

Magnetically Recoverable Fe₃O₄-Modified Bentonite as a Heterogeneous Catalyst of H₂O₂ Activation for Efficient Degradation of Methyl Orange

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Abstract

Clay-based materials provide an efficient and environmentally benign strategy for heterogeneous catalytic oxidation. In this study, a novel Fe₃O₄-modified bentonite (Fe₃O₄-BT) catalyst was obtained by using the hydrothermal method. The catalyst was characterized by transmission electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy. The Fe₃O₄ nanoparticles mainly existed on the surface and in the outermost pores of the BT, thus exhibiting improved dispersion and lower levels of aggregation. The catalytic activity of Fe₃O₄-BT was assessed in the degradation of methyl orange (MO) in the presence of H₂O₂. Fe₃O₄-BT showed higher MO degradation efficiency than both bare Fe₃O₄ and BT. The initial H₂O₂ concentration, catalyst loading, temperature, and initial pH were optimized for the degradation of MO. The MO decolorization rate was still ~90% after the Fe₃O₄-BT was reused five times. Additionally, the degree of ferric ion dissolution was only 3.23×10^{-3} mg/L after 60 min. This novel catalyst was easily reclaimed by simple magnetic separation and exhibited good reusability and stability.

Keywords: Fe₃O₄-bentonite/H₂O₂, magnetic, heterogeneous Fenton catalysts, methyl orange, decolorization ratio

Introduction

The dyeing and printing industries result in the discharge of huge amounts of dyestuff pollutants into water bodies. The removal of these pollutants is both difficult and important because of their intense color, potential mutagenicity, and resistance to biochemical degradation

[1]. Various treatment strategies such as adsorption, coagulation, oxidation, and electrochemical methods have been used for the remediation of dye wastewater [2-4]. Of these, advanced oxidation processes (AOPs) are powerful and attractive techniques for the treatment of high-organic-loading and non-biodegradable wastewater [5-6]. Fenton's reagent is commonly employed in AOP methodology as it degrades nearly all organic compounds owing to its ability to form highly reactive free radicals [7-8]. However, there are several limitations to its application. For example,

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its production is cost-intensive and causes secondary pollution [9].

Recently, low-cost minerals or inorganic materials with high degradation efficiencies have attracted increasing interest. As natural microporous substrates, bentonites (BTs) show interesting properties in adsorption and catalysis because of their low-charge-density surfaces [10]. Furthermore, their weak forces and charge deficits can lead to inorganic cations such as Na^+ and Ca^{2+} ions penetrating into their layers to balance the negative charge [4]. Magnetite (Fe_3O_4) nanoparticles have also attracted increasing attention because Fe_3O_4 contains both Fe^{2+} and Fe^{3+} ions, which are crucial cations for initiation of the Fenton reaction according to the classical Haber-Weiss mechanism [11]. Moreover, when in the inverse spinel crystal structure form, the electrons can transfer between Fe^{2+} and Fe^{3+} in the octahedral sites, allowing the Fe species to be reversibly oxidized and reduced while maintaining the same structure [12-13]. Additionally, Fe_3O_4 nanoparticles are magnetic and can be easily separated from spent reaction solutions by magnetic separation. Thus, combining BT with Fe_3O_4 as a catalyst for Fenton-like reactions is a promising strategy for the decontamination of wastewater [14].

In this work, $\text{Fe}_3\text{O}_4/\text{BT}$ was synthesized by a hydrothermal method and characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR). The catalytic properties of the obtained heterogeneous catalysts were assessed in the peroxide oxidation of methyl orange (MO). The effects of catalyst loading, initial pH, reaction temperature, and oxidant concentration were assessed. Furthermore, the stability and reusability of the catalysts, as well as the degradation mechanism, were also investigated.

