

## Study on the photocatalysis performance and degradation kinetics of X-3B over modified titanium dioxide

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Received 18 August 2004; received in revised form 11 November 2004; accepted 13 November 2004

Available online 18 December 2004

### Abstract

In this paper, reactive brilliant X-3B was used as a model compound to study the photocatalytic activity of TiO<sub>2</sub>. Experimental results showed that the adulteration of iron and silver on TiO<sub>2</sub> could greatly improve the activity of TiO<sub>2</sub>, and the optimum adulteration amount of iron and silver was 0.1 wt.% (Fe/TiO<sub>2</sub>) and 0.05 wt.% (Ag/TiO<sub>2</sub>), respectively, at the adulteration range of experiments. The photocatalytic degradation kinetics of X-3B on TiO<sub>2</sub>, Fe/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> were also studied. The results showed that the degradation of X-3B on all of them were in accordance with the Langmuir–Hinshelwood kinetics model well, and the sequence of apparent reaction rate constants *k* of X-3B degradation catalyzed by TiO<sub>2</sub>, Fe/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> was Ag/TiO<sub>2</sub> > Fe/TiO<sub>2</sub> > TiO<sub>2</sub>, while adsorption equilibrium constants *K<sub>A</sub>* of X-3B on Fe/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> were approximately the same, and both were greater than that of TiO<sub>2</sub>.

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**Keywords:** Modified TiO<sub>2</sub>; Reactive brilliant X-3B; Photocatalytic degradation; Kinetics; Langmuir–Hinshelwood model

### 1. Introduction

The widespread presence of organic dyes in industrial wastewater results in a potentially serious environmental problem. Conventional biological treatment processes are ineffective for removing the coloring from industry wastewater because of the nature of synthetic dyes and the high salinity of dye wastewater [1]. Adsorption and coagulation are conventional practices used to treat dyes in wastewater, usually causing secondary pollutions. Consequently, an alternative to conventional methods was studied extensively, that is advance oxidation processes (AOPs). AOPs are based on the generation of reactive species such as hydroxyl radicals ( $\bullet\text{OH}$ ) that can oxidize a broad range of organic pollutants quickly and non-selectively [2,3].

The heterogeneous photocatalytic oxidation process using semiconductors as catalysts was one of the novel advanced oxidation technologies developed in the 1970s. Titanium dioxide is widely used as a photocatalyst because it is photochemically stable, non-toxic and relatively inexpensive [4,5]. The recombination ratio of photo-induced electrons ( $e^-$ ) and positive holes ( $h^+$ ) produced from the interior of pure TiO<sub>2</sub> under the irradiation of UV light ( $\lambda < 380 \text{ nm}$ ) is so high that the photocatalytic efficiency of TiO<sub>2</sub> to degrade pollutants is decreased greatly. In order to improve the photocatalytic activity of titanium dioxide, more and more researchers were interested in the modification of titanium dioxide which mainly included the noble metal deposition on the surface [6–8], the adulteration of transition metals [9,10], the surface photosensitization [11] and the combination of two different semiconductors [12]. But most of the studies were focused on the effect of the modification of TiO<sub>2</sub> and the effect factors of the removal efficiency of pollutants [13–18]; few researchers did in-depth studies about it.

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The production and consumption of azo dyes account for over 50% of the total dyes around the world. Reactive brilliant red X-3B is a kind of typical azo dye. Therefore, X-3B was chosen as a representative model compound to study the changes in the photocatalytic activity of TiO<sub>2</sub> after modification. To explain the variety of photocatalytic activity, the degradation behavior of X-3B was also investigated for macroscopic degradation kinetics.

## 2. Methodology

### 2.1. Chemicals

Reactive brilliant red X-3B was purchased from the Dyes Research Institute of Tianjin and used without further purification, whose structure is shown as Fig. 1. TiO<sub>2</sub> (mean particle size: 30 nm, about 70% anatase form and 30% rutile form) and modified TiO<sub>2</sub> (mainly the anatase form, mean particle size: 10 nm) powder were prepared using sol-gel methods by us. The preparation process and characterization of catalysts were reported in a previous published paper [19] and [20]. Deionized water was used for the preparation of X-3B solution.

