

## Sonochemical Preparation of Nano-TiO<sub>2</sub> and Photocatalytic Degradation of Methylene Blue

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This paper reports the preparation of nano-TiO<sub>2</sub> powder by ultrasound hydrolyzed titanium(IV) chloride and methylene blue were used to photocatalysis degradation. We studied the respond time, pH value, the amount used and the light distance, *etc.* We also studied the factors affecting the degradation rate of methylene blue and compared the P-25 and TiO<sub>2</sub> power. Experiments show that the photocatalytic activity of TiO<sub>2</sub> is better. The respond time is 150 min, the catalyst dosage is 0.2000 g, the light distance is 16 cm. When pH value is between 6-8, the degradation rate is up to 99.35 %.

**Key Words:** Nano- TiO<sub>2</sub>, Methylene blue, Photo-catalytic degradation, P-25.

### INTRODUCTION

TiO<sub>2</sub> is a photo-catalyst material, which has a number of advantages, such as high efficiency, energy saving, safety, low operation cost, clean and non-toxic, catalytic wide of range<sup>1,2</sup>, good stability and corrosion resistance, *etc.*, many people have been paying increasing attention to it in recent years. In the wastewater treatment, including dye wastewater, pesticide wastewater, oily wastewater, pharmaceutical wastewater, *etc.*, nano-TiO<sub>2</sub> powder catalysts can effectively set off photo-catalytic reaction and were transformed to inorganic molecules, such as H<sub>2</sub>O, CO<sub>2</sub>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, halogen ions *etc.*, to achieve complete mineralization. It is an effective method for wastewater treatment. The fact that TiO<sub>2</sub> powders can dispose a variety of wastewater has been reported largely<sup>3-5</sup>, but as to methylene blue solution study, the reports are quite limited. In view of this, using TiO<sub>2</sub> powder as catalyst, we have studied the degradation rate of methylene blue and the following were discussed: the respond time, pH value, the catalyst dosage, the light distance *etc.* to methylene blue of the influence of the degradation rate<sup>6</sup>.

### EXPERIMENTAL

Paradigm 722-type spectrophotometer (Unico Shanghai), instrument Co. Ltd.; ray magnetic precision pH meter (Shanghai precision scientific instrument Co. Ltd.), 8 W UV lamp, 8-1A magnetic heating mixer (Hangzhou Electric instrument Factory).

P-25 commercial nano-TiO<sub>2</sub>, degussa (China) investment Co. Ltd., Shanghai branch (China), TiCl<sub>4</sub>, ethanol, methylene blue for were analytical pure reagents.

**Preparation of TiO<sub>2</sub> photo-catalyst:** In ice water bath condition, TiCl<sub>4</sub> were slowly poured into distilled water to be produced TiCl<sub>4</sub> solution<sup>7</sup>. Ultrasonic, heat hydrolysis were processed and then left for 12 h. The solution was neutralized until pH to 7 by 15 % of dilute ammonia aqueous, nano-TiO<sub>2</sub> powder were washed by distilled water until no chloride ion detected and heated at 300 °C for 4 h, which was sifted by 100 meshes. Taking nano-TiO<sub>2</sub> powders, with methylene blue as the goal, this paper discusses the respond time, dosage, the light distance, pH value to methylene blue of the influence of the degradation rate and studies its photo-catalytic impact on performance.

**Testing method of TiO<sub>2</sub> photo-catalysis performance:** Photocatalytic reaction occurred in homemade reactor (Fig. 1). Put a certain amount of methylene blue solution in petri dishes (reactor) and add TiO<sub>2</sub> powders, under the irradiation of UV light. At regular intervals, sample centrifugal separation, take supernatant fluid, with paradigm 722 visible spectrophotometer to measure the absorbance of the methylene blue, to calculate the degradation rate and measure TiO<sub>2</sub> photo-catalytic impact on performance.