Experimental Procedures

Materials and Chemicals

BT was purchased from Heishan Wancheng Bentonite Co., Ltd., Liaoning, China. The BT sample was ground and passed through a 120-mesh sieve prior to use. Its cation-exchange capacity (CEC) was 108.4 mmol/100 g BT. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NaOAc, ethylene glycol (EG), polyethylene glycol 200 (PEG200), and epichlorohydrin (ECH) were analytical grade reagents obtained from Tianjin Kernel Chemical reagent Co., Ltd. (Tianjin, China). All the chemicals used in this study were analytical reagent grade and were used without further purification.

The $\text{Fe}_3\text{O}_4/\text{BT}$ nanocomposite was synthesized by hydrothermal reaction of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the presence of BT. In a typical process, a mixture of 2.16 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 5.76 g NaOAc, and 1.6 g PEG 200 in 60 mL EG was stirred for 30 min. Then, 0.5 g BT and 1 mL ECH were added to the homogeneous solution and the mixture was stirred at 55°C for 2 h. The mixture was then transferred to a 100 mL autoclave and heated to 200°C for 12 h before

cooling to room temperature, whereupon a dark black solution formed that was then filtered. The precipitate was washed with distilled water/ethanol (1:1) and dried under vacuum at 80°C to obtain the $\text{Fe}_3\text{O}_4/\text{BT}$ nanocomposite.

Characterizations and Measurements

The FTIR spectra were recorded between 400 and 4,000 cm^{-1} from KBr pellets using a Tensor 27 spectrometer (Bruker, Germany). XRD patterns were obtained using a Rigaku Max 2550VB+/PC instrument (Japan) at a scan speed of 8°/min in a 2θ range of 5-80°. TEM was performed with a JEM-2100 high-resolution transmission electron microscope (JEOL, Japan) at 300 kV.

Batch Experiments

Batch heterogeneous Fenton experiments for the removal of MO as a model wastewater pollutant were carried out in a 250 mL glass flask reactor (75 mL actual reaction volume) under continuous magnetic mechanical stirring. Typically, an appropriate amount of catalyst suspended in water (0.5 g/L) was placed into the glass reactor. The system was then heated to the appropriate temperature and MO (100 mg/L) and hydrogen peroxide (5.66 g/L) were added to the reactor. Solution samples (1.0 mL) were taken at regular time intervals and, following solid removal, quenched by adding 0.5 mL methanol. The time-dependent concentration of the organic pollutants in the supernatant was analyzed using a UV-Vis spectrophotometer. MO mineralization was followed by measuring the total organic carbon (TOC) with a Shimadzu TOC-5000A analyzer. The TOC results presented are the average of at least three measurements with an accuracy of $\pm 5\%$.

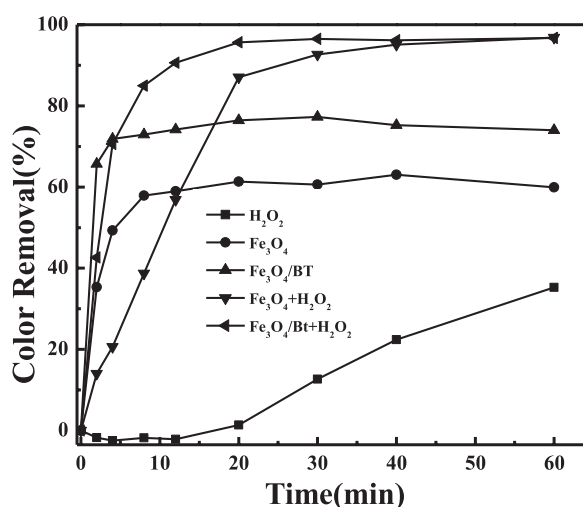


Fig. 1. MO degradation with various catalysts. Reaction conditions: MO = 100 mg/L, H_2O_2 = 5.66 g/L, catalyst = 0.50 g/L, T = 25°C, pH = 3.

