Visible light induced photocatalytic degradation of rhodamine B by magnetic bentonite

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ABSTRACT

The photocatalytic activity of magnetic bentonite, Fe₃O₄ nanoparticles decorated Al-pillared bentonite (Fe₃O₄/Al-B), for the degradation of rhodamine B (RhB) in the presence of H₂O₂ under visible light (VL) was evaluated. The effects of different reaction parameters such as catalyst dose, dye concentration and externally added H₂O₂ were also investigated. The magnetic bentonite showed good photocatalytic activity, magnetic separability and stability for repeated use. More than 95% of 40 mg/L RhB was converted within 3 h under VL with a catalyst dose of 0.5 g/L. Suitable mechanisms have been proposed to account for the photocatalytic activities in the presence and absence of H₂O₂. The efficiency of H₂O₂ in VL process was much higher than that of the dark process. Results obtained in the current study may be useful to develop a suitable photocatalyst for photocatalytic remediation of different water contaminants including organic dyes.

Key words | degradation, heterogeneous catalyst, magnetic bentonite, rhodamine B, visible light

INTRODUCTION

Organic dyes are a major class of synthetic colored organic compounds used in textile, pharmaceuticals, cosmetic and paper industries. Because of their complex structures and synthetic origins, organic dyes discharged into the environment are generally resistant to biological treatment, which has a significant impact on water quality (Iram et al. 2010). As we know, rhodamine B (RhB) is one of the most commonly used xanthene dyes for the textile industry. RhB dissolves well in water or organic solvents, with many toxic effects, such as irritation to the skin, eyes and respiratory tract. The most serious is that RhB was believed to be carcinogenic, which made it be banned from use in foods and cosmetics. However, RhB is still extensively used in dyeing and staining processes (Zhang et al. 2011). Therefore, the treatment of effluents containing RhB is essential before their final discharge into the environment.

The removal methods of RhB include physical adsorption, chemical degradation, biological degradation, photodegradation and the synergic treatments of different methods (Xue et al. 2009; Hou et al. 2011; Wang et al. 2014; Liu et al. 2015). Among these methods, heterogeneous photo-Fenton systems play an important role. It is found that dyes can absorb visible light (VL) and be excited under visible irradiation. The subsequent electron transfer from the excited dye molecules to the Fe(III) species would enhance Fenton chain reactions (Chen et al. 2009; Alvarez et al. 2010). With this advantage, some heterogeneous Fenton-like catalysts, which contain active iron species, have been employed in the VL photo-Fenton process for the degradation of RhB as well as other dyes, such as iron-pillared bentonite (Gao et al. 2015), Al-pillared Fe-smectite (Li et al. 2015), Fe₃O₄@AgBr–ZnO (Shekofteh-Gohari & Habibi-Yangjeh 2015), Ag–AgI/Fe₃O₄@SiO₂ (Guo et al. 2011), and so on. Nevertheless, most of these photocatalysts are difficult to be available at a reasonable cost. What’s more, the separation of suspended catalysts from the treated water is another major problem in recycling the catalysts for reuse. Hence, the development of the photocatalysts with lower cost and better separability is a prerequisite for their practical application in waste water treatment. Recently, a kind of magnetic bentonite catalyst, Fe₃O₄ nanoparticles decorated Al-pillared bentonite (Fe₃O₄/Al-B), was prepared conveniently and applied for the adsorption and degradation of RhB through Fenton-like process (Wan et al. 2015). The magnetic bentonite material has good catalytic property and can be easily separated from water by means of magnetic separation. However, the VL photocatalytic activity of the magnetic bentonite still needs further research.
Keeping the above in view and in sequel to the previous studies on the adsorption and catalytic properties of Fe₃O₄/Al-B (Wan et al. 2015), the present study aimed to evaluate its photocatalytic efficiency. The degradation of RhB in the presence of Fe₃O₄/Al-B and H₂O₂ under VL irradiation was studied in this work. The effects of operating parameters, including catalyst dose, initial RhB concentration and H₂O₂ concentration, on the degradation of RhB were investigated. The stability and reusability of the catalyst were also explored.