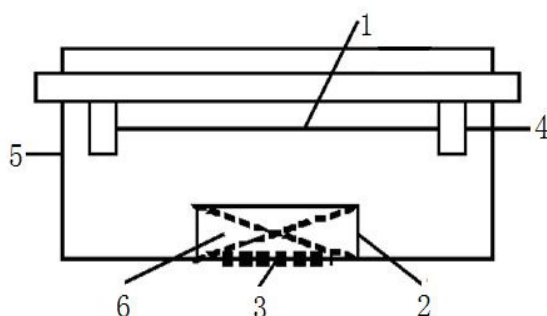
**Analysis method:** We used the 722 visible spectrophotometer to determine the absorbance of methylene blue. Degradation rate of methylene blue (D) was attained through the following equation:

TABLE-1  
FIRST ORDER KINETICS RATE CONSTANTS AND RELATIVE COEFFICIENT FOR PHOTOCATALYTIC DECOMPOSITION OF METHYLENE BLUE ON SELF-MADE TiO<sub>2</sub> AND P-25

Different of photo-catalytic conditions	Primary photo-degradation kinetics of equation	Relative coefficient (r)	Primary dynamic constant k (min <sup>-1</sup> )	Half-life (min)
Self-made TiO <sub>2</sub> powders	$\ln(C_0/C_t) = 0.0277t - 0.1035$	0.9187	0.0277	25.02
P-25	$\ln(C_0/C_t) = 0.0165t - 0.2527$	0.9704	0.0165	41.76

$$\text{Degradation rate (D)} = \frac{A_0 - A_t}{A_0} \times 100\%$$

In the formula,  $A_0$  is for the initial absorbance of methylene blue in samples and  $A_t$  is for the absorbance of methylene blue after photo-catalysis degradation.



1) UV lamp; 2) Reactor; 3) TiO<sub>2</sub> powders; 4) Power; 5) Separated light box; 6) Methylene blue solution

Fig. 1. TiO<sub>2</sub> photo-catalysis experiment device

## RESULTS AND DISCUSSION

**Standard curve production:** We adopted UV-visible spectrophotometry to have a quantitative analysis of methylene blue. First, by UV-visible spectrum scanning, we got the maximum absorption wavelength of methylene blue. Experiments show that the maximum absorption wave length of methylene blue is 665 nm<sup>8</sup>. After preparing 0, 0.5, 1.0, 1.6, 2.0, 2.5 mg/L standard solution of 10 mL, this solution of the absorbance was measured and standard curve was drawn. The regression equation is:  $y = 0.3853x - 0.012$  and the correlation coefficient is:  $r = 0.9996$ .

**Effect of time on degradation rate of methylene blue:** Take 50 mL 40 mg/L of methylene blue solution and then 0.2000g TiO<sub>2</sub> powders are added into the reactor. The determination absorbency is sampled every 0.5 h. Use the same methods and by the P-25 comparison, as is shown in Fig. 2.

