

TiO₂/beads as a photocatalyst for the degradation of X_{3B} azo dye

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Abstract: The feasibility of photocatalytic degradation of X_{3B} azo dye by TiO₂/beads photocatalyst was studied. The effects of parameters such as the amount of TiO₂/beads, airflow, as well as the concentrations of H₂O₂, Fe³⁺, Mg²⁺ and Na⁺ on the photocatalytic degradation of X_{3B} azo dye were also studied. The results showed that 25 mg/dm³ X_{3B} azo dye can be photocatalytically degraded completely by 30 min illumination with a 375W medium pressure mercury lamp. Adding a small amount of H₂O₂ or Fe³⁺, the efficiencies of photocatalytic degradation of X_{3B} azo dye were increased rapidly. The mechanisms of the reaction and the role of the additives were also investigated. After 120 hours TiO₂/beads showed no significant loss of the photocatalytic activity.

Keywords: X_{3B} azo dye; photocatalytic degradation; titanium dioxide; hollow glass microbeads

Introduction

Environmental protection experts in many countries pay high attention to the disposal of the wastewater with dye or with deep chroma. Though at present biodegradation is used in the disposal of the wastewater, the concentration and chroma in the disposed water are still very high and deep respectively.

In recent years studies of the photocatalytic degradation of inorganic and organic pollutants by oxygenated aqueous semiconductor powder dispersions have attracted researchers (Hoffmann, 1995; Muneer, 1997). Many papers dealing with azo dye wastewater by photocatalysis with titanium dioxide suspensions have been published and the results are very promising (Qu, 1998; Zhao, 1998a; 1998b). Such a new method is suggested for the disposal of the wastewater. But it is evident that in any wastewater purification process, filtration and resuspension of semiconductor powders should be avoided if possible.

In this paper, photocatalytic degradation of X_{3B} azo dye using TiO₂ supported on the hollow glass microbeads was studied. The effects of parameters on the photocatalytic degradation were investigated. The results showed that 25 mg/dm³ X_{3B} azo dye can be photocatalytically degraded completely by 30 min illumination with a 375W medium pressure mercury lamp.

1 Experimental

1.1 Materials

X_{3B} azo dye was supplied by a dye printing mill, its chemical structure is shown in Fig. 1. Hollow glass microbeads were aluminosilicate beads with diameter in the range of 80—100 μm and the density in the range of 0.3—0.7 g/cm³. TiO₂ supported on hollow glass microbeads (TiO₂/beads photocatalyst) was prepared by the dip-coating technique (Chen, 1999) with TiO₂ sol-gel, which is made from titanium tetraisopropoxide [Ti(iso-OC₃H₇)₄] prepared by us. From X-ray powder diffraction patterns and SEM observation, we knew that the supported TiO₂ is mostly in the anatase form and the hollow glass microbead surface is uniformly covered with well-distributed TiO₂ particles. The amount of TiO₂ supported on 1.0g hollow glass microbeads is 0.11g.

1.2 Photoreactor and procedure

Experiments were carried out in a photochemical quartz reactor (Chen, 1996). The cylindrical annular-type reactor consists of three parts. The first part is an empty chamber in which a 375W medium pressure mercury lamp is hung. The second part is an inside thimble and running water is passed through the thimble to cool the reaction solution. Owing to the continuous cooling, the temperature of the reaction solution is maintained at approximately 30°C. The third part is an outside thimble. At the start of the experiment the reaction solution (Volume, 400 cm⁻³ of 25 mg/dm³ of X_{3B} azo dye with 6.0 g/dm³ TiO₂/beads) was put between the inside thimble and the outside thimble. Air was introduced into the reaction solution through the gas entry at the base of the reactor. All experiments were performed at initial pH of 5.0; air flow rate was 0.02 m³/h, except for experiments where air flow was varied. After illumination, samples were taken intermittently for analysis.

1.3 Product analysis

The amount of TiO₂ supported on the hollow glass microbeads was analyzed by a spectrophotometric method (Chen, 1999). The concentration of X_{3B} azo dye in solution was determined by colorimetric analysis.

The photodegradation efficiency of X_{3B} azo dye for each sample was expressed as

$$\eta = \frac{C_o - C_t}{C_o} \times 100\%$$

where η is the photodegradation efficiency, C_o is the initial concentration of X_{3B} azo dye, C_t is the concentration of X_{3B} azo dye after illumination for time t .

2 Results and discussion

2.1 Effect of illumination time

The relationship between the photodegradation efficiency of X_{3B} azo dye and the illumination time is shown in Fig. 2.