**METHODS**

**Preparation of magnetic bentonite (Fe₃O₄/Al-B)**

Natural bentonite was procured from Shanghai No. 4 Reagent & H.V. Chemical Co., Ltd, China. RhB was obtained from Shanghai Zhanyun Chemical Co., Ltd, China. All chemicals were of analytical grade and used as received. In all experiments, distilled water was used for preparing the solutions and suspensions.

The magnetic bentonite catalyst (Fe₃O₄/Al-B) was prepared according to the previous work (Wan et al. 2015). Briefly, the suspension containing 3.1 g Al-B was bubbled with N₂ flow to remove the dissolved oxygen and placed in a 95 °C water bath, then 11.1 g FeSO₄·7H₂O was added into the suspension. Afterwards, the solution containing 3.2 g NaOH and 3.2 g NaNO₃ was added dropwise into the heating solution while maintaining vigorous stirring and stable N₂ flow during the entire reaction period. After the suspension was heated at 95 °C for another 2 h, the Fe₃O₄/Al-B nanocomposites formed. All the products were stored in a desiccator under ambient temperature for further experiments.

**Characterization**

X-ray diffraction (XRD) patterns of the samples were recorded by a Rigaku D/max-RB diffractometer (Rigaku, Japan) at 40 kV and 30 mA using filtered Cu Kα radiation (λ = 0.15418 nm). Micrographs of the samples were taken using a Nova400 Nano SEM (FEI, USA). X-ray photoelectron spectroscopy (XPS) of the samples was performed with a MULTILAB2000 X-ray photoelectron spectrometer (VG, USA) with a monochromatized Al Kα X-ray source (25 eV) operated at 300 W. Magnetic characterization of the samples was carried out using a JDAW-2000D vibrating sample magnetometer at a temperature of 298 K with fields up to 6,000 Oe. UV–vis–DRS of magnetic bentonite were recorded on an Aucy, UV-1901 spectrophotometer using BaSO₄ as reference.

The point of zero charge (pHpzc) of magnetic bentonite was determined using the solid addition method as follows (Oladjoja & Aliu 2009). Into a series of 100 mL conical flasks, 45 mL of 0.1 M KNO₃ solution was transferred. The pH0 values of the solution were roughly adjusted from 2 to 10 by adding either 0.1 M HNO₃ or NaOH. The total volume of the solution in each flask was made exactly to 50 mL by adding the KNO₃ solution. The pH0 of the solutions was then accurately noted. Magnetic bentonite (1 g) was added to each flask and securely capped, immediately. The suspension was then manually agitated. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pHz) values (ΔpH = pH0 − pHz) was plotted against the pH0. The point of intersection of the resulting curve is the one at which pH0 gave the pHpzc.

**Heterogeneous photocatalytic degradation of RhB under VL**

Photocatalytic activities of the as-prepared samples were evaluated by the degradation of RhB in aqueous solutions under VL irradiation. The VL source was a 125 W high pressure Hg lamp. The emission spectrum of the source is shown in Figure 1. As can be seen, the source has high intensity in the visible range, and the central wavelength was 546 nm. The lamp was equipped with a cut-off filter to remove any radiation <450 nm and to ensure irradiation only by VL. All the experiments were performed at constant temperature and under mechanical stirring condition. For the degradation of RhB, the reaction cell was placed in a sealed cardboard box of which the top was opened. Prior to irradiation, the suspensions containing RhB and catalyst

![Figure 1](https://iwaponline.com/wst/article-pdf/73/10/2345/461432/wst073102345.pdf)
powder were continuously stirred for 2 h in the dark to achieve the adsorption/desorption equilibrium established. The reaction was initiated by adding H₂O₂ and switching on the lamp.