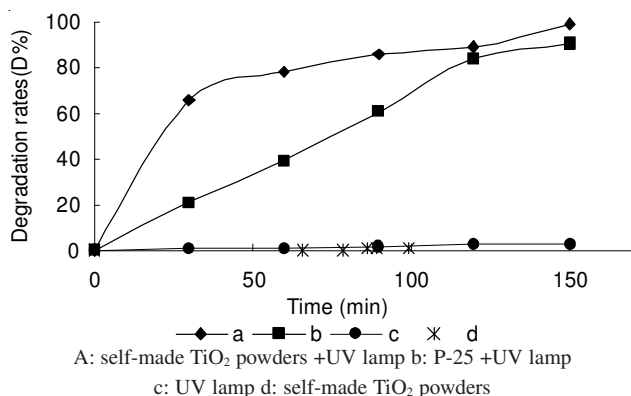


Fig. 2. Effect of time on degradation rate of methylene blue

Fig. 2 shows that photo-catalytic reaction time is 2.5 h. Under the same condition, the homemade TiO<sub>2</sub> powder degereneration rate achieved 99.35 % to the methylene blue, while its degradation rate only achieves 91.18 % after using P-25. The figure also shows that the degereneration rate is faster between 0-30 min, afterward the speed of degrades slows down. Also, under the same conditions with UV-lamp, homemade TiO<sub>2</sub> powders were compared and the results show that the UV-lamp, self-made TiO<sub>2</sub> powders degrade to the methylene blue mostly. Because TiO<sub>2</sub> powders has been radiated by UV-lamp, photoproduction electron which migrate to the superficial and hole both can participate in the photo-catalytic reaction acceleratly (quickly) and make electronic and hole compound. This kind of bonds can occur between the nanosecond and the picosecond time, when the photoproduction electron and the hole compound and the life of hole will reduce and slow down the photocatalytic reaction.

According to Fig. 3, the data which has been determined from the chart was put into first-level dynamics photolysis equation<sup>9</sup> separately and the results in dynamics photolysis fitted curve, as is shown in Table-1.

$$\ln(C_0/C_t) = kt + m \quad t_{1/2} = \frac{\ln 2}{\kappa}$$

here,  $k$  is for the dynamic constant;  $t$  for illumination time,  $C_0$  is for the initial concentration of methylene blue ( $\text{mg L}^{-1}$ ),  $C_t$  is for the concentration of methylene blue after photo-catalysis degradation ( $\text{mg L}^{-1}$ ),  $t_{1/2}$  is for the photo-degradation half-life (min) and  $m$  is a constant.

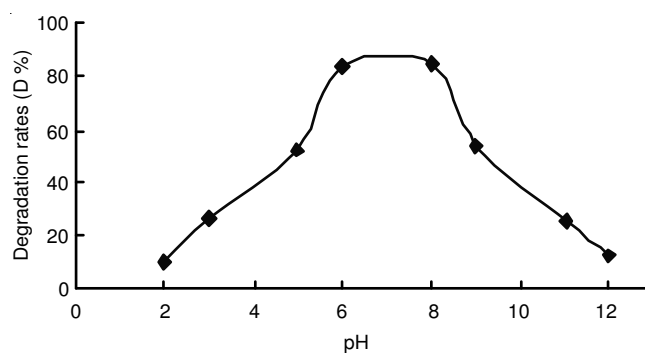


Fig. 3. Effect of pH values on the degradation rate of methylene blue

Through the regression analysis of experimental results, the different of photo-catalytic conditions photo-degradation of kinetic equation there are superior correlation coefficient, which indicates that they are in line with a dynamic equation when using the different of photo-catalytic degradation methylene blue. Table-1 shows that the effect of degradation rate of self-made TiO<sub>2</sub> powders surpasses P-25. Under the same conditions, with self-made TiO<sub>2</sub> powders photo-degradation,

TABLE-2  
FIRST ORDER KINETICS RATE CONSTANTS AND RELATIVE COEFFICIENT FOR PHOTOCATALYTIC DECOMPOSITION OF METHYLENE BLUE ON DIFFERENT TiO<sub>2</sub> POWDER AMOUNT

TiO <sub>2</sub> amount powder (mg/L)	Primary photo-degradation kinetics of equation $\ln(C_0/C_t) = Kt + m$	Relative coefficient (r)	Primary dynamic constant (min <sup>-1</sup> )	Half-life (min)
0.05	$\ln(C_0/C_t) = 0.0057t + 0.1601$	0.9487	0.0057	121.60
0.10	$\ln(C_0/C_t) = 0.0079t + 0.2317$	0.9383	0.0079	87.74
0.20	$\ln(C_0/C_t) = 0.0277t - 0.1035$	0.9187	0.0277	25.02
0.30	$\ln(C_0/C_t) = 0.0286t - 0.1382$	0.9924	0.0286	24.52
0.40	$\ln(C_0/C_t) = 0.0297t + 0.0153$	0.9422	0.0297	23.34

the same concentration of methylene blue, the half-life was reduced to 16.74 min, by the P-25 comparison.

