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Efficient removal of atrazine in water with a $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ nanocomposite as a heterogeneous Fenton-like catalyst

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Fe_3O_4 and multi-walled carbon nanotube hybrid materials ($\text{Fe}_3\text{O}_4/\text{MWCNTs}$) were synthesized by a coprecipitation combined hydrothermal method. The nanocomposites were applied for adsorption and degradation of atrazine (ATZ) in the presence of H_2O_2 . The obtained catalysts were characterized by TEM, XRD, BET, XPS and Raman spectroscopy. The effects of solution pH, catalysts dosage, H_2O_2 concentration and iron leaching on the degradation of ATZ were investigated. $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ showed a higher utilization efficiency of H_2O_2 , higher ability of adsorption for ATZ and higher degradation efficiency of ATZ than Fe_3O_4 nanoparticles in the batch degradation experiment. The degradation efficiency increased with the solution pH decreasing from 8.0 to 3.0. The catalytic results showed that $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ presented good performance for the degradation of ATZ, achieving 81.4% decomposition of ATZ after 120 min at reaction conditions of H_2O_2 concentration 3.0 mmol L^{-1} , catalysts dosage 0.1 g L^{-1} , ATZ concentration 10.0 mg L^{-1} , pH 5.0 and T 30 °C. Three degradation products (desethylatrazine, desisopropylatrazine, and 2-hydroxyatrazine) were detected during a heterogeneous Fenton reaction in solution. The stability, and reusability of $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ for ATZ degradation were also investigated.

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1. Introduction

Atrazine (ATZ) (2-chloro-4-(ethylamino)-6-isopropylamino-s-triazine) is widely used as a herbicide at 70 000–90 000 tons annually in the world.¹ It is extensively used in agriculture to control broad leaf and grassy weeds in corn, rice, sorghum and sugarcane fields. Moreover, ATZ is also widely applied to non-agricultural fields such as lawns and turf. Because of its widespread use, moderate water solubility and high persistence in water (the half-life of atrazine is as long as about 100 days), ATZ has been frequently detected in soil and surface waters in North America and Europe, where it often exceeds the 10 $\mu\text{g L}^{-1}$ level of concern for aquatic ecosystems.²

ATZ shows slight toxicity to many fish species, and less toxicity to aquatic invertebrates.^{2,3} As a widely used herbicide, ATZ is also highly toxic to algae and aquatic vascular plants.² As far as for human health, the main threat related to ATZ exposure is its endocrine disruption capabilities.^{2,4} Because of its endocrine disrupting effect, ATZ is included in the list of prior substances by the European Union.^{5,6} Although ATZ has been

banned in the European Union, it is still in use in North America and China. Thus, it is very important to develop efficient methods for ATZ removal.

Traditional physical and chemical methods (coagulation, adsorption, reverse osmosis, *etc.*) can generally be used for ATZ removal. Nevertheless, ATZ is usually non-destructive after being treated with these methods, and the post-treatment of the adsorbent or the solid wastes is necessary and expensive. Advanced oxidation processes (AOPs) have been regarded as effective methods to oxidize these compounds, because they can produce hydroxyl radicals ($\cdot\text{OH}$), a powerful unselective oxidants (2.8 V vs. NHE (pH 0)), which can mineralize almost any organic pollutant.⁷ Among the AOPs technologies, Fenton reaction ($\text{H}_2\text{O}_2 + \text{Fe}^{2+}/\text{Fe}^{3+}$) has been proven to be one of the most effective methods to degrade organic pollutants in wastewater. Unfortunately, there are two critical drawbacks in traditional Fenton system: (1) removal of the ferric ions remaining in the treated water complicates the whole process and makes the method uneconomic and even leads to secondary metal ion pollution easily. (2) A traditional homogeneous Fenton system works well only under the highly acidic conditions (pH 2–3).^{8,9} In order to overcome the disadvantages of the homogeneous Fenton reaction, the heterogeneous Fenton-like systems, in which soluble ferric ions are replaced by Fe-containing solids (*e.g.*, Fe^0 , Fe_3O_4 , Fe_2O_3 , FeOOH , and so on), have been recently developed.^{10,11} Especially, magnetite (Fe_3O_4) has been reported as an efficient catalyst for heterogeneous

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Fenton-like process.^{12–22} Magnetite exhibits several characteristics that are important for the Fenton reaction: (1) it contains Fe^{2+} that might play an important role as an electron donor to initiate the Fenton reaction; (2) the octahedral site in the magnetite structure can easily accommodate both Fe^{2+} and Fe^{3+} , Fe^{2+} can be reversibly oxidized and reduced in the same structure; and (3) Fe_3O_4 has peroxidase-like activity which can active H_2O_2 .¹² The excellent catalytic activity, biocompatibility, easy preparation and convenient separation from water by external magnetic field, make Fe_3O_4 a promising catalyst for wastewater treatment.

