Catalytic activity of $\text{Cu}_x\text{Mn}_x\text{Fe}_{3-2x}\text{O}_4$/multi-walled carbon nanotubes ($0 \leq x \leq 0.1$) nanocomposites for $p$-nitrophenol degradation in catalyst/$\text{H}_2\text{O}_2$ system

Jiye Yu, Xiaojun Tian, Mingwang Liu, Zhenzhen Jia, Hongqin Fang, Yunfang Liu and Changyuan Yu

ABSTRACT

Heterogeneous Fenton oxidation has become a very important wastewater-treatment method and its catalyst is crucial for good treatment effect. In order to improve the catalytic properties, the Cu and Mn elements were doped for $\text{Cu}_x\text{Mn}_x\text{Fe}_{3-2x}\text{O}_4$/multi-walled carbon nanotubes ($\text{Cu}_x\text{Mn}_x\text{Fe}_{3-2x}\text{O}_4$/MWCNTs) nanocomposites ($0 \leq x \leq 0.1$) by co-precipitation method. The structure, morphology and surface properties of the nanocomposites were characterized by X-ray powder diffractometer (XRD), $\text{N}_2$-physisorption analysis, transmission electron microscope (TEM), and X-ray photoelectron spectroscopy (XPS). The $\text{Cu}_x\text{Mn}_x\text{Fe}_{3-2x}\text{O}_4$/MWCNTs nanocomposites were used as heterogeneous Fenton catalysts for $p$-nitrophenol ($p$-NP) degradation. The catalytic performances of the Cu and/or Mn doped nanocomposites have remarkable improvement compared with $\text{Fe}_3\text{O}_4$/MWCNTs nanocomposite, especially for both Cu and Mn doped catalyst. For $\text{Cu}_x\text{Mn}_x\text{Fe}_{3-2x}\text{O}_4$/MWCNTs nanocomposites, the catalytic performance increases with increasing $x$ value and reaches a maximum at 0.075 of $x$ value. At optimal condition, the $p$-NP conversion rate reaches 96.4% in 10 min for $\text{Cu}_{0.075}\text{Mn}_{0.075}\text{Fe}_{2.85}\text{O}_4$/MWCNTs nanocomposite. However, the mentioned rate for $\text{Fe}_3\text{O}_4$/MWCNTs catalyst is only 14.5%. The chemical oxygen demand (COD) removal rates in 120 min for $\text{Cu}_{0.075}\text{Mn}_{0.075}\text{Fe}_{2.85}\text{O}_4$/MWCNTs and $\text{Fe}_3\text{O}_4$/MWCNTs catalysts are 82.7% and 67.3%, respectively. Furthermore, the $p$-NP conversion and COD removal rates of $\text{Cu}_{0.075}\text{Mn}_{0.075}\text{Fe}_{2.85}\text{O}_4$/MWCNTs nanocomposite still keep at 94.4% and 70.3% after five-time reuse, respectively. This catalyst shows good reusability for $p$-NP degradation and is very easy to recover from the treated water.

Key words | Cu/Mn doping, heterogeneous Fenton catalyst, magnetite nanocomposite, multi-walled carbon nanotubes, wastewater treatment

INTRODUCTION

Fenton technology, as one kind of advanced oxidation process in wastewater treatment, has been widely used due to its facile operation, general applicability, fast start-up and low running cost (Munoz et al. 2015; Nidheesh 2015; Tian et al. 2017; Miklos et al. 2018). The strong oxidation ability of Fenton technology is due to the hydroxyl radical ($\cdot$OH) originating from the reaction of metal catalyst and hydrogen peroxide ($\text{H}_2\text{O}_2$). Hydroxyl radicals can oxidize most organic pollutants with high efficiency and the catalyst is the key. The state of the catalyst in the Fenton system could be homogenous or heterogeneous. Compared with the homogeneous Fenton process, the heterogeneous Fenton process has many advantages, such as less iron sludge, relatively high $\text{H}_2\text{O}_2$ utilization efficiency and low operation cost (Kuan et al. 2015; Wan et al. 2016). Furthermore, the heterogeneous Fenton catalyst could be targetedly modified by different methods according to the characteristics of the wastewater to be treated. Therefore, heterogeneous Fenton oxidation for wastewater treatment has attracted more and more attention.

