Preparation and the Catalytic Properties of Attapulgite / TiO₂ Nanocomposites

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Abstract. With the rapid development of industry, the discharge of textile printing and dyeing wastewater will cause serious pollution to other pure water bodies. It is imperative to deal with textile printing and dyeing wastewater. In this paper, with titanium tetrachloride as a precursor, attapulgite (ATP) / TiO₂ nanocomposites were prepared by a neutralizing hydrolysis method and their catalytic activities were investigated by the oxidative degradation of methylene blue dye using ozone as oxidant. The test results showed that there were significant interactions between TiO₂ and ATP support. The effects were also studied of ozone concentration, catalyst amount, reaction temperature, and initial concentration of methylene blue on the degradation rate of methylene blue catalyzed by the prepared attapulgite / TiO₂ nanocomposites, and under the optimal conditions, the methylene blue could be degraded more than 90% in 30 minutes. Compared with that of pure ATP, the catalytic activities of ATP / TiO₂ nanocomposites were enhanced remarkably. The degradation mechanism of methylene blue was also discussed.

Keywords: Attapulgite, Catalytic Oxidation, Methylene Blue.

1. Introduction
Now some industries, such as textile, rubber, paper, leather, plastics, cosmetic and printing factories, bring forth a great deal of effluents in which there are high levels of organic pollutants (for example, methylene blue, methylene orange), large pH variations, and of various colors [1]. If these effluents were directly discharged, many adverse environment effect will come into being, as dissolved oxygen in water will be reduced and the aquatic plants and animals will also be severely affected. Moreover, human beings’ health will be influenced because of the carcinogenic substance in the dye wastewater such as aromatic amines [2, 3]. Therefore, how to effectively deal with the wastewater produced by the modern industries has been a more and more urgent environmental protection problem.

The attapulgite clay is rich in magnesium and aluminosilicates and abundant in Jiangsu, China [4]. Compared with activated carbon, attapulgite clay has superior physicochemical properties such as multiple-void structure, large surface area and high stability. In addition, its catalytic properties can be enhanced via different modification methods which include attapulgite activation, the organic matter compound modification, the inorganic composite modification, and metal ion modification [5]. Attapulgite / CeO₂ nanocomposites were prepared and their catalytic degradation activity of methylene blue was studied by Chen et al [6]. It was shown in the article that in the presence of ozone the degradation rate reached 96% when the doping ration of CeO₂ was 40% and the catalyst amount was 0.2 g because ozone produced more •OH on the catalyst surface and improved the ozone utilization.
rate and the degradation rate of methylene blue owing to the synergistic reaction of modified attapulgite and ozone.

Therefore, herein the ATP / nano-TiO$_2$ composite powders were synthesized by neutralization and hydrolysis and their catalytic activity of were explored by studying the degradation experiments of methylene blue. The experimental factors were carefully investigated on the structure, the morphology and the properties of the samples and the catalytic mechanism were discussed on the degradation of methylene blue.

2. Experimental

2.1. Experimental Instruments

The instruments used in the experiment contain a 101-1AB electric blast drying oven (Beijing Zhongxing Weiye Century Instrument Co., Ltd.), a DF-101Z type heat collection, a constant temperature magnetic stirrer (Shanghai Lichen Bangxi Instrument Technology Co., Ltd.), an HY-010 type ozone generator (Chengdu Yifeng Hongyuan Environmental Protection Technology Co., Ltd.), an I3 type UV-visible spectrophotometer (Jinan Haineng Instrument Co., Ltd.) and a OTL1200 type tube furnace. Figure 1 is the experimental devices as follows:

![Experimental Devices Diagram](image)

1-Ozone generator, 2-colloidal sampler, 3-thermometer, 4-exhaust pipe, 5-tail gas recovery cup, 6-four-necked flask, 7-magnetic stirring heater, 8-stirring rotor

**Figure 1.** Diagram of experimental devices

2.2. Experimental Reagents

Attapulgite powders were from Gansu, China. Titanium tetrachloride were purchased from Aladdin Biochemical Technology Co. Ltd and methylene blue from Ebene Chemical Reagent Co. Ltd. at analytical grade and used directly.

2.3. Preparation of ATP / TiO$_2$

Disperse 6g ATP was dispersed in 100mL 10% hydrochloric acid, placed for 6 h, washed with deionized water to neutral, and filtered. The cake obtained was then dried in a drying chest for 4 hours and sealed. At room temperature, 2.375 g pure TiCl$_4$ was added to a 1 mol / L HCl solution to prepare a 1 mol / L light yellow transparent titanium dioxide acidic sol, which was aged for 3 hours.