### 2.2. Experimental procedures

All the experiments were performed in a batch photoreactor of 1000 ml in volume, fitted with a 125 W high-pressure mercury lamp (Yaming, Shanghai, emission wavelength: 365 nm). The irradiation intensity of the lamp at the surface of dye solution was measured with a ZD-II model luminometer (Peiguang, Jiangsu). Solutions with the desired concentration in dye and the load of TiO<sub>2</sub> or modified TiO<sub>2</sub> were fed into the reactor. The volume of the dye solutions of a batch experiment was 500 ml. The aqueous solutions were magnetically stirred, and the pH of the solutions was adjusted using dilute nitric acid or aqueous sodium hydroxide solution. At regular time intervals, samples of about 5 ml in volume were taken and centrifuged, and then filtrated in a 0.45 μm syringe filter. A supernatant was used to analyze the concentration of X-3B. The dye X-3B was analyzed on a UV-vis 7520 spectrophotometer; the determination wavelength was 536 nm which is the maximum absorption wavelength of X-3B. The determined absorbance was converted

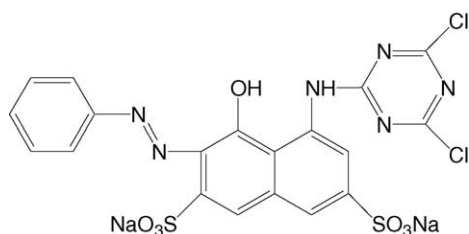


Fig. 1. The structure of the reactive brilliant X-3B.

to concentration through the standard curve method of X-3B. The destruction efficiency of X-3B was calculated by  $R = (1 - C/C_0) \times 100\%$ , where  $C_0$  and  $C$  were the concentration of X-3B when reaction time was 0 and  $t$ , respectively. The photocatalytic oxidation process of X-3B in the present article was described with the pseudo-first-order kinetics model, which is  $-(dc/dt) = k_1t$ , where  $k_1$  is the pseudo-first-order rate constant, and could be calculated by a regression analysis method.

## 3. Results and discussion

### 3.1. Effect of deposition dosage of iron and silver on TiO<sub>2</sub> activity

As shown in Figs. 2 and 3 where the experimental conditions were pH 4.00 (the effect of pH of solutions to the photocatalytic activity of TiO<sub>2</sub> were studied in reference [19] and the conclusion was reached that the photocatalytic activity of TiO<sub>2</sub> to the degradation of X-3B increased with decreasing pH of X-3B solutions. To practical purpose, pH value could

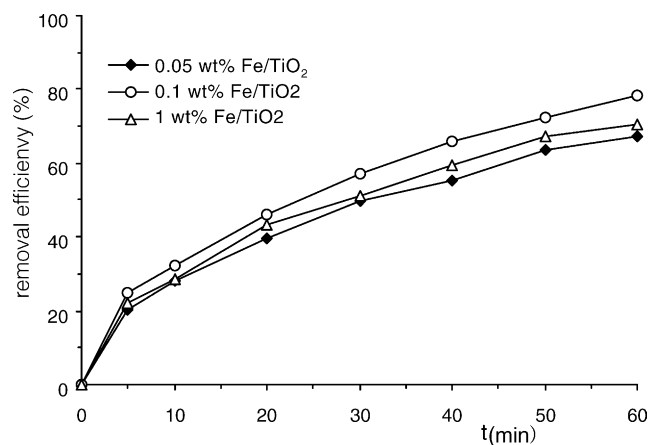


Fig. 2. Effect of deposition dosage of iron on the TiO<sub>2</sub> photocatalysis activity.

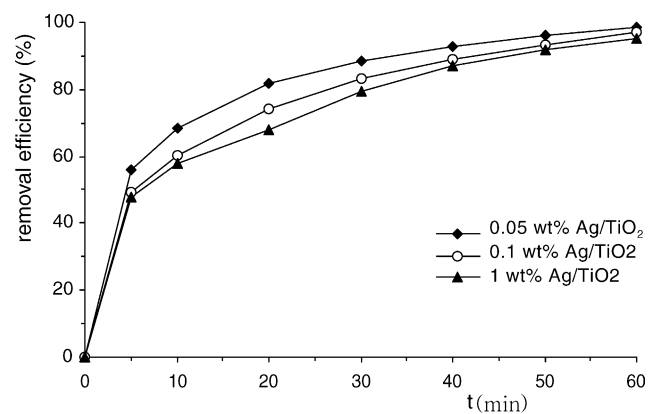


Fig. 3. Effect of deposition dosage of silver on the TiO<sub>2</sub> photocatalysis activity.

