Nanoscale zero-valent iron incorporated with nanomagnetic diatomite for catalytic degradation of methylene blue in heterogeneous Fenton system

Yiming Zha, Ziqing Zhou, Haibo He, Tianlin Wang and Liqiang Luo

ABSTRACT

Nanoscale zero-valent iron (nZVI) incorporated with nanomagnetic diatomite (DE) composite material was prepared for catalytic degradation of methylene blue (MB) in heterogeneous Fenton system. The material was constructed by two facile steps: Fe₃O₄ magnetic nanoparticles were supported on DE by chemical co-precipitation method, after which nZVI was incorporated into magnetic DE by liquid-phase chemical reduction strategy. The as-prepared catalyst was characterized by scanning electron microscopy, Fourier-transform infrared spectroscopy, X-ray diffraction, magnetic properties measurement and nitrogen adsorption–desorption isotherm measurement. The novel nZVI@Fe₃O₄–diatomite nanocomposites showed a distinct catalytic activity and a desirable effect for degradation of MB. MB could be completely decolorized within 8 min and the removal efficiency of total organic carbon could reach to 90% after reaction for 1 h.

Key words | diatomite, Fenton degradation, magnetite, methylene blue, nanoscale zero-valent iron, synergistic catalysis

INTRODUCTION

Advanced oxidation processes are currently powerful approaches for degradation of stable and pertinacious pollutants in water, which involves the generation of highly reactive species, such as hydroxyl radicals (·OH). The advantages of the advanced oxidation processes include fast reaction rates and non-selective oxidation leading to the complete oxidic decomposition of target organics (Antonopoulou et al. 2014). As a special type of advanced oxidation process, homogeneous Fenton oxidation system (Fe²⁺/H₂O₂) has caused extensive concern on treating many kinds of environmental pollutants while the traditional Fenton process suffers from the narrow pH range, leaching of iron ions into water and stacking of coagulative sludge (Zha et al. 2014). In order to solve these problems, heterogeneous Fenton oxidation systems based on various iron-based catalysts have been gradually used as promising alternatives in recent years (Huang et al. 2012). Such heterogeneous Fenton catalysts are environmentally benign and also much easier to be magnetically separated from treated wastewater for recycling use. Among these iron-based materials, the employment of nanoscale zero-valent iron (nZVI) has been increasingly developed (Chu et al. 2012; Wu et al. 2014; Zha et al. 2014; Zhou et al. 2015). In this method, nZVI corrodes rapidly in the acidic medium and the interaction between Fe²⁺surf and H₂O₂ in situ provides a large amount of ·OH for oxidation of pollutants, as described below:

\[
\begin{align*}
    Fe^0 + 2H^+ + H_2O_2 & \rightarrow Fe^{2+} + 2H_2O \\
    Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + \cdot OH + OH^-
\end{align*}
\]

Methylene blue (MB), a common heterocyclic organic dye, has been extensively applied in fields of textile dyeing, paper, pulp, plastic, pharmaceutical, food, cosmetic and other industries (He et al. 2012). The nature of its toxicity, teratogenesis and carcinogenesis may do harm to the water environment as well as to human health. It is reported that nano-structural metal oxides can be exploited as heterogeneous catalysts for effective degradation of MB (Xiao et al. 2008; Li et al. 2015; Vinothkannan et al. 2015). In particular, magnetite (Fe₃O₄) with a spinel structure has attracted tremendous attention owing to its low cost, reactive surfaces,
large specific area and excellent magnetic properties (Vinothkannan et al. 2015). In a typical catalytic process, Fe$_3$O$_4$ serves as a heterogeneous Fenton catalyst due to the existence of Fe$^{2+}$ and Fe$^{3+}$ on the octahedral sites of magnetite (Huang et al. 2012; Yang et al. 2015a). The catalytic principle contains the following two steps:

\[
\text{Fe}^{2+}_{\text{magnetite}} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+}_{\text{magnetite}} + ^{\bullet}\text{OH} + ^{\cdot}\text{OH} \\
\text{Fe}^{3+}_{\text{magnetite}} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+}_{\text{magnetite}} + ^{\bullet}\text{OOH} + \text{H}^+ \\
\text{Total: } 2\text{H}_2\text{O}_2 \xrightarrow{\text{Fe}^{3+}_{\text{magnetite}}} ^{\bullet}\text{OH} + ^{\bullet}\text{OOH} + \text{H}_2\text{O}
\]

