

Photocatalytic degradation of dye effluent by titanium dioxide pillar pellets in aqueous solution

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Abstract: Photocatalytic oxidation (PCO) process is an effective way to deal with organic pollutants in wastewater which could be difficult to be degraded by conventional biological treatment methods. Normally the TiO_2 powder in nanometre size range was directly used as photocatalyst for dye degradation in wastewater. However the titanium dioxide powder was arduous to be recovered from the solution after treatment. In this application, a new form of TiO_2 (i. e. pillar pellets ranging from 2.5 to 5.3 mm long and with a diameter of 3.7 mm) was used and investigated for photocatalytic degradation of textile dye effluent. A test system was built with a flat plate reactor (FPR) and UV light source (blacklight and solar simulator as light source respectively) for investigating the effectiveness of the new form of TiO_2 . It was found that the photocatalytic process under this configuration could efficiently remove colours from textile dyeing effluent. Comparing with the TiO_2 powder, the pellet was very easy to be recovered from the treated solution and can be reused in multiple times without the significant change on the photocatalytic property. The results also showed that to achieve the same photocatalytic performance, the FPR area by pellets was about 91% smaller than required by TiO_2 powder. At least TiO_2 pellet could be used as an alternative form of photocatalyst in applications for textile effluent treatment process, also other wastewater treatment processes.

Keywords: dyes degradation; photocatalytic reactions; TiO_2 catalyst

Introduction

The widespread presence of organic dyes in industrial wastewater, especially in textile industry, results in a potentially serious environmental problem. Conventional biological treatment methods are ineffective for decolouring and degrading such wastewater since the complex nature of synthetic dyes (Li, 1996; Slokara, 1999; Wang, 2000). In conventional wastewater treatment practices of industry, organic dyes are usually removed by adsorption or coagulation. However, new environmental law may consider spent adsorbent or sludge as hazardous wastes and require further treatment (Kuo, 2001). Consequently, novel technologies with more efficiency and less energy consumed have stimulated intensive research. As an alternative to conventional methods, advanced oxidation processes (AOPs) is based on the generation of very reactive species such as the hydroxyl radical that oxidates a broad range of organic pollutants quickly and non-selectively. The photocatalytic AOPs is a fast-developing area, in which the UV radiation or UV band in the solar radiation is used to provide the energy to generate the reactive species, which makes the process even more environmental friendly.

Coating the TiO_2 powder into thin film is the most often used form due to its considerable photocatalytic activity, high stability, non-environmental impact and low cost (Fujishima, 2000; Goswami, 1997; Zhang, 1997a; 1997b). However, the TiO_2 powder has to be separated from the treated water stream for reuse after the process. The solid-liquid separation

has become an extremely important and difficult issue, due to the TiO_2 powders used are in nanometre range. On the other hand, the fixation/coating of TiO_2 on substrates would result in the limited mass transfer (Blake, 1995; Ollis, 1991), loss of photocatalytic activity and the high cost (Bekbolet, 1996; Samuneva, 1993; Yu, 2000). In this application, TiO_2 pellet in a pillar shape was selected as photocatalyst to be investigated for photocatalytic degradation of textile dye effluent as it did not dissolve in water and was easy to recover and reuse. A test system was built with a flat plate reactor (FPR) installed with UV light (blacklight and solar simulator as light source respectively). Investigation on degradation mechanism and effectiveness under this configuration and characteristics of the process by using TiO_2 pellets as photocatalyst have been carried out in this study.

1 Experiment set up and chemicals used in the study

In order to investigate the characteristics of the process by using TiO_2 pellets as photocatalyst, an experimental rig with a FPR was designed and built (Fig. 1). The rig can be operated under the UV lamps/tubes or solar radiation when the UV lamps are removed. Both TiO_2 powder and TiO_2 pellets were studied in the experiments to compare their performance. The treated dye solution was prepared and stored in a tank. The solution was pumped through a tube to a flowmeter that was used to record the flow rate of the system. From the outlet of the flowmeter, fluid was then pumped into the spray tube that had a number of 1 mm-

diameter holes at 5 mm spacing along its length. The solution was trickled down through the FPR under UV/solar radiation irradiating and return back to the tank by gravity. The process was repeated until preset removal requirements were achieved. When TiO₂ powder was used as a photocatalyst it mixed with solution in the tank before hand. Otherwise, if the TiO₂ pellets were used as a photocatalyst the reactor was divided by perforated stainless plates into a series of rectangular slots where TiO₂ pellets were placed (Fig. 1b).

