Poly(catechol) modified Fe₃O₄ magnetic nanocomposites with continuous high Fenton activity for organic degradation at neutral pH

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Abstract
Fe₃O₄ magnetic nanoparticles (MNPs) have been widely used as a recyclable catalyst in Fenton reaction for organic degradation. However, the pristine MNPs suffer from the drawbacks of iron leaching in acidic conditions as well as the decreasing catalytic activity of organic degradation at a pH higher than 3.0. To solve the problems, Fe₃O₄ MNPs were modified by poly(catechol) (Fe₃O₄/PCC MNPs) using a facile chemical co-precipitation method. The poly(catechol) modification improved both the dispersity and the surface negative charges of Fe₃O₄/PCC MNPs, which are beneficial to the catalytic activity of MNPs for organic degradation. Moreover, the poly(catechol) modification enhanced the efficiency of Fe(II) regeneration during Fenton reaction due to the acceleration of Fe(III) reduction by the phenolic/quinonoid redox pair. As a result, the Fenton reaction with Fe₃O₄/PCC MNPs could efficiently degrade organic molecules, exemplified by methylene blue (MB), in an expanded pH range between 3.0 and 10.0. In addition, Fe₃O₄/PCC MNPs could be reused up to 8 cycles for the MB degradation with negligible iron leaching of lower than 1.5 mg L⁻¹. This study demonstrated Fe₃O₄/PCC MNPs are a promising heterogeneous Fenton catalysts for organic degradation.

Keywords Poly(catechol) · Fe₃O₄ MNPs · Fenton · Catalyst · Recycle

Introduction
Heterogeneous Fenton technique as a promising technique for advanced oxidation processes (AOPs) has been intensively applied for the removal of organic pollutants because of its intrinsic advantages over classical homogeneous Fenton reactions, including the wide working pH range, no iron sludge pollution, reusable catalysts, and low H₂O₂ consumption (Chen et al. 2017; Goncalves et al. 2020; Luo et al. 2010). Many solid catalysts have been demonstrated to be effective in heterogeneous Fenton reactions (Li et al. 2018; Li et al. 2017). Fe₃O₄ magnetic nanoparticles (Fe₃O₄ MNPs) have received great attention in Fenton reactions (Mondal et al. 2020). The Fe₃O₄ MNPs possess unique properties, magnetism, which can be effectively separated from the solution using a magnetic field (Mercado et al. 2018a; Magnacca et al. 2014). Especially, Gao et al. demonstrated that Fe₃O₄ magnetite nanoparticles possessed an intrinsic enzyme mimetic activity similar to that of peroxidases in nature, which were widely used to oxidize organic pollutant in the treatment of wastewater. Further, Fe₃O₄ MNPs possessed highly effective catalytic activity, which possessed a higher binding affinity for the substrate TMB than HRP and exhibited a 40-fold higher level of activity at the same molar catalyst concentration than that of HRP (Gao et al. 2007). Moreover, the Fe(II) in Fe₃O₄ MNPs plays an important role as the electron donor to initiate the Fenton reactions. The octahedral sites in the magnetite
structure can accommodate both Fe(II) and Fe(III) simultaneously. Hence, the reversible transformation of Fe(II)/Fe(III) can happen within the same structure during Fenton reaction (Wang et al. 2020; Wang et al. 2010), that is to say, Fe(III) transforms to Fe(II) and Fe(II) continues to catalyze H₂O₂. Thus, Fe₃O₄ MNPs can be used as Fenton catalysts for activating H₂O₂ (Cai et al. 2021; Xiang et al. 2021).

However, the iron leaching from the Fe₃O₄ MNPs at acidic pH and the low catalytic activity at neutral and alkaline pH could affect the stability and activity of Fe₃O₄ MNPs, thus limiting their applications (Pu et al. 2014). Previous studies have shown, that, for the degradation of 2,4-dichlorophenol (2,4-DCP) with Fe₃O₄ MNPs, 9.8 mg L⁻¹ of Fe dissolved into the solution at pH 3.0 after 180 min. Slow degradation of 2,4-DCP was observed at pH values of 3.9, 4.6, and 5.0, although a lower pH caused a shorter induction time and a higher kinetic rate (Xu and Wang 2012). Dimethyl phthalate (DMP) was quickly removed in the acidic solution with pH range from 3.0 to 4.5. However, at pH 8.0, the Fe₃O₄ MNPs had very little activity as Fenton catalysts (He et al. 2015). The low catalytic activity at high pH values is mainly caused by the oxidation of these fine particles with limited Fe(II) regeneration during heterogeneous Fenton processes. Hu et al. reported that the Fe(II) amount in the total surface Fe atoms of Fe₃O₄/MWCNTs for used and fresh catalysts was 13.3% and 31.7%, respectively (Hu et al. 2011). Many efforts have been paid to improving the catalytic performance of Fe₃O₄ MNPs (Hammouda et al. 2015). Niu et al. introduced humic acid (HA) to coat Fe₃O₄ magnetic nanoparticles, i.e., Fe₃O₄/HA, which exhibited a high catalytic ability for H₂O₂ decomposition. This was caused by rapid electron transfer among the complexed Fe(II)–HA and Fe(III)–HA, leading to the rapid regeneration of Fe(II) species and the fast production of •OH radicals (Niu et al. 2011).