Moreover, Costa et al. have previously reported that the degradation efficiency of MB in heterogeneous Fenton system can be effectively enhanced when using Fe$^0$/Fe$_3$O$_4$ composites, which may originate from the promoted electron transfer process from nZVI to magnetite (Costa et al. 2008). Nevertheless, the inevitable agglomeration of bare Fe$_3$O$_4$ magnetic nanoparticles would reduce their surfactivity and catalytic activity. To overcome this disadvantage, Fe$_3$O$_4$ nanoparticles are generally anchored to some supports such as carbonaceous materials for enhanced catalytic degradation of MB (Vinothkannan et al. 2015; Yang et al. 2015b).

Diatomite (DE) is a low-cost siliceous mineral composed of silica microfossils of aquatic algae with high permeability and porous structure that possesses the properties of large surface area, small particle size, high permeability and remarkable thermal stability (Sun et al. 2013). Such superior physico-chemical characteristics enable DE to be used as an outstanding adsorbent for water pollutants (Chao et al. 2014; Sheshdeh et al. 2014) and as a support for synthesizing varieties of nano-catalysts (Zhang et al. 2013; Padmanabhan et al. 2014). However, there are few reports regarding the DE-supported iron-containing materials (Dror et al. 2012; Sun et al. 2013; Yusan et al. 2014), none of which focuses on the catalytic degradation of MB in heterogeneous Fenton system.

In this work, we attempted to integrate the three components of nZVI, magnetite and DE to construct the novel DE-supported Fe$^0$/Fe$_3$O$_4$ hybrids (nZVI@Fe$_3$O$_4$-DE) by two facile steps. First, Fe$_3$O$_4$ magnetic nanoparticles were immobilized onto DE support by the chemical co-precipitation method. Second, nZVI was then incorporated into magnetic DE (Fe$_3$O$_4$-DE) by chemical reduction strategy. As expected, the as-prepared nZVI@Fe$_3$O$_4$-DE composite material exhibits high catalytic efficiency for MB in heterogeneous Fenton system. The research should be valuable and contributive to the wastewater remediation technology of MB dye pollutant.

**MATERIALS AND METHODS**

**Reagents and materials**

DE (Celite 545), ammonium hydroxide, hydrogen peroxide, sodium borohydride and tert-butanol were obtained from Sinopharm Chemical Reagent Co., Ltd (China). Ferric chloride and ferrous chloride were provided by Aladdin Chemical Reagent Co., Ltd (China). MB was purchased from TCI (Japan). Milli-Q water was used throughout the experiments.

**Preparation of Fe$_3$O$_4$-DE and nZVI@Fe$_3$O$_4$-DE**

The raw DE was firstly treated with 5 M HCl for purification. The mixture was magnetically stirred at 80°C for 24 h in a water bath and then filtered, washed with water and dried at 105°C.

Fe$_3$O$_4$-DE nanocomposites were synthesized based on the chemical co-precipitation method:

\[
\text{Fe}^2+ + 2\text{Fe}^3+ + 8\text{NH}_3\cdot\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 \downarrow + 8\text{NH}_4^+ + 4\text{H}_2\text{O}
\]

First, 0.745 g FeCl$_3$·6H$_2$O and 0.274 g FeCl$_2$·4H$_2$O were dissolved in 100 mL water, in which 0.120 g activated DE sample was ultrasonically dispersed. Afterward, 2.5 mL 8 M ammonium hydroxide was injected into the solution. The mixture was vigorously stirred under nitrogen atmosphere at 60°C for 2 h. The precipitate was collected by using an external magnet and washed with water and anhydrous ethanol several times and dried in vacuum at 50°C for 24 h to obtain the Fe$_3$O$_4$-DE hybrids.

nZVI@Fe$_3$O$_4$-DE was synthesized through in situ chemical reduction of ferric ion by borohydride in the liquid phase using Fe$_3$O$_4$-DE as the support material:

\[
2\text{Fe}^3+ + 6\text{BH}_4^- + 18\text{H}_2\text{O} \rightarrow 2\text{Fe}^0 \downarrow + 6\text{B(OH)}_3 + 21\text{H}_2 \uparrow
\]