During the oxidation reactions, 5 mL aliquots were withdrawn and clarified quickly by an outer strong permanent magnet at selected time intervals. The aqueous phase was sampled for analysis. The solid catalyst separated from aqueous phase was rinsed with 5 mL ethanol three times. The rinsed liquid was mixed for analysis. The residual RhB amount is the sum of that in aqueous and solid phases. After the oxidation reaction, the catalyst was repeatedly washed and dried for reuse. Each experiment was achieved in triplicate. All results were expressed as a mean value of the three experiments.

**Analytical procedures**

At given intervals of degradation, a sample was analyzed by UV-vis spectroscopy (Ultrospec 3300 pro, GE Healthcare Bio-Sciences China Ltd) at a wavelength of 554 nm, which is the maximum absorption wavelength of RhB (Xue et al. 2009). The concentration of RhB was converted through the standard curve method of dyes. The pH value of solutions was determined by an Orion 5-Star pH meter (Thermo Scientific, USA). Chemical oxygen demand (COD) was determined by dichromate method. To eliminate the interference of H₂O₂ with COD measurements, the reaction was finally blocked by raising the pH to 9–10, adding MnO₂ and allowing the samples to sit overnight (Neamtu et al. 2004). Hydrogen peroxide was analyzed spectrophotometrically with titanium oxalate (Sellers 1980). Iron leaching after catalytic tests was evaluated by the 1,10-phenantroline spectrophotometric method (Chen et al. 2011).

**RESULTS AND DISCUSSION**

**Characterizations of magnetic bentonite**

The XRD pattern and XPS spectrum of magnetic bentonite with characteristic diffraction peaks indicate the formation of well crystalline single phase Fe₃O₄ nanoparticles (Wan et al. 2015). The SEM micrographs show the Fe₃O₄ nanoparticles with diameters ranging from 40 to 100 nm growing on the Al-B surface with better dispersity and less co-aggregation (Wan et al. 2015). The saturation magnetization value of magnetic bentonite is 30.9 emu g⁻¹ (Wan et al. 2015).

The band gap energy and extent of interaction of substrate with the photocatalyst are two important parameters among others, which ultimately decide the overall photocatalytic activity (Valizadeh et al. 2014; Xavier et al. 2015). In order to correlate these properties of magnetic bentonite with activity, the band gap energy and point of zero charge (pHpbzc) of magnetic bentonite were determined. The UV–vis–DRS of magnetic bentonite, presented in Figure 2(a), shows significant absorption of light on the higher wavelength side, indicating its possible photocatalytic activity under VL irradiation. Additionally, a plot of the transformed Kubelka-Munk function of light energy (αhv)² versus energy (hv) is also shown in Figure 2(a). The estimated band gap energy of magnetic bentonite is 2.1 eV. The catalyst surface will be charged negatively when pH > pHpbzc, positively when pH < pHpbzc and neutrally when pH ≈ pHpbzc. As can be seen from Figure 2(b), the pHpbzc of magnetic bentonite measured 6.8, which compares well with those reported by various researchers for similar catalysts (Giri et al. 2011; Shahamat et al. 2014; Kakavandi et al. 2016). Accordingly, the surface of magnetic bentonite will be either positively or negatively charged at pH < 6.8 or > 6.8, respectively. Due to the variation of surface charge with pH, magnetic bentonite has the advantage of

![Figure 2](https://iwaponline.com/wst/article-pdf/73/10/2345/461432/wst073102345.pdf)
interacting with both anionic and cationic dyes from water to facilitate their photocatalytic degradation.