not be too low, so the pH values of X-3B solutions were all adjusted to 4 in this study to make a compromise between efficiency and practicality), the light intensity at the liquid surface of X-3B solution was 2.05 mW/cm<sup>2</sup>, the initial concentration of X-3B was 20 mg/L, the catalysts used were all calcined under 600 °C, and the usage amount of catalysts was 0.5 g/L; the optimum deposition dosage of iron was 0.1 wt.% among 0.05%, 0.1% and 1% deposition dosage, while the optimum value of silver was 0.05 wt.% which is much lower than the value 1–10% that Veronica V. and Cui P. had obtained through their experiments [21,22].

### 3.2. The effect of calcination temperature on the modified TiO<sub>2</sub> activity

The calcination temperature of TiO<sub>2</sub> had a significant effect on its catalytic activity. In this section, in order to screen the optimum calcination temperature of catalysts, the catalytic activity of the Fe-loaded TiO<sub>2</sub> and Ag-loaded TiO<sub>2</sub> under different calcination temperatures was compared. The first-order reaction rate constants of photocatalytic degradation of X-3B catalyzed by the Fe-loaded TiO<sub>2</sub> and Ag-loaded TiO<sub>2</sub> under different calcination temperatures are listed in Table 1, where the experimental conditions were pH 4.00, light intensity was 2.0 mW/cm<sup>2</sup>, the initial concentration of X-3B was 20 mg/L, the catalyst used was titanium dioxide containing 0.1 wt.% ferrum and 0.05 wt.% silver, respectively, and its usage amount was 0.5 g/L.

It can be seen from Table 1 that the catalysts without calcination had little activity, the reason being that they could be activated only after calcination. The photocatalytic activity of two kinds of modified catalysts decreased with increasing calcination temperatures in the range of 300–700 °C, the catalytic activity was the largest when calcination temperature was 300 °C, and the activity of the Ag-loaded TiO<sub>2</sub> was higher than that of Fe-loaded TiO<sub>2</sub>. Compared with the modified TiO<sub>2</sub> calcined under 300 °C, the activity of modi-

fied TiO<sub>2</sub> calcined under 400 °C decreased a little, but was not very significant. When the calcination temperature continued to increase after that, the activity of modified TiO<sub>2</sub> reduced rapidly. Perhaps this occurred because the increase of calcination temperature led to the rapid decrease of the specific surface area of titanium dioxide. In a previous study, the conclusion was obtained that the pure titanium dioxide processing mixture crystal form calcined under 600 °C had the highest activity, and the activity of the pure titanium dioxide calcined under 300 °C had the worst activity [19]. Contrary to the previous conclusion, after the TiO<sub>2</sub> was modified, the TiO<sub>2</sub> calcined under 300 °C had the highest activity.

The following explanation could be a reason for the change in the results of TiO<sub>2</sub>. In the course of photocatalytic degradation of pollutants by pure TiO<sub>2</sub>, the amount of photo-induced holes on the surface of TiO<sub>2</sub> was relatively few because of the high recombination ratio of photo-induced electrons and holes. Therefore, the X-3B pollutants adsorbed on the surface of TiO<sub>2</sub> could not be oxidized by oxidation species in time, and the specific surface area of TiO<sub>2</sub> was superfluous. The effective specific surface area of pure TiO<sub>2</sub> calcined under 600 °C was approximately close to that of being calcined under 300 °C. On the other hand, titanium dioxide calcined under 600 °C was advantageous for the separation of photo-induced electrons and holes because it consisted of anatase and rutile, which made titanium dioxide into a complex semiconductor and improved the quantum yield of TiO<sub>2</sub> greatly, so the photocatalytic activity of TiO<sub>2</sub> calcined under 600 °C was the best. After that, TiO<sub>2</sub> was modified by adulterating with ferrum and silver on the surface, both of which could separate the electrons and holes more effectively. Consequently, the reactive brilliant red X-3B adsorbed on the surface of TiO<sub>2</sub> could be oxidized and degraded rapidly by the holes and a series of free radicals, induced by the holes made by the adulteration. To put it more succinctly, the effective specific surface area of modified titanium dioxide increased a great deal. In such a case, the specific surface area of TiO<sub>2</sub> was very important, and the effect of mixture crystal form of TiO<sub>2</sub> was minor compared with the effective specific surface area of TiO<sub>2</sub>. After modification, TiO<sub>2</sub> with anatase, which has a much larger specific surface area, had a greater catalytic activity.