In brief, 0.200 g as-prepared Fe$_3$O$_4$-DE was dispersed in FeCl$_3$ solution (0.289 g FeCl$_3$·6H$_2$O in 20 mL water). The mixture was first stirred for 30 min, and subsequently the excessive freshly prepared NaBH$_4$ solution was added drop-wise to the mixture under nitrogen gas protection. After continuous stirring for another 1 h, the resulting solid was
magnetically collected, rinsed with water and anhydrous ethanol, and finally dried at 50°C.

Characterization

Scanning electron microscopy (SEM) images were observed using an S-4800 field emission scanning electron microscope (Hitachi, Japan) equipped with an energy dispersive X-ray (EDX) spectroscopy. Fourier-transform infrared (FT-IR) spectra were recorded on a Avatar 370 spectrometer (Nicolet Thermo, USA). X-ray powder diffraction patterns (XRD) were tested by a D/MAX 2200 V X-ray diffractometer (Rigaku Corporation, Japan). Magnetic properties were analyzed using a vibrating sample magnetometer (VSM, Lakeshore 7407, USA). The nitrogen adsorption and desorption isotherm was measured with an ASAP 2020 physisorption analyzer (Micromeritics, USA) and the surface area and pore size distribution were calculated by the Brunauer–Emmett–Teller (BET) equation and Barrett–Joyner–Halenda method, respectively.

Catalytic degradation of MB

The degradation experiments were conducted in a 250 mL conical flask, to which 100 mL of pH-adjusted MB aqueous solution (50 mg/L, pH 3.0) was added, followed by addition of a certain amount of different active materials. The reaction was initiated by introducing a desired amount of H2O2 to the system and the suspension was shaken in an incubator shaker at 200 rpm under ambient conditions. About 2 mL sample was withdrawn at predetermined time intervals and filtered through 0.45μm filter into a glass vial containing 10μL tert-butanol to quench the reaction. The filtrate was then quickly diluted properly for determination of the remaining concentration of MB using a SP-2500 spectrum instrument (Shanghai Spectrum Co., Ltd, China) measured at 664 nm. To evaluate the mineralization of the MB, the concentration of total organic carbon (TOC) was analyzed by a N/C 2100 TOC analyzer (Analytik Jena AG). The concentrations of total iron after reaction were determined by inductively coupled plasma atomic emission spectrometer of ICPE-9000 (Shimadzu, Japan).

The removal efficiency (RE%) was employed to evaluate the degradation effect that was calculated based on the following formula:

\[
RE\% = \left(\frac{C_0 - C}{C_0}\right) \times 100\%
\]

where \(C_0\) (mg/L) is the initial concentration of MB and \(C\) (mg/L) is the remaining concentration of MB after reaction.

RESULTS AND DISCUSSION

Characterization of the materials

Figure 1 represents the micrographs of DE, Fe3O4, Fe3O4-DE and nZVI@Fe3O4-DE, respectively. The acid-treated DE support has the macroporous structure with the pore diameter of about 500 nm (Figure 1(a)). Once Fe3O4 nanoparticles were loaded on DE, most of them were attached on its surface partially at the edge of pores (Figure 1(c)). The average size of these supported Fe3O4 particles was largely diminished compared to that of bare Fe3O4 in which the nanoparticles tended to aggregate due to the strong magnetic interaction (Figure 1(b)). As the incorporation of nZVI into the Fe3O4-DE catalyst (Figure 1(d)), it is observed that nZVI chains were mostly divided by Fe3O4 into finely dispersed nZVI crystals composed of one or several nanoparticles (pointed by white arrow). According to the EDX spectra and the corresponding element semiquantitative data shown in Figure 1(e) and 1(f), the content of Fe in nZVI@Fe3O4-DE increased apparently with the decreased content of O and Si compared to Fe3O4-DE, confirming the successful embedding of nZVI in the as-prepared nanocomposites.