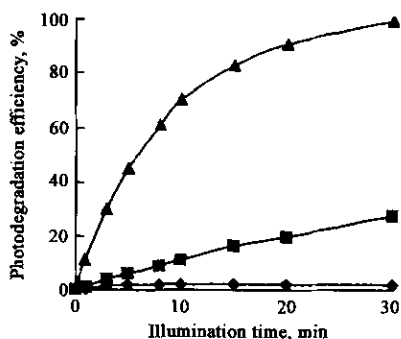


Fig. 2 Effect of illumination time on the photodegradation of X_{3B} azo dye

- ◆ only TiO₂/beads photocatalyst present;
- only UV illumination;
- ▲ TiO₂/beads + UV illumination

azo dye after different illumination time. From Fig. 3 it can be seen that under TiO₂/beads photocatalyst +

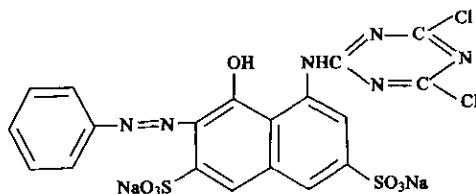


Fig. 1 The chemical structure of X_{3B} azo dye

UV illumination condition, with the increasing the illumination time, the intensity of 540 nm characteristic absorption peak decreases gradually, the absorption peak has been completely eliminated after 30 min illumination. From the result it is clear that the coloring unsaturated conjugated bond $-N=N-$ has been completely opened.

It is believed that photocatalytic degradation of organic pollutants occurs on the surface of TiO₂ (Ammar, 2001; Vesely, 1991), O₂ and H₂O are necessary for the photocatalytic degradation. When under near UV illumination, electron-hole pairs are created on the TiO₂ surface, oxygen adsorbed on the TiO₂ surface prevents the recombination of electron-hole pairs by trapping electrons. Superoxide ions ($\cdot O_2^-$) are thus formed, and then H₂O₂ is generated from $\cdot O_2^-$. Hydroxyl radicals ($\cdot OH$) are produced from holes reacting with either H₂O or OH⁻ adsorbed on the TiO₂ surface. $\cdot OH$ radicals are widely accepted as a primary oxidant in the heterogeneous photocatalysis (Sclafani, 1991), the oxidizing power of the $\cdot OH$ radicals is strong enough to completely oxidize X_{3B} azo dye into CO₂, H₂O and mineral acid (Qu, 1998; Zhao, 1998a; 1998b).

2.2 Effect of amount of TiO₂/beads

Table 1 shows the effect of the amount of TiO₂/beads on the photocatalytic degradation of X_{3B} azo dye. From Table 1 it can be seen that the photodegradation

efficiency of X_{3B} azo dye increases rapidly with increasing the amount of TiO₂/beads up to 6.0 g/dm³, but when the amount of TiO₂/beads is in excess of 6.0 g/dm³, the photodegradation efficiency decreases gradually due to light obstruction by TiO₂/beads.

2.3 Effect of airflow

When there is no air flow into reaction solution, using nitrogen instead, flow is 0.02 m³/h. The data in Table 2 show that when there is no air flow into the reaction solution, the photodegradation efficiency of X_{3B} azo dye is lower, and that the photodegradation efficiency increases rapidly with increasing the air flow up to 0.02 m³/h, but when the air flow is greater than 0.02 m³/h, the photodegradation efficiency increases slowly.

Table 2 Effect of air flow on the photodegradation efficiency*

Air flow, m ³ /h	0	0.005	0.01	0.02	0.03	0.04
η , %	26.3	51.6	66.3	70.6	70.8	71.5

* illumination time $t = 10$ min

2.4 Effect of H₂O₂ concentration

Table 3 shows the effect of H₂O₂ concentration on the photodegradation efficiency of X_{3B} azo dye.

From Table 3 it can be seen that adding a small amount of H₂O₂ (up to 1.0×10^{-3} mol/dm³), the

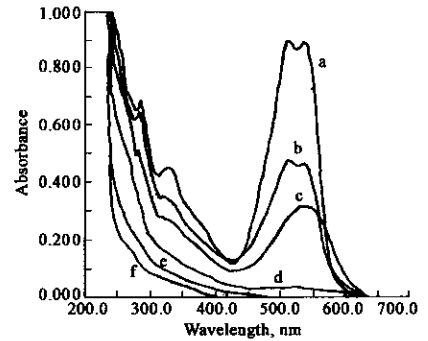


Fig. 3 UV-vis absorption spectrum of X_{3B} azo dye
 a. original X_{3B} azo dye reaction solution; b. illumination for 5 min; c. illumination for 10 min; d. illumination for 20 min; e. illumination for 30 min; f. illumination for 40 min.

