Fe$_2$O$_3$-modified activated clay as Heterogeneous Catalyst for Fenton-like oxidation of the removal of methylene blue in wastewater

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Abstract. The Fe$_2$O$_3$-modified activated clay catalysts were prepared by precipitation method and were characterized by SEM, and XRD techniques. The catalysts were used as heterogeneous Fenton catalysts for degradation of simulated methylene blue solution. The effects of initial pH value, H$_2$O$_2$ dosage, and catalyst dosage and reaction temperature on methylene blue removal rate were investigated. The results showed that, under the optimal conditions of initial pH value 3.0, H$_2$O$_2$ dosage 1200 mg/L, catalyst dosage 6.2 g/L and reaction temperature 30℃, 98.3% of decolorization efficiency was achieved within 60 min in a batch process. The results indicated that Fe$_2$O$_3$-modified activated clay was a promising catalyst for the heterogeneous Fenton system.

1. Introduction

A variety of dyes are used in many industries such as the textile, leather, paper, food, plastics, cosmetic s and mineral processing industries [1]. Wastewater from these industrial effluents, when containing a large amount of such dyes, not only causes water coloring, but also poses a threat to aquatic organisms. Dyes pose a serious threat to human health and the environment due to their toxicity and potential carcinogenic properties [2]. Therefore, their removal from contaminated water bodies using efficient processes has become very important [3]. However, it is extremely difficult to treat modern dyes that are resistant to sunlight, water and other harsh conditions for a long period of time. In fact, many dyes have developed their chemical stability and are not readily biodegradable. Many physical, chemical and biological methods have been used for the treatment of wastewater contaminated with dyes in different industries [4-7]. However, physical and biological methods are not advantageous because they simply transfer contaminants from one stage to another. Moreover, the high cost of the equipment involved in these processes limits their actual large-scale implementation. Alternatively, advanced oxidation processes (AOPs) have been developed and become a common method of wastewater treatment, especially for the deep treatment of non-biodegradable and stubborn organic pollutants [8,9]. In particular, one of the most intensively studied AOPs is Fenton technology. Fenton technology is considered one of the most promising techniques because of its high efficiency, non-selectively, low toxicity and low commercial cost [10]. However, the classical homogeneous Fenton process has disadvantages such as a narrow working pH (pH 2-4), formation of iron-containing precipitates, and inability to regenerate the catalyst [1
To overcome these disadvantages, heterogeneous Fenton-like processes using solid catalysts have been employed, where the active phase is supported by porous matrices. Several materials have been used as supports of iron such as kaolin, activated carbon, zeolite, SiO₂, Al₂O₃, zeolites, and clay, etc. [13-18]. Clay minerals have been widely used as catalyst supports and adsorbent, due to their low cost, abundance and environmental friendly. To the best of our knowledge, little information involving the uses of Fe₂O₃-modified activated clay as the heterogeneous catalyst is reported for the treatment of dye waste water. In this work, Fe₂O₃-modified activated clay was prepared and used as a catalyst for the degradation of cationic dye methylene blue (MB). Several operating parameters such as solution pH, amounts of H₂O₂ and catalyst were investigated. This work implies that Fe₂O₃-modified activated clay is a potential catalyst for Fenton-like oxidation of dye wastewater.

2. Materials and methods

2.1. Materials and analytical method
Hydrogen peroxide (30%, w/w), Fe (NO₃)₃·9H₂O, methylene blue and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytical grade reagents without any further purification. Deionized water was used, and activated clay (industrial grade) was used as supports. MB concentration of the solutions was analyzed by using a UV–Vis spectrophotometer (UV1750, Shimadzu Co., Japan) at 665 nm corresponding to the maximum absorbance of MB. The efficiency of MB removal was calculated using the following equation:

\[
\text{MB removal efficiency (%) = } \left(1 - \frac{C_t}{C_0}\right) \times 100
\]

Where \(C_0\) (mg L\(^{-1}\)) and \(C_t\) (mg L\(^{-1}\)) are the concentration values of MB at the initial time and after \(t\) minutes of treatment, respectively.

2.2. Preparation of Heterogeneous Fenton Catalyst
Fe₂O₃-modified activated clay catalysts were prepared by precipitation method. A certain amount of Fe (NO₃)₃·9H₂O was dissolved in 100 mL of distilled water to make a solution containing Fe Wt% = 5%. Then 25 g of activated clay and 25 g CO (NH₂)₂ were slowly added into the solution and the mixture was kept at 60 °C for 4 h under constant stirring. After completing the precipitation, the precipitation was recovered by filtering and washed with distilled water. Then, the precipitation was dried at 100°C overnight. Finally, the dried precipitation was calcined at 450 °C for 4 h and the final catalyst was obtained.

2.3. Methods
The degradation activity of Fe₂O₃-modified activated clay was performed in a glass batch reactor equipped with a magnetic stirrer and a pH electrode, placed in a water bath. In a typical run, 100mL of MB wastewater was added into the reactor together with a different amount of Fe₂O₃-modified activated clay. Then, H₂O₂ added to achieve the desired H₂O₂ concentration and the mixture was agitated throughout the procedure. The pH of the solutions was changed by adding 0.1 M H₂SO₄ or 0.1 M NaOH. Reaction temperatures varied from 20°C to 60 °C. After treatment, the samples were centrifuged and the liquid was analyzed in order to determine MB concentration.