Organic ligands (citrate, oxalate, ethylenediaminetetraacetic acid, etc.) have been used to modify the surface of iron compounds to control their solubility in Fenton or Fenton-like processes (Bai et al. 2013; Baldi Marchetto et al. 2010; Jho et al. 2012). Among those iron ligands, catechol, could form strong coupling with the iron ions which reduced the Fe³⁺/Fe²⁺ redox potential (Niu et al. 2011; Kang and Choi 2009). In addition, catechol can directly reduce Fe(III) to Fe(II), which itself transformed to the corresponding quinones (Melin et al. 2015). Therefore, introducing catechol in Fenton or Fenton-like processes can widen the reaction pH to neutral conditions by preventing iron from precipitation and, at the same time, enhance the electron transfer (Chen et al. 2017; Contreras et al. 2009). However, it also contributes a certain amount of total organic carbon (TOC) that consumes a certain amount of H₂O₂ in a Fenton system. Finally, catechol will be degraded and exhausted, which will result in the degradation of the catalytic performance (Xiao et al. 2016).

The polymerization of catechol, catalyzed by Fe(III), forms poly(catechol) (Elhabiri et al. 2007; Gulley Stahl et al. 2010; Slikboer et al. 2015). Poly(catechol), containing phenolic/quinonoid redox-active units in the main chain, is a redox-active polymer. Moreover, the binding of the bidentate enediol ligands from the catechol group converted the under-coordinated iron on the surface sites back to a bulk-like lattice structure with an octahedral geometry for the oxygen-coordinated iron, which consequently ended up with tight binding between ligands and iron oxide (Xu et al. 2004). Poly(catechol) has been exploited as adhesives and coatings on the surfaces of organic and inorganic materials due to its unique thermal, structural properties, and the ability to form strong charge transfer complexes with the metal oxides (Faure et al. 2013; Ye et al. 2011). Therefore, we propose that Fe₃O₄ MNPs modified with poly(catechol) will greatly increase the catalytic activity of Fe₃O₄ MNPs without sacrificing the structural stability. The introduction of poly(catechol) in Fe₃O₄/PCC MNPs could offer the following advantages: i) preventing nanoparticles from agglomeration and broadening the working pH range of Fenton reactions; ii) avoiding Fe(II) oxidation and iron leaching; iii) accelerating the Fe(III)/Fe(II) conversion with the recyclable organic ligands.

In this work, Fe₃O₄/PCC MNPs were prepared by a facile co-precipitation method. The obtained material was tested for heterogeneous Fenton degradation of MB, used as a model organic pollutant. The structure, surface charge, electron transfer ability, and catalytic activity of Fe₃O₄/PCC MNPs were investigated. The possible mechanisms for Fe₃O₄/PCC MNPs formation and enhanced MB degradation were also proposed.

**Experimental section**

**Chemicals**

All chemicals were analytical grade and used without further purification. Ferric chloride (FeCl₃·6H₂O), ferrous sulfate (FeSO₄·7H₂O), hydrogen peroxide (H₂O₂, 30 wt.%), ammonium hydroxide (NH₃·H₂O, 25%), methylene blue (MB), methyl orange (MO), and catechol were obtained from Chuandong Chemical Inc., Chengdu, Sichuan, China. 5,5′-dimethyl-1-pirroline-N-oxide (DMPO) and 4-chloro-7-nitrobenz-2-oxa-1,3-diazole (NBD-Cl) were purchased from Adamas, Shanghai, China.

**Preparation and characterization of catalysts**

Fe₃O₄/PCC MNPs were prepared by a facile chemical co-precipitation method using iron salts and catechol as precursors (Wang et al. 2014). In brief, FeCl₃·6H₂O (10 mmol) and FeSO₄·7H₂O (5 mmol) were dissolved into 75 mL deionized...
water, before adding 75 mL of catechol aqueous solution (1.5 mM). The mixture was also used as the poly(catechol) precursor. The solution was standing for 30 min before adding into 100 mL of ammonium hydroxide (3.3 M) rapidly. The solution was aged for 120 min under vigorous stirring. The whole synthesis processes were performed in an ambient atmosphere. The black magnetic nanoparticles were separated by an external magnet and were washed with deionized water until pH neutral. The collected nanoparticle powder was dried in a vacuum oven at 50 °C for 24 h to obtain Fe3O4/PCC MNPs. The pristine Fe3O4 MNPs without PCC were synthesized following the same procedure without adding catechol. The poly(catechol)-Fe was obtained following the same procedure without adding ammonium hydroxide. All the products were stored in a desiccator under ambient temperature for further experiments.

