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## Research Article

**Keywords:** Titanium dioxide, Attapulgite, Methylene blue, Catalytic ozonation

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# Catalytic Oxidation of Methylene Blue by Attapulgite/TiO<sub>2</sub>

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**Abstract:** Methylene blue (MB) is a common pollutant in wastewater of printing and dyeing. At present, ozone oxidation is commonly used in the treatment of printing and dyeing wastewater. Ozone is oxidized by direct reaction and indirect reaction, However, the reaction rate is not high and it is impossible to completely mineralize organic matter. The experimental scheme is to impregnate the attapulgite (ATP) with a volume of tetrabutyl titanate-ethanol solution. The TiO<sub>2</sub>/attapulgite nanocomposite with high catalytic activity was prepared. The synthesized samples were subjected to characterized by X-Ray diffraction (XRD). The morphology and particle size of the particles were observed by scanning electron microscopy (SEM). The attapulgite modified by TiO<sub>2</sub> was calcined at 300 °C for 2 h, and the degradation rate of 80 mg/L methylene blue was 99.8%. The experimental results show that the ozone, temperature and mass transfer factors are excluded, and the effects of temperature, MB concentration and pH on the degradation of methylene blue are investigated. The optimal reaction conditions are as follows: The ozone concentration is 0.067 g/min; the ozone flow rate is 0.15 NL/min; the stirrer rotation speed is 550 r/min; the catalyst is 0.1 g; the temperature is 50 °C; Based on the results, the reaction mechanism was derived and the kinetic study of the experiment was carried out.

**Key words:** Titanium dioxide; Attapulgite; Methylene blue; Catalytic ozonation

## 1. Introduction

China is a major dye producer, and its dye output ranks first in the world. At present, the discharge of dye industry wastewater has reached 157 million tons/year (Ma 2006, Zhou 1999, Zhu 2004). Dyes, as an environmental pollutant, have various types and complex structures. There are currently over 30,000 kinds of synthetic dyes used worldwide. The wide application of methylene blue in the printing and dyeing industry has resulted in the pollution of industrial wastewater containing methylene blue to other pure water bodies (Zhang 2008). The current treatment approaches of organic dye wastewater mainly include biological method, coagulation method, oxidation method, adsorption method and membrane separation method. The most commonly used methods for treating dyeing wastewater at home and abroad are biochemical method or flocculation precipitation method and activated carbon adsorption method (Song 2003, Chen 2009, Li 2007). Activated carbon is expensive and the regeneration process is complex, which limits its range of use. The activated attapulgite clay water purifying agent can treat printing and dyeing wastewater, and the chroma removal rate can reach above 99.8%. Meanwhile the filter slag can be reused, the photocatalyst can be prepared with TiO<sub>2</sub>, and the refractory printing water can also be treated well. Moreover, activated attapulgite is resistant to organophosphorus pesticides such as trichlorfon and dichlorvos (Peng 2006, Han 2017, Zhang 2003, Yin 2003, Yang 2014).

In this paper, TiO<sub>2</sub>/attapulgite nanocomposite were successfully prepared. The effects of temperature, MB concentration and pH on the degradation of methylene blue are investigated. Moreover the property and microstructure of the catalyst were measured. And the degradation mechanism of MB was derived and the reaction kinetic was proposed.

## 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:

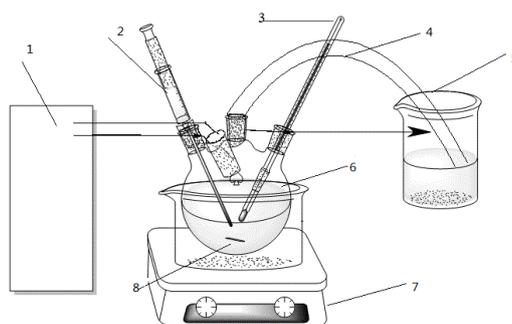


Fig. 1. Diagram of experimental devices

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

## 2.2 Experimental reagents

The experimental reagents include methylene blue  $C_{16}H_{18}ClN_3S \cdot 3H_2O$  (analytical grade, Chengdu Cologne Chemical Co., Ltd.), attapulgite (ATP)  $Mg_5Si_8O_{20}(OH)_2(OH_2)_4 \cdot 3H_2O$ ; tetrabutyl titanate ( $C_{16}H_{36}O_4Ti$ ), (analytically pure, Chengdu Cologne Chemical Co., Ltd.), and anhydrous ethanol ( $C_2H_5OH$ ) (analytically pure, Chengdu Cologne Chemical Co., Ltd.).

## 2.3 Preparation of ATP/TiO<sub>2</sub>

About 40 g of attapulgite with a particle size of about 180 g was screened and immersed in 200 mL of 4 mol/L dilute hydrochloric acid for 8 h, and then filtered by suction to neutrality and dried in an oven at a temperature of 80 °C for 4 h. A tetrabutyl titanate-ethanol impregnation solution with a volume ratio of 1:4 was placed for use. The water absorption of 31.8 g acid-modified attapulgite was measured to be 24.5 ml, and it was dried in an oven for 3 h. Subsequently, 24.5 mL of tetrabutyl titanate-ethanol impregnation solution was added to 31.8 g of attapulgite, sealed with a plastic wrap, and immersed for 13.5 h. The impregnated attapulgite was hydrolyzed in a water bath for 1 h, hydrolyzed to  $Ti(OH)_4$ , dried in an oven and oxidized to  $TiO_2$ , and dried for 3 h. The attapulgite was placed in a tube furnace and calcined at 500 °C for 2 h, and sealed in a bag.