Results and Discussion

Catalyst Evaluation

H_2O_2 , Fe_3O_4 , Fe_3O_4 -BT, Fe_3O_4/H_2O_2 , and Fe_3O_4 -BT/ H_2O_2 were assessed for the degradation of MO, and the results are shown in Fig. 1. The decolorization rates of MO in the presence of H_2O_2 , Fe_3O_4 , Fe_3O_4 -BT, Fe_3O_4/H_2O_2 , and Fe_3O_4 -BT/ H_2O_2 are 35.26, 59.93, 74.02, 96.72, and 96.72%, respectively. Fe_3O_4 -doped BT rapidly destroys the chromophore structure of the dye. A possible reason for this is that Fe_3O_4 provides Fe for the catalytic reaction and BT enhances MO adsorption [4]. Furthermore, the degradation of MO over Fe_3O_4 -BT/ H_2O_2 is complete after 20 min, while Fe_3O_4/H_2O_2 needs 40 min. Other samples only slightly improve MO degradation. Thus, Fe_3O_4 -modified BT exhibits the highest activity. In order to study the effects of the Fe_3O_4 species on the BT, the samples were analyzed with XRD, FTIR, and TEM.

Catalyst Characterization

The XRD patterns for Fe_3O_4 , BT, and Fe_3O_4 -BT are shown in Fig. 2. BT is mainly composed of montmorillonite (JCPDS file no. 29-1498) and silicon dioxide (JCPDS file No. 46-1045). An interlamellar spacing of 1.16 nm was calculated using Scherer's equation for the (001) diffraction line (6.03°), indicating that the BT is of the Na-based type. The reflections for Fe_3O_4 can be indexed as cubic phase Fe_3O_4 (JCPDS file No.19-0629). In the XRD pattern for the Fe_3O_4 -BT nanocomposite, the reflections corresponding to BT are present at $2\theta = 6.03$, 19.80 , 28.50 , and 35.22° [4], and the reflections at 19.80 , 28.50 , and 35.22° are of lower intensity than those in the pure BT. Peaks for Fe_3O_4 at $2\theta = 34.98$, 36.06 , 43.25 , 57.31 , and 61.98° are clearly observed [15-16], indicating that Fe_3O_4 particles are mainly dispersed on the external surfaces of the BT. Additionally, loading Fe_3O_4 onto the BT changes its d_{001} value from 1.47 to 1.16 nm, indicating that Mg^{2+} and Ca^{2+} metal ions are replaced by Fe ions that intercalate into the silicate layers. This material structure

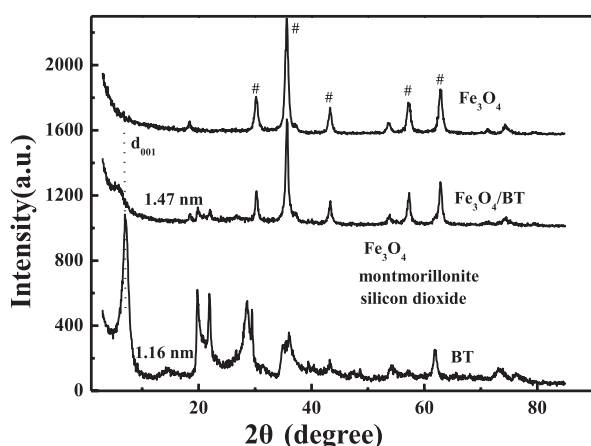


Fig. 2. XRD patterns of BT, Fe_3O_4 , and Fe_3O_4 -BT.