However, Fe_3O_4 nanoparticles usually aggregate during the reaction process, resulting in reduced catalytic activity.¹⁵ So, many efforts have been made to improve this situation.^{23–26} Iron oxides can be immobilized on organic or inorganic supports to form novel heterogeneous Fenton catalysts. Carbon materials such as multiwalled carbon nanotubes,^{25,27} graphene,^{28,29} and activated carbon^{30,31} have attracted great attention because of their excellent properties, including acid/base resistance and high thermal stability. Particularly, due to large reactive area, good dispersion of iron oxides, and high reaction rate, carbon nanotube-supported iron oxides have attracted much attention for heterogeneous oxidation of pollutants such as azo dyes and bisphenol A.^{27,32} Recently multi-walled carbon nanotube-supported magnetite ($\text{Fe}_3\text{O}_4/\text{MWCNT}$) has been synthesized and used as the heterogeneous catalyst for Fenton reaction.^{25,33} $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ demonstrated high oxidation efficiency of the contaminants (*i.e.*, 17 α -methyltestosterone and synthetic dyes) and can be easily separated from water by external magnetic field after treatment.^{27,33} Due to the hydrophobic surface, MWCNTs exhibit strong interactions with organic chemicals. MWCNTs are an excellent adsorbent for organic contaminants in water treatment compared with activated carbon and octadecyl adsorbent (C18).³⁴ Consequently, MWCNTs are an attractive and competitive support compared with other materials for its adsorption property and stability.³⁵ Hu *et al.*²⁷ prepared the MWCNTs supported Fe_3O_4 nanocomposites by *in situ* growth. The as-prepared catalyst was used to degrade 17 α -methyltestosterone with H_2O_2 by Fenton reaction. In our study, $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ catalyst has been prepared by coprecipitation combined with hydrothermal method. Compared with the catalysts synthesized by *in situ* growth, $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ prepared by coprecipitation combined with hydrothermal method showed better stability and crystallinity, the morphology of Fe_3O_4 nanoparticles is more uniform and Fe_3O_4 nanoparticles dispersed well on the surface of MWCNTs. For the first time, the $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ catalyst had been used in Fenton reaction to adsorb and degrade pesticide atrazine in water.

2. Experimental

2.1 Materials

The MWCNTs (diameter, 30–50 nm; length, $\sim 20\ \mu\text{m}$) used in this work were purchased from Chengdu Institute of Organic Chemicals, Chinese Academy of Science. All the other chemicals were analytic grade and used without

further purification. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, ammonia solution, and H_2O_2 were purchased from Beijing Chemical Reagents Company. Atrazine (99.2%) and its degradation products desethyl-desisopropyl-2-hydroxy-atrazine (99.6%), desisopropyl-2-hydroxy-atrazine (DIHA, 95.4%), desethyl-2-hydroxy-atrazine (DEHA, 98.7%), desethyl-desisopropyl-atrazine (DEIA, 98.3%), desethyl-atrazine (DEA, 99.9%), desisopropyl-atrazine (DIA, 96.1%), 2-hydroxy-atrazine (ATZOH, 94.7%) were purchased from Sigma Aldrich. *tert*-Butanol (*t*-BuOH) was purchased from Sigma Aldrich (>99.5%). All solutions were prepared in ultra-pure water (Milli-Q water, Millipore system). Solutions were subject to a brief period in an ultrasound bath to achieve better dissolution.

2.2 Catalyst synthesis

Purification of MWCNTs. For purification and oxidation the MWCNTs surface to facilitate a uniform Fe_3O_4 deposition on their outer walls, 2.0 g of the pristine MWCNTs were dispersed in 200 mL 68% HNO_3 by exerting ultrasonic dispersion (Kunshan, KQ-250DE, 50 kHz, 100 W) and refluxed at 70 °C with constant stirring for 14 h. After cooling to room temperature, the treated MWCNTs were separated from the black suspension through a vacuum filter, and then washed with deionized (DI) water until pH neutral, the obtained MWCNTs were dried under vacuum at 40 °C. The dried MWCNTs were gently milled into powder for use.