Table 1 Effect of amount of TiO₂/beads on the photocatalytic degradation*

Amount of TiO ₂ /beads, g/dm ³	0	1	2	4	6	8	10
η , %	11.1	39.3	50.8	66.7	70.6	67.9	61.8

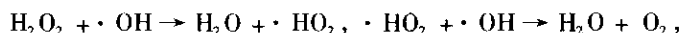
* illumination time $t = 10$ min

The reason for this behaviors is that dissolved oxygen in the solution plays an important role by trapping the conduction band electrons (Balcioglu, 1996; Muneer, 1997), superoxide ions ($\cdot O_2^-$) are formed and thus delay the electron-hole pairs

recombination ($O_2 + e^- \rightarrow \cdot O_2^-$), and at the same time H₂O₂ is formed from $\cdot O_2^-$, increasing the amount of $\cdot OH$, on the other hand, air flow accelerates adsorb and desorbs of the reactants.

photodegradation efficiency increases rapidly, but if the H_2O_2 concentration is greater than $1.0 \times 10^{-3} \text{ mol/dm}^3$, the photodegradation efficiency decreases gradually.

H_2O_2 is a strong oxidizer, when under UV illumination and trapping the conduction band electrons, $\cdot\text{OH}$ radicals will be produced, at the same time H_2O_2 trapping conduction band electrons, preventing the recombination of electron-hole pairs, thus increasing the chances of the formation of $\cdot\text{OH}$, so adding a small amount of H_2O_2 , the photodegradation efficiency increases rapidly, but when the H_2O_2 concentration is higher, H_2O_2 can acts as the trapping matter of $\cdot\text{OH}$ (Balcioglu, 1996).

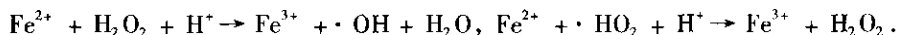


so that the photodegradation efficiency decreases.

2.5 Effects of Fe^{3+} , Mg^{2+} and Na^+ concentration

The data in Table 4 show that adding trace amounts of Fe^{3+} (up to 0.05 mmol/dm^3), the photodegradation efficiency increases rapidly, but if the Fe^{3+} concentration is larger than 0.05 mmol/dm^3 , the photodegradation efficiency increases slowly.

Fe^{3+} behaves as an electron scavenger ($\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$), thus preventing the recombination of electron-hole pairs. When suitable amounts of Fe^{3+} are present, the following reactions become very significant (Sclafani, 1991).



The above reactions increase the amount of $\cdot\text{OH}$ and H_2O_2 , so that the photodegradation efficiency increases rapidly.

The results also show that adding a small amount of Mg^{2+} or Na^+ into the reaction solution, no significant effects on the photodegradation efficiency of $\text{X}_{3\text{B}}$ azo dye are observed.

2.6 Photocatalytic lifetime of TiO_2 /beads

The results show that there is no significant loss of photocatalytic activity of the TiO_2 /beads after 120h illumination by a 375W medium pressure mercury lamp, and the TiO_2 /beads photocatalyst is relatively resistant to mechanical breakage. The supported TiO_2 is not easily detached from the hollow glass microbeads since no TiO_2 powder was found at the end of the photocatalytic experiments.

3 Conclusions

The present studies show that TiO_2 /beads can be used for the photocatalytic degradation of $\text{X}_{3\text{B}}$ azo dye. As the density of TiO_2 /beads is low 1.0 g/dm^3 and may be floating on water, avoiding the filtration and resuspension of the photocatalysts. After 30 min illumination 25 mg/dm^3 $\text{X}_{3\text{B}}$ azo dye can be completely photocatalytically degraded with a 375W medium pressure mercury lamp. Adding a small amount of H_2O_2 (1.0 mmol/dm^3) or Fe^{3+} (0.05 mmol/dm^3) the efficiencies of photocatalytic degradation of $\text{X}_{3\text{B}}$ azo dye are increased rapidly. After 120h illumination by a 375W medium pressure mercury lamp, no significant loss of photocatalytic activity of the TiO_2 /beads was observed.

Table 3 Effect of H_2O_2 concentration on the photodegradation efficiency*

H_2O_2 concentration, mmol/dm ³	0	0.02	0.1	0.5	1.0	2.0	4.0	8.0
η , %	30.1	59.5	77.2	81.1	86.3	82.8	81.3	79.3

* illumination time $t = 3 \text{ min}$

Table 4 Effect of Fe^{3+} concentration on the photodegradation efficiency*

Fe^{3+} concentration, mmol/dm ³	0	0.005	0.01	0.05	0.10	0.20	0.5
η , %	30.1	67.7	79.3	82.6	85.0	85.7	86.0

* illumination time $t = 3 \text{ min}$

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