Photocatalytic degradation of Chicago Sky Blue 6B and Benzopurpurin 4B using titanium dioxide thin film

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Abstract: Aqueous solutions of azo dyes undergo degradation to form harmless intermediates and colorless products following irradiation by visible light in the presence of titanium dioxide thin films. The dyes that were studied in this work are: Chicago Sky Blue 6B and Benzopurpurin 4B. Results obtained indicated that complete mineralization of the dyes took place under the experimental conditions. There was an increase in conductivity after the complete mineralization experiments possibly indicating the formation of ions such as NO_3^- and SO_4^{2-}. Chemical oxygen demand(COD) measurements show a decrease in organic matter for both dyes following complete degradation. The effect of how changing experimental conditions such as pH, temperature and starting concentrations of dyes affected the rate of dye degradation was measured. There was an increase in the rate of disappearance of the dye color at lower pH. High concentrations of dye solutions required long degradation time.

Keywords: titanium dioxide; photocatalysis; photocatalytic degradation; azo dyes

Introduction

Azo dyes are a significant portion of the effluents expelled into the environment. These dyes are based on benzidine and its derivatives, dimethylbenzidine and dimethoxybenzidine, which are known carcinogenic aromatic amines. The primary site for tumors from benzidine is the bladder(Gray, 1993). Over half of the dyes used in industry are azo dyes, which make them the largest and most important class of all commercial dyes(Waring, 1990). Many of these dyes are not only used as textile dyes for clothing, paper, and food industries, they are also utilized to color pharmaceuticals and commercial goods such as drugs, mouthwashes, and cosmetics.

The work discussed in this article, will focus on the photodegradation of the azo dyes Chicago Sky Blue 6B(CSB) and Benzopurpurin 4B(B4B). Comparison of our work will be made with similar studies found in the literature concerning other benzidine-based dyes. Previous studies which have been done on the photocatalytic degradation of azo dyes focused on different aspects of the degradation process. For example, Tanaka *et al*. (Tanaka, 2000) analyzed the intermediate and end products found after the complete degradation of azo dyes. Seven azo dyes were investigated in the study: Congo Red, Orange G, Acid Orange 7, New Coccine, Acid Black 1, Tartazine, and Acid Yellow 17. Congo Red(in particular) is of great interest due to the similarity of its structure to that of the dye(B4B) in this work. Tanaka *et al*. was able to identify the intermediates and the products for most of the dyes that were studied. Aromatic amines or phenolic compounds were found as some of the intermediates and the final products obtained include ammonium, nitrate, nitrite, and sulfate ions.

1 Materials and methods

The procedure in the literature(Blount, 2001) was used to prepare the TiO_2 sol-gel. A 250 ml fused quartz (transparent) flask, which may be heated to 1500℃, was used as the reactor. Aliquots of the prepared sol-gel were placed in the reactor and rotated carefully to ensure complete coating of the inside area of the reactor. The reactor was dried at room temperature for 1 d and calcined in an oven at 473 K for 3 h.

A 200-W mercury lamp (Osram: Spectral Energy, Corp., NY) was used as the source of irradiation. To block radiation below 400 nm, a cutoff filter was placed between the reactor and the lamp. This ensures that only visible light was used. In order to obtain reproducible data of photodegradation process under varying conditions, the volume of dye inside the reactor was maintained at 250 ml for each experiment. The solutions were stored in the dark immediately after preparation and were used in an experiment soon afterwards.

Solutions were prepared by dissolving the appropriate dye in distilled water. pH was adjusted using nitric acid and sodium hydroxide to reach the desired pH. A water bath was used to keep each solution at the desired temperature.

Shimadzu Model UV-2401 PC Spectrophotometer was used for recording absorbance and the UV-Vis spectra of the samples. The extent of degradation was followed by measuring the absorbance (at the dye's characteristic lambda max (λ_{max})) of aliquots of the sample that were withdrawn at varying time intervals.

A YSI Model 3100 conductivity meter was used to measure the conductivity of the solutions. The samples were stirred vigorously before measurements in order to ensure that a homogeneous sample was studied. Approximately 8 ml of each sample tested was placed in a 10 ml beaker. A water bath was used to maintain constant sample temperature for conductivity measurements. Beakers containing samples were placed in the water bath and the temperature was adjusted to 27.6℃.