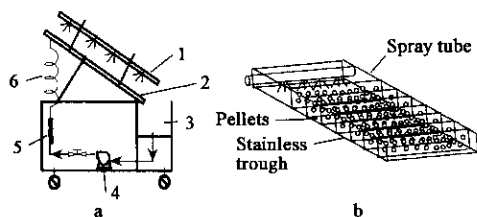


Fig. 1 Experimental rig (a); photoreactor (b)

1. UV source; 2. flat-plate photoreactor; 3. tank; 4. circulating pump; 5. flowmeter; 6. soft connection tube

UV light source consists of six parallel blacklight lamps of 36 W each (Philips Phild 3608, UV-A). Solar simulator composed of three 1000 W lamps (TRI-STAR 280, John Handland Ltd., England). The light intensity was measured by a pyranometer and an UV irradiance meter (model UV-A, the range of 320–400 nm, made in photoelectric instrument factory of Beijing Normal University, China). UV spectrophotometer (DR/4000, HACH Company, US) was used to measure the absorbency of solution at the maximum absorbent wavelength and then determine the solution concentrations by using the standard curve of absorbency vs mass concentration.

TiO₂ pellets in a small pillar shape were made by Degussa Company, Germany have the size ranging from 2.5 to 5.3 mm long and with a diameter of 3.7 mm. They are almost pure TiO₂ (83.2% anatase and 16.8% rutile), with a S-content of < 20 ppm and a Cl content of the order of 0.1 wt.%. No further elements are presented in contents above 0.05 wt.%. TiO₂ powder P25 had BET surface area 50 ± 15 m²/g, average primary particle size 21 nm, purity > 99.5% and contained 83.9% anatase, 16.1% rutile (made in Degussa Company, Germany) (Degussa, 1991). Methyl orange, acid Red 8, reactive orange 16 (made in Sigma-Aldrich Corporation) and Lanazol Blue CE (Vinylsulfone azo naphthalene, made in CIBA Specialty Chemicals Pty. Ltd.) were the dyes to be degraded in this study.

2 Results and discussion

Before conducting the experiment in the rig, a series of static experiment has been undertaken. A Lanazol Blue CE solution of 450 ml with the concentration of 30 mg/L was poured into a 182 mm diameter cylindric dish that contained 45 g TiO₂ pellets. The dish was then placed under mean UV

irradiation of 36.5 W/m². At specified time intervals, typically ten minutes or twenty minutes, a 5 ml sample of the testing solution was drawn out and analysed by spectrophotometer. The results are shown in Fig. 2(a) and (b). Lanazol Blue CE has a maximum absorbent peak of 600 nm. Fig. 2a shows that the absorbent curve changed with the irradiated time. The dye absorbency decreased with the increasing irradiated time significantly at all wavelengths. This means that the dye could be completely degraded by UV and TiO₂ pellets. The concentration of dye could be removed 91% in 114 min (Fig. 2b). The photocatalytic degradation process can be sufficiently characterised by the first-order kinetics,

$$C = C_0 e^{-kt} \quad (1)$$

Where C and C_0 are the solute concentration and the initial solute concentration respectively; T is the residence time; and k is the reaction rate constant. The constant k can be determined from experimental data as using the regression analysis. This finding was similar as other observers for TiO₂ powder (Blake, 1995; Goswami, 1995; 1997; Wyness, 1994a; 1994b).