The catalyst plays the key role in the heterogeneous Fenton process in wastewater treatment. Some natural iron-based oxides have been applied as heterogeneous catalysts, such as goethite, magnetite and hematite (Rusevova 2019).
et al. 2012). Many artificial catalysts have also been widely investigated, especially for Fe3O4-based materials (Sun & Lemley 2011; Rusevova et al. 2012; Bounab et al. 2015; Xu et al. 2015; Wan et al. 2016; Tian et al. 2017). The characteristic of Fe3O4 can allow Fe species to keep reversible oxidation and reduction, which can be attributed to the simultaneous existence of Fe(II) and Fe(III) in the octahedral crystal structure (Xu et al. 2015). Furthermore, the magnetic property of Fe3O4-based catalysts also makes them easy to separate from the treated water. Of course, the properties of those Fe3O4-based catalysts could be further improved. Usually, Fe3O4 nanoparticles (NPs) easily aggregate. In order to resolve this problem, various support materials have been used to immobilize Fe3O4 NPs, such as active carbon (Bounab et al. 2015), graphene (Wan & Wang 2016; Liu et al. 2019), zeolite (Neamtu et al. 2004), carbon nanotubes (CNTs) (Neamtu et al. 2004; Zhang et al. 2010; Tian et al. 2017), coke (Giri et al. 2015; Wan et al. 2016), and chitosan hollow fibres (Dorraji et al. 2015). CNTs are widely used as support material in different fields due to their unique structure and excellent properties. Catalyst/CNT nanocomposites are also promising as heterogeneous Fenton catalysts for wastewater treatment (Zhang et al. 2010; Mallakpour & Khadem 2016). On the other hand, the performance of heterogeneous Fenton catalysts in wastewater treatment could be improved by introducing the coexisting M(III)/M(II+) redox pairs of metal oxides (Zhang et al. 2010; Barros et al. 2016; Wan & Wang 2016). Some Fe3O4/ MoO4 (Cu, Ti, Cr, Mn, Co, and Ni) composites were prepared as heterogeneous Fenton catalyst for organic wastewater treatment (Pan et al. 2012; Zhong et al. 2015; Zhong et al. 2014; Barros et al. 2016). In addition, some precious metals were applied as substitutions in magnetite to increase the degradation efficiency (Lu et al. 2018; Alshehri et al. 2016).

It is well known that phenolic compounds are difficult to eliminate but have a tremendous negative impact on our environment, due to their non-biodegradation, toxicity and potential carcinogenicity (Ahmed et al. 2011). p-Nitrophenol (p-NP), as an extremely important precursor and intermediate, has been widely used in many industries. As a result, its corresponding wastewater has brought an enormous threat to our environment. Thus, efficient technologies for p-NP degradation are urgently expected. Many methods have been developed, such as biodegradation, Fenton oxidation, electrochemical degradation, photochemical treatment, microwave-assisted oxidation and ozonation (Nidheesh 2015; Pan et al. 2015; Chakraborty 2016; Meijide et al. 2017; Ghareshaghi et al. 2018; Afzal et al. 2019; Mei et al. 2019). Biodegradation usually has the lowest running cost among those methods but needs the longest treatment time to achieve the same p-NP removal rate. Furthermore, the treatment efficiency of the biodegradation method is greatly affected by the environmental factors and is usually difficult to recover after a serious impact. Other new methods usually have high costs and relatively low degradation speed compared with Fenton oxidation. Up to now, Fenton technology is still the most preferred method for p-NP degradation due to its many advantages. Recent researches show the modified Fe3O4-based materials as heterogeneous Fenton catalysts (Wan & Wang 2016; Tian et al. 2017). In this paper, CuMnFe3-2xO4/MWCNTs) nanocomposites were firstly prepared by the co-precipitation method and used as a novel heterogeneous Fenton catalyst to degrade p-NP. The catalytic properties of this new kind of Fe3O4-based nanocomposite could be obviously improved due to the synergistic effects generated between not only Cu, Mn and Fe but also metal oxide catalysts and MWCNT support. The structures and catalytic properties of the CuMnFe3-2xO4/MWCNTs’ composites were investigated. The effect of the doping contents and reaction conditions (catalyst dosage, initial H2O2 concentration and pH) on the p-NP degradation was discussed. Furthermore, the iron leaching and H2O2 decomposition as well as chemical oxygen demand (COD) removal efficiency and reusability of the catalyst were also evaluated.

METHODS

Synthesis of nanocomposites

Firstly, MWCNTs (Shenzhen SUSN Sinotech New Materials Co. Ltd) were modified by acid oxidation (ν(H2SO4) : ν(HNO3) : ν(H2O) = 3 : 1 : 1) in a water bath (100 °C) for 4 h. Then, the mixture was filtered and washed with deionized water and ethanol several times, and further dried at 80 °C under vacuum.