### 3.3. Comparison of the activity of pure and modified TiO<sub>2</sub>

The comparison curves of the photocatalytic activity of pure TiO<sub>2</sub> calcined under 600 °C, Fe-loaded TiO<sub>2</sub> containing 0.1% ferrum, and Ag-loaded TiO<sub>2</sub> containing 0.05% silver calcined under 300 °C are plotted in Fig. 4, where the experimental conditions were a pH of 4.00, a light intensity of 2.05 mW/cm<sup>2</sup>, an initial concentration of X-3B of 20 mg/L, and the usage amount of the catalyst was 0.5 g/L. It can be seen from Fig. 4 that the activity of the Ag-loaded TiO<sub>2</sub> was a little higher than that of the Fe-loaded TiO<sub>2</sub>; both of them were much higher than that of pure TiO<sub>2</sub>. The reason behind the activity variation of TiO<sub>2</sub> is explained below.

Table 1  
The first-order degradation rate constants of X-3B photocatalyzed by Fe/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> under different calcination temperatures

	Calcination temperature (°C)	First-order reaction rate constant (min <sup>-1</sup> )	Correlation coefficient <i>r</i>
0.1 wt.% Fe/TiO <sub>2</sub>	Without calcination	0.0016	0.9449
	300	0.0471	0.9992
	400	0.0445	0.9987
	500	0.0263	0.9930
	600	0.0219	0.9995
	700	0.0150	0.9947
0.05 wt.% Ag/TiO <sub>2</sub>	Without calcination	0.0020	0.9596
	300	0.0585	0.9994
	400	0.0524	0.9994
	500	0.0180	0.9999
	600	0.0145	0.9874
	700	0.0119	0.9882

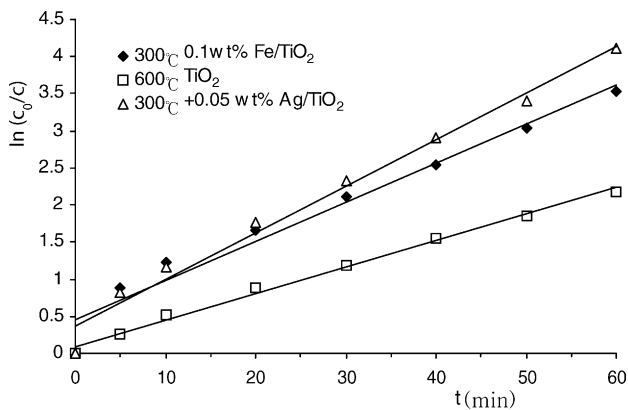


Fig. 4. The comparison curves of the activity of pure and modified TiO<sub>2</sub> under calcination temperatures.

Some limitation sites were imported into the crystal lattice of TiO<sub>2</sub> or, on the other hand, the crystal degree of TiO<sub>2</sub> was changed by the adulterated ferrum ions on titanium dioxide, affecting the recombination of the electron–hole pairs, which then trapped the electrons and holes, prolonging their life. Because Fe<sup>3+</sup> was an effective acceptor for electrons (Fe<sup>3+</sup> + e → Fe<sup>2+</sup>), it contests for electrons with the holes, thereby decreasing the recombination of the electrons and holes on the surface of TiO<sub>2</sub>. Consequently, there were more •OH and O<sub>2</sub><sup>-</sup> generated on the surface of the titanium dioxide, which greatly improved the oxidation degradation rate of X-3B. However, if the excessive iron was deposited on TiO<sub>2</sub>, more Fe(OH)<sup>2+</sup> would be formed. Fe(OH)<sup>2+</sup> had a greater adsorption to the incidence light in the range of 290–400 nm. This higher adsorption decreased the light energy irradiating on the surface of TiO<sub>2</sub> and the removal efficiency of X-3B, so the adulteration amount of iron had an optimum value of 0.1 wt. %.

