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,
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 Ca2+ ions penetrating into their layers to balance the negative charge [4]. Magnetite (Fe3O4) nanoparticles have also attracted increasing attention because Fe3O4 contains both Fe2+ and Fe3+ 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 Fe2+ and Fe3+ in the octahedral sites, allowing the Fe species to be reversibly oxidized and reduced while maintaining the same structure [12-13]. Additionally, Fe3O4 nanoparticles are magnetic and can be easily separated from spent reaction solutions by magnetic separation. Thus, combining BT with Fe3O4 as a catalyst for Fenton-like reactions is a promising strategy for the decontamination of wastewater [14].

In this work, Fe3O4/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., Liaooning, 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. FeCl3·6H2O, NaOAc, ethylene glycol (EG), polyethylene glycol 200 (PEG200), and epichlorohydrin (ECH) were analytical grade reagents obtained from Tianjin Kermel Chemical reagent Co., Ltd. (Tianjin, China). All the chemicals used in this study were analytical reagent grade and were used without further purification.

The Fe3O4/BT nanocomposite was synthesized by a hydrothermal method and characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR).

**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 8º/min in a 2θ range of 5-80º. 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 assessed 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 ±5%.

**Fig. 1. MO degradation with various catalysts. Reaction conditions: MO = 100 mg/L, H2O2 = 5.66 g/L, catalyst = 0.50 g/L, T = 25ºC, 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 (6.03º), 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 2θ = 6.03, 19.80, 28.50, and 35.22º [4], and the reflections at 19.80, 28.50, and 35.22º are of lower intensity than those in the pure BT. Peaks for Fe_3O_4 at 2θ = 34.98, 36.06, 43.25, 57.31, and 61.98º 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 provides more •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
MO degradation rate increases significantly when the H$_2$O$_2$ concentration increases from 1.42 to 11.33 g/L. Clearly, the degradation process is accelerated when the H$_2$O$_2$ concentration increases to 5.66 g/L. However, the rate constant is slightly reduced at a higher H$_2$O$_2$ concentration (11.33 g/L). A possible reason for this phenomenon is that the increased H$_2$O$_2$ concentration induces homogeneous catalytic oxidation. Since MO degradation is directly related to the concentration of •OH produced by the catalytic decomposition of H$_2$O$_2$, increased MO decomposition is expected at higher H$_2$O$_2$ concentration. However, no further improvement occurs when the H$_2$O$_2$ concentration increases to 11.33 g/L, which can be explained by the scavenging of •OH by H$_2$O$_2$ [18-19]:

$$H_2O_2 + •OH \rightarrow H_2O + •OOH$$  \hspace{1cm} (1)

The oxidation potential of •OOH is much lower than that of •OH. Therefore, this slows the reaction. Thus, 5.66 g/L of H$_2$O$_2$ 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 •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]:

$$≡Fe^{2+} + OH\rightarrow ≡Fe^{3+} + OH^-$$  \hspace{1cm} (2)

$$≡Fe^{3+} + •OOH \rightarrow ≡Fe^{3+} + OOH^-$$  \hspace{1cm} (3)

The degradation of MO by Fe$_3$O$_4$-BT is dramatically improved with increasing reaction temperature, as seen in Fig. 4. TEM images of a) BT, b) Fe$_3$O$_4$, and c) Fe$_3$O$_4$-BT.

Fig. 4. TEM images of a) BT, b) Fe$_3$O$_4$, and c) Fe$_3$O$_4$-BT.

Fig. 5. Effect of initial pH for MO degradation over Fe$_3$O$_4$-BT/ H$_2$O$_2$. Reaction conditions: MO = 100 mg/L, H$_2$O$_2$ = 11.33 g/L, catalyst = 1.0 g/L, T = 45ºC.

Fig. 6. Influence of H$_2$O$_2$ content on MO removal. Reaction conditions: MO = 100 mg/L, catalyst = 1.0 g/L, T = 45ºC, 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 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 decolonization 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-
BT was measured before and after the catalytic reaction using inductively coupled plasma elemental analysis. The ferric ion dissolution is only $3.23 \times 10^{-3}$ mg/L after a 60 min reaction (Fig. 10.), indicating that Fe$_3$O$_4$-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 H$_2$O$_2$ activation through the reduction of Fe$^{3+}$ to Fe$^{2+}$ is thermodynamically favorable. The binding of $\equiv$Fe$^{2+}$ to surface hydroxyl groups (OH) through the dissociative adsorption of water molecules on the Fe$_3$O$_4$-BT surface is expected to change with the oxidation state of the surface metal [26-27]. The $\equiv$Fe$^{2+}$ species on the Fe$_3$O$_4$-BT surface react with H$_2$O$_2$ to produce surface-bound HO•, and some more $\equiv$Fe$^{3+}$ species can be produced from the formed $\equiv$Fe$^{2+}$ species upon reaction with H$_2$O$_2$ (Eq. (4)). $\equiv$Fe$^{3+}$ is then reduced back to $\equiv$Fe$^{2+}$ by another molecule of H$_2$O$_2$, 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 H$_2$O$_2$ is added slowly to the system. This is one of the reasons that Fe$_3$O$_4$-BT exhibits good catalytic activity and stability.

$$\equiv\text{Fe}^{2+} \cdot \text{OH} + \text{H}_2\text{O}_2 \rightarrow \equiv\text{Fe}^{3+} \cdot \text{OH} + \text{HO}^- + \text{HO}^+ \quad (4)$$

$$\equiv\text{Fe}^{3+} \cdot \text{OH} + \text{H}_2\text{O}_2 \rightarrow \equiv\text{Fe}^{2+} \cdot \text{OH} + \text{HO}^- + \text{H}^+ \quad (5)$$

$$\text{HO}^- + \text{HO}^- \rightarrow \text{H}_2\text{O}_2 \quad (6)$$

$$\text{HO}^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (7)$$

$$\text{HO}^- + \text{organic pollutants} \rightarrow \text{[...many steps...]} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (8)$$

**Conclusions**

A novel heterogeneous Fenton catalyst (Fe$_3$O$_4$-BT) has been synthesized via a hydrothermal method and characterized by XRD, FTIR, and TEM. The results show that the Fe$_3$O$_4$ pillaring process leads to an increase of the d$_{001}$ spacing. Furthermore, the pure Fe$_3$O$_4$ 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, Fe$_3$O$_4$-BT dosage of 0.5 g/L, an initial H$_2$O$_2$ concentration of 5.66 g/L, an initial methyl orange concentration of 100 mg/L, and a reaction temperature of 45°C. The Fe$_3$O$_4$-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 $3.23 \times 10^{-3}$ mg/L after 60 min, which is insignificant in comparison to the amount of Fe$_3$O$_4$/BT added. The results confirm that Fe$_3$O$_4$-BT exhibits good catalytic activity and stability.

**References**

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