The morphology and size distribution of Fe3O4/PCC and Fe3O4 MNPs were obtained from a transmission electron microscope (TEM, Tecnai™ G2 Spirit, FEI, USA). The phase structures of the Fe3O4/PCC and Fe3O4 MNPs were determined by X-ray diffraction (XRD, Empyrean, Netherlands) and Raman spectroscopy (Renishaw, inVia Qontor, Germany). To verify the formation of poly(catechol), the surface chemistry of catechol, poly(catechol), Fe3O4, and Fe3O4/PCC MNPs was analyzed using Fourier transform infrared (FTIR) spectrometer (Cary 630, Agilent). The FTIR samples were prepared in pressed KBr pellets. The interaction between Fe3O4 and poly(catechol) was analyzed using X-ray photoelectron spectroscopy (XPS, ESCALAB 250, ThermoVG Scientific, USA) with Al Kα (1486.6 eV) as the X-ray source. All XPS spectra were corrected using the C 1s line at 284.6 eV. The thermal stability of Fe3O4 and Fe3O4/PCC was performed by a thermogravimetric analyzer (TGA, TGA/DSC 1, Mettler-Toledo, Switzerland). The tests were performed at heating rate of 5 °C min⁻¹ from room temperature to 1000 °C under the nitrogen flow, and the weight retention-temperature curves were recorded. The zeta potentials of the catalyst suspensions at different pH values were determined by an analyzer (Zetasizer, Malvern 3000). The electron transfer ability of the catalysts was examined by cyclic voltammetry measurements using an electrochemical workstation (CHI660, CH Instruments, Chenhua, Shanghai, China) in a cell with a three-electrode configuration. Glassy carbon electrodes deposited with Fe3O4 or Fe3O4/PCC MNPs respectively were used as working electrodes. A Pt foil and a saturated calomel electrode (SCE) were used as the anode and the reference electrode, respectively. The measurements were carried out in the potential range of 0 to 1.0 V versus Hg/HgO at a scan rate of 10 mVs⁻¹.

Degradation procedures

The degradation procedures were carried out in a beaker (100 mL) shaken at a speed of 180 rpm. In a typical reaction, MB solution (50 mL) with a certain concentration was prepared with the addition of the specified amount of Fe3O4/PCC MNPs. The pH of the reaction solution was adjusted to a required value using H2SO4 (1.0 M) or NaOH (1.0 M) solution. The degradation reactions were initiated by adding H2O2 to the suspension once the adsorption equilibrium was achieved. At different time intervals, a suspension sample (0.6 mL) was collected, and the reaction was immediately quenched with the solution of pure methanol (30 μL). The solid samples were separated from the solution using an external magnet. The supernatant liquid was collected for analysis. To test the stability of Fe3O4/PCC composites, the catalyst was gathered via an external magnet, followed by washing, and drying under vacuum, and then reused in a fresh solution of MB and H2O2 several times. Each experiment was run in triplicate, and average values and standard deviations are presented.

Analytical methods

The MB concentration was measured by UV-vis spectroscopy at the maximum absorption wavelength of MB (660 nm) (Anelise L. et al. 2012; Banerjee S. et al. 2018; Li K.Y. et al. 2017). The MB mineralization was evaluated by a total organic carbon (TOC) analyzer (MultiN/C3100TOC/TN, Analytijena, AG ). The total carbon content on the catalyst was measured by the elemental analyzer (Vario EL cube). The total leached iron was measured using the orthophenantroline complexometric method (λ = 510 nm). The formation of •O2⁻ was determined by a fluorescence method using 4-chloro-7-nitrobenz-2-oxa-1,3-diazole (NBD-Cl) as a radical scavenger. The concentration of the reaction product between •O2⁻ and NBD-Cl was measured with a fluorescence spectrometer (Hitachi F-4600, Hitachi, Japan) at the emission of 550 nm with the excitation of 470 nm. •OH radicals were identified by electron spin resonance spectroscopy (ESR, ESP 300E, Bruker), operating at the center field strength of 3514 G with 9.85 GHz microwave frequency. For electron spin resonance (ESR) assay, samples (0.5 mL) were taken instantaneously after 20 min into the heterogeneous Fenton reaction. The samples were mixed with 50 μL of DMPO (500 mM) to form the DMPO-•OH adduct. The ESR spectra of the reaction filtrate were recorded.

Results and discussion

Formation of Fe3O4/PCC MNPs

Scheme 1 shows the formation processes of Fe3O4/PCC MNPs. The polymerization of catechol was catalyzed by Fe³⁺ in the mixed solution, forming blank coarse precipitates containing poly(catechol) (Slikboer et al. 2015).
Simultaneously, some Fe$^{3+}$ ions were chemically adsorbed on the poly(catechol) precipitates through complexation and served as the nucleation centers for the subsequent growth of Fe$_3$O$_4$ once ammonium hydroxide was added. The formed Fe$_3$O$_4$/PCC chains entangled with each other to form the Fe$_3$O$_4$/PCC MNPs. The weight average molecular of poly(catechol) obtained from the polymerization of catechol catalyzed by Fe$^{3+}$ was 817 g mol$^{-1}$.