The CuMnFe3-2xO4/MWCNTs nanocomposites (0 ≤ x ≤ 0.1) were fabricated by the chemical co-precipitation method (Hu et al. 2011). The treated MWCNTs (0.5 g) and deionized water (500 mL) were added into a flask and sonicated for 30 min. After that, the flask was placed in a water bath (90 °C). Then, FeCl3·6H2O, FeCl2·4H2O, CuCl2·2H2O and MnCl2·4H2O were added with different masses and deaerated by N2 flow for 10 min. Next, ammonium hydroxide was carefully dropped until the pH value arrived at about 10. Then, the mixture was further stirred at 90 °C for 4 h. The nanocomposites were collected with an external...
magnet and washed with water and ethanol several times. Finally, the products were dried overnight at 80 °C under vacuum. The series of nanocomposites were synthesized using the same process except for differences in proportion of the metal salts: Cu0.075Mn0.075Fe2.85O4/MWCNTs (x = 0, 0.025, 0.05, 0.075 or 0.1), Cu0.075Fe2.85O4/MWCNTs and Mn0.075Fe2.85O4/MWCNTs.

Characterization of nanocomposites

An X-ray powder diffractometer (XRD, Rigaku D/max-2400, Japan) with a Cu Kα radiation source was used to characterize the crystal structures of the samples. A transmission electron microscope (TEM, Tecnai-G20, FEI) was employed to analyze the morphology of the products. The nitrogen adsorption and desorption isotherms of the catalysts were measured at absolute zero (JW-BK100, China). The specific surface area (SSA) and pore size distribution were calculated using the Brunauer–Emmett–Teller method and density functional theory, respectively. X-ray photo-electron spectroscopy (XPS, Thermo Scientific ESCALAB 250 XI, USA) was employed to identify the surface states of the nanocomposites.

Nanocomposites as heterogeneous Fenton catalyst for p-NP degradation

The p-NP molecule was used as the typical contaminant in order to evaluate the catalytic performances of the prepared nanocomposites as a heterogeneous Fenton catalyst. The effect of oxidation conditions (reaction time, catalyst dosage, pH value and initial H2O2 concentration) on the p-NP degradation was investigated. The p-NP solution (100 mg L⁻¹, 100 mL) was added into a conical flask and its initial pH value (2, 2.5, 3, 3.5 or 4) was adjusted by H2SO4 or NaOH solution. A certain mass of catalyst (0.5, 0.75, 1.0, 1.5 or 2.0 g L⁻¹) was added into the flask with agitation. Then, H2O2 (2, 4, 15, 18, 20 or 25 mmol L⁻¹) was added to start the reaction. The mixture was agitated continuously at a temperature of 25 °C. 5 mL of reaction solution was taken out at set intervals for analysis. In addition, the reusability of the catalyst was investigated by being collected with an external magnet and washed with deionized water and ethanol several times. After drying, the catalyst was used for the next treatment.

The p-NP concentration was determined by UV-Vis spectroscopy (YU-1810, Beijing Purikinje General Co., China) at a wavelength of 400 nm (Lu et al. 2016). COD values of the samples were tested by the dichromate method (Neamtu et al. 2004). The concentration of H2O2 was measured by UV-Vis spectroscopy with titanium oxalate at a wavelength of 395 nm (Sellars 1980). The leaching rates of iron and ferrous ion were measured by 1, 10-phenantroline spectrophotometric method (Liang et al. 2011).

RESULTS AND DISCUSSION

Characterization of CuMnFe3-2xO4/MWCNTs nanocomposites

Figure 1 shows the XRD patterns of the samples. The diffraction peaks at about 26.2° of 2θ are assigned to the MWCNTs. For all the nanocomposites, the main characteristic peaks are in good agreement with the standard XRD data of Fe3O4 with a cubic spinel structure (JCPDS Card No. 19-0629) (Cleveland et al. 2014; Dorraji et al. 2015; Giri et al. 2015; Wan et al. 2016; Tian et al. 2017). Those peaks at about 18.1°, 30.2°, 55.5°, 43.2°, 53.8°, 57.2° and 62.8° are marked respectively by (111), (220), (311), (400), (422), (511) and (440) indices. The doping of Cu or/and Mn elements has no obvious effect on the spinel structure of the Fe3O4 NPs (Pouran et al. 2016; Wan & Wang 2016). But some small differences are still found after carefully comparing these samples: the relative intensity and shifting of the diffraction peaks. It is possible to have the partial replacement of Fe2⁺ ions by Cu2⁺ or/and Mn2⁺ ions in the octahedral sites (Zhong et al. 2013; Zhong et al. 2014; Barros et al. 2016; Lu et al. 2016; Wan & Wang 2016). The crystallite sizes of the nanoparticles in the nanocomposites were calculated from the (311) diffraction according to the Scherrer equation are about 10.2 nm (Fe3O4/MWCNTs), 9.3 nm (Cu0.075Fe2.925O4/MWCNTs), 10.8 nm (Mn0.075Fe2.925O4/MWCNTs) and 8.0 nm (Cu0.075Mn0.075Fe2.85O4/MWCNTs), respectively. The differences may originate from the ion radius differences of Mn2⁺ (0.80 Å), Fe2⁺ (0.78 Å) and Cu2⁺ (0.73 Å). But the real reason for the lowest crystallite size of the nanoparticles in Cu0.075Mn0.075Fe2.85O4/MWCNTs nanocomposite still needs to be further investigated.

