Bifunctional core–shell nanocomposite Mn-doped ZnO/Fe₃O₄ for photodegradation of reactive blue 198 dye

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Abstract
Magnetic nanoparticles of manganese doped ZnO have been prepared by co-precipitation method. Photocatalytic activity results show that 9% of Mn in Mn-doped ZnO exhibited the highest photodegradation efficiency of reactive blue 198 dye. Additionally, excellent photocatalytic activity was observed when the molar ratio of Mn-doped ZnO/Fe₃O₄ was 1:1. The photodegradation of reactive blue 198 (RB198) dye was carried out with different illumination times, initial concentrations of dye, amounts of photocatalyst and pH of medium. The results reveal that the degradation efficiency of reactive blue 198 were 99% at the concentration of 30 ppm for 25 min when the amount of catalyst was 5 g L⁻¹. The photodegradation of dye increased with increasing catalyst load. Furthermore, the prepared magnetic nanoparticles could also serve as convenient recyclable photocatalysts because of their magnetic properties. As a result, the removal of dye was still 90% after three times recycling.

Keywords: magnetic nanoparticles, Mn-doped ZnO nanoparticle, photodegradation, wastewater

Classification numbers: 5.02, 5.11, 5.07

1. Introduction
Colored compounds comprising pigments and dyes are widely used in textile, plastic, food, dyeing, paper, printing, pharmaceutical and cosmetic industries. It is estimated that 2–50% of them are lost into wastewaters, causing environmental contamination. Many of them are toxic, carcinogenic, mutagenic, or even stable to biological degradation. Moreover, many dyes are difficult to decolorize due to their complex chemical structure and synthetic origin. Recently, attention has been paid globally to the application of nanotechnology in environmental protection of toxic materials from sewage. Titanium dioxide nanoparticle (TiO₂) is generally considered to be the best photocatalyst and has the ability to detoxify water from a number of organic pollutants [1]. However, widespread usage of TiO₂ is uneconomical for large-scale water treatment, therefore, interest has been drawn toward the search for suitable alternatives to TiO₂. Many attempts have been made to study photocatalytic activity of different semiconductors such as SnO₂, CdS and ZnO. ZnO nanoparticle has attracted a great deal of attention, owing to its unique and novel applications in optics, optoelectronics, catalysis, pyroelectricity and piezoelectricity [2, 3]. Among these properties, the degradation of the pollutants catalyzed by ZnO has been studied widely. However, ZnO nanoparticle has several drawbacks including the low surface area or large particles size and an unsuitable band gap energy (E_g = 3.7 eV). It was observed that doping with 3d metals such as Cu, Ni, Co and Mn created localized levels inside the bandgap [4, 5]. The difficulty of separation and reuse of nanostructured TiO₂, ZnO or Mn-doped ZnO from treated water often limits its application in industry and practice. Magnetic separation technology as an efficient, fast and economical method for separating magnetic materials has been widely used in textile, biology, and environmental protection [6]. In recent years, some investigators have prepared nanocomposite with magnetic core and photoactive shell, and proved that the composite nanoparticles could be
2. Materials and methods

2.1. Materials

All chemicals had analytical grade and were used without further purification. The reactive blue 198 was a commercial product, which could be utilized in the photocatalytic oxidation. This dye was donated by Thanh Cong Textile and Dyeing Company.

2.2. Preparation of Mn-doped ZnO nanoparticles

For synthesizing the catalyst, 0.2 M zinc acetate solution was mixed with different amounts of 1% manganese chloride solution. The resulting mixture was stirred and heated to 80 °C. 2 M NaOH solution was then added to the mixed solution with constant stirring (4000 rpm) until pH 10 was reached. The new solution was kept in a water bath at 80 °C for one hour. After cooling the solution to room temperature for four hours, the precipitate was centrifuged for 20 min at 4000 rpm. The resulting precipitate was washed several times with ethanol and distilled water to remove unreacted ion. The separated precipitate was dried overnight at 90 °C. The samples were coated and stored at room temperature for future studies.

2.3. Preparation of Mn-doped ZnO/Fe3O4 nanocomposite

Preparation of nanocomposite of Mn-doped ZnO/Fe3O4 was prepared by two steps. Firstly, Fe3O4 nanoparticle was prepared by coprecipitation method according to the presented manner with minor modification [7]. A solution of FeCl2 and FeCl3 (molar ratio 2:1) were dissolved in water at a concentration of 0.3 M iron ions under stirring at 80 °C. The sodium hydroxide solution was added to the above solution under vigorous stirring. The precipitates were formed and maintained at 80 °C for one hour. A mixture of MnCl2 and Zn(CH3COO)2 solutions was added slowly to the above precipitation. During the reaction process, the pH was maintained at about 10 by sodium hydroxide solution. The resulting precipitation was kept at 80 °C, and then cooled to room temperature and separated by a permanent magnet. The products were washed several times with distilled water and ethanol, and finally dried at 60 °C.