Preparation of $\text{Fe}_3\text{O}_4/\text{MWCNTs}$. A mixture containing 0.14 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.04 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and 0.10 g MWCNTs was placed in 160 mL deionized water, vigorously stirred at 60 °C in a three-neck flask under the purge of nitrogen gas. After the addition of 0.2 mL ammonia solution and stirred for 30 min, the $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ colloidal solution was formed. The obtained MWCNTs colloidal solution was then transferred into a 200 mL Teflon-lined autoclave. The autoclave was sealed and kept at 120 °C for 12 h, then cooled naturally to room temperature. The precipitate was separated from the suspension by a magnet, and then washed with DI water to remove the residual reagents. After repeated washing with DI water and absolute methanol under ultrasonication for 5 min, the formed $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ nanocomposites were dried in a vacuum oven at 60 °C for 24 h. The cleaned MWCNT/ Fe_3O_4 was used in the subsequent characterization and application work.

2.3 Characterization methods

A transmission electron microscope (TEM, JEOL-2010) were employed to characterize the morphology of the catalysts and the distribution of magnetic nanoparticles in MWCNTs. The crystalline phase of the synthesized samples were determined by X-ray diffraction (XRD, Phillips PW 1050-3710 Diffractometer) with Cu K α radiation ($\lambda = 1.5406\ \text{\AA}$). The sample magnetization curves were determined using a vibrating sample magnetometer (VSM, Quantum Design MPMS-5S). The surface properties of the catalysts were measured using nitrogen adsorption-desorption experiments at 77 K. The surface area was calculated using the standard Brunauer-Emmett-Teller

(BET) equation. All of the calculations were automatically performed using an accelerated surface area and porosimeter system (ASAP 2010, Micromeritics). X-ray photo-electron spectroscopy (XPS, Al K-Alpha, Thermo Fisher Scientific) with monochromatic Al K α X-ray radiation at 1486.71 eV was used to identify metal oxidation states of the nanocomposites. Raman spectra were recorded with a JY-HR800 (Jobin Yvon) spectrometer equipped with a confocal microscope.

2.4 Degradation of ATZ by heterogeneous Fenton experiments

All experiments were conducted in the dark in a 500 mL conical flask (with 200 mL aqueous solution) placed in a thermostated water bath (TZ-2EH) with an agitation of 150 rpm. The reactions were initiated by adding a desired dosage of H₂O₂ to a pH-adjusted solution (by H₂SO₄ or NaOH) containing Fe₃O₄/MWCNTs and atrazine. The suspension was sampled at pre-determined time intervals, meanwhile, 2.0 mL *t*-BuOH was added into 2.0 mL sample to quench the reaction. The aqueous phase was sampled for the analysis of pH, the concentrations of ATZ, H₂O₂, Fe(II), and total soluble Fe. The solid catalyst separated from aqueous phase was rinsed by 5 mL methanol for three times. The rinsed methanol was mixed for analysis. The residual ATZ amount is the summation of that in aqueous phase and solid phase. As in ATZ adsorption experiment, the concentration of ATZ is just the ATZ remained in aqueous phase. The reusability of the catalyst was evaluated by washing the catalyst with methanol and DI water, drying the used catalyst under vacuum, and using it for the next reaction under similar experimental conditions. Experiments were carried out at least in duplicate, and all results were expressed as a mean value. In addition, control experiments and the effects of pH, initial H₂O₂ concentration, Fe₃O₄/MWCNTs loading and dissolved iron on ATZ degradation were carried out according to the same steps as above.

2.5 Analytic methods

Concentration of ATZ and its degradation intermediates was tested by a high-performance liquid chromatography HPLC equipped with a UV diode array detector (DAD). Separation was achieved using a Lichrocart C18-RP Purospher Star (250 mm $\times$ 4.6 mm, 5 μ m) column and a water/methanol mobile phase. The mobile phase flow was 1 mL min⁻¹ and the composition was gradually changed from 50 : 50 to 30 : 70 v/v in 21 min. ATZ concentration was calibrated and measured at 222 nm and ATZ intermediates at 215 nm. Total organic carbon (TOC) was analyzed using a Multi TOC/TN Analyzer (2100, Analytik Jena AG Corporation). The solution pH was measured by a Thermo Orion model 8103BN pH-meter. Ferrous ion and total dissolved iron concentrations were measured according to the 1,10-phenanthroline method,¹¹ using a UV-VIS spectrophotometer ((UVmini-1240, Shimadzu)) at 510 nm. H₂O₂ concentration was measured at λ = 400 nm with a UV-VIS spectrophotometer (UVmini-1240, Shimadzu) after adding titanium sulfate solution (a yellow complex is formed).

