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A study on dye photoremoval in TiO_2 suspension solution

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Abstract

TiO_2 samples with different characteristics and adsorption ability were prepared via hydrolysis of titanium tetraisopoxide and calcination at four different temperatures. The photoremoval of Acid Red 3B catalyzed by these catalysts was carried out. The results show high firing temperature lead to large TiO_2 particle and a low adsorption ability of TiO_2. The dye photoremoval reaction fits zero order kinetics well in catalyst-free solution and changes to first order kinetics in the presence of TiO_2. The solution pH value has a large effect on the removal efficiency. High dye removal efficiency can be obtained at high pH value. Catalyst addition improves the dye photoremoval efficiency and leads to the change of removal kinetics. Anatase TiO_2 fired at 400 °C shows the best catalytic activity and the catalytic activity of TiO_2 fired at 800 °C, which is rutile, is the worst of all catalysts. The catalytic ability of TiO_2 is influenced mainly by two factors of catalysts: crystalline form and adsorption ability for Acid Red 3B. The crystalline form is a more important factor influencing the catalytic activity than the adsorption ability of TiO_2 and the catalytic activity can be enhanced by the high dye adsorption ability of TiO_2.

Keywords: Photoremoval; TiO_2; Catalytic ability; Firing temperature; Kinetics; Adsorption; Crystalline form

1. Introduction

The wastewater from textile dyeing contains a high concentration of organic compounds which are toxic and colorful. The typical treatment methods of dye wastewater include biological treatment, chemical coagulation, activated carbon adsorption and ultrafiltration [1,2]. Based on the utilization of solar energy and the complete mineralization of organic compounds to carbon dioxide, water and mineral acid [3], photocatalytic treatment is a more attractive alternative for the removal of soluble organic compounds in wastewater since it can avoid oxidant addition and the second pollution [4–6].

In the process of photochemistry, the presence of a catalyst is necessary to obtain ideal treatment efficiency [7]. TiO_2 is usually adopted because of its high activity [8] and stability [9]. The characteristics of a catalyst, such as its crystalline form, particle size, adsorption ability and surface area, vary with the preparation condition and have important effect on the catalytic ability of TiO_2 [10–12].

In this paper, four samples of TiO_2 with different characteristics were prepared via hydrolysis and calcination at four temperatures, and the photoremoval of a dye (Acid Red 3B) was carried out in aqueous solution to examine the effect of the characteristics of TiO_2 and the solution pH value on the photoremoval efficiency of the dye removal.

2. Experimental details

The dye used in these experiments was Acid Red 3B, whose structure is shown in Fig. 1.

With vigorous stirring at room temperature, a mixture of isopropanol and titanium tetraisopropoxide was added dropwise to a mixture of distilled water and isopropanol. The mixture was filtered and the gel was washed with distilled water repeatedly. The resulting gel was dried at 110 °C and divided into four portions. These portions were fired at 200 °C, 400 °C, 600 °C and 800 °C for 4 h, respectively.

X-ray powder diffraction patterns were obtained with a Japanese XD-3AX diffractometer using Cu Kα radiation.

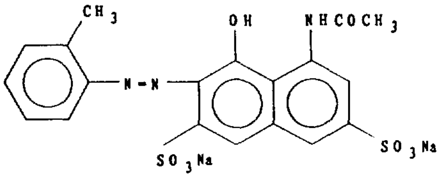

Fig. 1. The structure of Acid Red 3B.

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Diffuse reflectance spectra of TiO_2 were recorded on a Japanese UV-240 UV–visible spectrometer, scanning from 190 nm to 700 nm.

TEM observations were carried out by using an H-800 microscope, after coating the catalysts with gold.

In the adsorption study, 70 mg of catalysts fired at four temperatures were suspended in 50 ml of 50 ppm dye solution, and the suspension was allowed to equilibrate for 24 h with stirring. Then, TiO_2 was filtered and the dye concentration was determined spectrophotometrically.

The catalytic activity of TiO_2 in the suspension was examined in an NDC reactor equipped with a 500 ml thermostated cylindrical Pyrex vessel directly irradiated by a UV light source, a high pressure mercury lamp (300 W). The solution was saturated with air during the irradiation process. The dye concentration was about 500 ppm, and the amount of catalyst added was 70 mg per 100 ml of solution.

3. Results

3.1. Characterization of TiO_2

The samples of TiO_2 fired at four different temperatures have different crystalline forms. XRD patterns show that TiO_2 fired at 200 °C is almost amorphous, while TiO_2 fired at 400 °C and 600 °C is anatase. The crystalline form of TiO_2 fired at 800 °C is transformed into rutile.

Although the habit of TiO_2 UV-DRS patterns is rather similar, the slight red-shift of these patterns with increasing firing temperature reveals the difference in the particle size of TiO_2. The situation is also determined by TEM observation. Table 1 shows the change of the particle size with increasing temperature. TiO_2 samples fired at 200 °C, 400 °C and 600 °C are porous, mesopores can be observed clearly, while significant aggregation of TiO_2 particles is observed in TiO_2 fired at 800 °C and it is large crystal with fewer surface pores.

