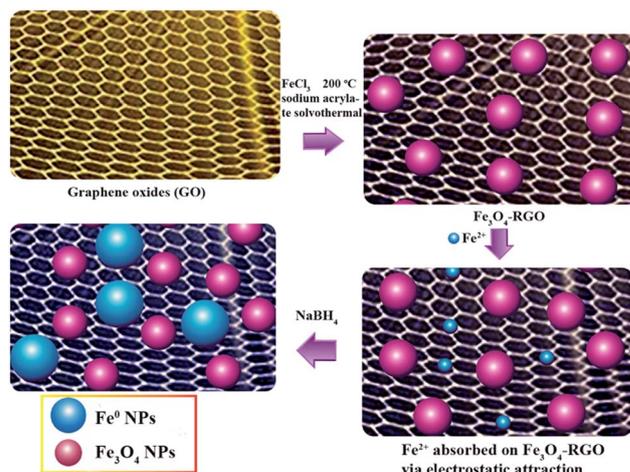


Fig. 1 Schematic illustration of the synthesis of nano-dispersed $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO.



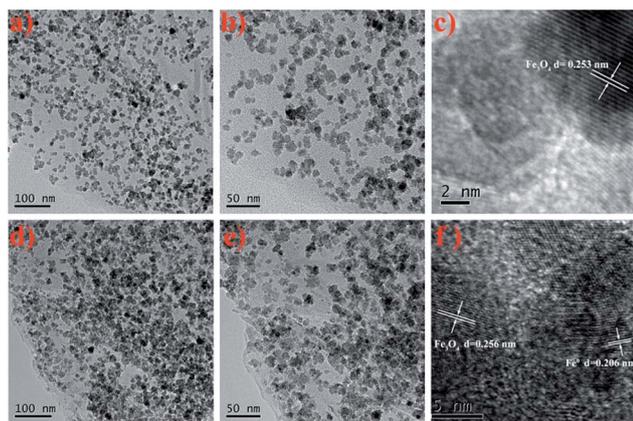


Fig. 2 TEM images of Fe_3O_4 -RGO (a and b) and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO (d and e). HRTEM images of Fe_3O_4 -RGO (c) and (f).

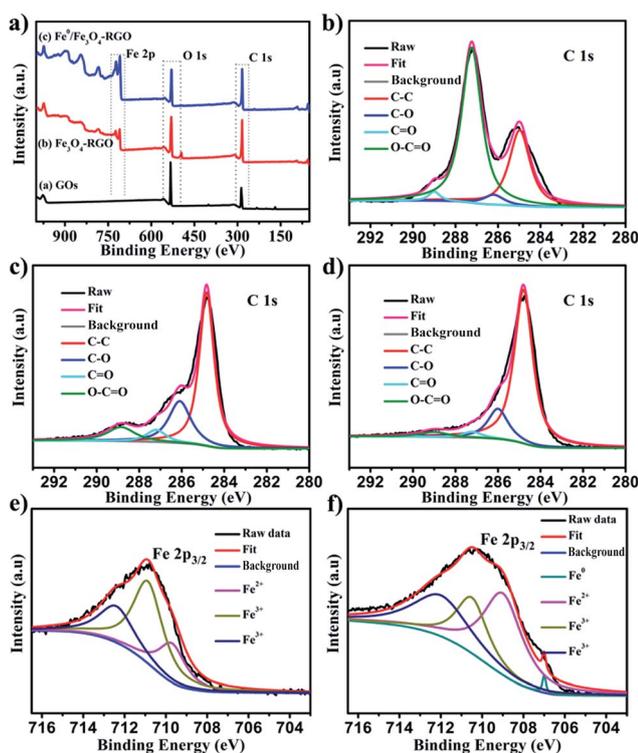


Fig. 3 (a) XPS survey spectra of GO, Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO. (b–d) C 1s peaks of GO, Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO. (e and f) Fe $2p_{3/2}$ peaks of Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO.