3. Results and discussion

3.1 Characterization of catalyst

It can be seen from Fig. 1a that there was a distortion in the linear structure of MWCNTs, indicating that, in some situations, the damage extended beyond the outermost graphene sheet and into the underlying sidewalls. Fig. 1b showed that the distribution of diameter of the synthesized Fe₃O₄ nanoparticles ranging from 10 nm to 30 nm. As can be seen from Fig. 1c, Fe₃O₄ nanoparticles grew regularly on the surface of MWCNTs with diameters ranging from 10 to 30 nm. Although the nanocomposites had been washed with water and methanol for several times, and underwent ultrasonication before TEM measurement, most of the Fe₃O₄ nanoparticles were still found on MWCNTs surface. This reflected the strong interaction between MWCNTs and Fe₃O₄ nanoparticles. As can be seen in Fig. 1d, the Fe₃O₄ nanoparticles in Fe₃O₄/MWCNTs nanocomposites showed some but not serious agglomeration after being reused for three times for oxidation reaction.

Fig. 2 shows the XRD patterns of MWCNTs, Fe₃O₄ nanoparticles and Fe₃O₄/MWCNTs nanocomposites. A diffraction peak at 2θ = 25.9°, which is assigned to MWCNTs,²⁵ can be seen for treated MWCNTs and Fe₃O₄/MWCNTs nanocomposites. As shown in Fig. 2b and c, the characteristic peaks for Fe₃O₄ (2θ = 18.3°, 30.3°, 35.7°, 43.5°, 53.4°, 57.4°, 62.8° marked by their indices *d*(111), *d*(220), *d*(311), *d*(400), *d*(422), *d*(511) and *d*(440)),³⁶ can be observed for the synthesized Fe₃O₄ nanoparticles and Fe₃O₄/MWCNTs nanocomposites. As can be seen from Fig. 2c, the peak at 2θ = 25.9° for Fe₃O₄/MWCNTs is smaller than that of MWCNTs, this is because that the MWCNTs content in Fe₃O₄/MWCNTs is 50 wt%.

Fig. 3 shows the Raman spectrogram of treated MWCNTs and Fe₃O₄/MWCNTs nanocomposites. As can be seen from

Fig. 1 TEM images of the treated MWCNTs (a), Fe₃O₄ (b), Fe₃O₄/MWCNTs (c) and reused Fe₃O₄/MWCNTs (d).

Fig. 2 X-ray diffraction patterns of MWCNTs (a), Fe₃O₄ (b) and Fe₃O₄/MWCNTs (c).

Fig. 3 Raman spectra of the treated MWCNTs and Fe₃O₄/MWCNTs nanocomposites.

Fig. 3, the crystallinity of MWCNTs in treated MWCNTs and Fe₃O₄/MWCNTs is different. Some extra peaks in Fe₃O₄/MWCNTs at lower wavenumbers (271.0, 481.3 and 662.5 cm⁻¹) can be attributed to the Fe–O bonds and the Fe–C bonds, confirming that Fe₃O₄ nanoparticles were anchored on the surface of MWCNTs.²⁷ As is known, G (1571.1 cm⁻¹) band can reflect the purity and regular structure of MWCNTs, while D band (1340.3 cm⁻¹) can reflect the defects at the surface of MWCNTs.²⁷ As can be seen in Fig. 3, the I_G/I_D ratio of MWCNTs changed from 1.34 to 1.44 after Fe₃O₄ loading. The increase of the ratio suggests that the atomic ordering of the MWCNTs was enhanced and the structure defects were reduced. The peak centered at 2682.4 cm⁻¹ can be assigned to D* band of MWCNTs.

As shown in Fig. 4a, the peaks at binding energy of 285.1, 530.1 and 711.1 eV can be attributed to C 1s, O 1s, and Fe 2p,

Fig. 5 Nitrogen adsorption/desorption isotherms for Fe₃O₄ and Fe₃O₄/MWCNTs nanocomposites.

respectively. There are two peaks at binding energies of 710.9 and 725.1 eV for Fe 2p XPS spectrum (Fig. 4b), and these can be ascribed to Fe 2p_{1/2} and Fe 2p_{3/2} respectively. The results are in accordance with literature for magnetite³⁷ and agreed with the XRD results.