## 2.4 Characterization

The synthesized samples were identified by X-ray diffractometry, and the scanning range was 5~90°. The morphology of the particles was observed by transmission electron microscopy (SEM), and the working voltage was 120 KV.

## 2.5 Catalytic oxidation of methylene blue wastewater

An analytical balance was used to weight 0.1 g of modified attapulgite for later use. A certain amount of methylene blue stock solution was removed from the 1000 mg/L methylene blue mother liquor to prepare a methylene blue reaction solution of the desired concentration. The prepared MB solution was poured into a dry four-necked flask, and then a magnetic stirrer was put into the flask; the four-necked flask containing the solution was placed in a water bath to fix the height of the MB solution below the height of the water layer. After turning on all the switches, the speed and temperature of the magnetic stirrer were set; the bottom of the meter and the bottom of the trachea were at the same level as the stirrer; when the reaction temperature of the MB solution reached the specified temperature, it would pass through the four ports. After the modified attapulgite catalyst was added into the flask, the ozone generator switch was turned on and the timer was started. The sampler was used to take 5 mL of sample liquid through the sampling port every time. The residue was filtered through the disposable filter head and then put into the sample tube for testing. The temperature was controlled during the reaction so that the temperature difference was lower than  $\pm 1$  °C. After the reaction was completed, the solution with a constant volume was measured by an ultraviolet spectrophotometer at its maximum wavelength of 665 nm. The degradation rate is calculated according to the following formula:

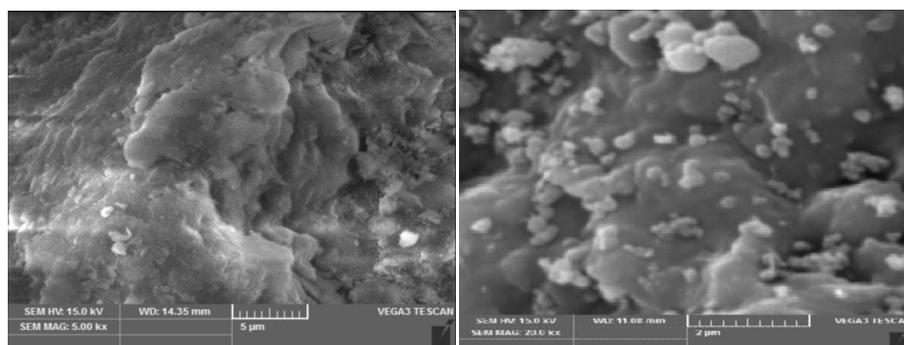
$$D = \left(1 - \frac{A}{A_0}\right) \times 100\% \quad (1)$$

Where D is the degradation rate (%), and A and  $A_0$  are the absorbance before and after degradation, respectively.

## 3. Results and Discussion

### 3.1 SEM of the sample

The SEM results of the attapulgite/TiO<sub>2</sub> catalyst calcined at 300 °C, 400 °C, and 500 °C for two hours were shown in Fig. 2. It can be observed that the attapulgite has a loose structure as well as a large surface area and specific surface area, so it has a good adsorption effect. The TiO<sub>2</sub> nanoparticles with a particle size of less than 10 nm are more uniformly distributed on the surface of the attapulgite clay, and the morphology and size of the TiO<sub>2</sub> and the attapulgite clay change little after loading. Nevertheless, the TiO<sub>2</sub> nanoparticles are not fully attached to the surface of the attapulgite clay. With a small amount of TiO<sub>2</sub>, the crystal form has anatase transformed into rutile type, and a small amount of spherical-like particles appear on the surface. A small portion is dispersed around the TiO<sub>2</sub>/attapulgite powder, which indirectly increases the specific surface area and surface area. When the temperatures are 300 °C and 400 °C, the structure changes little, but the crystal structure of TiO<sub>2</sub> on the surface will change. At 500 °C, the catalyst has a loose structure. Although the surface area has increased, the pore structure of the crystal will collapse, thereby reducing the specific surface area.



(a)

(b)