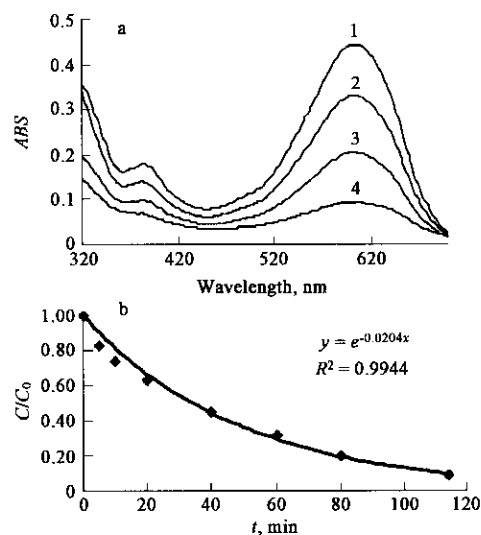


Fig. 2 Lanazol Blue CE photocatalytic degradation at UV = 36.5 W/m², 450 ml solution with the concentration of 30 mg/L and 45 g TiO₂ pellets
1. 0 min; 2. 10 min; 3. 40 min; 4. 80 min

Four kinds of dyes including Lanazol Blue CE, Methyl Orange, Acid Blue 120 and Reactive Orange were also tested under solar radiation simulator with 1.06 kW/m² mean intensity in four 75 mm diameter cylindric dishes respectively. Each dish contained 60 ml solution with the dye concentration of 30 mg/L and 16 g TiO₂ pellets. Results for degradation are shown in Fig. 3. All of them could be degraded effectively under the testing condition although they had different maximum absorbent wavelengths. The four-dye mixture was also investigated under the same testing conditions. The same volume from each dye solution of 30 mg/L concentration was mixed to produce the mixture

solution. 60 ml mixture was poured in a 75 mm diameter cylindrical dish containing 16 g TiO_2 pellets. The dish was then irradiated under solar radiation simulator with a mean intensity of 1.06 kW/m^2 . The result is shown in Fig. 4. A new absorbent curve with a maximum absorbent wavelength of 480 nm was formed for the four-dye mixture (Fig. 4). The absorbency in whole wavelength spectrum from 320 nm to 700 nm decreased with increasing the irradiated time. This may mean that the four-dye mixture was degraded in whole wavelength band non-selectively. Namely the treatment process just likes to degrade a new colour with maximum absorbent wavelength of 480 nm. Comparing with the process for only degrading one single dye, the constant k for the mixture degradation was lower and it would need more time to oxidate it (Table 1).

Table 1 Photocatalytic reaction constant k for degradations of four dyes at solar simulating light

Dye	Methyl Orange	Reactive Orange	Acid Blue 120	Lanasol Blue CE	Four-dye mix.
λ_{max} , nm	466	492	578	600	480
k , min^{-1}	0.0339	0.048	0.0461	0.0396	0.0228

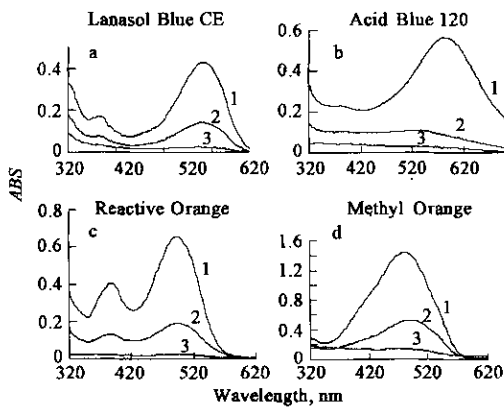


Fig.3 Photocatalytic degradations of four dyes at mean solar simulating light of 1.06 kW/m^2 in the dish containing 60 ml solution with the concentration of 30 mg/L and 16 g TiO_2 pellets
1: 0 min; 2: 30 min; 3: 70 min

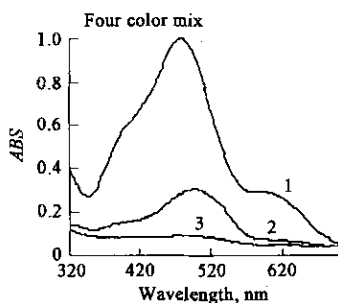


Fig.4 Photocatalytic degradations of four-dye mixture at solar mean lighter of 1.06 kW/m^2 in the dish containing 60 ml solution and 16 g TiO_2 pellets
1: 0 min; 2: 55 min; 3: 105 min