**VL photocatalytic activity of magnetic bentonite**

The purpose of the current work is to analyze the benefits of VL irradiation in conjunction with a heterogeneous catalyst and H$_2$O$_2$ (VL/magnetic bentonite/H$_2$O$_2$) over the dark system (magnetic bentonite/H$_2$O$_2$). Figure 3 shows the conversion of RhB over the reaction time performed under VL irradiation or dark conditions at initial pH (5.4) of RhB solution. In order to ascertain the effect of various operational variables, Figure 3 also includes the results obtained with (a) VL irradiation in the presence of H$_2$O$_2$ (VL/H$_2$O$_2$), (b) only catalyst, and (c) only VL irradiation. Since we have analyzed the residual RhB amount in both aqueous and solid phase, it can be seen from Figure 3 that the concentration of RhB almost keeps unchanged in 180 min with VL or catalyst only, which indicated that neither the VL nor the catalyst could degrade RhB alone. In the presence of magnetic bentonite and H$_2$O$_2$, the decrease of RhB concentration under VL was much higher than in dark under similar experimental conditions. The total conversion of RhB under VL/magnetic bentonite/H$_2$O$_2$ condition reached 95% compared with only 34% under magnetic bentonite/H$_2$O$_2$. In the meantime, the VL/H$_2$O$_2$ process was carried out with and without the heterogeneous catalyst, which revealed the benefits of the catalyst in the removal of RhB. The total conversion of RhB increased from 19% (absence of catalyst) to 95% (presence of catalyst) after 180 min of reaction time. These results prove the high catalytic activity of the magnetic bentonite in the degradation of RhB aqueous solution, in comparison to a dark Fenton-like process or a VL/H$_2$O$_2$ process. It is also seen that initial photo-degradation up to 120 min is relatively fast, followed by a slow process up to 180 min. Hence, all further experiments to evaluate the photocatalytic efficiency of magnetic bentonite under varying conditions were carried out keeping the reaction time fixed at 120 min.

In order to see the effect of catalyst dose, the experiments were performed by varying the catalyst amount from 0.1 to 1.5 g/L at fixed pH (5.4) and initial RhB concentration (40 mg/L), and the results obtained are depicted in Figure 4(a). As evident, the removal rate of RhB is increased almost linearly with the increase of magnetic bentonite dose up to 0.5 g/L, which is primarily due to availability of a greater amount of active sites on the catalyst surface. On further increase of magnetic bentonite dose, the activity is not linearly increased with the amount of magnetic bentonite, presumably due to aggregation of catalyst, which in turn reduces the number of active sites for photo-Fenton reaction. The other factor of decreased activity could be due to the increased turbidity of reactant solution with the increase of catalyst dose, resulting in a decrease of VL penetration into the reactant solution (Li et al. 2015).

**Figure 3** | Degradation of RhB in different processes (C$_0$ = 40 mg/L, initial pH 5.4, [H$_2$O$_2$] = 50 mM, catalyst loading 0.5 g/L).

**Figure 4** | Effect of magnetic bentonite dose (a) and initial RhB concentration (b) on degradation of RhB (C$_0$ = 40 mg/L, initial pH 5.4, [H$_2$O$_2$] = 50 mM, catalyst loading 0.5 g/L).
In a previous study, we have found that the surface reactions of RhB, including sorption and oxidation by surface -OH, played an important role in determining the rate of the whole reaction (Wan et al. 2013). The effect of initial RhB concentration on the degradation of RhB under VL irradiation in the range 10–100 mg/L is depicted in Figure 4(b). It can be seen that similar results are found in both VL and dark conditions. Increased amount of pollutant may occupy a greater number of iron active sites, which become unavailable for H2O2 and result in a lower -OH generation rate. However, in the presence of VL, the -OH can be also generated in the VL/H2O2 system (Koutantou et al. 2013). Thus, with the increase of initial RhB concentration, the RhB conversion reduced much more slowly in VL than in dark.