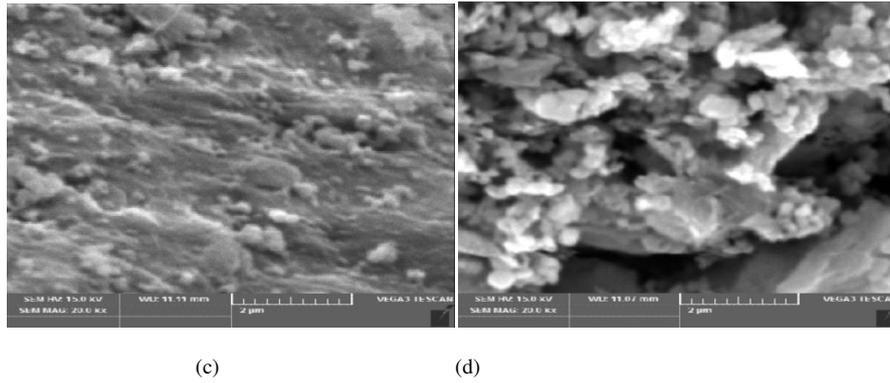
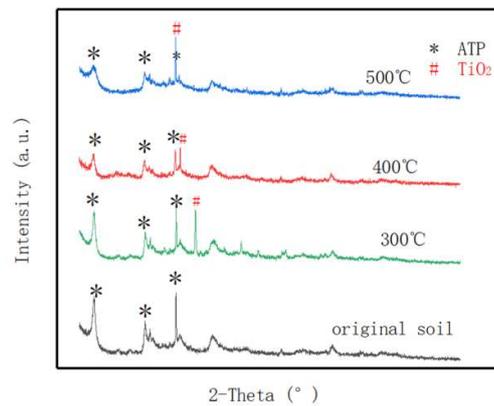


Fig. 2. (a) SEM image of Original soil, (b) Calcination at 300 °C, (c) Calcination at 400 °C, (d) Calcination at 500 °C  
 As shown in Fig. 2(a), the surface of the original soil has a layered structure and there are no other impurity groups on the surface. That is to say, the original soil has a complete and compact structure and contains no other substances, so it has a large surface area and specific surface area.  
 It is analyzed from Fig. 2(b) that after the modified attapulgite is calcined at 300 °C, the surface of the attapulgite becomes porous, and the internal structure changes. The small white spheres on the surface are TiO<sub>2</sub> particles which increase the surface area and the adsorption efficiency.  
 It can be seen from Fig. 2(c) that the surface of calcined attapulgite presents a fluffy porous structure rather than a dense layered one, and the shapes of TiO<sub>2</sub> particles are irregular.  
 As shown in Fig. 2(d), when the attapulgite is calcined at 500 °C, its surface becomes more fluffy and porous. Meanwhile the pores collapse, the surface is sintered, and the growth of TiO<sub>2</sub> crystals is hindered.

### 3.2 XRD characterization of the sample

In order to further investigate the coating condition of the sample, the X-ray diffraction spectrum of sample is obtained by X-ray diffractometer. The range is 5~90°. The scanning results were analyzed by Jade software to obtain the phase analysis. the figure shows that ATP/TiO<sub>2</sub> is calcined at 300 °C,



400 °C, and 500 °C for two hours at constant temperature.  
 Fig. 3. XRD patterns of ATP and ATP/TiO<sub>2</sub> prepared under different calcination temperature  
 It can be seen from the figure that all the four graphs have a strong diffraction peak when the 2θ is 8.495 °C, and it was analyzed that ATP was obtained here. For the ATP/TiO<sub>2</sub> sample with a calcination temperature of 300 °C, a strong diffraction characteristic peak of TiO<sub>2</sub> appears when 2θ is 25.339 and 30.807 respectively. For the ATP/TiO<sub>2</sub> sample calcined at 400 °C, a strong diffraction characteristic peak of TiO<sub>2</sub> appears when 2θ is 27.446, 36.085, and 54.322 respectively. At the

calcination temperature of 500 °C, a strong diffraction characteristic peak of TiO<sub>2</sub> show at 25.27 and 48.049. The higher the temperature, the more TiO<sub>2</sub> is loaded in the ATP. In the four graphs, the diffraction peak of ATP decreases with the rising temperature. This is ascribed to the reduction of the ATP diffraction peak intensity caused by the hydroxyl group on the attapulgite clay's surface as well as the separation of adsorbed water, crystal water and structural water. When the temperature is too high, the internal channel collapses. Other peaks in the graph are caused by the presence of impurities in the sample itself. The overall crystal lattice of the catalyst is intact and not destroyed. The product has obvious diffraction peaks, and the interlayer spacing fluctuates. The diffraction peaks remain orderly after calcination, and the crystal lattice is intact.

### 3.3 Catalytic oxidation of methylene blue by ATP/TiO<sub>2</sub>

#### 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:

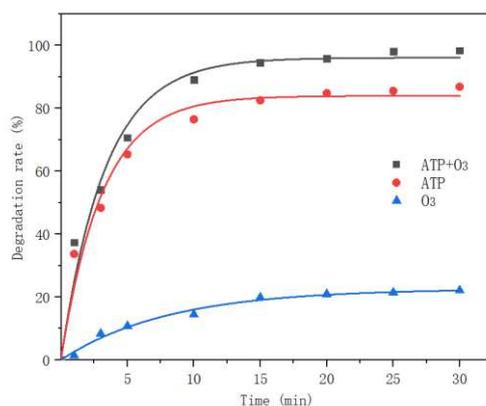


Fig. 4. Comparative experimental results of ozone and catalyst

It can be seen from Fig. 4, when the same modified attapulgite is added, the ozone ratio is different, and the degradation rate of methylene blue increases to some extent. In the absence of ozone, the degradation rate can reach 90% or so. After the introduction of ozone, the rate can reach 98%. This indicates that the catalyst has a certain adsorption capacity, but the degradation rate can be further improved under the indirect oxidation of ozone. The addition of catalyst significantly improves the efficiency, indicating that the catalyst plays a critical role in the degradation of methylene blue.