A static test was carried out using different amount of pellets. A Lanazol Blue CE solution of 50 ml with the

concentration of 30 mg/L was poured into 75 mm diameter dishes containing different amounts of TiO_2 pellets. The dishes were then placed under mean UV irradiation intensity of 36.5 W/m^2 . At the beginning and after 40 min of test, a 5 ml sample of the testing solution was drawn out and measured respectively. The photocatalytic reaction constant as a function of the amount of TiO_2 pellets at $\text{UV} = 36.5 \text{ W/m}^2$ are shown in Fig. 5. The constant increased as increasing the TiO_2 pellet amount. However, above 6.4 kg/m^2 of TiO_2 pellets the constant plateaued. This was because with the increment of the used TiO_2 pellet amount the area received the light was the same and the received light did not increased. In this study about 16 g TiO_2 pellets (3.7 kg/m^2) was enough to fill a 75 mm diameter dish in a layer with minimum gaps. More TiO_2 pellets increased the TiO_2 pellet thickness in the dish. Initially, the TiO_2 pellets located on bottom layer could receive some light which past through the gaps between the pellets. At 25 g (5.7 kg/m^2) in this testing condition, more TiO_2 pellets could not raise the photocatalytic reaction rate because the TiO_2 pellet on the bottom could not received any light (Fig. 5). When Lanazol Blue CE solutions were adjusted on the different pH by NaOH or H_2SO_4 was tested on the same condition and method, the photocatalytic constant decreased linearly with the increasing pH.

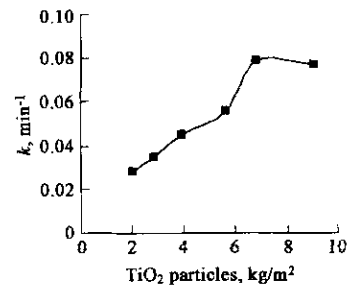


Fig.5 Effectiveness on the different amount of TiO_2 pellets for Lanazol Blue CE degradation

After the static tests, the experiment on the rig shown in Fig.1 was carried. The effectiveness on the different flow rate through the reactor was investigated at UV mean intensity of 36.5 W/m^2 . The reactor was tilted at 10° degree from the horizontal and 800 g TiO_2 pellets were spread evenly on the reactor of 0.3 m wide by 0.95 m long uniformly in the test. Initially the Lanazol Blue CE solution with the initial concentration of 30 mg/L and the volume of 8 L was put in the tank. An opaque cover placed over the reactor and UV lamps were turn on. The solution was then circulated through the rig at a desired flow rate until the steady flow was achieved in about ten minutes. The opaque cover was removed from the reactor, the test begun and an initial sample was taken. At specified time intervals, typically ten minutes or twenty minutes, a 15 ml sample of the test solution was drawn from the tank and measured. The results with various flow rates are shown in Fig.6. It can be seen

that the photocatalytic activity seems decreased with the higher flow rate. The reason was thought that the higher flow rate resulted in thicker film of liquid containing in the reactor and weakening UV light received by the TiO₂ pellets.

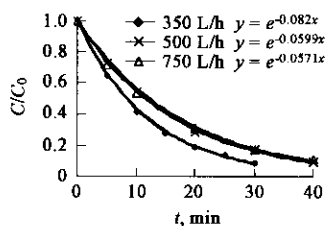


Fig. 6 Lanazol Blue CE degradation on the different flow-rate through the reactor

To reveal the difference of TiO₂ performance relating to aging (i. e. the times of usage), the same batch of TiO₂ (both powder and pellets) was repeatedly used in a series of tests. When using the powder, after each treatment process the treated solution remained without light in the tank for 12 h precipitation to separate TiO₂ powder. The clear water at the top of the tank was then removed and new dye and fresh water were added (to maintain dye concentration of 30 mg/L and 8 L solution in the tank) for the next treatment process. The flow rate was 1000 L/h for the powder tests. For the pellets, the initial concentration of 30 mg/L, the flow rate of 350 L/h and treated solution volume 8 L were used for each test. The same batch TiO₂ pellet was repeatedly used without regeneration in the tests. The dye solution was renewed after each treatment process.

The result that the photocatalytic reaction constant changed with usage times is shown in Fig. 7. In both (powder and pellet) cases, the performance has declined with increasing usage times. After eight times, the powder performance (i. e. constant) declined 62% and that of pellet declined about 39%. In powder case, as the powder was very fine (in the nanometre range) the loss of some powders together with "clear" water was thought to be one of reasons that caused the sharp decline of the photocatalytic performance. In the case of pellets, the process is more complicated. Some powder of TiO₂ was affixed in new pellets initially and then washed out by the solution, so that when the new pellets were used, the powders would also contribute to the photocatalytic performance. After the washing out there were only pellets to have a relative stable photocatalytic activity. It should be noted in our tests between each usage, the photocatalyst (powders or pellets) were kept in dark, i. e. no regeneration nor cleaning of TiO₂ occurs. Further study is needed to explore the topic with various condition of regeneration of TiO₂.