C, O, and Fe elements on the surface of Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO. Moreover, as shown in Fig. 3b, four different peaks at 284.5, 286.2, 287.2 and 289 eV were observed in high-resolution scans in the C 1s region. Those peaks could be distinguished by deconvolution and were assigned to the non-oxygenated ring C, epoxy/hydroxyls (C–O), the carbonyl (C=O), and the carboxylate carbon (O–C=O).^{29,36} For Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO, the intensity of the C 1s peaks, especially the peak assigned to oxidized carbon, decreased dramatically, implying that the GO was reduced to RGO (Fig. 3c and d). In

addition, three different peaks at 709.5, 710.7 and 712.2 eV could be distinguished by deconvolution using data from the high-resolution scans in the Fe $2p_{3/2}$ region of Fe_3O_4 -RGO (Fig. 3e). Those peaks were assigned to the binding energies for Fe^{2+} -O, and Fe^{3+} -O.³⁷ Similarly, those characteristic peaks were observed in Fe $2p_{3/2}$ spectra of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO (Fig. 3f). In addition, the presence of a Fe^0 peak with weak intensity at 707 eV was further evidence for the presence of Fe^0 in nano-dispersed $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO (Fig. 3f).

XRD measurements were carried out to investigate the phase structure of the nano-dispersed $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO. Fig. 4a shows the XRD patterns of Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO.

The diffraction patterns for Fe_3O_4 -RGO showed seven broad peaks at 18.2° , 30.4° , 35.6° , 43.3° , 53.2° , 56.9° and 62.7° , corresponding to (111), (220), (311), (400), (422), (511) and (440) of Fe_3O_4 (JCPDS no. 001-1111), respectively. The typical peak of Fe_3O_4 was also observed in $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO. However, the peak of Fe^0 at 44.5° was not found in the XRD pattern of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO. Similar phenomenon have been observed and reported in the literature.^{9,38,39}

Raman spectra of the GO, Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO are shown in Fig. 4b. The peaks at ~ 1350 and ~ 1590 cm^{-1} are the characteristic peaks of the D and G bands from graphene. Peak shift was observed for both D and G bands, indicating a charge transfer between the graphene sheet and the Fe^0 and Fe_3O_4 NPs.^{40,41} The charge transfer between graphene and Fe_3O_4 could be beneficial for conversion of $\equiv\text{Fe}^{3+}$ to $\equiv\text{Fe}^{2+}$. In addition, the spectra of Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO were compared to that of GO. There was an obvious increase of the intensity ratio (I_D/I_G), implying the reduction of GO to RGO,^{36,42,43} which was consistent with the results of XPS.

The nitrogen adsorption–desorption curve was obtained to evaluate the specific surface area and pore size distribution. The N_2 adsorption–desorption isotherm of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO is shown

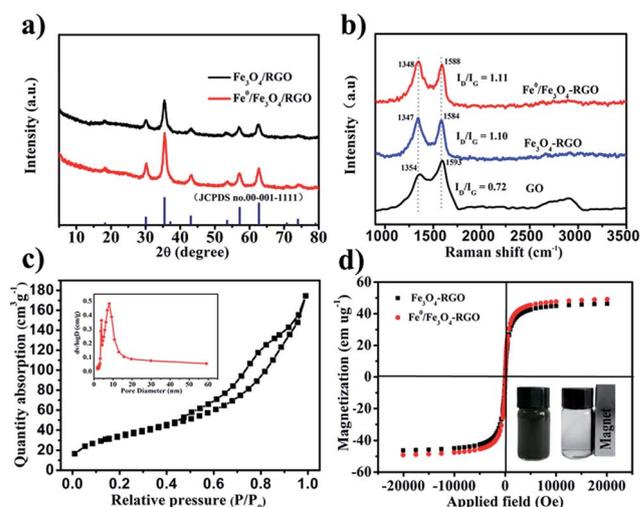


Fig. 4 (a) XRD patterns of Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO. (b) Raman spectra of GO, Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO. (c) Nitrogen adsorption–desorption isotherms and pore size distribution curve (insert pattern) of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO composite. (d) Magnetization curves of Fe_3O_4 -RGO and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ -RGO composites.



in Fig. 4c. The S_{BET} of the $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ was obtained as $124 \text{ m}^2 \text{ g}^{-1}$. The curve belongs to the Type IV isotherm classified by IUPAC with distinct hysteresis loops close to H3 type, suggesting that the $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ composite has a characteristic lamellar stacking. Fig. 4c (inset) shows the pore size distribution of $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$. The total pore volume and average pore diameter of $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ were $0.22 \text{ cm}^3 \text{ g}^{-1}$ and 7.26 nm , respectively.