As can be seen in Fig. 5, N₂ adsorption/desorption isotherms for Fe₃O₄ nanoparticles and Fe₃O₄/MWCNTs nanocomposites displayed type II isotherms. The isotherm of Fe₃O₄ nanoparticles is below that of Fe₃O₄/MWCNTs nanocomposites, indicating lower surface area (67.35 m² g⁻¹ for Fe₃O₄ nanoparticles, and 112.81 m² g⁻¹ for Fe₃O₄/MWCNTs nanocomposites) and pore volume of the former. This can be attributed to the porosity of the treated MWCNTs that were used as support.

3.2 Atrazine degradation experiments by heterogeneous Fenton reaction

Fig. 6 shows the ATZ degradation (a) and H₂O₂ decomposition (b) with time under different experimental conditions. As shown in Fig. 6a, the adsorption processes proceed very quickly, and the equilibrium concentrations are reached in about 60 min for Fe₃O₄ and Fe₃O₄/MWCNTs. The percentages of adsorbed ATZ were 18.4% and 49.6% respectively for Fe₃O₄ and Fe₃O₄/MWCNTs. As can be seen in Fig. 6a, little ATZ was degraded in the presence of H₂O₂ only, this can be ascribed to the low oxidation potential of H₂O₂ compared with hydroxyl and perhydroxyl radicals. In the presence of H₂O₂ and Fe₃O₄/MWCNTs, a conversion efficiency of 81.4% for ATZ can be achieved after 120 min reaction. There are two stages in the heterogeneous Fenton

Fig. 4 XPS spectra of the Fe₃O₄/MWCNTs nanocomposites (a) and high-resolution scan of Fe 2p region (b).

Fig. 6 Degradation of atrazine (a) and decomposition of H_2O_2 (b) along with time under different conditions ($[\text{ATZ}]_0 = 10 \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 3.0 \text{ mmol L}^{-1}$; $[\text{Fe}_3\text{O}_4] = 0.1 \text{ g L}^{-1}$; $[\text{Fe}_3\text{O}_4/\text{MWCNTs}] = 0.1 \text{ g L}^{-1}$; pH 5.0; $T = 30^\circ\text{C}$).

reaction: induction period and rapid degradation stage, the degradation rates were accelerated after reaction for about 30 minutes. As can be seen from Fig. 6a, $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ were much more efficient than Fe_3O_4 nanoparticles. Some researchers found that activated carbon and graphite could generate free radicals such as superoxide ion and activate hydrogen peroxide, carbon materials have been used in heterogeneous Fenton reactions.^{38,39} But Hu *et al.*²⁷ reported that the contribution of direct catalysis of MWCNTs in $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ to the improved degradation performance was very limited.

As shown in Fig. 6b, H_2O_2 was not converted without the presence of catalysts. In the presence of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{MWCNTs}$, 61.8% and 47.9% H_2O_2 were decomposed in 120 min, respectively. Taking the degradation efficiencies of ATZ into consideration, $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ showed higher utilization efficiency of H_2O_2 than Fe_3O_4 nanoparticles. It can be deduced that the adsorbed ATZ molecules which were closed to Fe-ions immobilized on WMCNTs, were easily attacked by the produced $\cdot\text{OH}$. The synergistic effect resulting from the adsorption performance of MWCNTs caused the different degradation efficiency.

3.3 Effect of pH

The experiments were carried out under four different pH values of 2.5, 3.0, 5.0 and 8.0. It can be seen from Fig. 7 that solution pH has a crucial influence on the removal of ATZ by Fenton-like reaction, lower pH was beneficial for the degradation of ATZ. At pH near neutrality (pH = 5.0), $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ are still active but the ATZ removal efficiency decreased to 81.4%. At pH = 8.0, the reaction rate was very slow and 39.7% ATZ can be removed in 120 min. This phenomenon is consistent with other iron oxide based heterogeneous Fenton systems.⁴⁰ As can be seen, when solution $\text{pH} \leq 3.0$, the reaction follows a pseudo-first order law, this is because homogeneous Fenton reaction may take place in the acidic conditions (Fe_3O_4 nanoparticles dissolved). The existence of high catalytic activity near neutral pH, allows these catalysts to be applied at neutral pH, which is impossible for homogeneous Fenton catalysts.

3.4 Effect of the catalyst dosage

Fig. 8 shows the influence of the catalyst dosage on the heterogeneous Fenton degradation of ATZ by $\text{Fe}_3\text{O}_4/\text{MWCNTs}$. The degradation efficiency increased from 81.4% to 97.3% as

the catalyst concentration increased from 0.1 g L^{-1} to 1.0 g L^{-1} . The increased efficiency was mainly due to the increased active sites when more catalyst was added to the solution, and more active sites is favorable for generating more free radical species which can promote the degradation reaction. A catalyst dosage of 1.0 g L^{-1} led to ATZ being almost completely degraded within 120 min.

