

Decolorization and mineralization of Direct Blue86 by UV/TiO₂ process: Investigations on the effect of operational parameters

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Abstract

Direct Blue 86 (DB86), commonly used as a textile dye, can be degraded photocatalytically in aqueous solutions using TiO₂ suspensions. A 400 W UV-A lamp was used in a batch circulating photo-reactor, without any dead zone. An initial concentration of 50 mg/L of dye, as a typical concentration in textile wastewaters, was used and the influence of catalyst concentration, pH and temperature were investigated. The experiments showed that degradation of dye can be effectively occurring in the both branches of photolysis (only UV) and photocatalysis (UV/TiO₂).

Accordingly, the optimum operating conditions of: catalyst concentration: 40 mg/L, pH of 4 and temperature of 40 °C were obtained. Under these conditions, a degradation of about 96% and a mineralization of about 87% (based on COD measurements) of dye were achievable during about only 120 min.

Keywords: photocatalytic degradation; photo-reactor; Direct Blue 86; COD

1. Introduction

Dye materials from textile industries are known as important source of environmental pollution. These effluents are toxic and mostly non-biodegradable. On the other hand, removing color pollutants from wastewaters is often more important than the other colorless ones. It is because the presence of small amounts of dyes (below 1 mg/L) is clearly visible and influences the water environment considerably^[1,2].

To perform the wastewater treatment, there are various chemical and physical processes such as chemical precipitation, electro-coagulation, adsorption on activated carbon and etc. Unfortunately these methods are not destructive, but only transfer the contamination from one phase to another; therefore, a new and different kind of pollution is faced and further treatments are required^[2,3].

In this regard, photocatalysis, as an advanced oxidation processes (AOPs), has become a hot topic, because it can completely degrade the organic pollutants into harmless inorganic

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substances such as CO_2 and H_2O under moderate conditions and would not bring with any serious secondary pollutions. The method is based on the generation of very reactive agents such as hydroxyl radicals ($\cdot\text{OH}$) that are extremely reactive and strong oxidizing ($E^\circ=2.8\text{V}$), capable of mineralizing organic contaminants [4].

The photocatalysis has been tested on many different compounds and in many different processes. To date, this technology has been used to detoxify drinking water, decontaminate industrial wastewaters and purify air streams [5, 6].

It is well known that TiO_2 is one of the suitable semiconductors for photocatalysis and has been applied into various photocatalytic reactions [7]. The reasons that TiO_2 does so well and is a desired agent in remediation of wastewater is based on several factors: 1. The process occurs under ambient conditions, 2. The formation of photocatalysed intermediate products, unlike direct photolysis techniques, is avoided, 3. Oxidation of the substrates to CO_2 is complete, 4. It is inexpensive and has a high turnover and 5. The process offers great potential as an industrial technology to detoxify wastewaters [8].

The aim of the present work is to investigate the influence of various parameters on photocatalytic degradation of a dye, called "Direct Blue 86 (DB 86)" in the presence of TiO_2 particles and irradiated by the UV-A light in a circulated reactor. DB86 is the sodium salt of copper phthalocyanine dye- sulphonic acid. Dyes like this find extensive use in various areas of textile dyeing (direct dyes for cotton), for spin dyeing and in the paper industry. No work has been published about the photodegradation of this substance so far.

2. Experimental

2.1. Reagents

All reagents were used as received without further purification. The dye Direct Blue 86, $\text{C}_{32}\text{H}_{14}\text{O}_6\text{N}_8\text{S}_2\text{CuNa}_2$ (C.I. No.: 74180, CAS No.: 1330-38-7, $\text{MW}=780$) was provided from Alvan Sabet company with purity of more than 98%. Fig. 1 displays the molecular structure of this dye. The molecular structure of this dye is shown in Fig. 1. TiO_2 catalyst was Merck product, anatase form (99%); BET surface area of $14.68\text{ m}^2\text{ g}^{-1}$ and the average particle diameter of $27.6\text{ }\mu\text{m}$ [9]. Sulfuric acid and sodium hydroxide, used to adjust the pH of solutions, were Merck products. Distilled water was used to prepare the solutions.

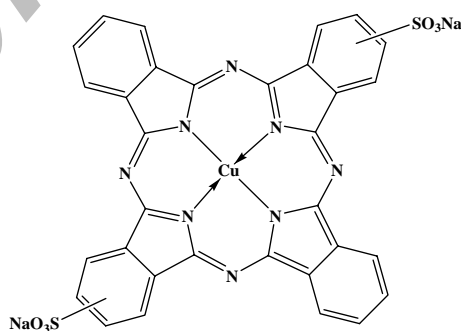


Fig.1. The molecular structure of Direct Blue 86.