The TEM images of the samples and corresponding size distribution histograms of the metal oxide NPs are shown in Figure 2. More than 300 nanoparticles in each sample were measured for the histograms. The metal oxide NPs are less NP aggregates compared with the Fe3O4/MWCNTs.
nanocomposite. The average sizes of the NPs in the nanocomposites are about 10.1 nm (Fe₃O₄/MWCNTs), 9.5 nm (Cu₀.₀₇₅Fe₂.₉₂₅O₄/MWCNTs), 10.8 nm (Mn₀.₀₇₅Fe₂.₉₂₅O₄/MWCNTs) and 7.6 nm (Cu₀.₀₇₅Mn₀.₀₇₅Fe₂.₈₅O₄/MWCNTs), respectively. The data are in agreement with the mentioned values obtained from the XRD results.

The N₂ adsorption-desorption isotherms of the samples are shown in Figure S1 (available with the online version of this paper). It can be seen that all the samples belong to type IV with H3 type hysteresis loops according to the IUPAC classification (Wan et al. 2016). The results indicate that these nanocomposites could be looked at as mesoporous materials. Table S1 (available online) lists the specific surface areas (SSAs) and pore structures of those samples. After adding Cu or/and Mn species, the SSAs of the nanocomposites increase from 84.5 m² g⁻¹ (Fe₃O₄/MWCNTs), 162 nm (Cu₀.₀₇₅Fe₂.₉₂₅O₄/MWCNTs), 15.4 nm (Mn₀.₀₇₅Fe₂.₉₂₅O₄/MWCNTs) and 15.1 nm (Cu₀.₀₇₅Mn₀.₀₇₅Fe₂.₈₅O₄/MWCNTs), respectively. The average BJH pore sizes decrease and are about 16.3 nm (Fe₃O₄/MWCNTs), 16.2 nm (Cu₀.₀₇₅Fe₂.₉₂₅O₄/MWCNTs), 15.4 nm (Mn₀.₀₇₅Fe₂.₉₂₅O₄/MWCNTs) and 15.1 nm (Cu₀.₀₇₅Mn₀.₀₇₅Fe₂.₈₅O₄/MWCNTs), respectively. To some extent, those data could reflect the fewer aggregates in the doped nanocomposites compared with the Fe₃O₄/MWCNTs. The XPS spectra of the Cu₀.₀₇₅Mn₀.₀₇₅Fe₂.₈₅O₄/MWCNTs composite are shown in Figure S2 (available online). The survey scan (Figure S2(a)) shows the existence of the C, Cu, Mn, Fe and O elements. The bonding energy values at 283.5, 529.1, 640.4, 709.8 and 952.7 eV respond to C1s, O1s, Mn2p, Fe2p and Cu2p, respectively.

The amplified Cu2p spectra in Figure S2(c) show the peaks at about 931.9 and 933.1 eV of bonding energy, which are corresponding to Cu2p3/2 and Cu2p1/2 (Barros et al. 2016; Zhang et al. 2016). The peaks at 640.3 and 652.0 eV in Figure S2(d) can be identified as Mn2p3/2 and Mn2p1/2 (Wan & Wang 2016). As showed in Figure S2(b), the peaks centred at 710.0 and 723.6 eV are corresponding to Fe2p3/2 and Fe2p1/2 (Hu et al. 2013; Barros et al. 2016; Wan et al. 2016), and the bonding energy values of 710.0 and 711.2 eV or 723.6 and 725.4 eV indicate the presence of Fe(II) and Fe(III) (Xu & Wang 2011).