3.5 Effect of H_2O_2 concentration

The influence of H_2O_2 concentration on the degradation of ATZ was illustrated in Fig. 9. The degradation efficiency increased from 60.5% to 92.7% when H_2O_2 concentration increased from 1.0 mmol L^{-1} to 10.0 mmol L^{-1} . At lower concentrations of H_2O_2 , an adequate number of $\cdot\text{OH}$ radicals can not generate, and this slowed the oxidation rate and further reduced the

Fig. 7 The effect of pH on ATZ degradation ($[\text{ATZ}]_0 = 10 \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 3.0 \text{ mmol L}^{-1}$; $[\text{Fe}_3\text{O}_4/\text{MWCNTs}] = 0.1 \text{ g L}^{-1}$; $T = 30^\circ\text{C}$).

Fig. 8 The effect of catalyst dosage on ATZ degradation ($[\text{ATZ}]_0 = 10 \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 3.0 \text{ mmol L}^{-1}$; pH 5.0; $T = 30^\circ\text{C}$).

removal efficiency. However, when the concentration of H_2O_2 increased to 10.0 mmol L^{-1} , a significant improvement did not appeared. There are two main disadvantages for using high concentrations of H_2O_2 . First, as H_2O_2 was excess to the pollutant, the excess H_2O_2 would not have enough substrate to act upon, most of H_2O_2 would therefore be wasted. Second, higher concentrations of H_2O_2 can result in the scavenging of $\cdot\text{OH}$ radicals (eqn (1) and (2)).²³ Therefore, the concentration of H_2O_2 should maintain at its optimal level.

3.6 Iron leaching

As can be seen in Fig. 10, the Fe ions concentration during ATZ degradation were investigated. As can be seen, Fe_3O_4 nanoparticles in $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ dissolved gradually in the solution during the reaction, the concentration of the total dissolved iron increased to 0.48 mg L^{-1} after 120 min. This demonstrated that homogeneous Fenton reaction occurred during ATZ degradation in the bulk solution. As ferrous ions can be oxidated to ferric ions by the remaining oxidants (such as $\cdot\text{OH}$ and H_2O_2) in the solution, the concentration of ferrous reached a peak value at 60 min, and then decreased to 0.081 mg L^{-1} after 120 min of reaction.

3.7 Oxidation products

At the solution pH 5.0, the leaching of iron ions can be ignored, heterogeneous Fenton reaction plays the dominant role, the

Fig. 9 The effect of H_2O_2 dosage on ATZ degradation ($[\text{ATZ}]_0 = 10 \text{ mg L}^{-1}$; $[\text{Fe}_3\text{O}_4/\text{MWCNTs}] = 0.1 \text{ g L}^{-1}$; pH 5.0; $T = 30^\circ\text{C}$).

Fig. 10 Investigation of iron dissolution during ATZ degradation ($[\text{ATZ}]_0 = 10 \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 3.0 \text{ mmol L}^{-1}$; $[\text{Fe}_3\text{O}_4/\text{MWCNTs}] = 0.1 \text{ g L}^{-1}$; pH 3.0; $T = 30^\circ\text{C}$).

reaction mainly proceed in the surface of $\text{Fe}_3\text{O}_4/\text{MWCNTs}$. MWCNTs are excellent adsorbent for ATZ, ATZ molecules adsorbed by MWCNTs were closed to Fe-ions immobilized on WMCNTs, they were easily attacked by the produced $\cdot\text{OH}$, so $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ show excellent catalytic activity. The intermediates derived from ATZ decomposition were analyzed by HPLC. As can be seen from Fig. 11, the main intermediates were DEA, DIA, ATZ-OH (also some unidentified oxidation products). The concentration of the intermediates increased slowly at first 30 min, reached peak values at about 60 min, and then decreased in the next 60 min. Barreiro *et al.*⁴¹ studied the mechanisms of the ATZ oxidation in solution by Fenton reaction. They found that it was $\cdot\text{OH}$ that initiated the oxidation of ATZ, the oxidation could be initiated through dealkylation (alkylic sidechain cleavage), alkylic-oxidation (alkylamino side-chain oxidation), and/or dechlorination (hydroxylation at the chlorine site), and hence the related intermediates were observed in the present study.⁴¹

3.8 Catalytic stability of $\text{Fe}_3\text{O}_4/\text{MWCNTs}$

Successive experiments were carried out to evaluate the stability of the catalyst. From Fig. 12, it can be seen that the activity

Fig. 11 Variation of the concentration of degradation intermediates detected by HPLC equipped with a UV DAD ($[\text{ATZ}]_0 = 10 \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 3.0 \text{ mmol L}^{-1}$; $[\text{Fe}_3\text{O}_4/\text{MWCNTs}] = 0.1 \text{ g L}^{-1}$; pH 5.0; $T = 30^\circ\text{C}$).