2.4. Photocatalytic experiments

The photocatalytic experiment was carried out in a 500 mL cylindrical self-designed UV light photocatalytic reactor (30 × 30 × 40 cm3) which was wrapped with aluminum foil. 14 W high pressure mercury lamp with the strongest emission at 380 nm was used as light source. Batch tests were performed as follows. 0.5 g Mn-doped ZnO/Fe3O4 nanocomposite was added into 100 mL RB198 solution with initial concentrations from 10–150 ppm. Before experiment, the mixture was stirred in dark to allow the physical absorption of dye molecules on catalyst particles to reach the equilibrium. When the UV light was irradiated in the absence of catalyst, there was still no change in the color of dye. The reaction solution was mixed by stirrer. The samples from the suspension were collected at regular intervals of time, separated by a permanent magnet. The concentration of RB198 in each sample was analyzed using UV-visible spectrophotometer at a wavelength of 625 nm. The degradation percentage of the dye was calculated as DE = (C0−Ct)/C0 × 100%, where DE is the abbreviation of the photocatalytic degradation efficiency, C0 is the initial dye concentration, Ct is the dye concentration at certain reaction time t (min).

3. Results and discussion

3.1. Structure and morphology of Mn-doped ZnO/Fe3O4 nanocomposite

Fourier transform infrared (FTIR) spectra of the Mn-doped ZnO and its composite with Fe3O4 are employed to study the formation of Zn–O, Mn–O and Fe–O bonds and vacancy sites. As can be seen, a broad band was observed in the region of 3200–3600 cm\(^{-1}\), which can be explained as overlapping O–H and C–H stretching modes. Additionally, a weak peak of C–H between 2800 and 3100 cm\(^{-1}\) has been observed in numerous semiconductors. Weak absorption peaks in the range of 1100–1600 cm\(^{-1}\) correspond to an OH bending mode. The adsorption band around 400–700 cm\(^{-1}\) was assigned to the stretching vibration of metal–O bonds such as Mn–O, Zn–O and Fe–O (figure 1).

Figure 2 shows x-ray diffraction (XRD) patterns of Fe3O4, Mn-doped ZnO and Mn-doped ZnO/Fe3O4 nanocomposite. The typical 20 peaks at 23.1°, 33°, 36° and 59° were observed in XRD pattern of Fe3O4. However, in XRD patterns of Mn-doped ZnO and Mn-doped ZnO/Fe3O4, besides the corresponding peaks of magnetite, the peaks located at 31.9°, 34.5°, 36.2°, 47.5°, 56.5°, 62.9°, 68.0° (figure 2(a)) and 16.93°, 30.19°, 30.25°, 30.28°, 35.53°, 35.62°, 46.44°, 56.38°, 63.37° (figure 2(b)) are indexed to diffraction of ZnO crystals with a hexagonal wurtzite structure.

The magnetic properties were measured using vibrating sample magnetometer (VSM) magnetometer. The magnetic property of prepared nanocomposite with molar ratio of 1:1 and of Fe3O4 is shown in figure 3. The magnetization saturation (\(M_s\)) value of Fe3O4 was 44.8 emu g\(^{-1}\). However,
the magnetization saturation decreased to 40.7 emu g\(^{-1}\) after coating with Mn-doped ZnO. This could be explained by taking into account the diamagnetic contribution of the thick Mn-doped ZnO layer surrounding the magnetic Fe\(_3\)O\(_4\) core. The results also demonstrated that all the samples were superparamagnetic and the coating of Mn-doped ZnO did not change the superparamagnetism of magnetic nanoparticles. Therefore, the nanocomposite could easily be separated and recovered from the adsorption system by a simple magnetic process after experiments.

The surface morphology of nanocomposite is viewed through scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images. The SEM micrograph of nanocomposite powder is presented in figure 4(a). SEM images reveal the agglomerated structure of the synthesized material. The nanocomposite also exhibits homogeneous structure, with a distribution of the agglomerates sizes in a narrow range. As can be seen from TEM, the prepared nanocomposite had the average size of 30–40 nm. More interestingly, we can see that the synthesized nanocomposite consists of a shell layer of Mn-doped ZnO around core of Fe\(_3\)O\(_4\) nanocrystals (figure 4(b)).