2.2. The photocatalytic reactor

Experiments were carried out in an annular vertical reactor, similar to that used in our previous work [10] with the capacity of about 1 L and a conic shape in its main body. The UV lamp (22 cm body length and 16 cm arc length) was a mercury 400 W (200 -550 nm) lamp,

having the highest irradiation peak at 365 nm (measured with a TOPCON UV-R-1 spectroradiometer). The intensity of ultraviolet light around the lamp at this wavelength was about 520 mW/cm². The emitted lights are mainly within the range of UV-A. The UV lamp was positioned inside a quartz tube and totally immersed in the reactor; therefore, the maximum light utilization was achieved. A pump located below the reactor, provides an adjustable circulating stream, feeding from top of the reactor and discharging to the bottom, just below the lamp, for the well-mixing and fluidizing of catalyst particles along the quartz tube. It was not expected that a single pass of polluted water through a short reactor would give adequate degradation. If particles in the water surrounding a lamp are well-mixed, then each particle on average achieves equal exposure. For regulating the temperature, the reactor vessel was equipped with a water-flow jacket, using an external circulating flow of a thermostat bath. Since the photocatalysis is sustained by a ready supply of dissolved oxygen, air was supplied to the reaction system at a constant flow-rate using a micro-air compressor.

2. 3. Procedure

In order to perform the experiments, a solution containing 50 mg/L of dye (about 6×10⁻⁵ M) which is within the range of typical concentration in textile wastewaters ^[11, 12] and a known amount of TiO₂ concentration was prepared. The pH was adjusted to the desired value by means of a pH meter, using dilute H₂SO₄ and NaOH solutions. The solution was then transferred to the reactor and after adjusting temperature, the lamp was switched on to initiate the degradation. To achieve steady state irradiation, the lamp was already switched on while surrounded by distilled water for about 3 hours. During each experiment, circulation of suspension was maintained to keep suspension homogenous and to have uniform temperature. Samples (4 mL) were taken at regular time intervals and then centrifuged in order to separate of TiO₂ particles from the samples. The operating conditions of experiments are given in Table 1.

Table1. The operating conditions of experiments.

Parameter	Value
DB86 initial concentration	50 mg/L
TiO ₂ amount	0-60 mg/L
pH	2-10
Temperature	20-40 °C
Irradiation time	up to 120 min

The concentration of the dye in each sample was analyzed with a UV-Vis spectrophotometer, measuring the absorbance at $\lambda_{max} = 620$ nm (as is given in the next section) and using the appropriate calibration curve (Fig. 2). It should be noted that the maximum wavelength and the molar absorption coefficient of DB86 were not much dependent on the pH of solution within the range of 2-10. The calibration curve for pH of 2 finds some deviation due to the low solubility of dye at this pH. The appropriate calibration curve for the natural solution pH of 6.38 is also given.

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2. 3. Procedure

In order to perform the experiments, a solution containing 50 mg/L of dye (about 6×10^{-5} M) which is within the range of typical concentration in textile wastewaters ^[11, 12] and a known amount of TiO₂ concentration was prepared. The pH was adjusted to the desired value by means of a pH meter, using dilute H₂SO₄ and NaOH solutions. The solution was then transferred to the reactor and after adjusting temperature, the lamp was switched on to initiate the degradation. To achieve steady state irradiation, the lamp was already switched on while surrounded by distilled water for about 3 hours. During each experiment, circulation of suspension was maintained to keep suspension homogenous and to have uniform temperature. Samples (4 mL) were taken at regular time intervals and then centrifuged in order to separate of TiO₂ particles from the samples. The operating conditions of experiments are given in Table 1.