Figure 2(a) shows the FT-IR spectra of DE, Fe3O4-DE and nZVI@Fe3O4-DE. The spectrum of DE illustrates two strong absorptions at 1,091 and 475 cm⁻¹, which stands for the asymmetric stretching vibration of Si-O-Si moieties. The absorption band at 793 cm⁻¹ is ascribed to the stretching vibration of Al-O-Si (Yusan et al. 2014). In the spectrum of Fe3O4-DE, the characteristic vibration of Fe-O bond appears at 582 cm⁻¹, indicating that Fe3O4 nanoparticles were successfully loaded on the DE support. The spectrum of nZVI@Fe3O4-DE is similar to that of Fe3O4-DE, while the peak intensity decreases a little because of the incorporation of nZVI. The new peak at 1,398 cm⁻¹ can be attributed to the symmetric vibration modes of species containing Fe-coordinated hydrolysis (Sun et al. 2013), which could be formed in the alkaline media of borohydride.

The crystalline structures of the products were characterized by XRD, as depicted in Figure 2(b). The DE sample used here displays typical crystal planes of cristobalite SiO2 (JCPDS 39-1425). The pattern of Fe3O4-DE retains the diffraction peak of DE at 21.9° and the characteristic peaks for the spinel phases Fe3O4 at 30.3, 35.5, 43.1, 53.5, 57.1 and 62.5° are observed corresponding to (220), (311),
However, the significant peak of nZVI at 44.8° has not been observed in the curve of nZVI@Fe₃O₄-DE, probably owing to the low content of nZVI, as well as the possible finely dispersed iron particles that form very small crystallites with size below the detection limit of XRD (Sun et al. 2013).

As shown in Figure 2(c), the magnetic hysteresis loops of Fe₃O₄, Fe₃O₄-DE and nZVI@Fe₃O₄-DE show that these magnetic species are all superparamagnetic with neither coercivity nor remanence. The saturation magnetizations (Mₛ) of Fe₃O₄, Fe₃O₄-DE and nZVI@Fe₃O₄-DE were measured at 59.25 emu/g, 42.31 emu/g and 67.28 emu/g, respectively. Although nZVI could not be recognized by SEM and XRD, the VSM results demonstrate that nZVI was supposed to be embedded to Fe₃O₄-DE due to the substantial increase of Mₛ of nZVI@Fe₃O₄-DE compared to that of Fe₃O₄-DE.

The nitrogen adsorption/desorption curve of nZVI@Fe₃O₄-DE gives a representative type-IV isotherm with H3 hysteresis loop (Figure 2(d)). The BET surface area was 78.5 m²/g with the total pore volume of 0.157 m³/g. The main pore size distribution was located in the range of 2–15 nm and the average pore size was 8.0 nm calculated.
from the desorption branch. The material was confirmed to possess the large specific surface area with mesoporous structures, which would favor the physical adsorption process towards the target pollutants.

**Degradation of MB**

The degradation of MB depends on the reaction system of using both H$_2$O$_2$ and catalysts. In Figure 3(a), MB was hardly degraded by H$_2$O$_2$ alone and the absolute adsorption capacity of nZVI@Fe$_3$O$_4$-DE also seemed very slight, mainly by reason of the small dose of the catalyst. The removal efficiencies that arise from H$_2$O$_2$ and nZVI@Fe$_3$O$_4$-DE were only 1.4% and 5.8%, respectively.

The comparison of different materials on MB degradation was evaluated with 50 mg/L MB, 0.12 g/L nZVI@Fe$_3$O$_4$-DE, 6 mM H$_2$O$_2$ and initial pH of 3.0 in this study. The dose of other materials (Fe$_3$O$_4$, Fe$_3$O$_4$-DE, nZVI) should contain the uniform content of each individual competent in nZVI@Fe$_3$O$_4$-DE. To the degree of catalytic ability of different materials towards H$_2$O$_2$, as shown in Figure 3(b), the oxidation process of MB catalyzed by bare Fe$_3$O$_4$ and Fe$_3$O$_4$-DE proceeded gently, which caused only 10.9% and 13.4% decolorization efficiency of MB after 1 h, respectively. The better effect when using Fe$_3$O$_4$-DE was ascribed to the relatively homogeneous dispersion of Fe$_3$O$_4$ nanoparticles on the surface of DE support, thus increasing its catalytic active sites. Also, it was likely that porous DE support might bring about the rapid adsorption–desorption process of MB and its degradation intermediates repeatedly, so the enrichment effect of DE, to some extent, enhanced the mass transfer of MB. In contrast, a rapid dynamic process was monitored with the presence of nZVI and nZVI@Fe$_3$O$_4$-DE. Especially, MB could be thoroughly decolorized within 8 min and the decolorization efficiency achieved at 67.5% at the initial 2 min by using nZVI@Fe$_3$O$_4$-DE as the catalyst, which indicated that nZVI was endowed with very high reactivity in H$_2$O$_2$/H$^+$ acidic system leading to the strong...
tendency of heterogeneous Fenton oxidation induced by nZVI. Hence, MB could be rapidly decomposed in combination with the inherent catalytic ability of Fe₃O₄-DE and the nZVI-Fenton process.