Similarly, after Ag<sup>+</sup> was adulterated on the surface of TiO<sub>2</sub>, Ag<sup>+</sup> could be reduced into an Ag atom by e<sup>-</sup> under the irradiation of UV light. Ag and TiO<sub>2</sub> were generally regarded as the large number of micro-cells formed on the surface of TiO<sub>2</sub>, metallic Ag was the anode of the micro-cell and TiO<sub>2</sub> was its cathode. When TiO<sub>2</sub> particles were illuminated with light with an energy equal to or greater than the bandgap energy, the electrons excited from the valence band to the conduction band and migrated to the anode of the micro-cell, and the holes migrated to the cathode. Therefore, the electrons and holes were effectively separated. However, there was also an optimum loading value of Ag<sup>+</sup>; if the silver ion loaded on the titanium dioxide was excessive, the activity of Ag/TiO<sub>2</sub> particles, on the contrary, would decrease. Excessive coverage of the photosensitive surface by overloading of silver decreases the amount of light reaching the TiO<sub>2</sub> surface, which reduces the number of electron–hole pairs generated and lowers the rate of organic oxidation [23,24]. It is also possible that above the optimum loading, silver particles can also act as a recombination center of the electrons and holes [25]. The optimum loading value was 0.05% in this study.

#### 3.4. Photocatalytic degradation kinetics of X-3B catalyzed by TiO<sub>2</sub> before and after modification

A series of X-3B solution were prepared, and the initial concentrations of X-3B were about 10, 20, 30, 40 and 60 mg/L, respectively. The catalyst added was pure TiO<sub>2</sub> calcined under 600 °C, Fe-loaded TiO<sub>2</sub> containing 0.1% ferrum, and Ag-loaded TiO<sub>2</sub> containing 0.05% silver calcined under 300 °C, respectively. The experimental conditions were pH 4.00, light intensity was 2.34 mW/cm<sup>2</sup> and all of the catalysts dosage used was 500 mg/L. The samples were drawn from the reactor for analysis with UV–vis spectrophotometer every fixed time. The relationship curves between the concentration of X-3B and the illumination time catalyzed by different catalysts are plotted in Figs. 5–7. Based on the removal curves, the degradation reaction rate constants and initial reaction rate  $r_0$  were calculated and are summarized in Table 2.

$1/r_0$  were plotted versus  $1/C_0$  based on the data from Table 2, as shown in Fig. 8. It can be seen that  $1/r_0$  almost correlated to  $1/C_0$  well, so the degradation kinetics of X-3B catalyzed by three kinds of TiO<sub>2</sub> catalysts were in accordance with the Langmuir–Hinshelwood kinetics model (L–H model) [26–28], which is commonly expressed as Eq. (1):

$$r_0 = -\frac{dC}{dt} = \frac{kK_A C_0}{1 + K_A C_0} \quad (1)$$

where  $r_0$  is the initial photocatalytic degradation rate (mg L<sup>-1</sup> min<sup>-1</sup>),  $C_0$  is the initial X-3B concentration (mg/L),  $k$  is the apparent reaction rate constant (mg L<sup>-1</sup> min<sup>-1</sup>) and  $K_A$  is the adsorption equilibrium constant (L mg<sup>-1</sup>).

According to the Langmuir–Hinshelwood kinetics formula and the formulae fitted in Fig. 8,  $k$  and  $K_A$  values during the degradation of X-3B photocatalyzed by TiO<sub>2</sub>, Fe/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> were calculated and are listed in Table 3.

It is obvious that the sequence of apparent reaction rate constants  $k$  of X-3B degradation catalyzed by TiO<sub>2</sub>, Fe/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> was Ag/TiO<sub>2</sub> > Fe/TiO<sub>2</sub> > TiO<sub>2</sub>, which is con-

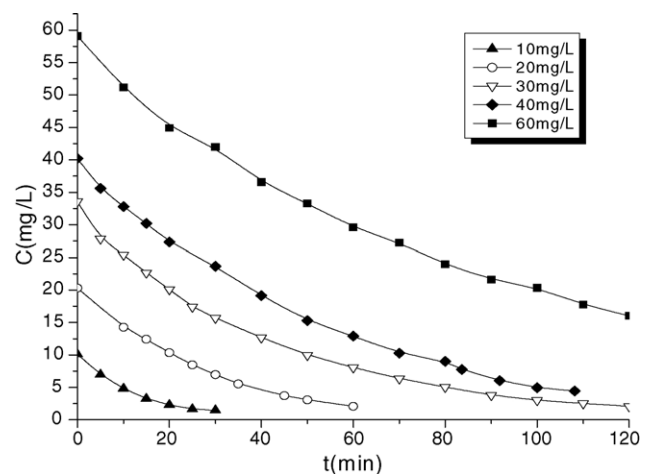


Fig. 5. The  $t$ – $C$  plots for X-3B destruction of different initial X-3B concentration catalyzed by TiO<sub>2</sub>.