**Effect of pH value on degradation rate of methylene blue:** Take a series of methylene blue solution and pour them into the reactor. Using pH meter (NaOH and HCl), the adjusted pH value were 2.14, 3.05, 4.66, 6.59, 9.00 and then 0.2000 g TiO<sub>2</sub> powders are added into the reactor. And then 0.2000 g TiO<sub>2</sub> powders are added into the reactor, the reaction time was 2.5 h. The absorbance was measured and the result is shown in Fig. 3.

Fig. 3 shows that the pH change has great influence on the degradation rate of methylene blue. In the acidic environment, with the increasing of the pH value, the degradation rate of methylene blue increased gradually, while in the alkaline environment, with the increasing of the pH value, the degradation rate of methylene blue declined gradually. Because, in the acidic conditions, the water reacted with TiO<sub>2</sub>, which increased the electrons' transfer to the surface of catalyst surface and its reaction with the surface adsorbed oxygen. This not only make light of electronic and hole compound, but also promoted electrons' reaction with oxygen, generating OH radicals. Therefore, photo-catalytic reaction also speeds up the efficiency. In the alkaline environment, with the increasing of pH value, the degradation rate of methylene blue declined gradually. Because organic matter in solution and dissolved oxygen react to change transfer complex, under the irradiation of UV light, change transfer complex became electronic excited states, while in the alkaline conditions was smaller<sup>10</sup>.

**Effect of the amount of TiO<sub>2</sub> powder on degradation rate of methylene blue:** Take a series of methylene blue solution and pour them into the reactor and then add 0.0500, 0.1000, 0.2000, 0.3000 and 0.4000 g TiO<sub>2</sub> powders, to it. The reaction time was 2.5 h, the absorbance was measured and the result is shown in Fig. 4.

Fig. 4 shows that when added 0.2000 g of TiO<sub>2</sub> powder, the degradation rate has achieved a better effect. In addition, when adding a dosage of TiO<sub>2</sub> powders, there is no significant effect on degradation rate. Considering the economic benefits and environmental aspects, it is advisable to choose a dosage of 0.2000 g. Dosage of TiO<sub>2</sub> powders and photocatalytic rate constant of methylene blue was fitted for used as the dynamics equation. Through the regression analysis of experimental results, we obtained the correlation coefficient and the results are shown in Table-2.

From the experiment results of the regression analysis, it is concluded that, with the increasing of TiO<sub>2</sub> powders dosage, the degradation rate constantly increases, while the half-life is shortened and the TiO<sub>2</sub> powder dosage can reach to 0.2000 g.

Then on increasing the TiO<sub>2</sub> powder dosage, the degradation rate will constantly increase while the half-life would not be changed<sup>5</sup>.

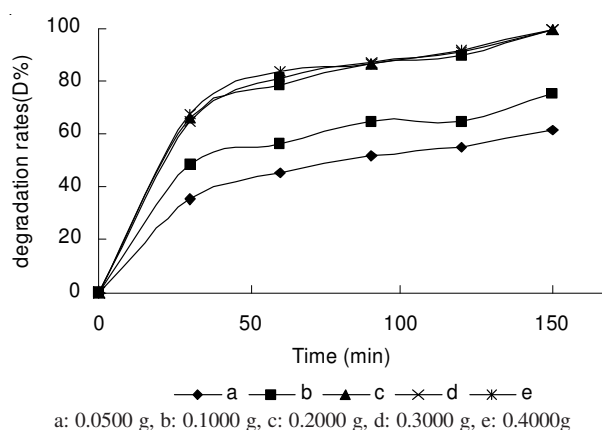


Fig. 4. Effect of TiO<sub>2</sub> powder amount on degradation rate of methylene blue

**Effect of light distance on degradation rate of methylene blue:** Adjusting the light distance (namely light source distance to the liquid surface) to 10, 16, 32 cm, respectively and adding 0.2 g of TiO<sub>2</sub> powders each time, the reaction time is 2.5 h, then the absorbance was measured, taking one type every 0.5 h to determine its corresponding absorbency. The results are shown in Fig. 5.