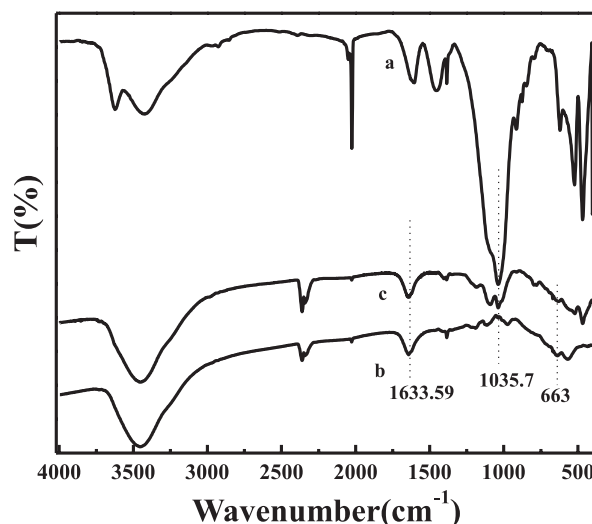


Fig. 3. FTIR spectra of a) BT, b) Fe_3O_4 , and c) Fe_3O_4 -BT.

provides more $\bullet OH$ radicals after the introduction of H_2O_2 because of their more effective contact with Fe_3O_4 , enhancing catalytic efficiency. Furthermore, the material also maintains its good magnetic responsiveness and recyclability.

FTIR spectroscopy was employed to further confirm the structure of the nanocomposites (Fig. 3). The absorption bands at $3,417.63$, $3,450.41$, and $1,633.59$ cm^{-1} can be ascribed to vibrations of water molecules. The absorption bands at $1,035.7$ and 791 cm^{-1} are Si-O stretching vibrations. The characteristic bands at 576.68 and 663 cm^{-1} are due to Fe-O stretching vibrations. The intensities of the Si-O bands in the Fe_3O_4 -BT nanocomposite are weaker than those of BT, indicating that the Fe-O bonds interact with the Si-O bonds on the surface of the BT [17]. Thus, Fe_3O_4 is probably bonded to the surface of the BT during the synthesis procedure.

The morphology of the prepared samples was also studied using TEM. Fig. 4b) shows the presence of hollow, spherical, monodispersed Fe_3O_4 particles with a uniform size of ~ 200 nm, allowing for improved adsorption of MO. However, as seen from the image of Fe_3O_4 -BT (Fig. 4c), the spheres tend to be non-uniform and the particles become smaller upon the addition of BT. TEM micrographs of the Fe_3O_4 -BT composite show that Fe_3O_4 is uniformly dispersed on the BT surface. These results are in good agreement with the XRD observations.

Catalytic Behavior

Decreasing the initial pH leads to a much higher degradation rate. A high MO removal efficiency is achieved at pH 3 (Fig. 5). This can be explained by the increased production of oxidizing species at higher pH. However, excessive acidity can cause equipment corrosion, so an optimum pH of 3 was employed.

The effect of H_2O_2 was analyzed by varying its initial concentration between 1.42 and 11.33 g/L (Fig. 6). The

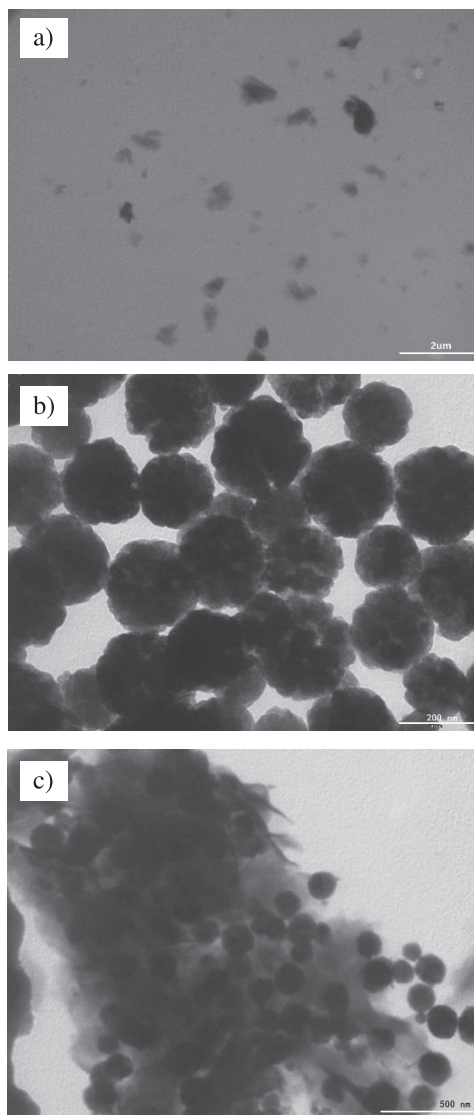


Fig. 4. TEM images of a) BT, b) Fe_3O_4 , and c) Fe_3O_4 -BT.