**Characterization of Fe$_3$O$_4$/PCC MNPs**

The FTIR spectra of catechol, poly(catechol), Fe$_3$O$_4$, and Fe$_3$O$_4$/PCC MNPs were shown in Fig. 1a. The peak at 584 cm$^{-1}$ is ascribed to the stretching vibrations of the Fe–O bond in the spectra of Fe$_3$O$_4$ and Fe$_3$O$_4$/PCC MNPs (Leng et al. 2013). The ν$_{OH}$ peak at 3326 cm$^{-1}$ from the catechol disappeared from the poly(catechol) and Fe$_3$O$_4$/PCC MNPs (Kong et al. 2002), which indicated the polymerization of catechol, and catechol retained only one hydroxyl group during the polymerization processes, being consistent with the reports in the literature (Dubey et al. 1998a, b). The peak at 1280 cm$^{-1}$ from the Fe$_3$O$_4$/PCC MNPs and poly(catechol) is attributed to the asymmetrical stretching of C–O–C$_{arom}$ and C–OH (Dubey et al. 1998a, b). The peaks observed at 1400 cm$^{-1}$, 1460 cm$^{-1}$ can be assigned to the stretch of C–C, C=C in the aromatic ring (Aktas et al. 2003), which demonstrates that organic ligand indeed existed in the magnetic nanocomposites.

The XRD patterns of Fe$_3$O$_4$/PCC and pristine Fe$_3$O$_4$ MNPs are shown in Fig. 1b. The diffraction peaks at 2θ at 30.3°, 35.6°, 43.3°, 53.7°, 57.2°, 62.7° were observed from both samples. These peaks are assigned to the (220), (311), (400), (422), (511), and (440) planes of the cubic spinel structure of Fe$_3$O$_4$ (PDF#65-3107). The similarity of the dominant XRD patterns indicates that the presence of poly(catechol) did not affect the crystal structure of Fe$_3$O$_4$ (Mercado et al. 2018a; Mercado et al. 2018b; Mercado et al. 2014; Mercado and Weiss 2018). The Fe$_3$O$_4$ MNPs in the composites are highly pure Fe$_3$O$_4$ phase with an inverse spinel structure since no XRD peaks from other magnetite were detected (Hu et al. 2011). Moreover, the structural characteristics of Fe$_3$O$_4$, Fe$_2$O$_3$, and Fe$_3$O$_4$/PCC MNPs were characterized by Raman spectroscopy (Fig. S1a). As shown as Fig. S1a, the Raman spectroscopy of Fe$_3$O$_4$ and Fe$_2$O$_3$ were very similar, and it was possible to distinguish hematite domains might be present. Nevertheless, the reason might be the oxidation of Fe(II) to Fe(III) during the Raman test, according with the published study that in situ laser oxidation might take place (Jubb and Allen 2010). From the hysteresis loop of Fe$_3$O$_4$ and Fe$_3$O$_4$/PCC MNPs (Fig. S1b), there were no coercive force and residual magnetism in Fe$_3$O$_4$ and Fe$_2$O$_3$/PCC MNPs, indicating the magnetic separation characteristic of Fe$_3$O$_4$/PCC MNPs (Mercado et al. 2018a; Magnacce et al. 2014).

To characterize the morphology and size distribution of Fe$_3$O$_4$/PCC and Fe$_3$O$_4$ MNPs, TEM images were obtained from a transmission electron microscope. The TEM and HRTEM images of Fe$_3$O$_4$/PCC and Fe$_3$O$_4$ MNPs were illustrated in Fig. 1c, e, d, and f, respectively. As shown as Fig. 1c, d, both Fe$_3$O$_4$ and Fe$_3$O$_4$/PCC MNPs were in a quasi-spherical shape, and the average particle size of Fe$_3$O$_4$ and Fe$_3$O$_4$/PCC MNPs was 8.06 nm and 6.32 nm, respectively. According to the formation processes of Fe$_3$O$_4$/PCC MNPs, there were a large number of phenolic hydroxyl groups distributed around Fe$_3$O$_4$ nanoparticles due to the modification of poly(catechol), and the ionization of phenolic hydroxyl groups made the composites

![Scheme 1](image-url) The scheme of the formation process of Fe$_3$O$_4$/PCC MNPs
negatively charged, which promoted the repulsion between nanoparticles and prevented them from agglomerating, thus availed to improve the dispersity of Fe$_3$O$_4$/PCC nanoparticles. Therefore, Fe$_3$O$_4$/PCC MNPs were much more dispersed than those of Fe$_3$O$_4$ MNPs. This observation suggested that poly(catechol) in the catalysts could prevent the agglomeration
of nanoparticles indeed. As presented in Fig. 1e, f, the measured d-spacings equal to 0.251 nm and 0.209 nm were assigned to the lattice spacing of the (311) and (400) plane of Fe3O4 and Fe3O4/PCC, respectively, which was accordance with the results of XRD patterns.