Chemical oxygen demand(COD), which can be used to determine the amount of organic (carbon content) material present in a sample, was measured by using the spectrophotometric method described in the literature(Jirka, 1975). Samples were oxidized in a sealed 10 ml borosilicate glass bottles. The bottles contain the following premixed COD reagents: 77.0% sulfuric acid, 0.05% potassium dichromate, 0.40% silver sulfate, and 0.002% sulfamic

acid. A calibration curve was prepared using various concentrations of potassium hydrogen phthalate. The absorbance of the samples were measured on the spectrophotometer at 440 nm and compared to the calibration curve to determine the COD concentrations.

2   Results and discussion

The photodegradation process was carried out under visible light irradiation using TiO_2 thin-film as the photocatalyst. To prove that the catalyst is required for the degradation of the organic dyes to occur, two controlled experiments were conducted by irradiating the dye B4B in the presence of the catalyst and in the presence of the catalyst without irradiation. All other conditions were kept constant. Fig.1 shows that by removing the TiO_2 thin-film, photodegradation is not significant after irradiation for approximately 120 min. Conversely, it was found that in the presence of the catalyst, without irradiation, insufficient degradation is observed after allowing the sample to sit for 120 min(Fig.1). Control experiments involving CSB show that either in the absence of light or the catalyst, significant amount of degradation did not take place as shown by the first two of the overlaid spectra in Fig.2. The rest of the spectra show that there is significant degradation of CSB when both catalysts and irradiation were applied.
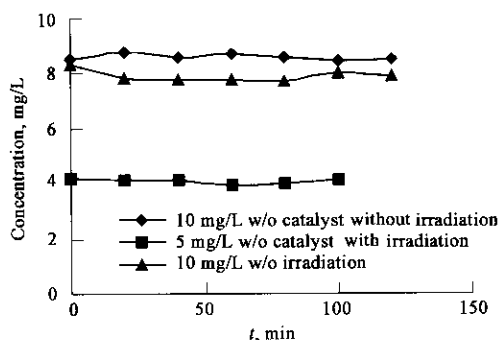
Fig.1   Controlled experiments of Benzopurpurin 4B irradiated w/o TiO_2 catalyst and in the presence of TiO_2 catalyst w/o irradiation
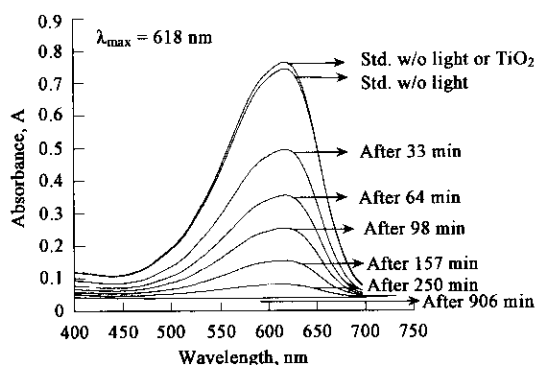
Fig.2   UV-Vis spectra of the degradation of 10 mg/L CSB at 54 ℃ (pH = 2)

2.1   pH effect on CSB degradation

The degradation of CSB was investigated at pH 2, 6, and 10 by measuring the decrease in dye concentration at room temperature (23 ℃). The photodegradation results in both acidic and alkaline aqueous solutions are shown in Fig.3. It shows that there is an increase in degradation at lower pH(pH of 2 and 6) compared to the slower degradation

at the higher pH of 10. The zeta potential of TiO_2 is positive in acidic solutions and negative in alkaline solutions, signaling the positive and negative charges of TiO_2. The noticeable increase in degradation in acidic media stems from dye being negatively charged from its attached sulfonate groups(Kirikidiu, 1999). The pH of the isoelectric point of TiO_2 thin-film is 7, therefore, it is positively charged in low pH media(pH 2). As the pH is lowered, the positive charge of the TiO_2 increases. This explains why the anions from the dyes are strongly attracted to the TiO_2 surface at pH < 6. The increased attractive forces cause an increase in the photodegradation of the dye. After a reaction time of approximately 1800 min, an average degradation of 98% is observed at pH 2. An experiment was also performed at neutral pH(approximately pH 6) where a degradation of 98% was observed. In basic media(pH 10), degradation process takes place at a much slower rate. The percentage of degradation was only 40% after 2000 min.
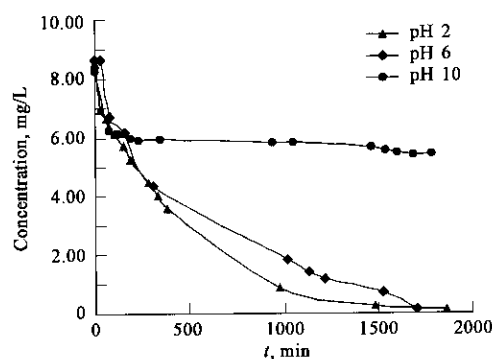
Fig.3   Degradation of 10 mg/L Chicago Sky Blue 6B overlapping pH