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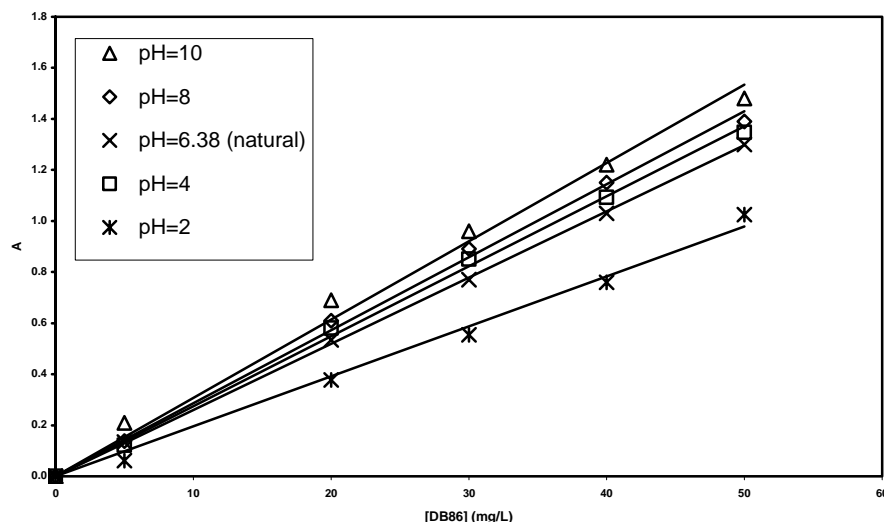


Fig.2. The calibration chart for measuring DB86 at different pH and $T=20\text{ }^{\circ}\text{C}$

Using this method, the degradation efficiency or conversion (X) of DB86 at any time, with respect to its initial concentration can be obtained by:

$$X = \frac{[\text{DB86}]_0 - [\text{DB86}]}{[\text{DB86}]_0} \quad (1)$$

Where $[\text{DB86}]_0$ and $[\text{DB86}]$ are the dye initial and time concentrations.

COD measurements were carried out to investigate the mineralization of the substrate, using the open reflux method according to the procedure given in standard methods^[13].

3. Results and discussion

3. 1. UV-Vis Spectra changes

In a precedent study, the absorption spectra of DB86 were studied at different times of irradiation. No catalyst was used in this case. As it is presented in Fig. 3, the bands relating to different molecular parts in this dye are decreased with respect to time. Direct blue 86 has three strong absorbance peaks in the UV and visible regions. The absorption peaks at 217 nm, 330 nm and 620 nm are respectively attributed to the benzene aromatic rings, C=N bonds and the chromophore part in the molecular structure^[14].

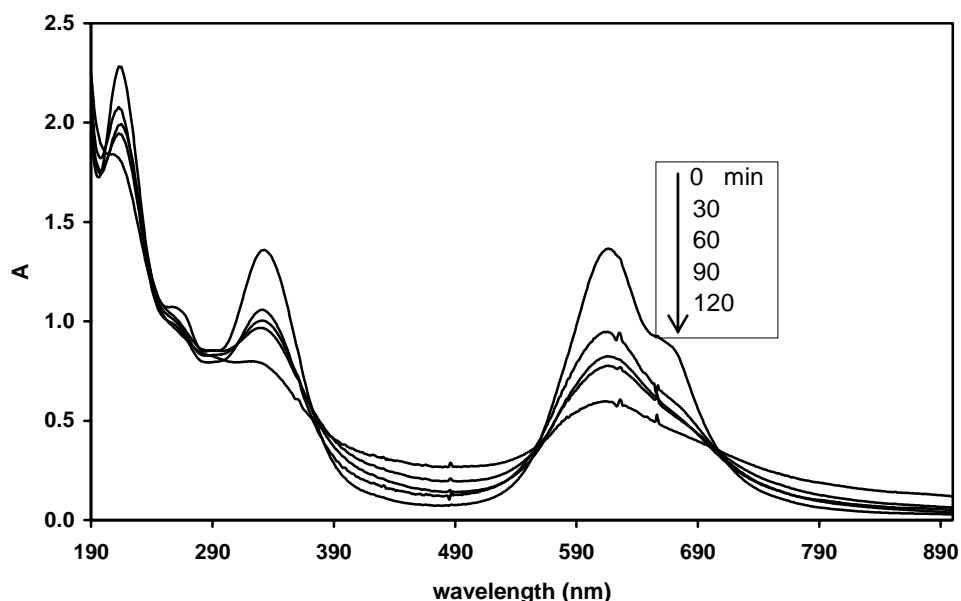


Fig.3. UV-Vis spectra changes of DB86 concentration in the aqueous solution at different times; natural pH (6.38) and $T=20^{\circ}\text{C}$.

The decrease of peaks at $\lambda_{\text{max}}=217\text{ nm}$ in Fig. 3 confirms the decomposition of benzene ring and also the decrease of peaks at $\lambda_{\text{max}}=620\text{ nm}$ indicate the degradation of dye from the chromophore part, as the most active site for the oxidation effect which leads to the decolorization of the solution.