The effect of H2O2 concentration on the VL photocatalytic activity of Fe3O4/Al-B was examined by varying initial H2O2 concentration from 0 to 200 mM. As shown in Figure 5, there is little RhB removed without H2O2 in the dark condition. While under VL irradiation, the RhB conversion reached 17.3% without H2O2. The photocatalytic degradation without H2O2 occurs most likely through photoexcitation of Fe3O4/Al-B leading to the electron–hole pairs on its surface, followed by the formation of hydroxyl radical (-OH) by the decomposition of the water, which leads to the degradation of RhB (Solomon et al. 2012):

\[
\text{Fe}_3\text{O}_4/\text{Al-B} + h\nu \rightarrow \text{Fe}_3\text{O}_4/\text{Al-B(e}^-\text{CB + h}^+\text{VB}) (1)
\]

\[
\text{H}_2\text{O} + \text{Fe}_3\text{O}_4/\text{Al-B(h}^+\text{VB)} \rightarrow -\text{OH} + \text{H}^+ + \text{Fe}_3\text{O}_4/\text{Al-B} (2)
\]

\[
-\text{OH} + \text{RhB} \rightarrow \text{degradation products} (3)
\]

When H2O2 was added to the system, the formation of hydroxyl radical was accelerated significantly, which due to the decomposition of H2O2 by electrons (Koutantou et al. 2013):

\[
\text{Fe}_3\text{O}_4/\text{Al-B(e}^-\text{CB)} + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \cdot\text{OH}^- + \text{Fe}_3\text{O}_4/\text{Al-B} (4)
\]

\[
\text{H}_2\text{O}_2 + e^- \rightarrow -\text{OH} + \text{OH}^- (5)
\]

While in the dark condition, the hydroxyl radical was primarily generated on the surface of Fe3O4/Al-B as given below (Xue et al. 2009; Garrido-Ramírez et al. 2010):

\[
\equiv\text{Fe}^{II} + \text{H}_2\text{O}_2 \rightarrow \equiv\text{Fe}^{II}(\text{H}_2\text{O}_2) (6)
\]

\[
\equiv\text{Fe}^{II}(\text{H}_2\text{O}_2) \rightarrow \equiv\text{Fe}^{III} + \text{OH}^- + \cdot\text{OH} (7)
\]

On the other hand, when the reaction system is exposed to the VL irradiation, the dye molecules of RhB can absorb VL energy and be activated to the excited state via Equation (8) (Gao et al. 2015). Then the excited dye molecule can transfer an electron to \equiv\text{Fe}(III) to generate \equiv\text{Fe}(II), which can promote Fe(III)/Fe(II) cycle in Fe3O4, as given in Equation (9):

\[
\text{RhB} + h\nu \rightarrow \text{RhB}^* (8)
\]

\[
\text{RhB}^* + \equiv\text{Fe}^{III} \rightarrow \equiv\text{Fe}^{II} + \text{RhB}^{**} (9)
\]

\[
\cdot\text{OH} + \text{RhB}/\text{RhB}^{**} \rightarrow \text{degradation products} (10)
\]

As can be seen, it is the synergistic effect between Fe3O4/Al-B and VL that leads to the efficient generation of hydroxyl radical and the high degradation efficiency of RhB. In a previous study (Wan et al. 2015), the removal rate of RhB could reach 46.8% when H2O2 concentration was 200 mM in the dark condition, while in this study, 84.5% of RhB can be removed with only 50 mM of H2O2 under the VL irradiation. The utilization of H2O2 is promoted remarkably in the presence of VL irradiation.

It can be seen from Figure 5 that the RhB conversion increases observably when H2O2 concentration increases from 0 to 50 mM in the condition of VL irradiation, which is primarily attributed to the increase of hydroxyl radical. However, further increase of H2O2 beyond 50 mM, results in a decrease of RhB removal, primarily due to the -OH
radical scavenging by H$_2$O$_2$ leading to the formation of less reactive hydroperoxyl (•OOH) (Xue et al. 2009):

\[ H_2O_2 + •OH \rightarrow H_2O + •OOH \] (11)