The dye adsorption study is in agreement with TEM and UV-DRS results. Table 1 also shows that the amount of dye adsorption is decreased with increasing TiO_2 particle size.

3.2. The kinetics of dye removal

In the absence of TiO_2, Fig. 2 shows the pH effect on the kinetics and the efficiency of dye photoremoval.

In catalyst-free solution, the dye photoremoval fits zero order kinetics well at three different pH values (Table 2. In the process of dye photoremoval, the rate constant of high pH value is higher than that of low pH value; the removal efficiency is increased with pH increasing and the dye removal kinetics remains unchanged at three pH values.

Table 1
The TiO_2 average particle size and dye adsorption amount of TiO_2 fired at four different temperatures

Firing temperature (°C)	200	400	600	800
Particle size (nm)	17	70	100	>400
Adsorption amount (mg g^{-1})	16.5	15.3	6.7	2.4

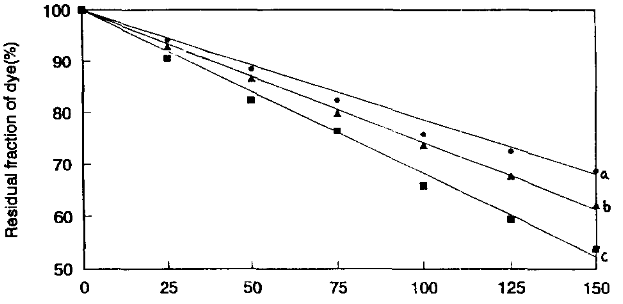

Fig. 2. The influence of pH on the dye removal in the absence of TiO_2: (a) pH = 3.32; (b) pH = 7.05; (c) pH = 9.97.

Table 2
The rate constants of dye photoremoval in catalyst free system

pH	3.32	7.05	9.97
Rate constant ($\times 10^{-3}$)	2.21	2.58	3.11
Ratio of rate constants	1	1.18	1.41

3.3. The catalytic photoremoval of dye

Fig. 3 shows the difference in kinetics between solutions with and without catalyst. For all pH values, the dye photoremoval in the presence of TiO_2 fits first order kinetics. This reveals that the addition of the catalyst changes the photoremoval kinetics.

For the catalytic system, Table 3 shows that the relation of catalytic activity to pH value is similar to that in the catalyst-free system. At high pH value, a high dye removal efficiency and photoremoval rate constant can be obtained. The amount of dye adsorption by TiO_2 is dependent on the solution pH value. For alkaline solution, a decrease in solution pH value during the irradiation process is observed, the pH value decreasing from 9.97 to 7.43 after 150 min irradiation. However, no such phenomenon can be observed in alkaline solution with TiO_2 absent, and in acidic and neutral solution the pH value remain unchanged.

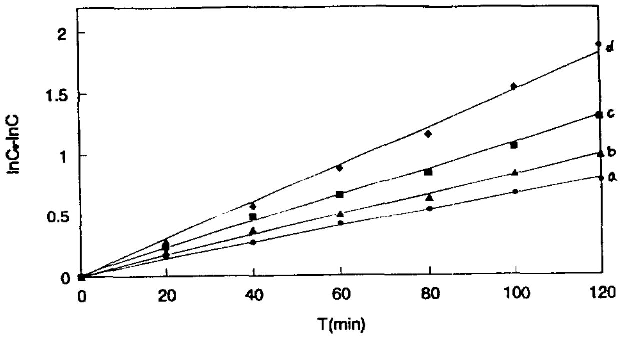

Fig. 3. The dye removal at three pH values in the presence of TiO_2 fired at 400 °C: (a) pH = 3.32; (b) pH = 7.05; (c) pH = 9.97; (d) in boracic acid and sodium hydrite buffer solution.

Table 3
The rate constants of dye removal catalyzed by TiO_2 fired at 400 °C at different pH values

pH	3.31	7.05	9.97	9.98 (in buffer solution)
Rate constants ($\times 10^{-3}$)	6.60	8.08	10.51	12.37
Adsorption amount (mg g^{-1})	31.88	13.72	15.30	15.41
Ratio of rate constants	1	1.22	1.59	1.87

Table 4
The rate constants catalyzed by TiO_2 fired at different temperatures in boracic acid and sodium hydrite buffer solution

Firing temperature (°C)	catalyst free	200	400	600	800
Rate constant ($\times 10^{-3}$)	3.11	7.90	12.73	6.35	5.67

To examine the effect of pH decrease on the photoremoval efficiency and kinetics, the catalytic photoremoval of dye was carried out in boracic acid and sodium hydrite buffer solution, the pH value is controlled at 9.98 during the irradiation process. In comparison with pH 9.97, in buffer solution, Table 3 shows the rate constant is increased but the kinetics of dye photoremoval remains unchanged.

For four different catalysts, the dye is removed via the same kinetics model. Table 4 shows the rate constants of dye photoremoval for four different catalysts; it indicates that the catalyst addition can increase the dye photoremoval efficiency. The evident difference in catalytic activity for the four catalysts reveals that the catalytic activity of TiO_2 with different characteristics is different.