The magnetic properties of the $\text{Fe}_3\text{O}_4\text{-RGO}$ and $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ are shown in Fig. 4d. The magnetic hysteresis loops were S-like curves. The saturation magnetization of $\text{Fe}_3\text{O}_4\text{-RGO}$ (46.3 emu g^{-1}) was smaller than that of $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ (49.1 emu g^{-1}), which could be attributed to the formation of Fe^0 . The magnetic remanence of $\text{Fe}_3\text{O}_4\text{-RGO}$ and $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ was nearly zero, suggesting that $\text{Fe}_3\text{O}_4\text{-RGO}$ and $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ exhibit superparamagnetic behavior. Moreover, the magnetic response of the $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ was also examined by an external magnet (Fig. 4d inset). The results showed that $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ could be easily separated and recovered. This could be an advantage for the recycling and reuse of the catalyst in real applications.

3.2 Catalytic activity of the $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ composite

Batch experiments were conducted to compare the removal efficiencies of phenol by various processes. As shown in Fig. 5, H_2O_2 without catalyst only led to a limited removal efficiency of 2.8% within 90 min, implying that the oxidation ability of H_2O_2 for phenol was poor. Interestingly, in the absence of H_2O_2 , $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ achieved removal efficiency 20% for phenol in 30 min. This is owing to the surface adsorption of phenol on the $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ via $\pi\text{-}\pi$ interaction.^{31,44} Noticeably, the removal efficiency of phenol using the $\text{Fe}_3\text{O}_4\text{-RGO}$ composite as the heterogeneous Fenton-like catalyst in the presence of H_2O_2 was significantly higher (76%) than that of a commercial Fe_3O_4 catalyst (35%), which could be explained by various aspects. Firstly, Fe_3O_4 NPs were highly dispersed on the substrate, furnishing a high density of active sites. Secondly, the strong $\pi\text{-}$

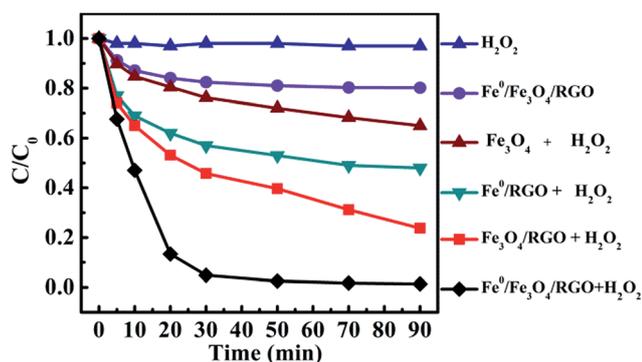
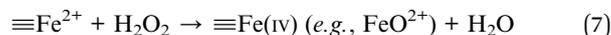
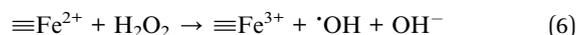


Fig. 5 Comparison of the removal efficiency of phenol with different catalytic systems. Reaction conditions: $[\text{phenol}]_0 = 50 \text{ mg L}^{-1}$, $[\text{Fe}_3\text{O}_4] = 1 \text{ g L}^{-1}$, $[\text{Fe}_3\text{O}_4\text{-RGO}] = 1 \text{ g L}^{-1}$, $[\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}] = 1 \text{ g L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 5 \text{ mM}$, $\text{pH } 3.0$ and $T = 25 \text{ }^\circ\text{C}$; C_0 and C are the initial phenol concentration and its concentration at any time during the reaction, respectively.

π interaction between RGO and the aromatic group of phenol promoted the absorption of phenol and thus increased the effective concentration near the surfaces of the $\text{Fe}_3\text{O}_4\text{-RGO}$ composite,⁴⁵ resulting in the improved catalytic activity of $\text{Fe}_3\text{O}_4\text{-RGO}$.

Interestingly, the $\text{Fe}^0\text{-RGO}$ with H_2O_2 led to 65% removal efficiency for phenol within 90 min. This was probably due to the reason that Fe^0 was oxidized producing $\equiv\text{Fe}^{2+}$ via two electron transfer mechanisms from the particle surface to H_2O_2 (reaction (5)).⁴⁶ The oxidants responsible for the removal of phenol were generated by Fenton reaction (reactions (6) and (7)).