**Nanocomposites as heterogeneous Fenton catalyst for p-NP degradation**

**Effect of Cu or/and Mn doping in nanocomposites**

The effect of Cu or/and Mn doping in the Fe₃O₄/MWCNTs nanocomposites on the p-NP degradation was firstly investigated. The experiments were done using different catalysts at a constant condition (100 mg L⁻¹ of initial p-NP concentration, 1.0 g L⁻¹ of catalyst dosage, 20 mmol L⁻¹ of H₂O₂ concentration, 3.0 of pH and 25 °C of reaction temperature). Figure 3(a) shows that the p-NP degradation speed was remarkably improved by doping other metal elements in the Fe₃O₄/MWCNTs catalyst, especially doping both Cu and Mn elements. The p-NP removal rate in 60 min is about 94.1% for the Fe₃O₄/MWCNTs, while the mentioned rate for the Cu₀.₀₇₅Mn₀.₀₇₅Fe₂.₈₅O₄/MWCNTs catalyst reaches about 96.4% in only 10 min. The results show that doping both
Figure 2 | TEM images of nanocomposites and corresponding NPs statistical size-distribution histograms. (a) and (b) Fe$_3$O$_4$/MWCNTs, (c) and (d) Cu$_{0.075}$Fe$_{2.925}$O$_4$/MWCNTs, (e) and (f) Mn$_{0.075}$Fe$_{2.925}$O$_4$/MWCNTs and (g) and (h) Cu$_{0.075}$Mn$_{0.075}$Fe$_{2.85}$O$_4$/MWCNTs.
Cu and Mn elements in the Fe₃O₄/MWCNTs catalyst could effectively improve its catalytic performance for p-NP degradation. The H₂O₂ consumption rates for different catalysts are shown in Figure 3(b). The H₂O₂ consumption rate in 120 min of the Fe₃O₄/MWCNTs catalyst is only 32.7%, while that of the Cuₐ₀.₇₅Mnₐ₀.₇₅Fe₂.₈₅O₄/MWCNTs catalyst is as high as 98.6%. The results indicate that the Cu and Mn species in the catalyst could effectively accelerate the conversion of H₂O₂ into ·OH to degrade p-NP because of the synergic effect (Barros et al. 2016).

**Effect of Cu/Mn doping contents**

Doping both Cu and Mn elements in the Fe₃O₄/MWCNTs nanocomposite could more effectively improve the catalytic properties, so the effect of the Cu/Mn doping contents on the p-NP degradation was further investigated (Figures 4 and 5). The experimental conditions are: 100 mg L⁻¹ initial p-NP concentration, 1.0 g L⁻¹ catalyst dosage, 20 mmol L⁻¹ H₂O₂ concentration, 5.0 pH value, 25 °C reaction temperature. It is generally known that the COD value is the key water-quality parameter in organic wastewater treatment. Usually, the toxicity of the organic compounds from the p-NP degradation is relatively low. So, only the p-NP and COD removal rates in 120 min were measured. The above said values firstly increase with the increase of x value and reach the maximal values (about 97.9% and 82.7%, respectively) at 0.075 of the x value. When the x value increases to 0.1, both the p-NP and COD removal rates respectively decrease to 90.5% and 78.3%. The p-NP degradation speed increases outstandingly after using the catalyst doped with Cu and Mn. It is very interesting that the p-NP removal rate reaches 96.4% in 10 min for the Cuₐ₀.₇₅Mnₐ₀.₇₅Fe₂.₈₅O₄/MWCNTs catalyst. But for the Fe₃O₄/MWCNTs catalyst,
CuxMnxFe3−2xO4/MWCNTs nanocomposites have relatively cies of p-NP and COD. It can be attributed to: (1) the Cu/Mn doping has great effect on the removal ef
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with prolonged reaction time. The results demonstrate that the Cu/Mn doping has great effect on the removal efficiencies of p-NP and COD. It can be attributed to: (1) the CuxMnxFe3−2xO4/MWCNTs nanocomposites have relatively large specific surface areas and less agglomeration compared with the Fe3O4/MWCNTs nanocomposites; (2) the synergistic system of Fe, Cu and Mn ions in the octahedral sites of the spinel structure lead to an enhancement of hydroxyl radical generation (Barros et al. 2016; Wan et al. 2016). The effect of the Cu/Mn doping contents on the p-NP removal rate (%)
can be seen from Figure 4(b) that the H2O2 decomposition efficiency increases with increasing x in the Cu,Mn,Fe3−2xO4/MWCNTs nanocomposites (x = 0, 0.025, 0.05, 0.075 and 0.1). And the H2O2 consumption rates for the corresponding samples are 32.9%, 69.0%, 85.1%, 94.9% and 96.2%, respectively. This indicates that the H2O2/−OH conversion can be accelerated with the addition of the Cu and Mn species. As a result, the p-NP degradation rate will be fast due to there being enough −OH.

It is well known that the generation of the hydroxyl radical (−OH) plays a decisive role in the organic pollutant degradation (Wang & Xu 2012). The Cu and/or Mn doping in the nanocomposites increases the SSA and enriches the surface species with Cu+/Cu2+ and Mn2+/Mn3+. These ions can also generate −OH in the presence of H2O2 under a synergistic effect. A possible mechanism of this reaction system could be proposed as the following equations (Weiss 1952; Lin & Gurol 1998; Barros et al. 2016; Wan et al. 2016) and Figure 6.