The effect of ozone concentration was also considered, and the results are as shown in the fig. 5:

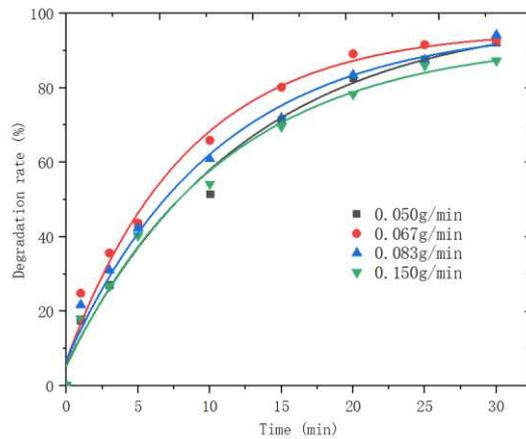


Fig. 5. Effect of ozone concentration on degradation rate

It can be seen from Fig. 5 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  $\bullet\text{OH}$  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 the 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  $\bullet\text{OH}$  involved in the reaction and thus impacts the degradation of MB.



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 attapulgate 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 20 °C, 30 °C, 40 °C, 50 °C, and 60 °C respectively. The change curve of MB degradation rate over time is shown in Fig. 6.

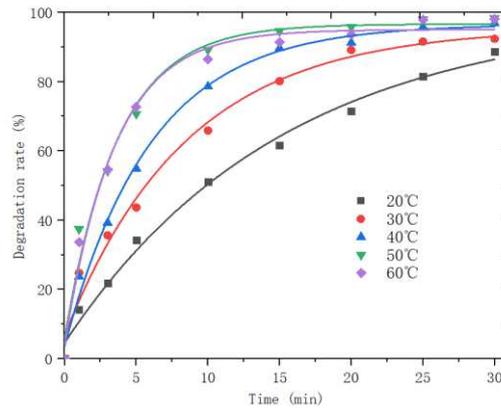
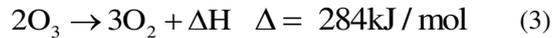


Fig.6. Effect of reaction temperature on MB degradation rate

It can be seen from Fig. 6 when the reaction temperature is lower than 50 °C, the degradation rate of MB gradually increases with the rising reaction temperature; when the reaction temperature is 50 °C, the change in reaction temperature has little effect on the degradation of MB. Therefore, with the increase of reaction temperature, the degradation rate of MB first increases and then remains unchanged. According to the study by W.J. Masschelein (Masschelein 1992), ozone is quite poor in stability and is easy to decompose at even room temperature (see Equation 2). The half-life of ozone decomposition in water is related to temperature. When the temperature is below 50 °C, the decomposition rate will increase accordingly as it rises, and more •OH will be produced in the solution, and increasing temperature will enhance the activation in the reaction system. The ratio of molecules increases the probability of effective collision and accelerates the degradation rate. Nevertheless, when the temperature rises to a certain value, the solubility of ozone in water will be greatly reduced. Because •OH can be decomposed by ozone in water, the degradation rate is reduced accordingly.



The optimum reaction temperature is 50 °C, at which neither the solubility of ozone in water is not too low nor the degradation rate is not too slow, thus the reaction rate can be maintained at a suitable temperature. Furthermore, this is also the temperature that is easier to control, so the temperature of subsequent experiments is set to 50 °C as well.

### 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 attapulgit 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 50 mg/L, 60 mg/L, 70 mg/L and 80 mg/L. The variation curve of MB degradation rate over time is shown in Fig.7.

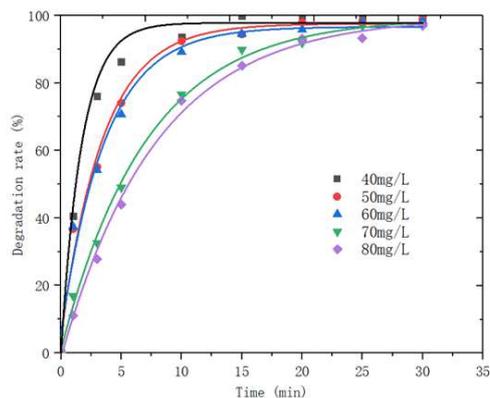


Fig. 7. Effect of MB solution concentration on MB degradation rate

The gas-liquid-solid heterogeneous reaction is a complex process. As can be seen from Fig. 7, under the above optimal experimental conditions, the initial concentration of MB was changed to observe the degradation of MB. The results showed that the degradation rate is faster as the initial concentration of MB is lower. Because of the heterogeneous catalysis, the reactants are adsorbed before the catalytic reaction, and adsorbed in the catalyst pores for catalytic oxidation. Due to the limited adsorption sites, the higher the MB concentration, the lower the adsorption efficiency. In addition, because the molecular weight of the adsorbed reactants is also limited, the degradation rate declines as the increasing concentration.

### 3.3.4 Effect of pH

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, attapulgite dosage is 0.1 g, 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 Fig. 8.