Figure 2a shows the XPS spectra of the MNPs. The dominant peaks at the binding energies of ~285, 530, and 711 eV are ascribed to the C 1s, O 1s, and Fe 2p, respectively. Figure 2b shows the high resolution Fe 2p spectra of Fe3O4 and Fe3O4/PCC MNPs. The peaks from the Fe 2p1/2 and Fe 2p3/2 are located at 710.8 and 724.5 eV, respectively. The results are consistent with the literature data for magnetite, which confirmed the successful formation of Fe3O4 (He et al. 2010). Moreover, 32.6% of the total surface iron atoms were in the Fe(II) state in Fe3O4/PCC MNPs (Fig. S2a). This is much higher than that in the pristine Fe3O4 MNPs (25%, Fig. S2b), which was due to the complexation and reduction of irons by the poly(catechol) in the Fe3O4/PCC MNPs. The O 1s spectrum of Fe3O4/PCC MNPs is shown in Fig. 2c. The deconvolution of the O 1s spectra revealed four peaks: (i) the oxygen belonging to lattice oxygen in the Fe3O4 (Fe–O: 530.2 eV), (ii) the oxygen from the Fe–O–C bonds (530.5 eV) associated with possible bidentate coordination between the surface Fe and phenolic hydroxyl group of Fe3O4/PCC MNPs, (iii) the oxygen from the hydroxy groups (~OH: 531.5 eV), and (iv) the oxygen in epoxy and hydroxyl group (C–O–C, C–O: 532.9 eV (Zubir et al. 2014)). The deconvolution of the C 1s spectra (Fig. 2d) of Fe3O4/PCC also consisted of four peaks: C=C (284.6 eV), C–C (285.2 eV), C–O (286.3 eV), and C=O (288.9 eV) (Chandra et al. 2010), indicating the existence of quinone in the Fe3O4/PCC.

Figure 3a shows the zeta potentials of the catalyst suspensions at varied pH values. The point of zero charge (PZC) of Fe3O4 MNPs was 4.2, while the surface of Fe3O4/PCC MNPs was negatively charged in the pH range of 2.0 to 10.0, which could be caused by the electronegativity of the phenolic hydroxyl group in poly(catechol). Moreover, the surface charge density of Fe3O4/PCC MNPs increased with the increasing pH.

The thermal behaviors of Fe3O4 and Fe3O4/PCC MNPs were further investigated by the TGA analysis shown in (Fig. 3b). The Fe3O4/PCC MNPs showed weight loss at the temperature below 150 °C, caused by the loss of physically
adsorbed water. The weight loss observed from 150 to 450 °C is ascribed to the loss of oxygen-containing functional groups. The final weight loss happening from 450 to 800 °C is mainly attributed to the complete decomposition of organic residues (Zhang et al. 2015). Comparing with the poly(catechol)-Fe complexes, it can be found that the weight loss of the Fe₃O₄/PCC MNPs is greatly restrict, indicating strong complexation between Fe₃O₄ and poly(catechol). For Fe₃O₄, a slight weight gain below 400 °C is due to the oxidization of Fe₃O₄ to γ-Fe₂O₃ (Xie et al. 2012). From the TGA curve, the fraction of the organic component in Fe₃O₄/PCC composites (red) was estimated to be 13 wt.% (Li et al. 2008).

**Heterogeneous Fenton catalytic activity of Fe₃O₄/PCC MNPs**

**Comparison of catalytic activity**

The catalytic activity of both Fe₃O₄ and Fe₃O₄/PCC MNPs (1.0 g L⁻¹) was evaluated based on the degradation of MB (0.1 mM) with H₂O₂ (40.0 mM) at an initial pH of 6.0 (Fig. 4a). No significant degradation of MB was observed in the presence of only 40 mM H₂O₂ without any catalyst. Similarly, less than 10% of MB was removed in the Fe₃O₄ suspension with or without the addition of H₂O₂. However, 63% of MB was adsorbed onto Fe₃O₄/PCC MNPs, and nearly 100% of MB was removed in the presence of H₂O₂ catalyzed by γ-Fe₂O₃ (Xie et al. 2012). From the TGA curve, the fraction of the organic component in Fe₃O₄/PCC composites (red) was estimated to be 13 wt.% (Li et al. 2008).

In the Fe₃O₄/PCC MNPs catalyzed MB degradation process, MB was first enriched at the vicinity of the catalyst surface through the electrostatic adsorption, which was due to the facts that the poly(catechol) modification increased the surface negative charges of Fe₃O₄/PCC MNPs (Fig. 3a) and improved the dispersity of the nanoparticles (Fig. 1d). The adsorbed MB could be much easier to be oxidized by the hydroxyl radicals generated on the surface of Fe₃O₄/PCC MNPs since the organic pollutant adsorbed on the surface of catalysts is much more reactive (Xue et al. 2009; Noorjahan et al. 2005; Gu et al. 2013). The adsorption of MB on the Fe₃O₄/PCC MNPs was quantitatively studied and shown in Figs. S3 and S4 (in supporting information: S1.1 and S1.2). In contrast, methyl orange (MO), an anion dye, was neither adsorbed on the Fe₃O₄/PCC MNPs nor degraded after the addition of H₂O₂ shown in Fig. S5 (in supporting information: S2). This confirmed that the degradation of MB was initiated by the adsorption of MB on Fe₃O₄/PCC MNPs. A similar effect was found by Gu et al. that a magnetic porous carbon derived from the sludge showed a highly active property as an efficient heterogeneous catalyst to adsorb and degrade naphthalene dye (1,2,4-Acid) in an aqueous solution through a Fenton-like reaction (Gu et al. 2013).