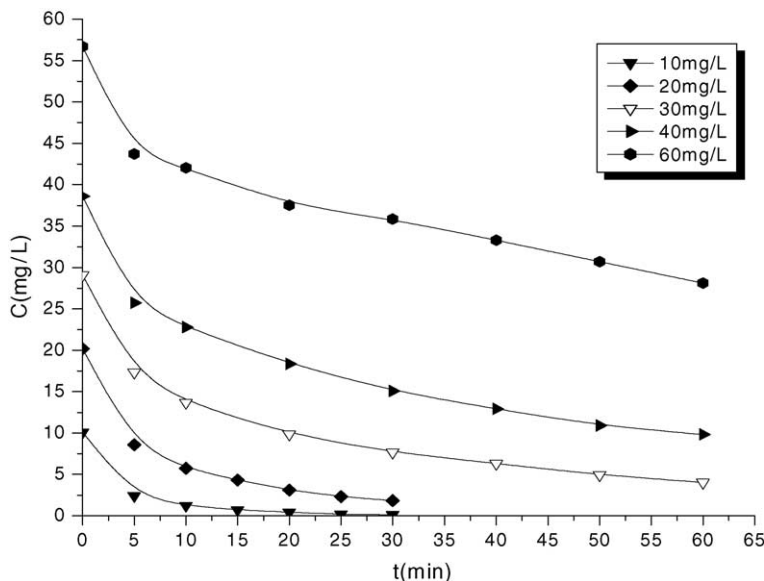


Fig. 6. The  $t$ - $C$  plots for X-3B destruction of different initial X-3B concentration catalyzed by Fe/TiO<sub>2</sub>.

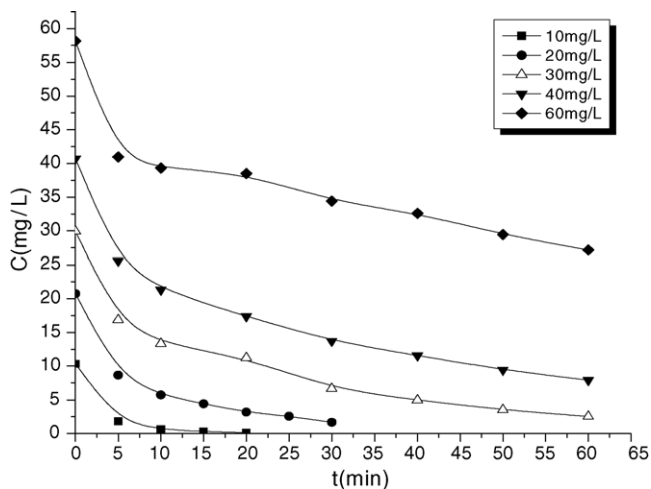


Fig. 7. The  $t$ - $C$  plots for X-3B destruction of different initial X-3B concentration catalyzed by Ag/TiO<sub>2</sub>.

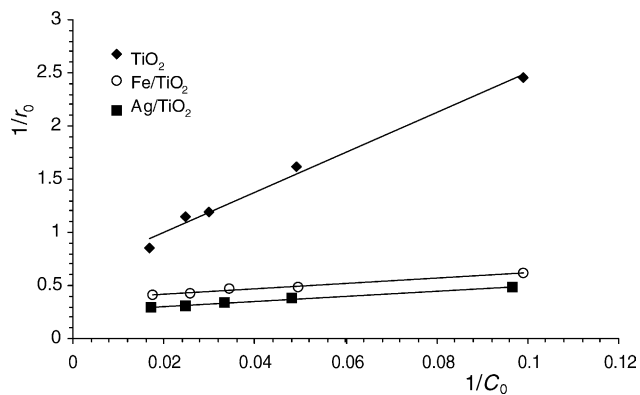


Fig. 8.  $1/r_0$ - $1/C_0$  relationship curves of photocatalytic degradation of X-3B catalyzed by different catalysts.