### 3.2. Photocatalytic degradation of RB198 solution

In the present study the effect of molar ratio of nanocomposites, irradiation time, the dosage of catalysts, pH of medium and initial concentration of dye on the degradation of dye were tested. In order to remove the effect of adsorption of dye on catalyst and the effect of UV light to dye, a blank experiment under UV radiation without catalyst and blank experiment with catalyst without UV radiation were performed; the results indicated that the degradation of dye was not significantly decreased. In order to determine the optimum amount of Mn for doping the photocatalyst, photodegradation of RB198 was studied by various ratios of Mn to ZnO (1% to 9%). The results show that photodegradation efficiencies of RB198 increased with increasing amount of Mn. The 9% Mn doped ZnO exhibited the highest photodegradation efficiency. This could be explained by the formation of the energy levels inside the bandgap [8, 9]. Therefore, the 9% Mn-doped ZnO was selected as catalyst for future study. Additionally, the nanocomposites with different molar ratios of 9% Mn-doped ZnO to Fe\(_3\)O\(_4\) were also prepared for photocatalytic degradation of dye. The photodegradation efficiency of dye increase with increasing molar ratio of 9% Mn-doped ZnO to Fe\(_3\)O\(_4\) from 0.5:1 to 1:1, and then decreased when the molar ratio increased over 1:1 (1:1.2 and 1:1.5). The highest photodegradation efficiency was observed with molar ratio of 1:1 under the same condition. Therefore, the molar ratio 1:1 was chosen for future studies.

### 3.3. Effect of pH of dye solution

pH plays an important role in the photocatalytic degradation of RB198. Hence, the effect of pH on the photocatalytic activity of the Mn-doped ZnO/Fe\(_3\)O\(_4\) was detected and the results are described in figure 5. As shown in figure 5, the decolorization efficiency of RB198 decreased significantly with the increase of pH of dye solution. It can be seen that the degradation of dye was similar at pH 6 and 6.68. The pH effect on the photocatalytic activity of the photocatalyst can be explained based on the point of zero charge of ZnO. The positive charges on the ZnO surface decreases with increasing pH and reaches zero at pH of point of zero charge. As a result, pH 7.0 was selected as the optimal operational pH value in the present study.

### 3.4. Effect of illumination time and initial concentration

The effect of illumination time and initial concentration on photodegradation efficiency of RB198 was conducted by measuring the photodegradation efficiency at different periods using 0.5 mg of catalyst and 100 mL of various concentrations of dye (from 10–150 ppm). As described in figure 6, it was found that the photocatalytic activity increases with the increase of the illumination time and reaches almost 100% after short illumination time. Such data reveals the relatively high activity of the prepared catalysts that enables the complete degradation of the RB198 in such short illumination time, and the catalyst has active sites for photocatalytic reaction. The effect of initial concentration of RB198 on the photocatalytic degradation efficiency was carried out by adjusting the initial concentration from 10 ppm to 150 ppm. It can be seen that the time for photodegradation concentration of dye is proportional to its concentration, which means that the higher concentration of dye, the longer time requirement for completed degradation of dye. As seen, the time for complete degradation was 10 min at lower initial dye concentration from 10 to 50 ppm. However, the time increased to 30 min for concentrations of 100 and 150 ppm. Additionally, the photodegradation efficiency of dye was 100% for all concentration ranges after 30 min (figure 6).
Figure 2. XRD patterns of (a) Mn-doped ZnO, (b) Mn-doped ZnO/Fe₃O₄ and (c) Fe₃O₄.
3.5. Effect of catalyst loading

The effect of photocatalysts dosage on the photocatalytic degradation of RB198 was detected by taking different amounts of catalyst ranging from 0.1 to 0.5 g into 100 mL of 30 ppm dye solution with pH 7. The results are shown in figure 7. It can be seen that the photodegradation efficiency of RB198 increased with increasing catalyst amount from 0.1 to 0.5 g. Consequently, the illumination time for 100% degradation of dye decreased with increasing catalyst amount from 0.1 to 0.5 g, because due to the increase of the catalyst amount, the number active sites on the photocatalyst surface increased, and the photogenerated electron–hole pairs increased correspondingly, which in turn increased the amount of hydroxyl and superoxide radicals. When the catalyst loading dose increases to above 0.3 g, it does not affect the photodegradation efficiency of RB198.