In addition, poly(catechol), coordinated with Fe(III) on the surface of Fe₃O₄/PCC MNPs, could facilitate the Fe(II)/Fe(III) conversion by the phenolic/quinonoid redox pair during the Fenton reaction (Feng et al. 2016). To better evaluate the catalytic activity of the catalyst, cyclic voltammetry measurements were adopted, which were shown in Fig. 4b. The cathodic and anodic peaks can be attributed to the reduction of Fe(III)/Fe(II) and the oxidation of Fe(II)/Fe(III), respectively. In comparison with Fe₃O₄ MNPs, both the cathodic and the anodic peaks of Fe₃O₄/PCC MNPs shifted towards smaller potentials, which indicated that the Fe(III)/Fe(II) redox reactions became more easily with the presence of PCC. The peak potential difference between the cathodic and anodic peaks of Fe₃O₄/PCC MNPs (92 mV) was also smaller than that of Fe₃O₄ MNPs (280 mV), which confirmed the acceleration of the Fe(III)/Fe(II) redox cycling with the introduction of poly(catechol). The fast Fe(II) regeneration can greatly promote the degradation of MB in the heterogeneous Fenton system (Ma et al. 2015).

**Effect of initial pH on the catalytic activity of Fe₃O₄/PCC MNPs**

Figure 5 shows the effect of initial pH on the degradation of MB with Fe₃O₄/PCC MNPs. Nearly 100% of MB was
removed within 120 min in an expanded pH range of 3.0 to 10.0. Based on the first-order kinetics, the degradation rate constant, \( k \), slightly decreased with the increase of pH. This was quite different from some Fe\( \text{O}_4 \)-based degradation system, in which the removal efficiency decreased sharply as the solution pH increased (Zhang et al. 2014a, b; Wang et al. 2012). On one hand, MB was more easily enriched at the vicinity of the catalyst surface with the increase of pH maintaining fast oxidation. On the other hand, poly(catechol) enhanced the Fe(II) regeneration in the Fenton reaction with Fe\( \text{O}_4 \)/PCC MNPs due to the acceleration of the Fe(II)/Fe(III) recycling (Fig. 4b). Hence, the Fe\( \text{O}_4 \)/PCC MNPs became less sensitive to the solution pH.

The amount of iron leaching from the catalyst was as low as 1.02 mg L\(^{-1}\), 0.62 mg L\(^{-1}\), 0.37 mg L\(^{-1}\), and 0.49 mg L\(^{-1}\), at the pH of 3.0, 6.0, 9.0, and 10.0, respectively. The possible reason for the negligible iron leaching was that the phenolic hydroxyl groups at the surface of the Fe\( \text{O}_4 \)/PCC MNPs were hydrolyzed to form a thin layer of H\(^+\), which could prevent the diffusion of H\(^+\) into the Fe\( \text{O}_4 \). Thus, Fe\( \text{O}_4 \)/PCC MNPs were stable even at acidic conditions.

**Mineralization of MB and \( \cdot \text{OH} \) radical detection**

Under our reaction conditions, MB concentration was decreased monotonically in the Fenton-like degradation process within 120 min (see in supporting information: S3, Fig. S6). To evaluate the mineralization of MB, the total carbon concentration (TOC) was measured. The total organic content was increased by 0.24 mg after the first circle of Fenton-like degradation with Fe\( \text{O}_4 \)/PCC MNPs. This value was increased to 1.57 mg after eight reaction cycles. In each reaction cycle, 0.1 mM 50 mL of MB (0.995 mg carbon) was added to the system. The net TOC removal was obtained by calculating the TOC difference coming from both the solid catalyst and liquid solution before and after the degradation reactions. Hence, during the first reaction cycle, 48.3% of TOC was mineralized using 1.0 g L\(^{-1}\) Fe\( \text{O}_4 \)/PCC MNPs and 40 mM H\(_2\)O\(_2\) at pH 6.0 and 30 °C within 120 min. After eight cycles, TOC removal efficiency was maintained at 40.7% (Table 1).