sistent with the conclusion of the comparison of three reaction rates obtained previously. It can be seen that for the adsorption equilibrium constant  $K_A$ ,  $K_A$  of X-3B catalyzed by Fe/TiO<sub>2</sub> was approximately equal to that of Ag/TiO<sub>2</sub>; both of them were two to three times greater than that of pure TiO<sub>2</sub>. The reaction rate constants of X-3B catalyzed by three kinds of TiO<sub>2</sub> had 25–50 times of adsorption equilibrium constants of that. Therefore, the photocatalytic degradation of X-3B by TiO<sub>2</sub> relied mainly on the surface oxidation destruction reaction attacked by the hydroxyl radical adsorbed on the surface of the catalysts. It is significant to note that the adsorption of X-3B on the surface of TiO<sub>2</sub> was the same important, only after X-3B was first adsorbed on the surface of the catalysts, could the X-3B be oxidized by radical species. The prod-

Table 2  
The removal kinetics parameters of different initial X-3B concentration catalyzed by different catalysts

Catalyst	Initial X-3B concentration $C_0$ (mg/L)	Reaction rate constant $k_1$ (min <sup>-1</sup> )	Initial reaction rate $r_0$ (mg/L min <sup>-1</sup> )
TiO <sub>2</sub>	10.1	0.0674	0.408201
	20.3	0.0387	0.6191
	33.6	0.0232	0.8445
	40.2	0.0203	0.8674
	59.1	0.0106	1.1775
Fe/TiO <sub>2</sub>	10.1	0.116	1.6094
	20.2	0.0611	2.0424
	29.1	0.0257	2.1285
	38.6	0.0216	2.3475
	56.7	0.0113	2.3875
Ag/TiO <sub>2</sub>	10.34	0.1853	2.0570
	20.76	0.0759	2.6005
	29.95	0.038	2.9804
	40.2	0.0242	3.1811
	58.2	0.0128	3.3790

Table 3

Apparent reaction rate constant and adsorption equilibrium constant of the degradation of X-3B catalyzed by three kinds of catalysts

Catalyst	Fitting L–H formula	Apparent reaction rate constant $k$ ( $\text{mg L}^{-1} \text{min}^{-1}$ )	Adsorption equilibrium constant $K_A$ ( $\text{mg/L}$ )	Regression relative coefficient $r$
TiO <sub>2</sub>	$1/r_0 = 18.737/C_0 + 0.6265$	1.5961	0.03343	0.9942
Fe/TiO <sub>2</sub>	$1/r_0 = 2.5178/C_0 + 0.3711$	2.6947	0.09999	0.9943
Ag/TiO <sub>2</sub>	$1/r_0 = 2.4042/C_0 + 0.2574$	3.8850	0.1071	0.9965

ucts formed continuously desorbed from the surface of the catalysts, and the vacant active sites could adsorb X-3B in solution ceaselessly until X-3B was oxidized entirely.

#### 4. Conclusions

In this study the photocatalytic activity of TiO<sub>2</sub> before and after modification was compared using reactive brilliant red X-3B as a model compound, and the Langmuir–Hinshelwood model could be used to express the photocatalytic degradation kinetics of X-3B well. The following conclusions can be drawn:

- (1) The photocatalytic activity of modified TiO<sub>2</sub> was much higher than that of pure TiO<sub>2</sub>; the doping amounts of Fe and Ag have optimum values, and they were 0.1 wt.% and 0.05 wt.%, respectively, at the adulteration range of experiments.
- (2) Compared with pure TiO<sub>2</sub>, the optimum calcination temperature of modified TiO<sub>2</sub> was 300 °C, not 600 °C.
- (3) The photocatalytic degradation kinetics of X-3B on TiO<sub>2</sub>, Fe/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> were all in accordance with Langmuir–Hinshelwood kinetics model well; the sequence of apparent reaction rate constants  $k$  of TiO<sub>2</sub>, Fe/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> was  $\text{Ag/TiO}_2 > \text{Fe/TiO}_2 > \text{TiO}_2$ , while the adsorption equilibrium constants  $K_A$  of Fe/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> were close and they were both two to three times greater than that of TiO<sub>2</sub>.

#### Acknowledgment

The authors are grateful to the National Natural Science Foundation of PR China for its financial support (No. 20207002).

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