6g activated attapulgite was mixed with water with the ratio of 1:100 ratio and stirred for 40 min to form a suspension. Then ammonia was added to adjust the value of the pH to 9 and further stirred for 2 h. Third, titanium dioxide acidic sol was added into the solution. The mixture was then put in a water bath at 70℃ for 12 hours, and then repeatedly rinsed with deionized water until the value of the pH was 7. After it was filtered, the cake obtained was dried at 100 ℃ for 4 h and subsequently calcined at 550 ℃ in nitrogen for 5h.
2.4. **Adsorption / Catalytic Activity Measurements**

The oxidation of methylene blue waste water was performed in a glass reactor with a capacity of 1000 mL equipped with an O3-flow controller. The decomposition extent of the methylene blue was determined by measuring the value of the absorbance at 665 nm using a UV-722 spectrometer, and according to the standard curve, the mathematical relationship between methylene blue concentration C and absorbance A was:

\[
C = \frac{A-0.0121}{0.0531}
\]

(1)

Where C was the concentration of methylene blue solution and A was the Absorbance of the methylene blue solution.

The degradation rate \( \omega \) (%) was calculated according to the following formula:

\[
\omega = \left(1 - \frac{C_t}{C_0}\right) \times 100\%
\]

(2)

Where \( C_0 \) was the initial concentration of methylene blue solution and \( C_t \) was the concentration of the methylene blue solution at t minutes.

3. **Results and Discussion**

3.1. **SEM of the Sample**

The morphology of attapulgite and attapulgite / TiO\(_2\) nanocomposites was observed by SEM and shown in Figure 2. It could be seen that before calcination the surface of attapulgite was very bumpy and could be used as the crystalline core of TiO\(_2\) particles. After the attapulgite clay was loaded with TiO\(_2\) particles and calcined, its surface became smooth, which meant the loading was successful.

![Figure 2. (a) Original soil, (b) Calcination](image)

3.2. **Structure Analysis**

The structure of the samples were characterized by XRD and displayed in Figure. 3. It was demonstrated that there were prominent characteristic diffraction peaks at the angle of 8.42°, 20.05°, 27.50°, 35.16°, and 42.25° which belonged to ATP. This result illustrated that carbonate impurities were removed by acidification and high-temperature treatment while the attapulgite frame structure was remained during the preparation of ATP / TiO\(_2\) nanocomposites. Moreover, the other bulges at were corresponding to TiO\(_2\) anatase (JCPDS (1976)) which showed that TiO\(_2\) were successfully implanted into the structure of ATP.
In order to confirm the modification, XRF were used to test the samples, whose result was exhibited in Figure 4. The excitation wavelength is 240nm, and the PL peak was slit by 6.0nm at 393nm, which further testified the result of XRD.

The comparison of two peaks indicates that TiO$_2$ is successfully loaded on attapulgite.

**Figure 3.** XRD patterns of ATP and ATP / TiO$_2$

**Figure 4.** XRF patterns of ATP and ATP / TiO$_2$

**Figure 5.** FTIR patterns of ATP and ATP / TiO$_2$
Figure 5 was the FTIR patterns of ATP and ATP/TiO2. The absorption peaks at 470 and 1032 cm\(^{-1}\), corresponded to the stretching vibration of the Si-O-Si bond in amorphous SiO\(_2\). The absorption band of modified attapulgite near 700 cm\(^{-1}\) is produced by asymmetric stretching vibration of Ti-O. The absorption peak at 1639 cm\(^{-1}\) is produced by N-H. The absorption peak in the range of 3000 cm\(^{-1}\) to 3800 cm\(^{-1}\) is generated by the surface hydroxyl group of SiO\(_2\). The absorption peaks of ATP/TiO\(_2\) were weakened because other chemical bonds were formed after the modification.

3.3. Catalytic Oxidation of Methylene Blue by ATP/TiO\(_2\)

3.3.1. Effect of ozone. In 150 mL MB solution, the experimental condition as follows: the concentration is 60 mg/L, the flow rate of ozone is 0.15 NL/min, the concentration of ozone is 0.067 g/L, pH is 5.5, the amount of attapulgite is 0.1 g, the stirring speed is 55 r/min, and the reaction temperature is 50 °C. The reaction results are as shown in the figure below:

![Figure 6. Comparative experimental results of ozone and catalyst](image)

The catalytic oxidation properties of the ATP/TiO\(_2\) nanocomposites were investigated via the degradation of methylene blue (Figure 6). In the atmosphere of only O3, methylene blue could be degraded by 42% in 30 min. Adding pure ATP as catalyst, the degradation efficiency was increased to 54% in 30 min. However, the decolorization perhaps was due to the adsorption methylene blue on the surface of ATP. While ATP/TiO\(_2\) nanocomposites were used as the catalyst, the degradation efficiency was up to 93% in the same time. This indicated that the catalytic activity of ATP was greatly enhanced because of the doping TiO\(_2\).