The data from the experiment involving the irradiation of 10 mg/L CSB were further analyzed to determine the rate of reaction. The rate constants obtained at pH 2, 6 and 10 are listed in Table 1. These rate constants decrease with increasing pH value and the value obtained for each pH showed pseudo-first-order kinetics. The data obtained from the pH experiment for CSB is consistent with other results that have been reported in the literature using similar azo dyes(Liu, 2000; Tanaka, 2000; Pak, 1999; Zhao, 1998).

Table 1   Disappearance rate of azo dye(CSB) by varying pH

pH	Chicago Sky Blue 6B		
	Rate order	k, 10^{-4} min^{-1}	R^2
2	1	22	0.9972
6	1	16	0.9929
10	1	4	0.9159

2.2   Effect of temperature on CSB degradation

The photodegradation of 10 mg/L CSB at various temperatures was investigated and the data are shown in Fig. 4. It can be seen that the degradation process occurs at a faster rate with increasing temperature and that less time is required for complete degradation. The percentage of degradation of the dye is observed to be 98%—100%. The activation energy(E_a) obtained for this reaction was 45.66 kJ. The photodegradation of 10 mg/L B4B at various temperatures was also investigated and the results are shown in Fig.5. The data follow a similar trend to that of CSB. This degradation process also shows an increase with increasing

temperature. A plot of $\ln k$ versus $1/T$ for B4B gave an activation energy of 32.95 kJ, which is lower than the value obtained for CSB.
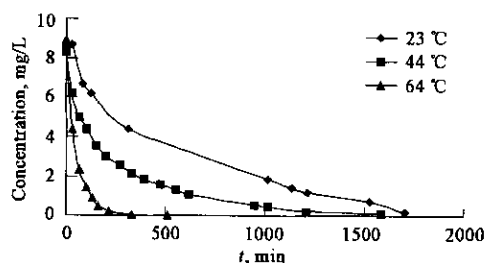

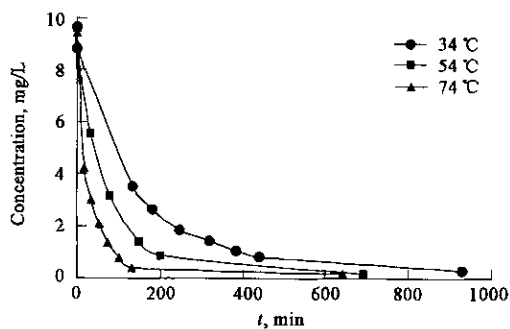Fig.4   Degradation of 10 mg/L Chicago Sky Blue 6B at 23, 44 and 64 ℃

Fig.5   Degradation of 10 mg/L Benzopurpurin 4B at 34, 54 and 74 ℃

2.3 Relationship between reaction rate and concentration of slution

The initial concentration of a solution is directly linked to the time required for a reaction to occur. Results in the literature have shown that reaction rate decrease as the concentration of the starting material decreases; therefore, increasing the concentration of reactants increases the rate. The relationship between reaction rate and concentration is shown in Table 2. The results of this experiment indicated that as the concentration increased the reaction rate decreased. The results indicate that complete degradation is heavily dependent on the initial concentration of the dye. The data obtained is consistent with the results from previous research studies stating that the time needed for complete decolorization increases with increasing initial dye concentration and at high concentrations the reaction rate decreases(Kirikidiu, 1999). This has been attributed to the fact that there is an increase in the monolayers of adsorbed dye formed on the TiO$_2$ surface (Kirikidiu, 1999). Thus, increasing dye concentrations requires an increase in the amount of photons absorbed by the dye. Therefore fewer photons are able to penetrate the dye monolayers on the surface of the TiO$_2$ thin film(Kirikidiu, 1999; Tang, 1995).