To identify the reactive oxygen species (ROS) responsible for the mineralization of MB, the concentrations of \( \cdot \text{OH} \) and \( \cdot \text{O}_2^- \) were detected by ESR and fluorescence method, respectively, during the MB degradation (Ma et al. 2015; Zhang et al. 2014a, b). DMPO and NBD-Cl were used as the probes for the determination of \( \cdot \text{OH} \) and \( \cdot \text{O}_2^- \) respectively. As shown in Fig. 6a, \( \cdot \text{O}_2^- \) was produced in the presence of Fe\( \text{O}_4 \) and Fe\( \text{O}_4 \)/PCC MNPs. The amount of \( \cdot \text{O}_2^- \) in the presence of Fe\( \text{O}_4 \)/PCC MNPs was increased sharply within the initial 5 min and then reached a plateau, which was lower than that of the pristine Fe\( \text{O}_4 \) MNPs. The result suggested that \( \cdot \text{O}_2^- \) is not responsible for the enhanced degradation of MB with Fe\( \text{O}_4 \)/PCC MNPs. The ESR spectra in the presence of Fe\( \text{O}_4 \) MNPs and Fe\( \text{O}_4 \)/PCC MNPs displayed a fourfold characteristic peak...
of the typical DMPO–•OH adduct with the intensity ratio of 1:2:2:1. There was no significant decrease in the ESR signal after the sixth repeated run of MB degradation with Fe₃O₄/PCC MNPs (Fe₃O₄/PCC-6th MNPs). However, the intensity of •OH in the Fe₃O₄/PCC–H₂O₂ system was much higher than that of the Fe₃O₄–H₂O₂ system (Fig. 6b). The results indicated that the addition of poly(catechol) in Fe₃O₄/PCC MNPs enhanced the transformation of H₂O₂ into •OH radicals. It confirmed that •OH radicals were the main active species involved in the process of MB degradation (Wang et al. 2020; Wang et al. 2010), which is also responsible for the stable performance of the Fe₃O₄/PCC MNP catalyst.

Stability of Fe₃O₄/PCC MNPs

Stability is an important property for an effective catalyst. To evaluate the stability of the catalyst, eight reaction cycles for MB removal with Fe₃O₄/PCC MNPs (1.0 g L⁻¹) were continuously performed using 40.0 mM H₂O₂ at pH 6.0 and 30 °C. Each cycle lasted 120 min. After each reaction, Fe₃O₄/PCC MNPs were separated from the reaction solution with a powerful magnet and rinsed with distilled water three times before reused in the next Fenton processes. During the eight times recycling, MB was almost completely removed with negligible iron leaching (< 1.5 mg L⁻¹) (Fig. 7). This is consistent with the fact that there was no significant decrease in the concentration of •OH radicals produced after six cycles of running (Fig. 6b), which was due to the enhanced Fe(II) regeneration. The results demonstrated the good stability and high catalytic activity of the Fe₃O₄/PCC MNPs.

Since the reduction of Fe(III) to Fe(II) is crucial for the continuous generation of •OH, the amount of surface Fe(II) on the catalyst after the reaction was investigated using XPS analysis shown in Fig. 8a. The survey spectrum from the used Fe₃O₄/PCC MNPs exhibited peaks at the binding energies of 285, 530, and 711 eV, which were ascribed to C 1s, O 1s, and

| TOC removal efficiency of the system ([Fe₃O₄/PCC] = 1.0 g L⁻¹, [H₂O₂]₀ = 40 mM, [MB]₀ = 0.1 mM, pH 6.0, T = 30 °C, t = 120 min/recycling) | The carbon content of catalysts | The carbon content of MB in the solution |
|---|---|---|
| Before reaction | 4.230 | 0.995 |
| After 1st reaction | 4.470 | 0.274 |
| After 2nd reaction | - | 0.476 |
| After 3rd reaction | - | 0.496 |
| After 4th reaction | - | 0.542 |
| After 5th reaction | - | 0.424 |
| After 6th reaction | - | 0.301 |
| After 7th reaction | - | 0.324 |
| After 8th reaction | 5.803 | 0.312 |
| TOC removal efficiency (after 1st cycle) (%) | 48.3 |
| TOC removal efficiency (after 8th cycle) (%) | 40.7 |

Fig. 6 (a) Fluorescence intensity of NBD–Cl–•O₂⁻. (b) DMPO spin-trapping ESR spectra of •OH radicals in heterogeneous Fenton reaction with Fe₃O₄, Fe₃O₄/PCC, and Fe₃O₄/PCC-6th as catalyst ([catalyst] = 1.0 g L⁻¹, [H₂O₂]₀ = 40 mM, [DMPO] = 500 mM, [NBD-Cl] = 2.0 mM, pH 6.0, T = 30 °C, t = 20 min)
Fe 2p respectively. Figure 8b shows the details of the Fe 2p peaks (Fe 2p_1/2 and Fe 2p_3/2) of used Fe_3O_4/PCC MNPs. The Fe 2p_3/2 peak was deconvoluted into three components at 713.42 eV, 711.30 eV, and 710.03 eV, which were assigned to the Fe(III)_oct, Fe(II)_oct, and Fe(II)_oct, respectively. About 34.8% of the total surface iron atoms were in the Fe(II) state in Fe_3O_4/PCC MNPs after MB degradation, close to the fresh catalyst (32.6%). This was different from some studies which observed that the amount of Fe(II) declined gradually during the Fenton reaction (Hu et al. 2011). The stable concentration of Fe(II) is associated with the presence of poly(catechol) which accelerated the reduction of Fe(II) driven by the phenolic/quinonoid conversion. Moreover, the chemical stability of poly(catechol) makes itself resilient against degradation due to the steric hindrance. Hence, it could contribute to the repeated effective catalytic performance of Fe_3O_4/PCC MNPs at neutral pH. The stable catalytic efficiency, negligible iron species leaching, as well as convenient recycling of Fe_3O_4/PCC MNPs, made it an attractive catalyst for the Fenton reactions.