Noticeably, with the $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ composite as the heterogeneous Fenton-like catalyst, the phenol was completely removed within 30 min. The catalytic activity of $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ was the highest compared to all other Fenton-like catalysts for phenol removal ever reported in the literature. These results are summarized in Table 1 (for detailed information, see ESI†). By comparing the catalytic performance with a series of control systems, it was concluded that the catalytic activity of the $\text{Fe}_3\text{O}_4\text{-RGO}$ was significantly enhanced by the introduction of Fe^0 . It was proposed that there was a synergistic effect between Fe^0 , Fe_3O_4 and RGO in phenol removal using $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ as a heterogeneous Fenton-like catalyst. A possible mechanism of enhanced removal of phenol using $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ as a heterogeneous Fenton-like catalyst is discussed in detail in Section 3.6.

3.3 Effects of pH and H_2O_2 concentration on phenol removal

The effect of pH on the removal of phenol using $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ is shown in Fig. 6a. The results showed that the catalytic activity of $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ for phenol removal was highly pH-dependent. The removal efficiency of phenol was only 20% after 90 min at pH 6.0, while the removal efficiency of phenol dramatically increased with decreasing pH. The phenol was almost totally removed after 30 min at pH 3.0. The higher removal efficiency at lower pH was ascribed to the higher oxidation potential of $\cdot\text{OH}$ under acidic conditions.^{51,52} It was also proposed that acidic conditions were favourable for the stability of H_2O_2 and were beneficial for the generation of $\cdot\text{OH}$ and the formation of metal oxide-pollutant inner-sphere complexes.¹⁴ The effect of the H_2O_2 concentration on removal of phenol using $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ was also investigated (Fig. 6b). It was observed clearly that the removal efficiency of phenol increased with increasing H_2O_2 concentration from 1 mM to 5 mM. Hydrogen peroxide is the precursor in the reaction with $\equiv\text{Fe}^{2+}$ generating $\cdot\text{OH}$ as described in reaction (1). With insufficient H_2O_2 concentration (below 5 mM), the amount of $\cdot\text{OH}$ generated will be limited, leading to a low removal efficiency of phenol. Interestingly and noticeably, the removal efficiency of phenol decreased with



Table 1 Comparison of phenol removal using different Fenton-like catalysts

| Catalyst | Catalyst dose (g L ⁻¹) | [Phenol] ₀ mM | [H ₂ O ₂] ₀ mM | Degradation (%) | Reaction time (h) | Reference |
|--|------------------------------------|--------------------------|--|-----------------|-------------------|-----------|
| Fe ₃ O ₄ | 5 | 1.00 | 1200 | 95 | 6 | 14 |
| Au/HO-npD | N/A | 1.06 | 5.88 | 93 | 24 | 6 |
| Fe/AC | 0.5 | 1.06 | 15 | 100 | 4 | 47 |
| Fe-ZSM-5 | 1.5 | 0.691 | 90 | 81 | 3 | 48 |
| FeAlSi-ox | 3.0 | 0.500 | 50 | 32 | 8 | 34 |
| FeSi-ox | 3.0 | 0.500 | 50 | 44 | 8 | 34 |
| Magnetite (Fe ₃ O ₄) | 3.0 | 0.266 | 150 | 42 | 24 | 49 |
| Fe–Al-pillared clay | 0.6 | 0.213 | 4.00 | 100 | 2.5 | 50 |
| Fe ⁰ /Fe ₃ O ₄ -RGO | 1.0 | 0.531 | 5.00 | 100 | 0.5 | This work |

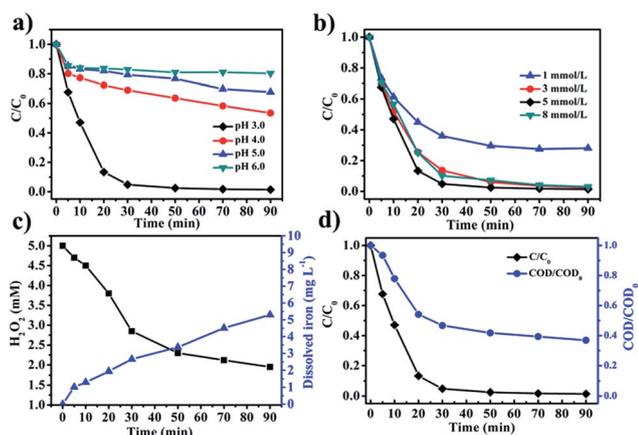
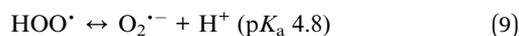
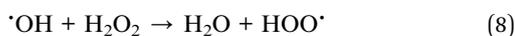
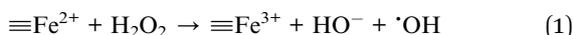