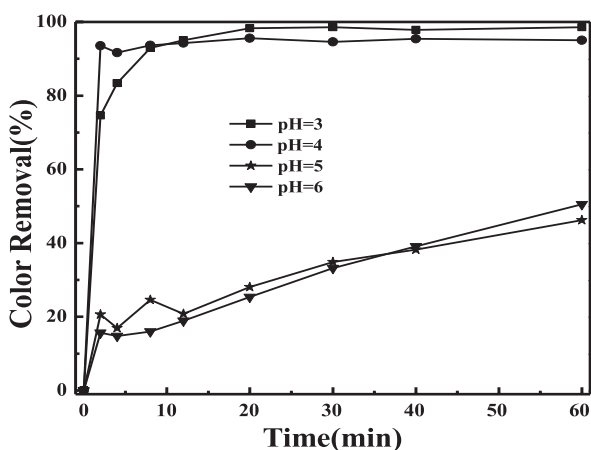


Fig. 5. Effect of initial pH for MO degradation over Fe_3O_4 -BT/ H_2O_2 . Reaction conditions: MO = 100 mg/L, H_2O_2 = 11.33 g/L, catalyst = 1.0 g/L, T = 45°C.

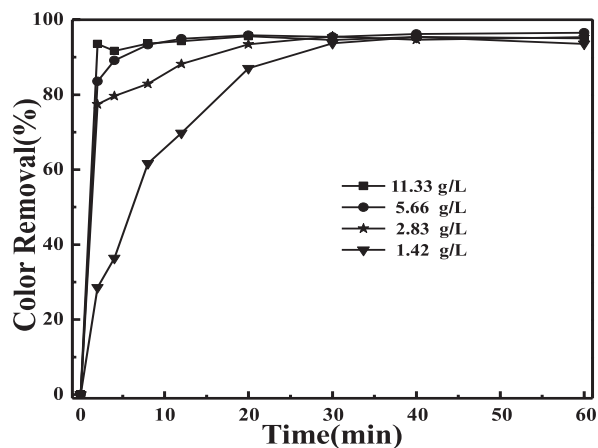


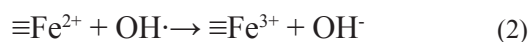
Fig. 6. Influence of H_2O_2 content on MO removal. Reaction conditions: MO = 100 mg/L, catalyst = 1.0 g/L, T = 45°C, pH = 3.

MO degradation rate increases significantly when the H_2O_2 concentration increases from 1.42 to 11.33 g/L. Clearly, the degradation process is accelerated when the H_2O_2 concentration increases to 5.66 g/L. However, the rate constant is slightly reduced at a higher H_2O_2 concentration (11.33 g/L). A possible reason for this phenomenon is that the increased H_2O_2 concentration induces homogeneous catalytic oxidation. Since MO degradation is directly related to the concentration of the $\cdot\text{OH}$ produced by the catalytic decomposition of H_2O_2 , increased MO decomposition is expected at higher H_2O_2 concentration. However, no further improvement occurs when the H_2O_2 concentration increases to 11.33 g/L, which can be explained by the scavenging of $\cdot\text{OH}$ by H_2O_2 [18-19]:



The oxidation potential of $\cdot\text{OOH}$ is much lower than that of $\cdot\text{OH}$. Therefore, this slows the reaction. Thus, 5.66 g/L of H_2O_2 was deemed optimal in this study.