Possible mechanism for activating H_2O_2 using Fe_3O_4/PCC MNPs

Since •OH radicals were the main active species involved in the degradation of MB, it is essential to figure out whether the •OH radicals generated by the homogeneous catalytic reaction is also contributed. The homogeneous Fenton reactions were performed in 3.0 mg L^{-1} FeSO_4·6H_2O solution. We chose this concentration since it is higher than the maximal amount of total iron leached from the Fe_3O_4/PCC MNP catalyst after the oxidation cycles. Only less than 10% of MB degradation was achieved in the homogeneous Fenton process with 40 mM H_2O_2 at pH 6.0 and 30 °C within 120 min, which indicated the importance of the solid state Fe_3O_4/PCC in the heterogeneous decomposition of MB (Dong et al. 1995; Rahhal and Richter 1988).

The mechanism for the MB degradation with activated H_2O_2 in the heterogeneous Fenton reaction on Fe_3O_4/PCC MNPs is proposed in Scheme 2. Firstly, MB was adsorbed on Fe_3O_4/PCC MNPs through electrostatic adsorption (Scheme 2a). Then, H_2O_2 was activated on the surface of Fe_3O_4/PCC MNPs to produce •OH radicals for MB degradation (Scheme 2b). The adsorption of MB was beneficial to its degradation as discussed above. The presence of quinones in PCC also improves the degradation of organic compounds in the Fenton processes, due to their role as an electron shuttle (Kang and Choi 2009; Fang et al. 2013). The poly(catechol) in Fe_3O_4/PCC MNPs introduced the phenolic/quinonoid redox cycle, which in turn accelerated the Fe(III)/Fe(II) cycle (Chen et al. 2017; Leng et al. 2013). This enhanced Fe(II) regeneration during the Fenton reaction (Fig. 4b) helped to maintain the high catalytic activity of Fe_3O_4/PCC MNPs in a wide pH range. The improved Fe(II) regeneration by poly(catechol) was verified by the XPS results (Fig. 8b).
In the Fenton reactions on Fe3O4/PCC MNPs, the surface Fe(II) from the Fe3O4/PCC MNPs catalyzed the decomposition of H2O2 to form the •OH radicals (Reaction 1) which were reactive for the degradation and mineralized of MB (Reaction 2). Simultaneously, H2O2 reacted with the surface Fe(III) to produce Fe(II) and \( \cdot \text{O}_2^- \) (Reaction 3) (Wang et al. 2014; He et al. 2014). The produced \( \cdot \text{O}_2^- \) was rapidly consumed by Fe(III) reduction (Reaction 4). Meanwhile, Fe(II) could also be quickly reduced to Fe(II) by poly(catechol) and semiquinone radicals (SQ) (Reactions 5 and 6), which were essential for the generation of •OH radicals through Reaction 1 (Leng et al. 2013). As the cycles increased, the quinone analogues were accumulated continuously in the system, forming more Fe(II) and •OH radicals. Hence, the MB degradation was accelerated. Therefore, Fe3O4/PCC MNPs exhibited a stable and high catalytic activity for the decomposition of organic molecules by H2O2.

\[
\begin{align*}
\text{Fe}^{\text{II}}(\text{II}) + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{\text{III}}(\text{III}) + \cdot \text{OH} \quad (1) \\
\cdot \text{OH} & \quad \text{MB} \rightarrow \text{intermediates} \rightarrow \text{degraded/mineralized product} \quad (2) \\
\text{Fe}^{\text{III}}(\text{III}) + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{\text{II}}(\text{II}) + \cdot \text{O}_2^- \quad (3) \\
\text{Fe}^{\text{III}}(\text{III}) + \cdot \text{O}_2^- & \rightarrow \text{Fe}^{\text{II}}(\text{II}) + \text{O}_2 \quad (4) \\
\text{Phenolic} + \text{Fe}^{\text{III}}(\text{III}) & \rightarrow \text{SQ} + \text{H}^+ + \text{Fe}^{\text{II}}(\text{II}) \quad (5) \\
\text{SQ} + \text{Fe}^{\text{III}}(\text{III}) & \rightarrow \text{Quinonoid} + \text{Fe}^{\text{II}}(\text{II}) + \text{H}^+ \quad (6)
\end{align*}
\]

**Conclusion**

Poly(catechol) modified Fe3O4 MNPs (Fe3O4/PCC MNPs) were successfully synthesized by a facile coprecipitation method. The coupling of Fe3O4 MNPs with poly(catechol) has improved the dispersity of the MNPs due to the negative surface charges. Such highly dispersed MNPs have improved the kinetics for the degradation of MB. Moreover, poly(catechol) in the catalyst accelerates the Fe(III)/Fe(II) recycling, which increases the generation of •OH radicals that are the dominant oxidant in the Fenton reactions for MB degradation in a wide pH range of 3.0–10.0. The negligible iron leaching, the enhanced Fe(II) regeneration, and the refractory degradation of poly(catechol) have all contributed positively to the good stability and high activity of Fe3O4/PCC MNPs. This work provides a new pathway for preparing a heterogeneous Fenton catalyst with potential applications in wastewater treatment.

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Declarations

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