Fig. 6 (a) The effect of initial pH on phenol removal. (b) The effect of H₂O₂ concentration on phenol removal. (c) The concentration of H₂O₂ and dissolved iron during phenol removal over time. (d) The phenol removal and COD removal over time [phenol]₀ = 50 mg L⁻¹, [Fe⁰/Fe₃O₄-RGO] = 1 g L⁻¹, [H₂O₂]₀ = 5 mM, pH 3.0 and T = 25 °C.

increasing H₂O₂ concentration from 5 mM to 8 mM. This was probably because the excess H₂O₂ could be a scavenger of [•]OH, as described in reaction (8).^{42,53} Although other oxidative species, such as HOO[•] and O₂^{•-}, are generated, as described in reactions (8) and (9), [•]OOH and O₂^{•-} have much lower oxidation potentials than [•]OH.^{11,54}



3.4 Iron leaching and H₂O₂ decomposition

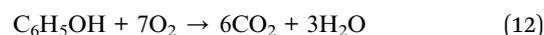
The concentrations of H₂O₂ and total dissolved iron during phenol removal using the Fe⁰/Fe₃O₄-RGO composite were investigated as well (Fig. 6c). It was observed that the concentration of total dissolved iron increased with the reaction time. The total dissolved iron could be the result of ferrous and ferric ions leaching from the Fe⁰/Fe₃O₄-RGO composite. The

concentration of total dissolved iron after 90 min was 5.2 mg L⁻¹, which was only 0.8% of the total iron of the 1.0 g L⁻¹ catalyst used. It was observed that the H₂O₂ concentration decreased rapidly within the first 30 min then slowed down gradually from 30 min to 90 min during the removal of phenol. This was consistent with the removal efficiency of phenol over time.

The COD of the phenol solution during the reaction was monitored in order to further investigate the utilization efficiency of H₂O₂ (Fig. 6d). The maximum COD removal (63%) was achieved after 90 min, indicating that a residual amount of organic compounds remained in solution, presumably generated by catalytic oxidation reaction. The stoichiometry utilization efficiency of H₂O₂ was defined as the ratio of the amount of H₂O₂ used for the degradation of phenol against the total amount of H₂O₂ consumed in the reaction.^{55,56} Based on reactions (11)–(13), the utilization efficiency of H₂O₂ can be calculated as 86% through eqn (10). The utilization efficiency of H₂O₂ was notably higher than previously reported results.^{13,53}

$$E (\%) = \frac{\Delta\text{COD}}{16 \times \Delta\text{H}_2\text{O}_2} \times 100 \quad (10)$$

where ΔCOD is the change of COD value (mg L⁻¹), ΔH₂O₂ is the amount of H₂O₂ (mol L⁻¹) consumed and 16 is the conversion factor.



3.5 The reusability of Fe⁰/Fe₃O₄-RGO

Reusability is one of the most important factors in evaluating a catalyst's performance in practical applications.⁵⁷ Five successive catalytic cycles were carried out under the same conditions to test the reusability of the Fe⁰/Fe₃O₄-RGO. The used catalyst was collected and washed with water before next use. As shown in Fig. 7a, the kinetic rate of phenol removal only decreased slightly after five successive batch experiments. This was attributed to iron leaching from the catalyst surface into