Table 2   Disappearance rate of azo dye CSB at 23℃ with varying concentration

Concentration, mg/L	Rate, $\times 10^{-9}$ mol/(L·min)
1.56	9.0
2.34	8.6
3.12	8.6
10	4.7
25	4.6

2.4 Conductivity of CSB solutions

The conductivity or electrical current estimates the amount of dissolved ions in solution. This current depends on the temperature of the water, ion mobility and concentration or numbers of ions present (Tang, 1995). The initial conductivity was recorded prior to the irradiation of the sample and the final conductivity was recorded after complete degradation. These results could be used to predict the degree of mineralization of the dye. Table 3 shows the increase in conductivity as the dye is degraded. There is a noted increase in final conductivity as the concentration increases. At 25 mg/L the final conductivity was found to be 208.3 uS/cm, which is primarily due to the high initial concentration of the dye. Although the degree to which the dye degraded is not known, it can be speculated that partial or complete mineralization is occurring. Ions such as NH$_4^+$, NO$_3^-$, NO$_2^-$, and SO$_4^{2-}$ have been discovered as the mineralization products in previous articles using comparable azo dyes(Tanaka, 2000), and similar results are expected in these studies. However, we intend to do more experiments to determine the concentrations and types of ions that are formed in the complete degradation of the dyes. Various types of intermediates have been discovered in previous work. These include compounds such as acetic, formic, glycolic, oxalic, glyoxylic, and malonic acids and phenols (Skoog, 1996). The conductivity of B4B solutions were tested as well and the results were consistent with the data found for CSB.

Table 3   Conductivity of CSB solutions

Chicago Sky Blue 6B concentration, mg/L	Conductivity, uS/cm	
	Initial (before irradiation)	Final (after irradiation)
3.12	22.00	45.59
10.00	13.16	74.41
25.00	30.21	208.30

2.5 Chemical oxygen demand(COD)

Chemical oxygen demand was measured to determine the amount of organic material that has been oxidized before and after photodegradation of the dye. Several experiments were performed with samples of B4B and CSB at various time intervals during the photodegradation process.

Table 4 shows various initial dye concentrations and the change in COD before and after photocatalysis of CSB. A range of concentrations was investigated in order to prove that a decrease in organic material can be reasonably verified at different dye concentrations. The results obtained indicated that there is a decrease in the amount of organic matter as shown by the decrease in COD in the various samples that ranges from 12% to 46%. This is consistent with the substantial decrease of organic matter observed by other investigators using similar azo dyes (Kiriakidu, 1999; Pak, 1999).

The data in Table 4 also show the decrease in COD level using the azo dye B4B. It shows that there is approximately 30% decrease in COD level in three of the samples, which is also consistent with previous data (Kiriakidu, 1999; Pak, 1999). COD experiments were performed at two different pH values at 25 mg/L. The result shows that before irradiation, at pH 6, the dye has a higher initial level of COD than at pH 2; this in turn led to a 72% decrease in COD level. The lower initial COD level of B4B at pH 2 is probably due to the

protonation and change in color of B4B at pH < 2. After the completion of the degradation process, the COD level was found to be the same for both pH values. This shows that despite the COD level at the beginning, there is a possibility of lowering the organic matter as a result of complete degradation of the dyes.

Table 4   Decrease of chemical oxygen demand in Chicago Sky Blue 6B and Benzopurpurin 4B

Dye concentration, mg/L		COD concentration, mgO$_2$/L		
		Removed, %	Initial (non-irradiated)	Final (irradiated)
Chicago Sky Blue 6B	2.34	20.2	12.05	9.61
	3.12	12.6	15.46	13.51
	10.0	31.0	22.78	15.71
	25.0	46.3	31.07	16.68
Benzopurpurin 4B	2.50	31.8	18.39	12.54
	10.0	32.3	20.34	13.76
	25.0(pH 6)	71.9	45.46	12.78
	25.0(pH 2)	34.4	18.39	12.05

3   Conclusions

In conclusion, the adsorption on TiO$_2$ has been found to depend on the electrical charge of the dye and the photocatalytic surface utilized. Also, the adsorption of the azo dye in the presence of TiO$_2$ depended on several experimental conditions such as the pH of the solution, temperature, and concentration as shown by the data discussed in this article. In basic media (pH 10), the degradation of the dye was found to occur at a much slower rate because of the negative charged TiO$_2$ in basic media. The rate of decomposition of the dye solution is influenced by the aforementioned experimental conditions and the degradation reactions closely followed pseudo-first-order kinetics.

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