The effect of ozone concentration was also considered, and the results are as shown in the figure 7:

![Figure 7. Effect of ozone concentration on degradation rate](image)
It can be seen from Figure 7 that the degradation rate of MB decreases with the increasing ozone flow rate. When the ozone concentration is above 0.067 g / L, the degradation rate of MB decreases with the increase of ozone concentration. Nevertheless, when the ozone concentration is below 0.067 g / L, the degradation rate of MB decreases as the ozone concentration declines. Thus, it can be concluded that the optimal ozone concentration is 0.067 g / L. The reason is that during the reaction, the ozone content in the solution is affected by the dissolution, reaction and decomposition of ozone. Within a certain ozone flow range, as the ozone flow rate increases, the solubility of ozone in water increases, and the yield of •OH also increases, resulting a faster degradation of MB. For a certain volume of reaction system, the solubility of ozone in the solution is constant. After he solution is saturated with ozone, the ozone in the reaction system is excessive, in which case, the impact of the amount of ozone on the reaction is negligible. When the ozone flow exceeds a certain value, excessive ozone will participate in the quenching reaction of •OH (see Equation 1), which reduces the amount of •OH involved in the reaction and thus impacts the degradation of MB.

$$2\cdot OH + O_3 \rightarrow H_2O + 2O_2$$

(3)

The gas-liquid mass transfer factor is eliminated, so that the reaction system is controlled by reaction and non-mass transfer control. In this experiment, in order to make the degradation rate of MB as high as possible, the ozone flow rate was chosen to be 6 L / min. If applied to industrial production, the economic efficiency of unit ozone removal MB should be evaluated to determine the optimal ozone flow.

3.3.2. Effect of reaction temperature. The experimental condition as follows: At a rotational speed of 550 r / min, the ozone flux is 0.15 NL / min, the ozone concentration is 0.067 g / L, and the pH is 5.5. The amount of attapulgite is 0.1 g, the initial concentration of 150 mL of MB solution is 60 mg / L. The reaction was carried out under the conditions of 30 °C, 35 °C, 40 °C, and 45 °C respectively. The change curve of MB degradation rate over time is shown in Figure 8.

![Figure 8. Effect of reaction temperature on MB degradation rate](image)

As can be seen in Figure 8, the degradation rate of methylene blue simulated wastewater was the lowest at 30°C, merely 82%. With the temperature increased, the degradation was accelerated. When it was 45°C, the rate was 96%. This is because when the reaction temperature was ascended, the molecules got active and the effective collisions became more. According to the experimental results, 45°C was chosen as the optimal reaction temperature.

3.3.3. Effect of MB solution concentration. The experimental condition as follows: the reaction temperature is 50 °C, the rotation speed is 550r / min, the ozone flux is 0.15L / min, the ozone concentration is 0.067g / L, the attapulgite dosage is 0.1g, pH is 5.5, the initial concentration of 150 mL MB solution is 40mg / L. The experiment was performed under the conditions of 30 mg / L, 35 mg
/ L, 40 mg / L, 45 mg / L, and 50 mg / L. The variation curve of MB degradation rate over time is shown in Figure 9.

![Graph showing MB degradation rate over time](image)

**Figure 9.** Effect of methylene blue initial concentration

It could be seen that the degradation rate increased with the increment of the initial concentration of methylene blue. This was due to the increase of the number of activated molecules colliding with •OH per unit volume when the concentration of methylene blue was ascended.

3.3.4. Effect of catalyst dosage. The experimental condition as follows: the reaction temperature is 50 °C, the rotational speed is 550 r / min, an ozone flux is 0.15 L / min, the ozone concentration is 0.067 g / L, an initial concentration of 150 mL of MB solution is 80 mg / L. The change curve of MB degradation rate over time is shown in Figure 10.