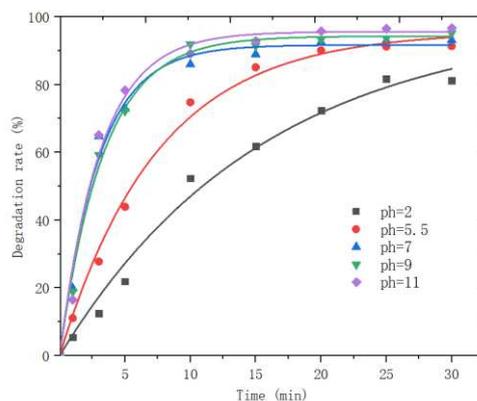


Fig. 8. Effect of pH on MB degradation rate

The results showed that the decolorization rate of MB increases along with the pH. Under acidic conditions, the decolorization rate is lower than that under alkaline conditions. By analyzing the principle of ozone oxidation, it is found that the oxidation intensity of ozone enhances with the rising pH. The above experimental phenomenon indicates that the hydroxyl radical generated by ozone decomposition by itself is the main driving force for MB degradation. Under acidic conditions, the direct reaction between ozone and MB molecules is much slower. Therefore, the degradation process of MB can be expressed by a continuous quasi-first-order equation.

### 3.3.5 Effect of catalyst calcination temperature

The tetrabutyl titanate-ethanol impregnation liquid has a volume ratio of 1:4. After intermediate treatment, it is calcined by a nitrogen atmosphere in a tube furnace, and calcined at 300 °C, 400 °C, and 500 °C, respectively. The effect of calcination temperature on the degradation rate of 80 mg/L MB solution was investigated. The experimental results are as follows.

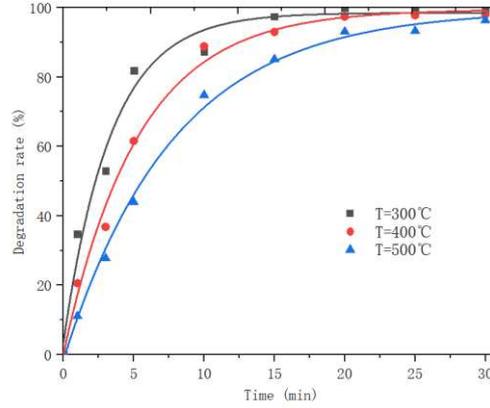


Fig. 9. Effect of calcination temperature on methylene blue wastewater

When the calcination temperature is too high, the catalyst pores collapse and the specific surface area of adsorption is reduced, so the degradation rate will be slowed down, whereas, the temperature increases TiO<sub>2</sub> and ATP load better, so the final degradation rate will tend to a close value.

### 3.4 Ozone reaction kinetics

Ozone enters the aqueous solution through aeration, in which the gas-liquid contact mass transfer is involved, and the gas is diffused in the water. According to classical dual-mode theory, ozone oxidation of organic matter may exist in two forms: the form of ozone gas diffuses into the liquid, reacts with organic matter at the gas-liquid interface or liquid film before entering the liquid phase, and the selectivity of ozone for such substances Strong results; another portion of unreacted ozone reacts with the organic matter through the liquid membrane into the liquid phase.

$$-\frac{d[D]}{dt} = k_Q[O_3][D] + k_{OH}[\cdot OH][D] \quad (4)$$

Where [O<sub>3</sub>] and [D] are the concentrations of ozone molecules and organic matter, respectively, and the ozone concentration and ·OH are deemed to be constant values. In the unbuffered MB solution, a quasi-stable condition for hydroxyl radicals is assumed. The concentration of hydroxyl radicals can be estimated by Benitez and Beltran from equation (5):

$$[\cdot OH] = \frac{3[O_3][OH^-]}{[D]} \cdot \frac{k_{HO\cdot}}{k_D} \quad (5)$$

In the formula, [HO·] and [HOO·] are the concentrations of hydroxyl radicals and hydroxide ions, respectively. [O<sub>3</sub>] is the dissolved ozone concentration, [D] is the concentration of the MB solution, and k<sub>HO·</sub> is the second-order rate constant of the [·OH] reaction path. k<sub>HOO·</sub> is a kinetic constant for the decomposition of ozone to form a free radical HOO· under high pH conditions. At higher pH, the ozone molecules decompose more hydroxyl radicals, resulting in a large amount of hydroxide ions. Substituting [·OH] in equation (5) into equation (6), yields equation (7):

$$-\frac{d[D]}{dt} = k_{O_3} [O_3] [D] + k_{OH} [OH] [D] \quad (6)$$

$$-\frac{d[D]}{dt} = k_{O_3} [O_3] [D] + 3k_{OH} [OH] [O_3] \quad (7)$$

Since the concentration of  $O_3$  is excessive, the ozone oxidation process of MB molecules is an apparent quasi-first-order kinetic reaction. Therefore, the formulas  $k_{O_3} \cdot [O_3]$  and  $3k_{OH} \cdot [O_3]$  are assumed to be constant.