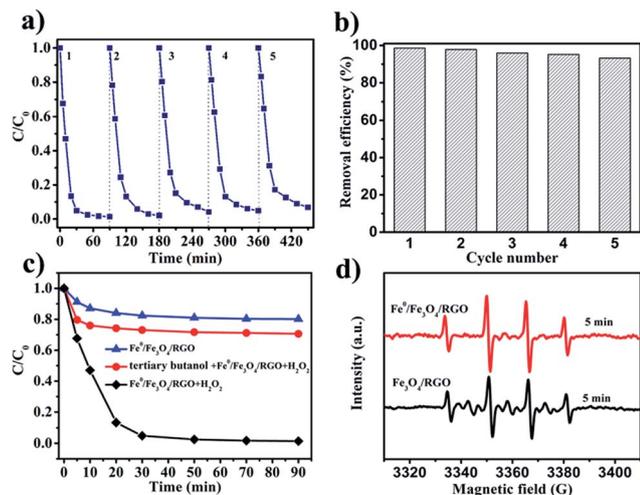


Fig. 7 Reusability of $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ catalyst for phenol removal: (a) the kinetic rate of removal for phenol; (b) the removal efficiencies of phenol after 90 min reaction; (c) effect of radical scavengers on phenol removal; (d) DMPO spin-trapping EPR spectra of $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}/\text{H}_2\text{O}_2$ system and $\text{Fe}_3\text{O}_4\text{-RGO}/\text{H}_2\text{O}_2$ system [catalyst] = 1.0 g L^{-1} , [DMPO] = 0.2 M , [tertiary butanol] = 300 mM , pH 3 and $T = 25^\circ \text{C}$.

solution, as discussed in the previous section. Another possible reason could be the poisoning of the active catalytic sites by adsorbed organic species. Impressively, the removal efficiency of phenol remained as high as 93% after 90 min reaction and reuse in five catalytic cycles (Fig. 7b). The removal efficiency of phenol after each cycle was 99%, 98%, 96%, 95% and 93%, sequentially, demonstrating the excellent catalytic activity and decent reusability of $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$.

3.6 Catalytic mechanism of $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ for phenol removal

Free radical inhibition experiments are known to be effective to identify reactive species in Fenton or Fenton-like systems.^{11,58} Therefore, tertiary butanol was selected as a scavenger of $\cdot\text{OH}$. As shown in Fig. 7c, the removal efficiency of phenol was 30% after 90 min in the presence of 300 mM tertiary butanol. For $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}/\text{H}_2\text{O}_2$ without adding tertiary butanol, the removal efficiency of phenol was as high as 100%. These results imply that the $\cdot\text{OH}$ is the main reactive species responsible for phenol removal rather than high oxidative state iron species (Fe^{IV}).³⁴ To further identify free radical species generated in the catalytic system, EPR technique with spin-trapping agent DMPO was used. As shown in Fig. 7d, four characteristic peaks of the $\text{DMPO}\cdot\text{OH}$ adduct with an intensity ratio of 1 : 2 : 2 : 1 were observed in the EPR spectra of both $\text{Fe}_3\text{O}_4\text{-RGO}/\text{H}_2\text{O}_2$ and $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}/\text{H}_2\text{O}_2$ in the presence of 0.1 M DMPO. This result was further evidence for the existence of $\cdot\text{OH}$. Furthermore, the peak intensity of $\text{DMPO}\cdot\text{OH}$ in the $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}/\text{H}_2\text{O}_2$ system was higher than that of $\text{Fe}_3\text{O}_4\text{-RGO}/\text{H}_2\text{O}_2$, indicating that the concentration of $\cdot\text{OH}$ generated in the $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}/\text{H}_2\text{O}_2$ system was higher. The result was consistent with the enhanced removal efficiency of phenol using $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$.

It was reported that the heterogeneous Fenton-like reaction and $\cdot\text{OH}$ production mostly occur on the surface of the solid catalyst.^{22,42,54} In addition, $\cdot\text{OH}$ was found to have a very short half-life ($<1 \mu\text{s}$).⁵⁹ According to this, the tight adsorption of phenol on the catalyst surface would increase the probability of the reaction between phenol and hydroxyl radicals formed at the surface of the catalyst.⁶⁰ Therefore, the effective adsorption of phenol on the catalyst surface could actually facilitate the catalytic process of phenol removal.¹¹