\[
\begin{align*}
\text{Fe}^{2+}_{\text{surf}} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+}_{\text{surf}} + \text{OH}^- + \cdot \text{OH} \\
\text{Fe}^{3+}_{\text{surf}} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+}_{\text{surf}} + \text{H}^+ + \cdot \text{OH} \\
\text{Fe}^{3+}_{\text{surf}} + \cdot \text{OH}_2 & \rightarrow \text{Fe}^{2+}_{\text{surf}} + \text{H}^+ + \text{O}_2 \\
\text{Cu}^{2+}_{\text{surf}} + \text{H}_2\text{O}_2 & \rightarrow \text{Cu}^{3+}_{\text{surf}} + \cdot \text{OH}^- + \cdot \text{OH} \\
\text{Cu}^{2+}_{\text{surf}} + \cdot \text{OH}_2 & \rightarrow \text{Cu}^{3+}_{\text{surf}} + \text{H}^+ + \text{O}_2 \\
\text{Cu}^{2+}_{\text{surf}} + \text{Fe}^{3+}_{\text{surf}} & \rightarrow \text{Fe}^{2+}_{\text{surf}} + \text{Cu}^{2+}_{\text{surf}} \\
\text{Mn}^{2+}_{\text{surf}} + \text{H}_2\text{O}_2 & \rightarrow \text{Mn}^{3+}_{\text{surf}} + \text{OH}^- + \cdot \text{OH} \\
\text{Mn}^{3+}_{\text{surf}} + \cdot \text{OH}_2 & \rightarrow \text{Mn}^{2+}_{\text{surf}} + \text{H}^+ + \text{O}_2 \\
\text{Mn}^{2+}_{\text{surf}} + \text{Fe}^{3+}_{\text{surf}} & \rightarrow \text{Fe}^{2+}_{\text{surf}} + \text{Mn}^{3+}_{\text{surf}} 
\end{align*}
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where, ‘surf’ represents the surface species. The reactions of Equations (1)–(3), Equations (5)–(7) and Equations (7)–(9)
the mentioned value is only 14.5% in 10 min, although that value could exceed 90% in 120 min. Compared with other reported methods, as shown in Table 1, the Cu/Mn doped Fe3O4/MWCNTs catalyst also has relatively fast degra-
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\text{Cu}^{2+}_{\text{surf}} + \text{H}_2\text{O}_2 & \rightarrow \text{Cu}^{3+}_{\text{surf}} + \cdot \text{OH}^- + \cdot \text{OH} \\
\text{Cu}^{2+}_{\text{surf}} + \cdot \text{OH}_2 & \rightarrow \text{Cu}^{3+}_{\text{surf}} + \text{H}^+ + \text{O}_2 \\
\text{Cu}^{2+}_{\text{surf}} + \text{Fe}^{3+}_{\text{surf}} & \rightarrow \text{Fe}^{2+}_{\text{surf}} + \text{Cu}^{2+}_{\text{surf}} \\
\text{Mn}^{2+}_{\text{surf}} + \text{H}_2\text{O}_2 & \rightarrow \text{Mn}^{3+}_{\text{surf}} + \text{OH}^- + \cdot \text{OH} \\
\text{Mn}^{3+}_{\text{surf}} + \cdot \text{OH}_2 & \rightarrow \text{Mn}^{2+}_{\text{surf}} + \text{H}^+ + \text{O}_2 \\
\text{Mn}^{2+}_{\text{surf}} + \text{Fe}^{3+}_{\text{surf}} & \rightarrow \text{Fe}^{2+}_{\text{surf}} + \text{Mn}^{3+}_{\text{surf}} 
\end{align*}
\]

where, ‘surf’ represents the surface species. The reactions of Equations (1)–(3), Equations (5)–(7) and Equations (7)–(9)

![Figure 5](image_url) Effect of Cu/Mn loading in CuxMnxFe3−2xO4/MWCNTs nanocomposites on p-NP and COD removal rates.

<table>
<thead>
<tr>
<th>Method</th>
<th>Catalyst/microorganism</th>
<th>p-NP removal rate (%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>10 min</td>
</tr>
<tr>
<td>Fenton</td>
<td>Cu,Mn,Fe3−2xO4/MWCNTs</td>
<td>&gt;96</td>
</tr>
<tr>
<td>Fenton</td>
<td>Fe0/Fe3O4/Coke</td>
<td>~65</td>
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<tr>
<td>Fenton</td>
<td>Fe/xerogel</td>
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<td>Photo</td>
<td>Cu2O/TiO2</td>
<td>&lt;10</td>
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<tr>
<td>Photo</td>
<td>N-doped RGO-CdS</td>
<td>&lt;10</td>
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<tr>
<td>Electro</td>
<td>CeO2</td>
<td>~30</td>
</tr>
<tr>
<td>Biological</td>
<td>Bacillus sp.</td>
<td>&gt;90 (30h)</td>
</tr>
<tr>
<td>Biological</td>
<td>Bacillus sp.</td>
<td>&lt;40 (20h)</td>
</tr>
</tbody>
</table>
occur on the surfaces of Fe-, Cu- and Mn-active sites, respectively. Specifically, Fe$^{2+}$, Cu$^{+}$ and Mn$^{2+}$ can catalyse H$_2$O$_2$ to form ·OH (Equations (1), (4) and (7)). Furthermore, the ions (Fe$^{3+}$, Cu$^{2+}$ and Mn$^{3+}$) can reversibly transfer into Fe$^{2+}$, Cu$^{+}$ and Mn$^{2+}$ by reacting with ·OH$_2$, respectively (Equations (3), (5) and (8)). Besides, Cu$^{+}$ and Mn$^{2+}$ ions could also react with Fe$^{3+}$ to regenerated Fe$^{2+}$, which can accelerate the reversible conversion of the Fe species between Fe$^{3+}$ and Fe$^{2+}$ (Equations (6) and (9)). It could be conducted that the Cu and Mn species have an active influence on the H$_2$O$_2$/·OH conversion and p-NP degradation. On the other hand, the MWCNTs possibly play several important roles during the reaction: (1) immobilizing the nanoparticles; (2) accelerating electron transmission; (3) absorbing H$_2$O$_2$, p-NP and its degraded products.