As expected, the MO degradation rate increases dramatically as the amount of catalyst employed increases from 0.25 to 1.5 g/L (Fig. 7) owing to the increased number of active sites for the formation of $\cdot\text{OH}$ and, perhaps equally importantly, for MO adsorption and the supply of Fe ions. However, when the catalyst addition is further increased to 1.5 g/L, the degradation of MO does not improve but slightly decreases. This may be due to the agglomeration of nanoparticles and the scavenging of hydroxyl radicals or other radicals by Fe species through the undesirable reactions (2) and (3) [20-21]:



The degradation of MO by Fe_3O_4 -BT is dramatically improved with increasing reaction temperature, as seen

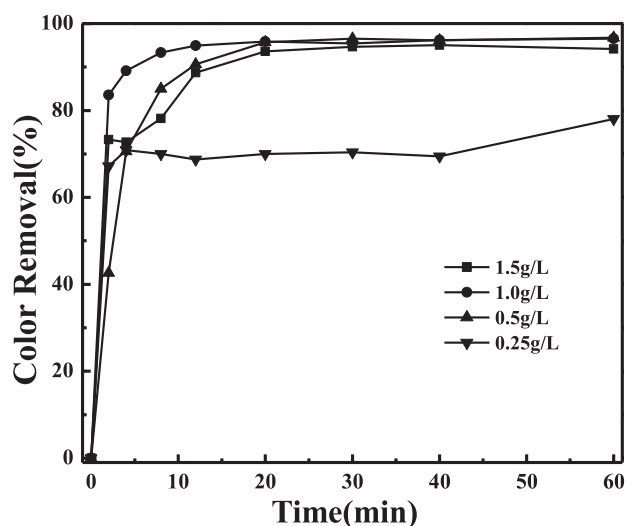


Fig. 7. Influence of Fe₃O₄-BT content on MO removal. Reaction conditions: MO = 100 mg/L, H₂O₂ = 5.66 g/L, T = 45°C, pH = 3.

from Fig. 8. According to a previous study [4], the change in enthalpy upon the oxidative degradation of MO is positive while the process is endothermic. Accordingly, an increase in reaction temperature is beneficial for the degradation of MO. The optimum temperature is 45°C.

During the decolorization of MO, reaction intermediates that may be long-lived and even more toxic than the parent compound can form. TOC values are similar for BT/H₂O₂, Fe₃O₄/H₂O₂, and Fe₃O₄-BT (Fig. 9) and slightly lower than those shown for the corresponding heterogeneous Fenton systems. However, a much higher value (~75%) is obtained with the introduction of H₂O₂ to Fe₃O₄-BT. The highest MO degradation (~97%) is also obtained with this system, although not all degraded MO is mineralized. These interesting results indicate that Fe₃O₄-BT is a good catalyst for MO removal by homogeneous Fenton

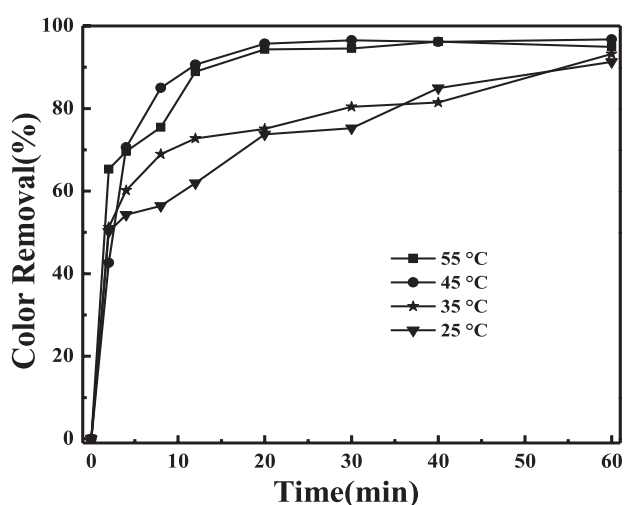


Fig. 8. Influence of reaction temperature on MO removal. Reaction conditions: MO = 100 mg/L, H₂O₂ = 5.66 g/L, catalyst = 0.5 g/L, pH = 3.