Under acidic conditions, the MB solution in deionized water has a PH of 5.5. In weakly acidic solution, because the MB solution is a non-buffered solution,  $[OH^-]$  is 0 in the solution. The kinetic formula is the apparent first-order kinetics:

$$-\frac{d[D]}{dt} = k_{\text{fit}} [O_3]^n [D]^m \quad (8)$$

With the standard curve of MB solution, the molar concentration at time  $t$  at  $T=50^\circ\text{C}$ ,  $C_{MB}=80$  mg/L, and  $\text{pH}=5.5$  is obtained. Because ozone is continuously and excessively introduced during the reaction,  $k \cdot [O_3]$  in the formula can be used as a constant. MATLAB software is used to theoretically model the formula. The kinetic equation is:

$$-\frac{d[D]}{dt} = 7.0525 \times [D]^{1.92} \quad (9)$$

The following results are obtained by fitting the experimental data, as shown in Fig. 10.

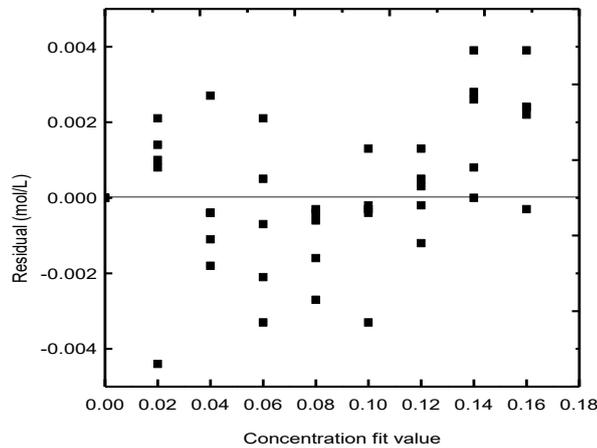


Fig. 10. Residual analysis

As shown in the figure, the residuals of the experiments are evenly distributed on the upper and lower sides of the zero line, indicating a good fitting degree.

The  $k$  values with different temperatures were obtained as follows:

Table 1. k values fitted at different temperatures

Temperature	k
20 °C	1.1148
30 °C	3.0672
40 °C	4.4077
50 °C	7.0525
60 °C	5.5701

According to Arrhenius formula:

$$k = k_0 \exp(-E_a / RT) \quad (10)$$

Ea was obtain by plotting  $\ln k - 1/T$  :

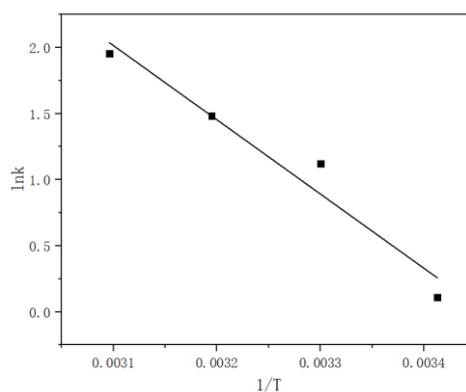


Fig. 11. Residual analysis

From Fig. 11, the slope is -5610.59, so the Ea is 46.646kJ/mol.

The results show that when the ozone is excessive, the ozone concentration is constant, and the degradation kinetics of the MB solution is the apparent first-order kinetics. Under acidic conditions, MB degradation is carried out by direct ozone oxidation, whereas under alkaline conditions, MB degradation is carried out by indirect ozone oxidation. In terms of the relative degradation rate, the higher the pH, the faster the degradation rate. For the final degradation rate, the weak acidity, neutrality and alkalinity can reach 99% degradation rate. This indicates that the above kinetic equation is suitable for most reactions, except for strongly acidic reactions.

#### 4 Conclusions

In this work, the experimental scheme is to impregnate the attapulgite with a volume of tetrabutyl titanate-ethanol solution. After drying, the tetrabutyl titanate was hydrolyzed to  $\text{TiO}_2$  under the action of water vapor, and calcined at a low temperature of 300 °C to obtain a uniform distribution of surface anatase  $\text{TiO}_2$ . The  $\text{TiO}_2$  attapulgite nanocomposite was loaded, and the material had high catalytic activity.

The attapulgite modified with  $\text{TiO}_2$  was calcined at 300 °C for 2 h, and the degradation rate of 80 mg/L methylene blue was 99.8%. The experimental results show that the ozone, temperature and mass transfer factors are excluded, so the effects of temperature, MB concentration and pH on the degradation of methylene blue are investigated. The optimal reaction conditions are as follows: The ozone concentration is 0.067 g/min; the ozone flow rate is 0.15 NL/min; the stirrer rotation speed is 550r/min; catalyst is 0.1 g; the temperature is 50 °C.

The decolorization process of MB is quasi-first-order kinetics, and the kinetic equation is obtained.  $E_a$  is 46.646kJ/mol.

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We would like to submit the enclosed manuscript entitled "Catalytic Oxidation of Methylene Blue by Attapulgite/TiO<sub>2</sub>", which we wish to be considered for publication in "Environmental Science and Pollution Research". No conflict of interest exists in the submission of this manuscript, and manuscript is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part. All the authors listed have approved the manuscript that is enclosed.

Author contributions:

Jianping Shang contributed to the conception of the study, experiment, data analyses and wrote the manuscript;

Yu Jiang performed the experiment;

Xiaoping Qin contributed significantly to analysis and manuscript preparation;

Bin Zhao performed the data analyses;

Xuefei Li helped perform the analysis with constructive discussions.