Based on previous literature and our experimental results, a possible mechanism of enhanced removal of phenol using $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ as a heterogeneous Fenton-like catalyst was proposed (Fig. 8). With our approach, the Fe^0 NPs and Fe_3O_4 NPs were uniformly dispersed and distributed on RGO, furnishing more active sites. $\equiv\text{Fe}^{2+}$ from the Fe_3O_4 and Fe^0 of $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ reacted with H_2O_2 to generate $\cdot\text{OH}$ (reaction (1)). Not only was $\equiv\text{Fe}^{2+}$ regenerated from $\equiv\text{Fe}^{3+}$ by reacting with H_2O_2 (reaction (2) and (3)), but also Fe^{3+} could react with Fe^0 *via* graphene-facilitated electron transfer to regenerate $\equiv\text{Fe}^{2+}$. It has been reported that this reaction is thermodynamically favourable (reaction (14)).²⁰ Interestingly, the Raman results for $\text{Fe}_3\text{O}_4\text{-RGO}$ and $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ showed an electron transfer between the $\text{Fe}^0/\text{Fe}_3\text{O}_4$ and RGO. This implied that RGO actually served as an effective mediator to promote electron transfer from Fe^0 to $\equiv\text{Fe}^{3+}$ of Fe_3O_4 for the generation of $\equiv\text{Fe}^{2+}$.⁶¹ Thus, more $\cdot\text{OH}$ was generated on the surface of $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ to oxidize the phenol adsorbed on $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ facilitated by $\pi\text{-}\pi$ interaction between RGO and phenol. Overall, nano-dispersed $\text{Fe}^0/\text{Fe}_3\text{O}_4$ on RGO as a Fenton-like catalyst for enhanced removal of phenol was successful.

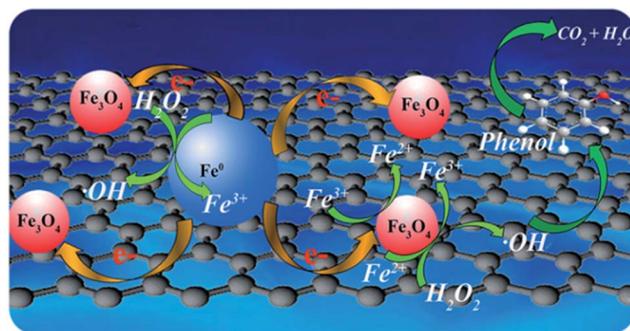
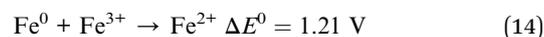
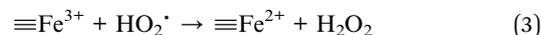
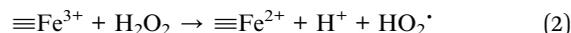
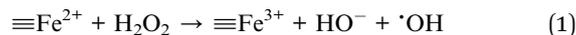


Fig. 8 The nano-dispersed $\text{Fe}^0/\text{Fe}_3\text{O}_4\text{-RGO}$ catalyst featured a unique mechanism of electron transfer-facilitated regeneration of active Fe^{2+} for catalytic phenol removal.



4. Conclusions

Nano-dispersed Fe⁰ and Fe₃O₄ on reduced graphene oxide (Fe⁰/Fe₃O₄-RGO) was prepared and characterized. The Fe⁰/Fe₃O₄-RGO composite as a heterogeneous Fenton-like catalyst achieved 100% removal efficiency for phenol within 30 min. The Fe⁰/Fe₃O₄-RGO catalyst was reusable and the removal efficiency of phenol after five catalytic cycles was as high as 93%. The Fe⁰/Fe₃O₄-RGO was also magnetically separable. The Fe⁰/Fe₃O₄-RGO could be an effective Fenton-like catalyst for the treatment of waste water containing refractory phenol and phenol-type pollutants. The nano-dispersed Fe⁰/Fe₃O₄-RGO catalyst featured a unique mechanism of electron transfer-facilitated regeneration of active Fe²⁺ for catalytic phenol removal. Nano-dispersed Fe⁰ and Fe₃O₄ NPs on RGO could furnish more active sites exposed on the catalyst surface. RGO served as an effective mediator to facilitate the electron transfer from Fe⁰ to ≡Fe³⁺ for the regeneration of ≡Fe²⁺, which resulted more ·OH. The strong π-π interaction between RGO and the aromatic ring of phenol promoted the absorption of phenol and thus increased the probability of the reaction with proximate hydroxyl radicals formed on the surface of the catalyst. All these helped achieve the high catalytic activity.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21472235), Xinjiang Distinguished Youth Scholar Program (qn2015jq012), "One Thousand Talents" Program (Y32H291501) of China and the STS program of Chinese Academy of Sciences (2017).

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