Effect of parameters on p-NP degradation

Due to having the best catalytic properties among those samples, the Cu$_{0.075}$Mn$_{0.075}$Fe$_{2.85}$O$_4$/MWCNTs nanocomposite was used for further investigation. The effect of the catalyst dosage on the p-NP degradation was studied under a constant condition (100 mg L$^{-1}$ of initial p-NP concentration, 20 mmol L$^{-1}$ of H$_2$O$_2$ concentration, 3.0 of pH value and 25$^\circ$C of temperature). With increasing catalyst dosage, the degradation rate constant of p-NP (k) increases and arrives at a maximal value of 0.2028 min$^{-1}$ at 1.0 g L$^{-1}$ dosage. It indicates that higher catalyst dosage can provide more active sites. However, the k shows a downtrend when the catalyst dosage further increases to 1.5 or 2.0 g L$^{-1}$. This may be for two reasons: agglomeration of the Cu$_{0.075}$Mn$_{0.075}$Fe$_{2.85}$O$_4$/MWCNTs nanocomposite in aqueous solution and ineffective consumption of H$_2$O$_2$.

The pH value is also one of the important parameters for homogenous/heterogeneous Fenton process in wastewater treatment. Fe(II) forms Fe(H$_2$O)$_6^{2+}$ (Fe$^{2+}$) in solution when the pH value is less than 2. When the pH value is in the range of 2.5 to 3.5, the H$_2$O is partially replaced by HO$^-$ and could form complexes of FeOH$^+$ and Fe(OH)$_2$. In this condition, Fe(OH)$_2$ could react with H$_2$O$_2$ to generate ·OH with a higher reaction rate constant (k = 586 m$^{-1}$ s$^{-1}$) than Fe$^{2+}$ (k = 40–80 m$^{-1}$ s$^{-1}$) (Wells & Salam 1968; Wan & Wang 2016). So, the effect of the pH value on the p-NP degradation was further investigated. The experimental conditions are: 100 mg L$^{-1}$ of initial p-NP concentration, 1.0 g L$^{-1}$ of catalyst dosage, 20 mmol L$^{-1}$ of H$_2$O$_2$ concentration and 25$^\circ$C of temperature. As can be seen from Figure 7(b), the optimal pH value is about 2.5, and the corresponding k value is about 0.3279 min$^{-1}$.

The effect of initial H$_2$O$_2$ concentration on the p-NP and COD removal efficiencies was also investigated (Figure 7(c)). The experimental conditions are: 100 mg L$^{-1}$ of initial p-NP concentration, 1.0 g L$^{-1}$ of catalyst dosage, 2.0 mmol L$^{-1}$ of H$_2$O$_2$ concentration and 25$^\circ$C of temperature. With increasing initial H$_2$O$_2$ concentration, the COD removal efficiencies was also investigated (Figure 7(c)).
concentration from 2 to 25 mmol L\(^{-1}\), the p-NP conversion rate and COD removal rate increase and gradually approach constant values of about 95% and 83% at 20 mmol L\(^{-1}\), respectively. This indicates that OH cannot be sufficiently generated to degrade p-NP and intermediate organic products (Equations (1), (4) and (7)) at a low H\(_2\)O\(_2\) concentration. At a high H\(_2\)O\(_2\) concentration, the generated excess ·OH could not be effectively utilized due to the by-reactions. As a result, the operating cost will inevitably increase.