3.6. Reuse of magnetic nanocomposite

Photocatalysis is a green technology, which normally does not involve any waste disposal problems. Therefore, it is necessary to keep high catalytic activity in each cycle of usage. The results presented in figure 8. As a result, the photocatalytic activity of the nanocomposite decreased slightly after each cycle. After being used three times, the photodegradation efficiency of RB198 was still higher than 95% and decreased to 60% after 4 cycles. The decrease in the efficiency of the recycled catalyst may be attributed to the deposition of photo insensitive hydroxides on the photocatalysts surface blocking its active sites and the loss of catalyst materials.

Figure 3. Magnetic hysteresis loops of (a) prepared Fe₃O₄ and (b) Mn-doped ZnO/Fe₃O₄ measured at 300 K by VSM.

Figure 4. SEM (a) and TEM (b) images of Mn-doped ZnO/Fe₃O₄ nanocomposite.

Figure 5. Effect of pH of dye solution on the photodegradation efficiency of RB198.

Figure 6. Effect of initial dye concentration on the photodegradation efficiency of RB198.
3.7. Real wastewater performance

To test the effect of prepared photocatalyst in real sample, the photodegradation of wastewater from Thanh Cong Textile and Dyeing Company was conducted and COD value was determined (method: SMEWW 5220C–2005). As results, the COD decreased from 276 to 126 mg L\(^{-1}\) for wastewater and wastewater after treatment, respectively. The results confirmed that the prepared catalyst could degrade environmental detoxification from organic compounds in real wastewater.

3.8. Magnetic properties and separable ability

The magnetization saturation (\(M_s\)) value of Fe\(_3\)O\(_4\) was 44.8 emu g\(^{-1}\). However, the magnetization saturation of Mn-doped ZnO/Fe\(_3\)O\(_4\) (40.7 emu g\(^{-1}\)) was less than that of pure Fe\(_3\)O\(_4\). This could be explained by taking into account the diamagnetic contribution of the thick Mn-doped ZnO layer (a non-magnetic component) surrounding the magnetic Fe\(_3\)O\(_4\) core. Finally, the predicted advantage of the magnetic nanocomposite is the association of magnetic and photocatalytic properties in a single system. Figure 9 is a visual evaluation of the magnetic activity, where heterogeneous photocatalysts were suspended in the solution and drawn towards the external magnet. The results displayed that the prepared nanocomposite could be separated and collected for reuse with a magnet after photocatalytic reaction.

4. Conclusion

In this study we have successfully prepared composite nanoparticle of Mn-doped ZnO/Fe\(_3\)O\(_4\). The structure of nanocomposite was characterized by XRD, SEM and TEM. The photocatalytic degradation of reactive blue 198 was investigated using prepared catalyst under UV light. The degree of degradation of dye was affected by the pH of the dye solution, illumination time, amount of catalyst loading and initial dye concentration. Experimental results show that the prepared catalyst could remain above 90% degradation percentage after three recycles. Finally, the prepared catalyst exhibited a potential application in environment treatment with lower COD in comparison with untreated sample.

References

[1] Li C J, Wang J N, Wang B, Gong J R and Lin Z 2012 Mater. Res. Bull. 47 333
[2] Kansal S K, Kaur N and Singh S 2009 Nanoscale Res. Lett. 4 709
[3] Saravanan R, Thirumal E, Gupta VK, Narayanan V and Stephen A 2013 J. Mol. Liq. 177 394
[4] Poureredal H R, Norozi A, Keshavarz M H and Semnani A 2009 J. Hazard. Mater. 162 674
[5] Hammad T, Griesing S, Wotocek M, Kuhn S, Hempelmann R, Hartmann U and Salem J 2013 Appl. Nanosci. 3 153
[6] Rocher V, Siaugue J M, Cabuil V and Bee A 2008 Water Res. 42 1290
[7] Nguyen V C and Huynh T K N 2014 Adv. Nat. Sci. Nanosci. Nanotechnol. 5 025007
[8] Saleh R, Djaja N F and Prakoso S P 2013 J. Alloys Compd. 546 48
[9] Ezema F I and Nwankwo U O 2011 Dig. J. Nanomater. Bio. 6 271

Figure 7. Effect of catalyst amount on the photodegradation efficiency of RB198.

Figure 8. Recycled performances of nanocomposite for the photodegradation of RB198.

Figure 9. Magnetic nanocomposite was separated from treated with RB198 solution.