Fig. 12 The catalytic activity of reused $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ on ATZ degradation ($[\text{ATZ}]_0 = 10 \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 3.0 \text{ mmol L}^{-1}$; $[\text{Fe}_3\text{O}_4/\text{MWCNTs}] = 0.1 \text{ g L}^{-1}$; pH 5.0; $T = 30^\circ\text{C}$).

decreased gradually during three consecutive runs. The loss of activity can be attributed to the dissolution of Fe_3O_4 nanoparticles from the surface of the catalyst as described in Section 3.6. In addition, the agglomeration of Fe_3O_4 nanoparticles in the reused $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ (as can be seen from TEM patterns of Fig. 1d) can also lead to the decrease of the catalytic activity of $\text{Fe}_3\text{O}_4/\text{MWCNTs}$.

4. Conclusions

$\text{Fe}_3\text{O}_4/\text{MWCNTs}$ nanocomposites were successfully synthesized by coprecipitation and hydrothermal method. $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ showed a strong ability for the adsorption of ATZ in aqueous solution. $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ can be used as an efficient heterogeneous Fenton-like catalyst to degrade ATZ in aqueous solution. The degradation efficiency strongly depends on the solution pH with a sharp increase in oxidation rate from pH 5.0 to 3.0 which is the pH range where Fe_3O_4 dissolution is strongly increased, and the soluble Fe(III) and Fe(II) species in solution initiate the homogeneous Fenton reaction. ATZ removal efficiencies are found not to increase much with the increasing concentrations of $\text{Fe}_3\text{O}_4/\text{MWCNTs}$. $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ showed higher utilization efficiency of H_2O_2 than Fe_3O_4 nanoparticles. The enhanced catalytic activity of $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ in heterogeneous Fenton system could be attributed to the well dispersion of Fe_3O_4 nanoparticles on MWCNTs, positive effect of MWCNTs *via* adsorption of pollutant molecules.