At appropriate intervals during the reaction, the UV-vis spectroscopy of the MB solution was measured following nZVI@Fe₃O₄-DE catalyst (Figure 3(c)). As reaction time prolonged, the characteristic absorption peaks (614 and 664 nm) originating from the primary chromophore in MB molecule were quickly diminished until they disappeared. Meanwhile, the absorbance in the ultraviolet region was also reduced, indicating that some degradation products of MB that includes aromatic rings were continued to be mineralized to CO₂ and H₂O.

To gain further insight into the contributions of ‘OH in the Fenton catalytic system, the reaction was additionally conducted in the presence of tert-butanol as the ‘OH scavenger (Huang et al. 2012). As shown in Figure 3(d), there existed only 14.8% RE after reaction of 1 h, accounting for the obvious quench of reaction by tert-butanol. Therefore, it was ascertained that the ‘OH played the dominant role in this Fenton catalytic system. It is well known that ‘OH could non-selectively attack the objective MB and its degradation intermediates that were eventually converted to CO₂ and H₂O. As a result, a high mineralization degree as 90% TOC RE was determined after reaction for 1 h by nZVI@Fe₃O₄-DE in the H₂O₂/H⁺ system. The nZVI@Fe₃O₄-DE was compared with other catalyst materials based on heterogeneous Fenton system for MB degradation in Table 1.

Stability is an importance factor in the application of Fenton catalysts. The leached Fe contents from each material after reaction were listed in Table 2. The concentrations of total iron in the reaction solution using Fe₃O₄-DE, nZVI and nZVI@Fe₃O₄-DE were 0.098 mg/L, 3.52 mg/L and 2.75 mg/L, respectively. As the existence of Fe⁰ nanoparticles, nZVI and nZVI@Fe₃O₄-DE were likely to produce a large amount of Fe²⁺ surf for high-efficient heterogeneous Fenton process, thereby leaching more Fe ions to solution. However, the Fe₃O₄-DE catalyst was much stabilized with the losses only 0.098 mg/L of the total iron. It should be emphasized that
the Fe leaching percentage of nZVI (12.57%) was 5.5 times greater than that of nZVI@Fe3O4-DE (2.29%), representing that bare nZVI was easy to corrode by acerbity, but the attrition resistance of nZVI in acid condition could be improved when incorporated with Fe3O4 nanoparticles for protection.

Mechanism discussion

The mutual promoting effects between nZVI and Fe3O4 make great contributions to the heterogeneous Fenton oxidation catalyzed by Fe2+surf. There are three possible explanations for the synergistic catalysis of nZVI and Fe3O4 (Figure 4): (i) the surface electron can easily transfer to Fe3+mag in the octahedral site of the magnetite spinel structure, reducing it to Fe2+surf for catalysis of H2O2 (Costa et al. 2008). That is to say the synergistic effect derived from nZVI can enhance the catalytic activity of Fe3O4; (ii) Fe2+surf can be regenerated by nZVI through the reduction of Fe3+surf formed in the Fenton reaction for cyclic catalysis; (iii) the electron transfer on the interface of Fe3O4/Fe0 prevents superficial oxidation and passivation of nZVI particles, which guarantees the continuous Fenton process (Lv et al. 2012).