## Ethics declarations

Competing interests

The authors declare that they have no competing interests.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Funding

Not applicable.

Availability of data and materials

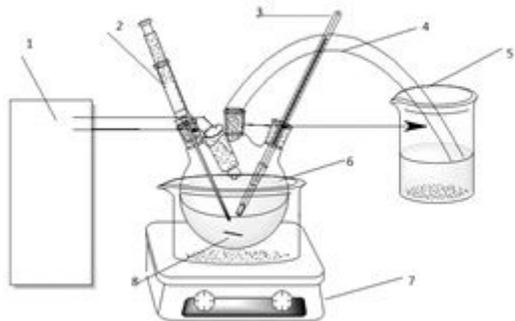
Not applicable.

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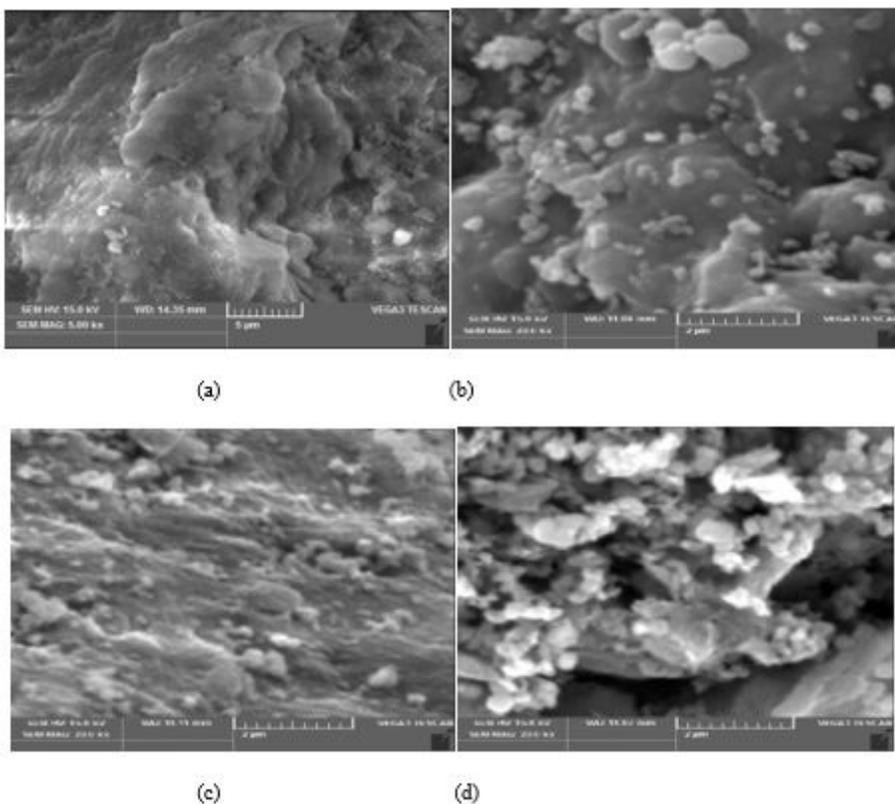
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# Figures



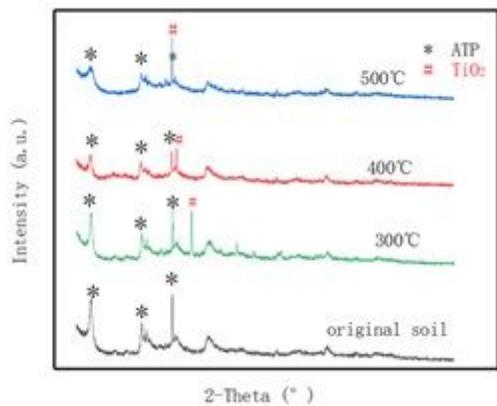
**Figure 1**

Diagram of experimental devices 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



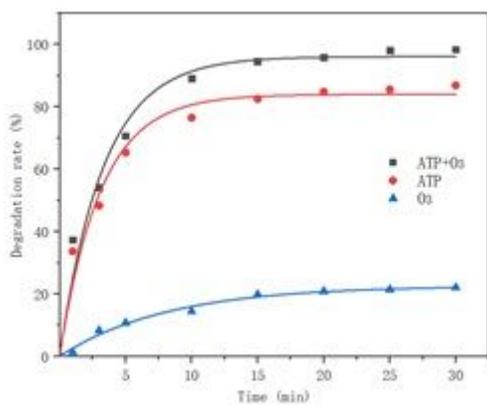
**Figure 2**

(a) SEM image of Original soil, (b) Calcination at 300 °C, (c) Calcination at 400 °C, (d) Calcination at 500 °C