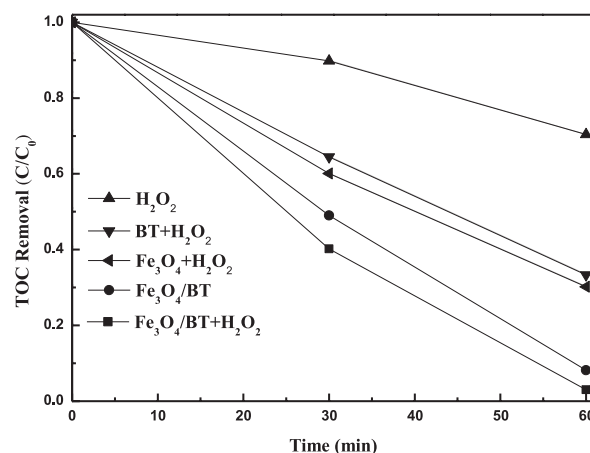


Fig. 9. TOC removal with various catalysts. Reaction conditions: MO = 100 mg/L, H₂O₂ = 5.66 g/L, catalyst = 0.50 g/L, T = 45°C, pH = 3.

oxidation. This catalyst causes H₂O₂ to generate many hydroxyl radicals, and may therefore exhibit a synergic effect of H₂O₂ oxidation and Fe₃O₄-BT adsorption, which is favorable for attacking aromatic compounds and thus improving MO degradation.

Reusability of Catalyst

The reusability of a heterogeneous catalyst is crucial for its practical application. To evaluate the catalytic stability of the Fe₃O₄-BT catalyst in the H₂O₂ oxidation system, the particles were repeatedly recovered to perform successive MO degradation tests. The obtained results are shown in Fig. 11. An MO decolorization efficiency of 89.94% is achieved after the fifth run.

Additionally, it is believed that the ferric content of a catalyst can undergo microphase separation, leading to deactivation. Consequently, it is necessary to evaluate the ferric content after the reaction. The ferric content of Fe₃O₄-

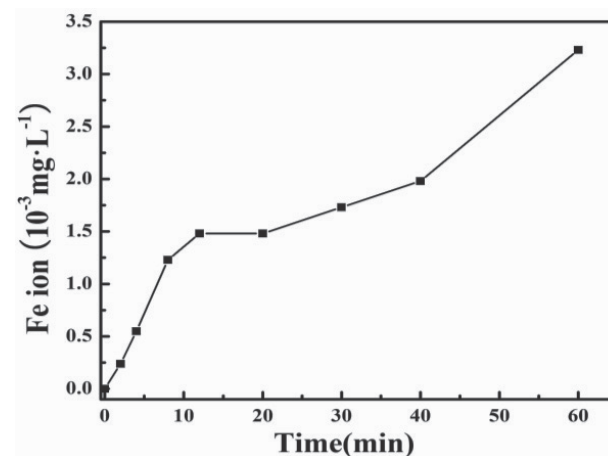


Fig. 10. Amount of dissolved Ferric ion in solution. Reaction conditions: MO = 100 mg/L, H₂O₂ = 5.66 g/L, catalyst = 0.50 g/L, T = 45°C, pH = 3.