The effectiveness of the process (*EOP*) was defined from the following equation for evaluation the performance of TiO₂ powders and pellets.

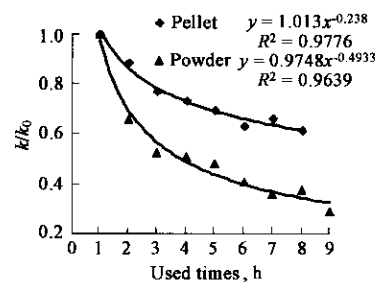


Fig. 7 The photocatalytic reaction constant as a function of the used times of TiO₂

$$EOP = \frac{(C_0 - C_s) \times V}{T_s \times D \times I \times A} \quad (2)$$

Where C_0 and C_s are the initial pollutant concentration and the accepted environmental pollutant concentration in solution respectively; V is the volume of the treated solution; T_s is the treatment time; D is the mass of photocatalyst used; I is the radiation intensity, and A is the reactor areas respectively.

Generally, *EOP* indicates the quantity of pollutant was degraded by using per unit photocatalyst under per unit radiation in per reactor area during a unit time. For our purposes of comparison (of powder and pellet), the effectiveness of the process, *EOP* indicates a mean ability of per unit photocatalyst to degrade the pollutant in the solution from the initial concentration C_0 to the accepted concentration C_s .

Table 2 lists the operating data used and results obtained for two photocatalytic degradation processes by using TiO₂ powders and pellets respectively. The operating parameters (i. e. flow rate, tilted angle etc.) were set based on the optimum for both cases (Li, 2001; 2003). The *EOP* of the powder is about 21 times greater than the *EOP* of the pellets (Table 2). However the required time to reach the goal in the process using the pellet is three times shorter than using the powder in this case (Table 2). Assuming that both processes (using powder and pellets) would degrade the same amount of pollutant in the same time period and intensity and both *EOP* are kept the same, the FPR area required is 0.15 m² and 60% smaller than that with the powder, which is a significant reduction of system cost. However about 240 times more pellets (in term of mass) is required. Besides, to compare with TiO₂ powder, the TiO₂ pellets system has the advantage of easy maintenance and reusing photocatalyst in practical applications, which also reduces the cost. The economics of using the powder or pellet depends on the cost of the pellets (comparing with the powder), and that of the construction and operation of the reactor.

3 Conclusions

TiO₂ in a form of small pillar pellets was first used as a photocatalyst to degrade textile dyes and its characteristics

Table 2 Comparison between TiO₂ powder and pellets

Photocatalyst	Powder	Pellets
I , W/m ²	38.3	36.5
A , m ²	0.368	0.291
FL , L/h	1000	350
D , g	8	800
C_0 , mg/L	30.08	30
V , L	8	8
T_s , $C_s = 5\%$, min	129	36.5
k , min ⁻¹	0.0232	0.082
EOP , $C_s = 5\%$	1.572×10^{-5}	7.35×10^{-7}

were also investigated in this paper. The TiO₂ pillar pellet could have the similar function to the powder to efficiently remove colours regardless of solo dye or multiple-dye mixture. The results indicated that the degradation trend with an exponent decrease could be used to describe the process, as the same as for TiO₂ powder. The Langmuir-Hinshelwood (L-H) expression to a pseudo-first-order expression could be applied the process. Despite of more(mass) TiO₂ pellets than TiO₂ powders are required in the application to reach the same goal, the reactor area required with pellets was about 91% less than that required with powder. Moreover the reactor/system with TiO₂ pellets has the advantage of easy maintenance, simple operation and no extra equipment needed for recovering and reusing photocatalyst in practical applications. Therefore, it at least can be concluded the TiO₂ pellet can be used as an alternative photocatalyst for using UV or solar energy to treat textile effluent, and also other wastewater treatment processes. The selection will depend on the detailed economic analysis of the particular case.

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