4. Discussion

As for the effect of pH on removal efficiency, in catalyst-free or catalytic systems, a high pH can enhance the efficiency of dye photoremoval.

Mechanically, $\cdot OH$ is believed to be a strong oxidant for organic pollutants in the photolysis process [17]. The generation of $\cdot OH$ depends on the solution pH value.

In an acidic and neutral solution [18]:

$$H_2O + h^+ \rightarrow \cdot OH + H^+$$

In an alkaline solution [19]:

$$OH^- + h^+ \rightarrow \cdot OH$$

In alkaline solution, the generation of the radical $\cdot OH$ is much easier than that in neutral and acidic solution. Therefore, at alkaline pH values, a high efficiency of dye photoremoval can be obtained. Fig. 2 shows that the dependence of dye removal efficiency on pH value is fairly strong. Both the initial pH value and the decrease in pH value during the irradiation process can lead to low dye removal efficiency. pH value also has an effect on the catalytic ability of TiO_2. However, the slight increase of the ratio of rate constants at three pH values between catalyst-free (1:1.18:1.41) and catalytic systems (1:1.22:1.87) indicates that the dependence of catalytic ability of TiO_2 on solution pH value is rather weak, a result which is in agreement with Harada's results [20]. Therefore, it can be concluded that in alkaline solution, the strong dependence of the efficiency of dye removal on the solution pH value is caused mainly by the effect of pH value on the generation of $\cdot OH$. A high pH value can enhance the generation of $\cdot OH$ and the catalytic ability of TiO_2 is slightly influenced by the solution pH value.

For different catalysts, the catalytic activity of TiO_2 is dependent on its characteristics, such as adsorption ability, pore distribution, particle size, specific surface area and crystalline form etc. The adsorption ability has an intimate relation with the particle size, pore character and surface area of the catalyst. Porosity and small particles of a catalyst mean a large surface area, which leads to the possibility of a high adsorption amount and a high surface area of photoreaction. It has been suggested that adsorption is a prerequisite for highly efficient photoactivity [13]. Therefore, the catalytic ability of TiO_2 depends mainly on the two major characteristics: its crystalline form [21,22] and its adsorption ability [23].

The amount of dye adsorption of TiO_2 fired at 400 °C is influenced by solution pH value because of the strong dependence of surface charge and band edge positions of TiO_2 on the solution pH value [14,15]. Positive surface charge is expected as the solution pH value is lower than the isoelectric point of TiO_2 ($pH = 6.0$ [16]) and negative surface charge is obtained at higher solution pH values. At pH 3.32, the amount of dye adsorption by TiO_2 is twice as much as that at pH 7.02 or 9.97 (Table 4). In spite of the high amount of dye adsorption by TiO_2 fired at 400 °C at low pH value, the rate constant of dye photoremoval is increased with increasing pH value. It is clear that the effect of solution pH on the removal efficiency of Acid Red 3B is greater than that of adsorption ability of TiO_2.

For TiO_2 fired at 400 °C, although its amount of dye adsorption is lower than that of TiO_2 fired at 200 °C, its activity is the highest. It can be said that the effect of the crystalline form of the TiO_2 on the dye photoremoval is more important than that of the adsorption ability of TiO_2; for the crystalline form, in other words, the catalytic ability of anatase TiO_2 is higher than that of amorphous TiO_2. For 400 °C and 600 °C TiO_2, which have the same crystalline form, the evidently higher catalytic activity of TiO_2 fired at 400 °C than that of TiO_2 fired at 600 °C is due to the larger adsorption ability of 400 °C TiO_2 than that of 600 °C TiO_2.

The catalytic activity of 800 °C TiO_2 is the lowest of all. Its crystalline form is rutile, whose activity is much lower than that of anatase and amorphous TiO_2 [24,25] and it has the lowest amount of dye adsorption. Its low adsorption ability and poor catalytic ability lead to the lowest dye photoremoval efficiency.

5. Conclusion

The photoremoval of a dye, Acid Red 3B, fits zero kinetics in the absence of TiO_2 and changes to first order kinetics with TiO_2 addition. In the catalyst-free and catalyst suspension solutions, the removal efficiency is strongly influenced by the solution pH value, but the kinetics of dye removal remains unchanged with change in the solution pH. The addition of TiO_2 can enhance the efficiency of dye photoremoval. Although the dye adsorption ability of TiO_2 is strongly affected by pH value, the dependence of catalytic ability of TiO_2 on solution pH value is weak. The characteristics of TiO_2 obtained by hydrolysis and calcination at four different temperatures are different. The influence of adsorption amount of TiO_2 is small compared with that of the crystalline form of TiO_2. The catalytic activity of anatase TiO_2 is higher than that of rutile and amorphous TiO_2. For 400 °C and 600 °C TiO_2, the higher catalytic activity of 400 °C TiO_2 than that of 600 °C may be due to the larger adsorption ability of 400 °C TiO_2.

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