In order to investigate the degradation of RhB during heterogeneous photocatalytic process, the removal of COD was also monitored and illustrated in Figure 6(a). As can be expected, dark degradation process led to less COD removal (9%). This can be indirectly verified by the fact that less than 13% H$_2$O$_2$ was decomposed in this case. Under the irradiation of VL, the COD removal efficiency was observed to increase to 87.8% after 180 min reaction, and only 47% of H$_2$O$_2$ remained in the system. Defining the efficiency of H$_2$O$_2$ as the amount COD converted per unit mass of H$_2$O$_2$ decomposed:

\[ E(\%) = \frac{\Delta COD}{0.47 \times \Delta [H_2O_2]} \times 100 \] (12)

where $\Delta$COD is the removable COD value (mg/L), $\Delta$[H$_2$O$_2$] is the decomposed H$_2$O$_2$ value (mg/L), and 0.47 is the conversion factor (Gao et al. 2015). The E values of VL and dark process are calculated to be 38.3% and 15.9%, respectively. As anticipated, the efficiency of H$_2$O$_2$ in VL process is much higher than that of dark process, which is in conformity with the analysis above.

Figure 6(b) shows the UV-vis spectra recorded during the degradation of RhB. As can be seen, the characteristic absorption peak of RhB at 554 nm is due to the color of RhB solution (Wang et al. 2014). The results show that the intensity of absorption peaks decreases gradually with the reaction proceeding, indicating the RhB molecules were gradually broken under the attack of •OH. However, the absorption peaks did not completely disappear, related to the uncompleted destruction of some aromatic group, which well corresponds to the COD result. Besides, it also can be seen from Figure 6(b) that the magnetic bentonite catalyst can be easily separated with the help of a common magnet after reaction. Attractive results were already mentioned for a Fe-supported bentonite used as heterogeneous catalyst for the photo-Fenton removal of RhB (Gao et al. 2015). Here, the magnetic bentonite provides more efficient photocatalytic effect as well as better separability.

**Stability of magnetic bentonite in VL photocatalytic process**

The stability of magnetic bentonite was investigated by means of recycling experiments. The magnetic bentonite catalyst was repeatedly applied to remove RhB by successive batch experiments. After each run, magnetic bentonite remaining in the reaction solution was magnetically separated and then oven dried at 100°C overnight. The same amount of dried powder was used as a catalyst for the next batch experiment. As can be observed in Figure 7, Fe$_3$O$_4$/Al-B was
capable of being reutilized for at least four cycles, and the reused catalyst almost retained efficient photocatalytic activity. After the fourth cycle, the total conversion of RhB could reach as high as 92%.

To evaluate the contribution of the homogeneous photocatalytic reaction catalyzed by leached iron from the solid to aqueous media, the solid catalyst was removed after the adsorption stage by means of magnetic separation. And then, an equal amount of $H_2O_2$ was added into the supernatant to start the reaction under the irradiation of VL. It can be clearly observed from Figure 7 that the homogeneous photocatalytic process resulted in a very limited removal of RhB. It indicated that the RhB degradation was mainly attributed to the heterogeneous photocatalytic reaction.

In addition to RhB removal efficiency, the COD removal efficiency and the leached iron concentration at the end of each cycle were also monitored, and the results were shown in Figure 8. It demonstrated that $Fe_3O_4/Al-B$ remained high photocatalytic activity and stability, with 82.7% of the COD removal being achieved and 0.35 mg/L of iron being leached after the fourth cycle. The results above indicate that $Fe_3O_4/Al-B$ could behave as a stable and efficient heterogeneous photocatalyst for removal of RhB in the presence of VL irradiation and $H_2O_2$.

CONCLUSION

Magnetic bentonite catalyst $Fe_3O_4/Al-B$ was found to be an effective photocatalyst for degradation of RhB under VL irradiation. More than 95% of 40 mg/L RhB was converted within 3 h under VL with a catalyst dose of 0.5 g/L. While in the absence of VL, only 34% of RhB was converted under identical conditions. The degradation rate of RhB was found to be decreased with the increase of initial dye concentration. The efficiency of $H_2O_2$ in VL process was much higher than that of dark process. More importantly, the magnetic bentonite catalyst can be easily separated from the reactant solution using an external magnetic field and can be used in cycles without any significant decrease in its activity. Future work will focus on toxicity issues so that the effluent could be safely discharged into receiving water bodies.

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