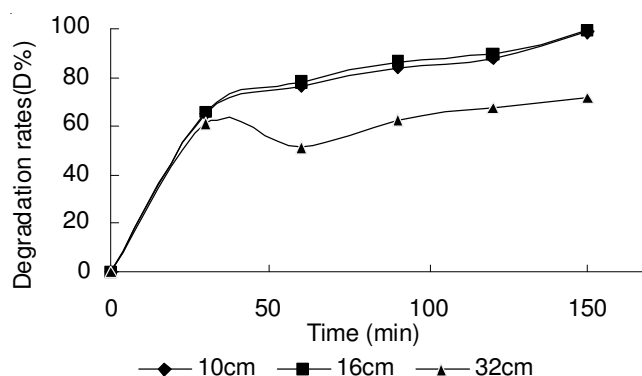


Fig. 5. Effect of different light distance on degradation rate of methylene blue

Fig. 5 shows that, with the increase of light, the light intensity is weak, the degree of TiO<sub>2</sub> powders which was activated will reduce and it is unfavourable to the degradation of methylene blue. The shortening of light is slightly advantageous to the degeneration rate of the methylene blue. But the distance of light cannot be infinitesimal. When it is too small,

the UV-lamp will have the heating function to the methylene blue solution, causing the solution to evaporate, increasing the density and resulting in inaccurate determination result.

**X-Ray powder diffraction:** Fig. 6 shows that line a of the instructions P-25 is a purer anatase TiO<sub>2</sub> type and line b is marked as '1' of which a type of rutile TiO<sub>2</sub> peak, indicating that self-made TiO<sub>2</sub> is mainly anatase TiO<sub>2</sub> type, as well as some rutile TiO<sub>2</sub> type. Description degradation in which anatase and rutile TiO<sub>2</sub> powders doped with each other are better than the degradation of single anatase TiO<sub>2</sub> powders (P-25), which is consistent with the reported<sup>10,11</sup>.

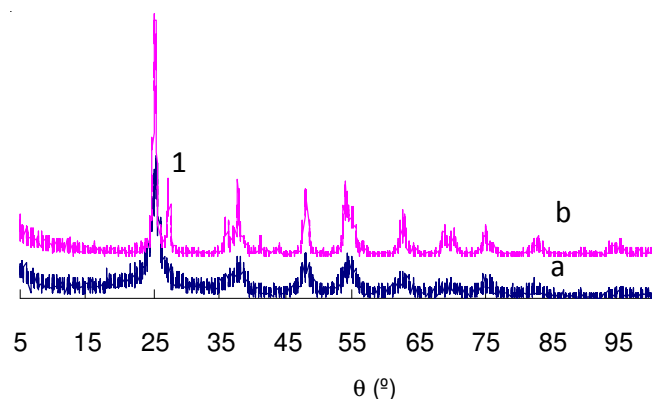


Fig. 6. XRD profiles of P-25 (a) and self- TiO<sub>2</sub> powder (b)

**Infrared spectra:** Fig. 7 shows that the IR spectra of nano-TiO<sub>2</sub> powder and P-25 are not very different spectra, of which 1000-400 cm<sup>-1</sup> of absorption peak of Ti-O bond by the vibration caused by the absorption, is a characteristic peak of TiO<sub>2</sub>; 3405 cm<sup>-1</sup> of absorption peak near is one O-H bond. This absorption peak is caused by the adsorption of the sample surface hydroxyl groups or water molecules.

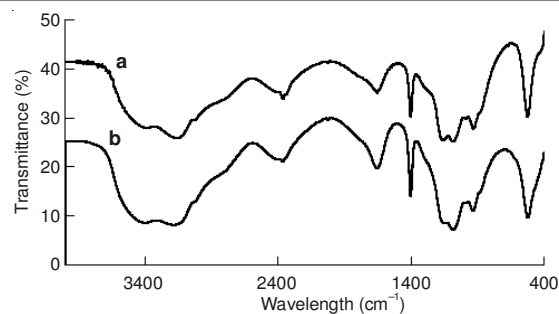


Fig. 7.

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