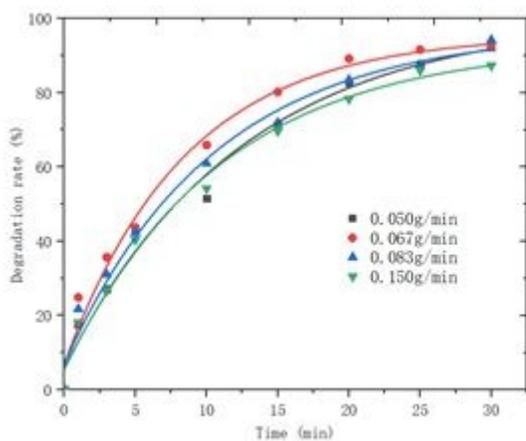
**Figure 3**

XRD patterns of ATP and ATP/TiO<sub>2</sub> prepared under different calcination temperature



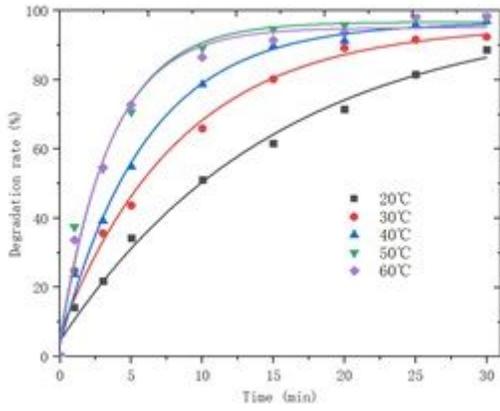
**Figure 4**

Comparative experimental results of ozone and catalyst



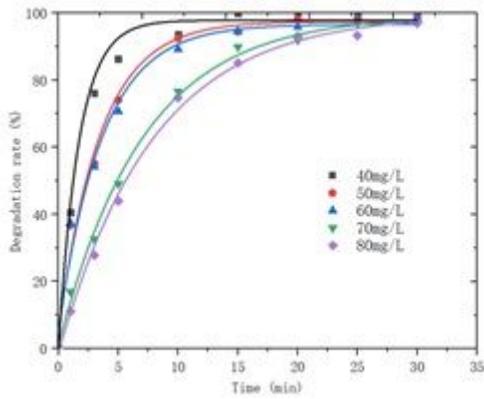
**Figure 5**

Effect of ozone concentration on degradation rate



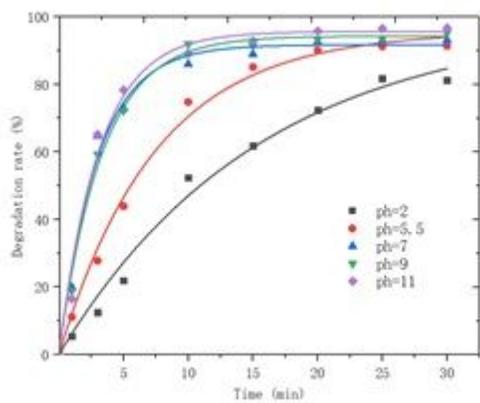
**Figure 6**

Effect of reaction temperature on MB degradation rate



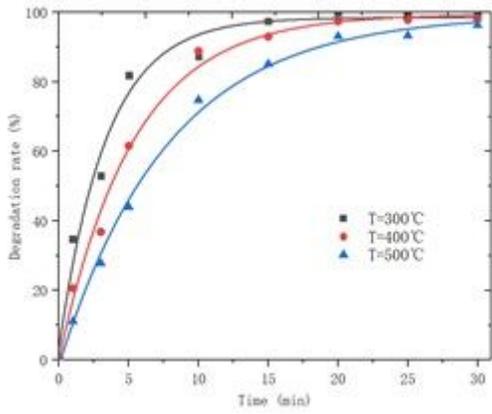
**Figure 7**

Effect of MB solution concentration on MB degradation rate



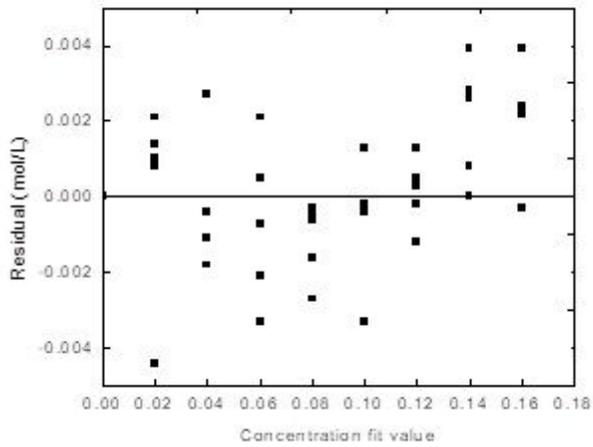
**Figure 8**

Effect of pH on MB degradation rate



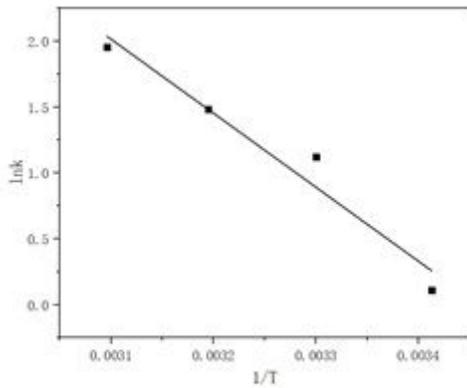
**Figure 9**

Effect of calcination temperature on methylene blue wastewater



**Figure 10**

Residual analysis



**Figure 11**

Residual analysis