3. Results and discussion

3.1. Activated clay and catalyst characterization
The morphologies of the activated clay and Fe₂O₃-modified activated clay were investigated by scanning electron microscopy (SEM) (Quanta 200 FEG, FEI Company, USA). XRD patterns of the activated
clay and Fe₂O₃-modified activated clay were obtained by an X-ray diffract meter (XRD-7000, Shimadzu, Shimadzu Corporation, Kyoto, Japan). Fig. 1 is the X-ray diffraction pattern of activated clay and catalyst Fe₂O₃-modified activated clay. It can be clearly seen from the comparison between the activated clay and Fe₂O₃-modified activated clay in Figure 1 that the basic positions of the diffraction peaks of the Fe₂O₃-modified activated clay have not changed, but the height of the peak has decreased, indicating that the crystal shape has deteriorated after modification. There are certain defects in the structure, which can play a certain catalytic role. Fig. 2 presents SEM images of the activated clay and Fe₂O₃-modified activated clay. In fact, clearly, the surface morphology of the activated clay (Fig. 2a) is different from that of the Fe₂O₃-modified activated clay (Fig. 2b). The activated clay is in an amorphous state, and the morphology is vague. However, the Fe₂O₃ crystals are dispersed on the activated clay surface in Fe₂O₃-modified activated clay. Although the particles are not uniformly dispersed, it is still clear that there are a large number of Fe₂O₃ crystals on the surface.

Fig 1. XRD patterns of the activated clay and Fe₂O₃-modified activated clay.

Fig 2. SEM images of the activated clay (a) and Fe₂O₃-modified activated clay(b).
3.2. Effect of the catalyst dosage

In the heterogeneous Fenton reaction, the amount of catalyst is an important factor affecting the catalytic performance of the catalyst. In this study, the catalyst dosage effect was studied by varying the catalyst dosage from 3.1 to 12.4 g L\(^{-1}\)at the temperature of 30 °C, pH 3.0, H\(_2\)O\(_2\) concentration of 1200 mg/ L. The effect is presented in Fig. 3. As shown in Fig.3, the removal efficiency of methylene blue increases with increasing the catalyst dosage, reaching 98.3% discoloration for a catalyst concentration of 6.2 g/L. This is due to the fact that the increase in the amount of catalyst can provide more iron sites on the surface of the catalyst to accelerate the decomposition of H\(_2\)O\(_2\), which can significantly increase the number of hydroxyl radicals. However, the decolorization efficiency is not significantly improved when the catalyst dosage is higher than 6.2g/L.

![Fig 3. Effect of catalyst dosage on the decolorization of methylene blue.](image)

3.3. Effect of H\(_2\)O\(_2\) Content

Fig. 4 shows the effect of the H\(_2\)O\(_2\) concentrations on decolorization of MB. It can also be seen from Figure 4 that the removal efficiency of methylene blue increased from 86.28% to 99.62% when the H\(_2\)O\(_2\) dosage increased from 0 to 1400 mg/L. This is because more H\(_2\)O\(_2\) produces ·OH under the catalysis of the Fe\(_2\)O\(_3\)-modified activated clay, which promotes the oxidative degradation of dye molecules. However, the increase in H\(_2\)O\(_2\) further reduces the degradation process because excess H\(_2\)O\(_2\) act as scavengers for hydroxyl radicals, generating per hydroxyl radicals with a lower oxidation potential than the former [19].
3.4. Effect of pH on catalytic degradation
The catalytic water purification process is highly dependent on the pH as it affects the charge on the catalyst particles, size of the aggregates, and position of the conductance and valence bands [20]. The catalyst surface can be protonated and deprotonated under acidic and alkaline conditions, respectively [21] The effect of pH on degree of decolourization is presented in Fig. 5. It was found that the decolorization rate of dyes decreases with increasing pH. When the pH is 3.0, the decolorization rate is relatively good, reaching 99.15%. With the increase of pH, the decolorization rate also dropped from the maximum 99.15% to 86.2%. When the pH is too high, the production of OH• will be suppressed, and at the same time, Fe³⁺ will be precipitated in the form of hydroxide and lose its oxidation. Therefore, the optimal pH value should be controlled at 3.0.
3.5. Effect of temperature on catalytic degradation
The temperature effect was investigated at the catalyst dosage of 6.2 g/L, an initial pH of 3, H₂O₂ concentration of 1200 mg/L, and a reaction temperature of 20, 30, 40, 60°C, respectively. The result is depicted in Fig. 6. It can be seen from Fig. 6 that the temperature has a significant effect on the reaction. When the reaction temperature increases from 20 ℃ to 30 ℃, the decolorization rate of methylene blue increases from 90.7 % to 98.1%, indicating that the temperature can accelerate the reaction rate and increase oxidative degradation. But when the temperature increases from 30 ℃ to 60 ℃, the temperature has no obvious effect on the decolorization rate of methylene blue. Therefore, the optimal temperature for the reaction is 30 ℃.

![Fig 6. Effect of the temperature on the decolorization of methylene blue.](image)

4. Conclusions
In this study, the Fe₂O₃-modified activated clay catalysts have been prepared by precipitation method, as verified by SEM and XRD characterizations. The Fe₂O₃-modified activated clay was used as the photocatalyst and H₂O₂ was added to the solution to eliminate methylene blue. Experimental results show that under suitable conditions, specifically the catalyst dose of 6.2 g/L, pH 3, hydrogen peroxide concentration of 1200mg/L and treatment time of 60 min, the decolorization efficiency of methylene blue reach 98.3%. These results gave new and practical approaches for dye wastewater treatment.

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