![Graph showing pH effect on MB degradation rate](image)

**Figure 10.** Effect of pH on MB degradation rate

It could be seen that the degradation rate gradually increased with the amount of ATP / TiO₂ under the same conditions. After the dosage was increased to 0.3g, the degradation rate remained unchanged. The reason for this was that more surface hydroxyl groups and acid sites were provided as catalytically active sites for ozonation reaction when the amount of catalyst was increased. Nevertheless, an excess of catalyst could cause the agglomeration of the catalyst particles and was disadvantageous to increase the active sites. On the other hand, the required active sites are limited for a certain amount of ozone and could not be increased by the excessive catalyst. Therefore, no additional catalyst pairs were formed when the dosage of ATP / TiO₂ continued to be added. Considering all the factors during the experiments, the amount of attapulgite was selected to be 0.4g.
3.4. Reaction Mechanism Analysis

Catalytic ozonation can be divided into homogeneous catalytic ozonation and heterogeneous catalytic ozonation. The modified attapulgite-catalyzed ozonation of methylene blue was a kind of heterogeneous catalytic ozonation. The mechanism of ozone degrading organic matter is mainly divided into direct reaction and indirect reaction. The direct reaction is direct reaction between ozone and organic matter, and the organic degradation rate is low. The indirect reaction is the addition of a catalyst to decompose ozone to generate more hydroxyl radicals, increase the utilization of ozone, and increase the degradation rate of organic matters in wastewater [7]. The decomposition mechanism of ozone in water can be expressed by the following formula [8]:

\[
O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (4)
\]

\[
O_3 + HO_2^- \rightarrow \cdot OH + O_2^- + O_2 \quad (5)
\]

\[
O_3^- + O_2^- \rightarrow O_3^- + O_2 \quad (6)
\]

\[
O_3^- + H^+ \rightarrow \cdot HO_3^- \quad (7)
\]

\[
HO_3^- \rightarrow \cdot OH + O_2 \quad (8)
\]

\[
\cdot OH + O_3 \rightarrow HO_2^- + O_2 \quad (9)
\]

It was proposed that the reaction mechanism of ozone on the metal surface was as follows [9]. Ozone was first oxidized on the surface of reduced metal catalyst to produce \( \cdot OH \), and then the organic molecules were oxidized by \( \cdot OH \) and organic radicals were produced. The organic radicals were further oxidized by ozone or \( \cdot OH \). Because the catalyst might adsorb organic matter only via chemical bonds [10-12], the organic molecules on the catalyst surface could also be directly oxidized by ozone and hydroxyl radicals. However, it was known that the enhancement of the degradation rate of methylene blue after the addition of the catalyst was owing to the hydroxyl radicals generated on the catalyst surface by ozone, shown in Figure 11.

![Figure 11. Effect of modified attapulgite](image)

Therefore, the modified attapulgite-catalyzed ozonation of methylene blue wastewater was the reaction of free radical oxidation. The reaction process could be divided into three stages: chain initiation, chain transmission, and chain termination.

The chain initiation reaction (RH standed for organic, M standed for catalyst):
\[ \text{O}_3 + \text{H}_2\text{O} \rightarrow 2 \bullet \text{OH} + \text{O}_2 \] (10)

\[ 2 \text{RH} + 2 \text{O}_3 \rightarrow 2 \text{R} \bullet + 2 \text{HOO} \bullet + \text{O}_2 \] (11)

\[ 2 \text{RH} + \text{O}_2 \xrightarrow{M} 2 \text{R} \bullet + 2 \bullet \text{OH} \] (12)

The reaction of chain transfer:

\[ \text{RH} + \bullet \text{OH} \rightarrow \text{R} \bullet + \text{H}_2\text{O} \] (13)

\[ \text{R} \bullet + 2 \text{O}_3 \rightarrow \text{ROO} \bullet + 2 \text{O}_2 \] (14)

\[ \text{R} \bullet + \text{O}_2 \rightarrow \text{ROO} \bullet \] (15)

The reaction of termination:

\[ \text{ROO} \bullet + \text{ROO} \bullet \rightarrow \text{inactive product} \] (16)

4. Conclusion

The attapulgite was successfully modified by TiO\(_2\), which was proved by SEM and XRD measurement. The degradation efficiency of methylene blue was greatly improved with the modified attapulgite as catalyst. The effect of temperature, catalyst dosage and initial concentration of methylene blue solution on the degradation rate was investigated and the optimum catalyst dosage was 0.4 g, and the best temperature was 45 °C. Furthermore, the degradation reaction mechanism of methylene blue was analyzed, and it was concluded that methylene blue was oxidized by the free radicals produced by ozone on the catalyst surface.

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