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References

- 1 M. Graymore, F. Stagnitti and G. Allinson, *Environ. Int.*, 2001, **26**, 483.
- 2 US Environmental Protection Agency, http://www.epa.gov/opp00001/reregistration/atrazine/atrazine_update.htm, last accessed November 2012.
- 3 C. Brassard, L. Gill, A. Stavola, J. Lin and L. Turner, *Atrazine Analysis of Risks. Endangered and Threatened Salmon and Steelhead Trout*, US EPA Policy and Regulatory Services Branch and Environmental Field Branch, 2003, p. 25.
- 4 A. L. Forgacs, Q. Ding, R. G. Jaremba, I. T. Huhtaniemi, N. A. Rahman and T. R. Zacharewski, *Toxicol. Sci.*, 2012, **127**, 391.
- 5 A. S. Friedmann, *Reprod. Toxicol.*, 2002, **16**, 275.
- 6 R. Renner, *Environ. Sci. Technol.*, 2002, **36**, 55A.
- 7 C. Comminellis, A. Kapalka, S. Malato, S. A. Parsons, I. Poulios and D. Mantzavinos, *J. Chem. Technol. Biotechnol.*, 2008, **83**, 769.
- 8 G. K. Zhang, Y. Y. Gao, Y. L. Zhang and Y. D. Guo, *Environ. Sci. Technol.*, 2010, **44**, 6384.
- 9 Z. H. Ai, L. R. Lu, J. P. Li, L. Z. Zhang, J. R. Qiu and M. H. Wu, *J. Phys. Chem. C*, 2007, **111**, 7430.
- 10 W. Wang, Y. Liu, T. L. Li and M. H. Zhou, *Chem. Eng. J.*, 2014, **242**, 1.
- 11 L. J. Xu and J. L. Wang, *Appl. Catal., B*, 2012, **123**, 117.
- 12 L. W. Hou, Q. H. Zhang, F. Jérôme, D. Duprez, H. Zhang and S. Royer, *Appl. Catal., B*, 2014, **144**, 739.
- 13 R. X. Huang, Z. Q. Fang, X. M. Yan and W. Cheng, *Chem. Eng. J.*, 2012, **197**, 242.
- 14 S. Shin, H. Yoon and J. Jang, *Catal. Commun.*, 2008, **10**, 178.
- 15 S. X. Zhang, X. L. Zhao, H. Y. Niu, Y. L. Shi, Y. Q. Cai and G. B. Jiang, *J. Hazard. Mater.*, 2009, **167**, 560.
- 16 S. P. Sun and A. T. Lemley, *J. Mol. Catal. A: Chem.*, 2011, **349**, 71.
- 17 J. B. Zhang, J. Zhuang, L. Z. Gao, Y. Zhang, N. Gu, J. Feng, D. L. Yang, J. D. Zhu and X. Y. Yan, *Chemosphere*, 2008, **73**, 1524.
- 18 X. F. Xue, K. Hanna and N. S. Deng, *J. Hazard. Mater.*, 2009, **166**, 407.
- 19 K. Rusevova, F. D. Kopinke and A. Georgi, *J. Hazard. Mater.*, 2012, **241**, 433.
- 20 M. Usman, P. Faure, C. Ruby and K. Hanna, *Appl. Catal., B*, 2012, **117**, 10.
- 21 R. C. C. Costa, F. C. C. Moura, J. D. Ardisson, J. D. Fabris and R. M. Lago, *Appl. Catal., B*, 2008, **83**, 131.
- 22 L. J. Xu and J. L. Wang, *Environ. Sci. Technol.*, 2012, **46**, 10145.
- 23 L. C. Zhou, Y. M. Shao, J. R. Liu, Z. F. Ye, H. Zhang, J. J. Ma, Y. Jia, W. J. Gao and Y. F. Li, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7275.
- 24 J. Y. Chun, H. S. Lee, S. H. Lee, S. W. Hong, J. S. Lee, C. H. Lee and J. W. Lee, *Chemosphere*, 2012, **89**, 1230.
- 25 X. B. Hu, Y. H. Deng, Z. Q. Gao, B. Z. Liu and C. Sun, *Appl. Catal., B*, 2012, **127**, 167.
- 26 L. R. Kong, X. F. Lu, X. J. Bian, W. J. Zhang and C. Wang, *ACS Appl. Mater. Interfaces*, 2011, **3**, 35.
- 27 X. B. Hu, B. Z. Liu, Y. H. Deng, H. Z. Chen, S. Luo, C. Sun, P. Yang and S. G. Yang, *Appl. Catal., B*, 2011, **107**, 274.
- 28 W. Liu, J. Qian, K. Wang, H. Xu, D. Jiang, Q. Liu, X. W. Yang and H. M. Li, *J. Inorg. Organomet. Polym.*, 2013, **23**, 907.
- 29 S. Guo, G. K. Zhang, Y. D. Guo and J. C. Yu, *Carbon*, 2013, **60**, 437.
- 30 L. Gu, N. W. Zhu, H. Q. Guo, S. Q. Huang, Z. Y. Lou and H. P. Yuan, *J. Hazard. Mater.*, 2013, **246**, 145.
- 31 H. Y. Zhao, Y. J. Wang, Y. B. Wang, T. C. Cao and G. H. Zhao, *Appl. Catal., B*, 2012, **125**, 120.
- 32 V. Cleveland, J. P. Bingham and E. Kan, *Sep. Purif. Technol.*, 2014, **133**, 388.
- 33 J. H. Deng, X. H. Wen and Q. N. Wang, *Mater. Res. Bull.*, 2012, **47**, 3369.
- 34 B. Pan and B. S. Xing, *Environ. Sci. Technol.*, 2008, **42**, 9005.
- 35 R. Gonzalez-Olmos, U. Roland, H. Toufar, F. D. Kopinke and A. Georgi, *Appl. Catal., B*, 2009, **89**, 356.

- 36 Y. Liu, W. Jiang, Y. Wang, X. J. Zhang, D. Song and F. S. Li, *J. Magn. Magn. Mater.*, 2009, **321**, 408.
- 37 D. Wilson and M. A. Langell, *Appl. Surf. Sci.*, 2014, **303**, 6.
- 38 F. J. Maldonado-Hodar, L. M. Madeira and M. F. Portela, *Appl. Catal., A*, 1999, **178**, 49.
- 39 F. Lücking, H. Köer, M. Jank and A. Ritter, *Water Res.*, 1998, **32**, 2607.
- 40 J. Y. Feng, X. J. Hu and P. L. Yue, *Water Res.*, 2006, **40**, 641.
- 41 J. C. Barreiro, M. D. Capelato, L. Martin-Neto and H. C. B. Hansen, *Water Res.*, 2007, **41**, 55.