The dissolved iron and H\(_2\)O\(_2\) consumption during the reactions were investigated under the optimal condition (100 mg L\(^{-1}\) of initial p-NP concentration, 1.0 g L\(^{-1}\) of catalyst dosage, 20 mmol L\(^{-1}\) of initial H\(_2\)O\(_2\) concentration, 2.5 of pH value and 25 °C of reaction temperature). The total amount of dissolved iron increases to 13.14 mg L\(^{-1}\) in 120 min, as shown in Figure S3(a) (Figure S3 is available online). The amount of ferrous iron performs a rapid increase in 60 min and then shows a downtrend. This may be due to the ferrous iron being deoxidized to ferric iron by excess H\(_2\)O\(_2\) and ·OH (Nidheesh 2015; Lu et al. 2016). Compared with other literature, more ferrous iron ions were dissolved in this catalyst system. This may be attributed to the Cu\(^{+}\) and Mn\(^{2+}\) ions effectively promoting the transformation of Fe\(^{3+}\) into Fe\(^{2+}\) (Equations (6) and (9)). After Fenton oxidation, the flocculation-settlement process will be carried out. That step will effectively remove the metal-based secondary pollutants in the treated water. Figure S3(a) also shows that the H\(_2\)O\(_2\) concentration decreases rapidly in 60 min and then slows. In one respect, the H\(_2\)O\(_2\) utilization efficiency is a very important parameter to evaluate the catalyst’s ability. According to the reported studies (Gao et al. 2015; Wan et al. 2016), the H\(_2\)O\(_2\) utilization efficiency (\(E\)) was defined as the amount of COD removed per unit mass of consumed H\(_2\)O\(_2\):

\[
E(\%) = \frac{\Delta\text{COD}}{(0.47 \times \Delta[H_2O_2])} \times 100
\]  

(10)

where, \(\Delta\text{COD}\) is the removed COD value (mg L\(^{-1}\)), \(\Delta[H_2O_2]\) is the consumed H\(_2\)O\(_2\) amount (mg L\(^{-1}\)), and 0.47 is the conversion factor. The efficiencies of the p-NP conversion and
COD removal are shown in Figure S3(b). The removed COD value is about 160.1 mg L\(^{-1}\) and the amount of H\(_2\)O\(_2\) consumed is about 670.3 mg L\(^{-1}\). The H\(_2\)O\(_2\) utilization efficiency is calculated as 50.8%.

**Stability and reusability of Cu\(_{0.075}\)Mn\(_{0.075}\)Fe\(_{2.85}\)O\(_4\)/MWCNTs**

The stability and reusability of the Cu\(_{0.075}\)Mn\(_{0.075}\)Fe\(_{2.85}\)O\(_4\)/MWCNTs nanocomposite as a heterogeneous Fenton catalyst were evaluated under the optimal condition (100 mg L\(^{-1}\) initial p-NP concentration, 1.0 g L\(^{-1}\) catalyst dosage, 20 mmol L\(^{-1}\) initial H\(_2\)O\(_2\) concentration, 2.5 pH and 25°C reaction temperature). It can be seen from Figure 8(a) that the p-NP degradation rate is still as high as 94.4% after the fifth use of the catalyst. The COD removal rate has a slight decrease from 82.3% (first time) to 70.3% (fifth time). The reasons may be that: (1) the iron component was leached and the catalytic sites decreased; (2) the absorbed organic molecules in the catalyst were not removed completely just by simple washing; (3) the Cu and Mn components may also leach. Figure 8(b) shows that the Cu\(_{0.075}\)Mn\(_{0.075}\)Fe\(_{2.85}\)O\(_4\)/MWCNTs nanocomposite could be easily separated from the water by an external magnet. Its recovery is more than 95.8%, which is very important for practical application. How to improve and keep the COD removal efficiency of the Cu/Mn doped Fe\(_2\)O\(_4\)-based nanocomposite is a very important work in future.

**CONCLUSIONS**

The Cu\(_{x}\)Mn\(_{3-x}\)Fe\(_{2x}\)O\(_4\)/MWCNTs nanocomposites (0 \(\leq x \leq 0.1\)) were prepared by co-precipitation process and used as a heterogeneous Fenton catalyst for p-NP degradation. After doping of the Cu and/or Mn elements, the specific surface area of the nanocomposite increased with good dispersion of metal oxide nanoparticles on MWCNTs. The Cu\(_{0.075}\)Mn\(_{0.075}\)Fe\(_{2.85}\)O\(_4\)/MWCNTs catalyst has the best catalytic properties among those catalysts. At the optimal reaction condition (catalyst dosage of 1.0 g L\(^{-1}\), pH value of 2.5 and initial H\(_2\)O\(_2\) concentration of 20 mmol L\(^{-1}\)), the p-NP and COD removal rates in 120 min are respectively 97.9% and 82.7%. In addition, the Cu\(_{0.075}\)Mn\(_{0.075}\)Fe\(_{2.85}\)O\(_4\)/MWCNTs nanocomposite also shows very good stability and reusability. Therefore, the Cu\(_{0.075}\)Mn\(_{0.075}\)Fe\(_{2.85}\)O\(_4\)/MWCNTs nanocomposite is a prospective candidate as a heterogeneous Fenton catalyst for the degradation of organic pollutants in wastewater.

**CONFLICTS OF INTEREST**

There are no conflicts to declare.

**REFERENCES**

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