In the present heterogeneous H2O2/H+ system, the mechanism of catalytic degradation of MB by nZVI@Fe3O4-DE is described in Table 3, in which the whole reaction can be divided into five stages as follows (Costa et al. 2008; Huang et al. 2012; Zha et al. 2014):

(a) The slight adsorption and surface enrichment of MB by DE support.
(b) The self-catalysis of Fe3O4 due to its intrinsic catalytic ability.
(c) Formation of Fe2+surf (including the surface corrosion of nZVI and the electron transfer on the interface of Fe3O4/Fe0).
(d) The Fenton process catalyzed by Fe2+surf.
(e) The final ‘OH oxidation process of MB.

Reusability of nZVI@Fe3O4-DE

The reusability of active materials for practical environmental applications is of great importance. Repetitive experiments were performed that MB solution was treated with nZVI@Fe3O4-DE for successive degradation. After completion of each cycle, the catalyst was magnetically separated and the solution was entirely withdrawn, followed by
addition of fresh MB and H₂O₂ solution for another degradation cycle. As depicted in Figure 5, the catalyst could maintain the stable catalytic activity at the first three cycles while the decolorization efficiency of MB in the fourth cycle dropped dramatically (74.8%), which probably came from two reasons: (i) the irreversibility of the Fe⁰ consumption in Fenton system caused the loss of iron constituent in the composite after several cycles; and (ii) the active sites of nZVI would be gradually obstructed, resulting in the decrease of its practical performance.

CONCLUSIONS

In this study, the nZVI@Fe₃O₄-DE heterogeneous Fenton catalyst showed great performance in MB degradation. MB could be completely decolorized within 8 min and the TOC RE could reach 90% after reaction for 1 h, much better than other materials such as bare nZVI, Fe₃O₄ and Fe₃O₄-DE. It was found that ‘OH mainly contributed to the degradation process, destroying the target substance effectively in a non-selective way. In addition, the incorporation of nZVI amplifies the inherent catalytic activity of Fe₃O₄-DE by the interface electron transfer between nZVI and Fe₃O₄ magnetic nanoparticles in heterogeneous Fenton system. Since the facile preparation of nZVI@Fe₃O₄-DE and the approving performance of MB degradation and TOC removal, the research could be a promising approach for the removal of MB contaminant in water.

ACKNOWLEDGEMENTS

This research is supported by the National Natural Science Foundation of China (Nos 61171033, 61571278) and Shanghai Key Laboratory of High Temperature Superconductors (No. 14DZ2260700).

REFERENCES


Costa, R. C. C., Moura, F. C. C., Ardisson, J. D., Fabric, J. D. & Lago, R. M. 2008 Highly active heterogeneous Fenton-like systems based on Fe\textsubscript{0}/Fe\textsubscript{3}O\textsubscript{4} composites prepared by controlled reduction of iron oxides. Applied Catalysis B: Environmental 83, 131–139.
Huang, R., Fang, Z., Yan, X. & Cheng, W. 2012 Heterogeneous sono-Fenton catalytic degradation of bisphenol A by Fe\textsubscript{3}O\textsubscript{4} magnetic nanoparticles under neutral condition. Chemical Engineering Journal 197, 242–249.
Li, Y., Qu, J., Gao, F., Lv, S., Shi, L., He, C. & Sun, J. 2015 In situ fabrication of Mn\textsubscript{3}O\textsubscript{4} decorated graphene oxide as a synergistic catalyst for degradation of methylene blue. Applied Catalysis B: Environmental 162, 268–274.
Lv, X., Xu, J., Jiang, G., Tang, J. & Xu, X. 2012 Highly active nanoscale zero-valent iron (nZVI)-Fe\textsubscript{3}O\textsubscript{4} nanocomposites for the removal of chromium(VI) from aqueous solutions. Journal of Colloid and Interface Science 369, 460–469.
Xiao, Q., Zhang, J., Xiao, C. & Tan, X. 2008 Photocatalytic degradation of methylene blue over Co\textsubscript{3}O\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6} composite under visible light irradiation. Catalysis Communications 9, 1247–1253.
Yang, X., Chen, W., Huang, J., Zhou, Y., Zhu, Y. & Li, C. 2015b Rapid degradation of methylene blue in a novel heterogeneous Fe\textsubscript{3}O\textsubscript{4}@rGO@TiO\textsubscript{2} catalyzed photo-Fenton system. Scientific Reports 5, 1–10.