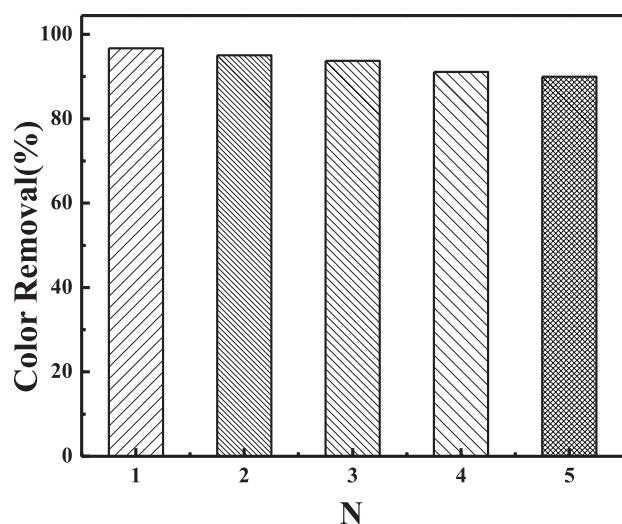
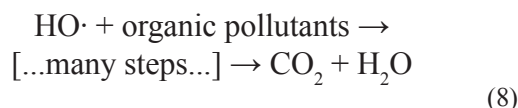
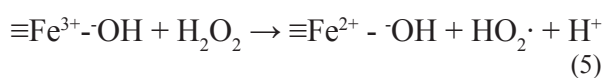
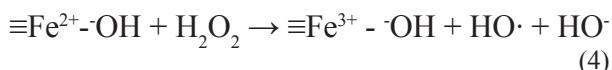


Fig. 11. Reuse of Fe₃O₄-BT. Reaction conditions: MO = 100 mg/L, H₂O₂ = 5.66 g/L, catalyst = 0.50 g/L, T = 45°C, pH = 3.

BT was measured before and after the catalytic reaction using inductively coupled plasma elemental analysis. The ferric ion dissolution is only 3.23×10^{-3} mg/L after a 60 min reaction (Fig. 10.), indicating that Fe₃O₄-BT has good chemical stability and reusability.

Reaction Mechanism

Many previous studies [22-25] have shown that the primary HO• radical plays a significant role in the oxidation of organic compounds. Catalytic H₂O₂ activation through the reduction of Fe³⁺ to Fe²⁺ is thermodynamically favorable. The binding of ≡Fe²⁺ to surface hydroxyl groups (OH) through the dissociative adsorption of water molecules on the Fe₃O₄-BT surface is expected to change with the oxidation state of the surface metal [26-27]. The ≡Fe²⁺ species on the Fe₃O₄-BT surface react with H₂O₂ to produce surface-bound HO•, and some more ≡Fe³⁺ species can be produced from the formed ≡Fe²⁺ species upon reaction with H₂O₂ (Eq. (4)). ≡Fe³⁺ is then reduced back to ≡Fe²⁺ by another molecule of H₂O₂, forming a hydroperoxyl radical and a proton (Eq. (5)). But the reactions represented by Eq. (6) and Eq. (7) efficiently consume hydroxyl radicals. Therefore, in practical applications of the Fenton reaction, catalytic amounts of iron salts are typically used and H₂O₂ is added slowly to the system. This is one of the reasons that Fe₃O₄-BT exhibits good stability and recyclability.



Conclusions

A novel heterogeneous Fenton catalyst (Fe₃O₄-BT) has been synthesized via a hydrothermal method and characterized by XRD, FTIR, and TEM. The results show that the Fe₃O₄ pillaring process leads to an increase of the *d*₀₀₁ spacing. Furthermore, the pure Fe₃O₄ synthesized is distributed uniformly on the surface of the BT. The optimum reaction conditions for the degradation of MO were found to be an initial pH of 3, Fe₃O₄-BT dosage of 0.5 g/L, an initial H₂O₂ concentration of 5.66 g/L, an initial methyl orange concentration of 100 mg/L, and a reaction temperature of 45°C. The Fe₃O₄-BT was reused five times by magnetic separation, and maintained an MO decolorization rate of 89.94%. Additionally, the quantity of ferric ion dissolution was only 3.23×10^{-3} mg/L after 60 min, which is insignificant in comparison to the amount of Fe₃O₄/BT added. The results confirm that Fe₃O₄-BT exhibits good catalytic activity and stability.

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