3. 2. The influence of TiO_2 particles

Fig. 4 demonstrates the influence of TiO_2 particles on the photo-degradation of DB86. In the presence of TiO_2 , about 66% of dye degrades in 120 min for instance, under its natural pH and at temperature of 20°C . It is while for the only UV irradiation and at the same conditions, the efficiency is about 45%. These results show that DB86 is significantly degradable under UV light when assisted with TiO_2 particles; however, light (UV-A) alone (without TiO_2) is efficient for this degradation. Of course, a major part of degradation will be conducted in photolysis branch while the photocatalysis degradation is in progress. Experiments were also conducted in darkness (without UV light), while the TiO_2 particles were present. The reduction in dye concentration was nil; i.e. no adsorption of dye substrate on the catalyst particles was occurred.

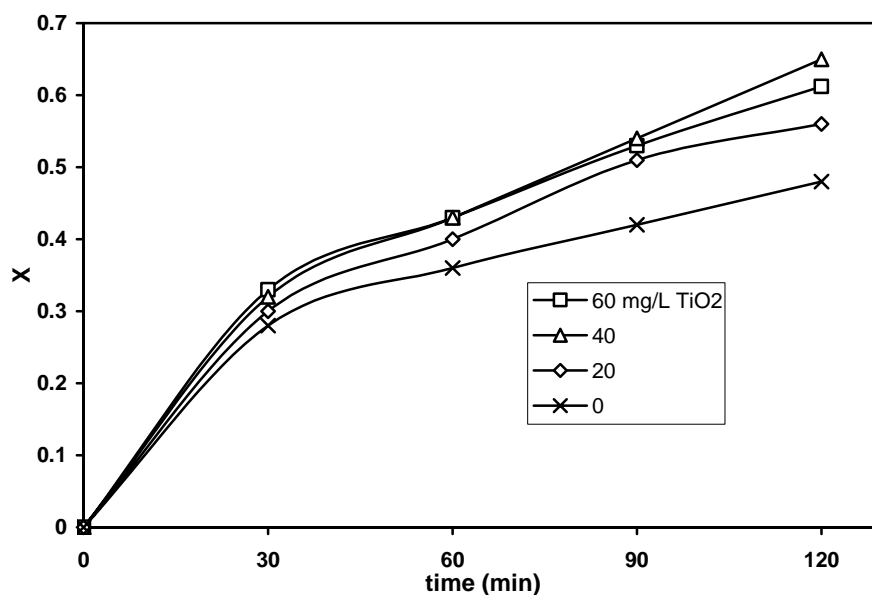
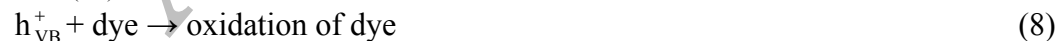
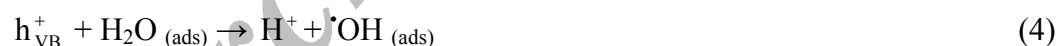
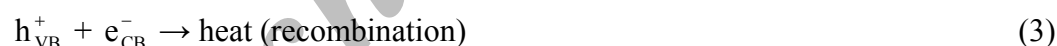


Fig.4. Effect of TiO₂ catalyst on degradation of DB86; natural pH (6.38) and T=20 °C.

The more activity of the UV/TiO₂ process is due to the well known fact that when TiO₂ is illuminated with the light having $\lambda < 390$ nm, electrons are promoted from the valance band to the conduction band of the semi-conducting oxide to give electron-hole pairs [15, 16]. The valance band (h_{VB}^+) potential is positive enough to generate hydroxyl radicals at the surface and the conduction band (e_{CB}^-) is negative enough to reduce the oxygen molecules, present in the solution. The generated hydroxyl radicals are powerful oxidizing agents and attack organic pollutants, present at or near the surface of TiO₂ and these cause the degradation of dyes according to the following reactions [5, 7, 17]



The effect of the amount of TiO₂ on degradation of DB86 is shown in Fig. 5 for two typical times of 30 min and 120 min. The degradation efficiency increases with increase in the amount of photocatalyst, until about 40 mg/L of catalyst and then decreases mildly.

The reason of this observation is thought to be the fact that when enough TiO₂ is present in the suspension for adsorbing dye molecules, the additional higher quantities of TiO₂ would not have more effect on the degradation efficiency. On the other hand, an increased opacity of the suspension brought about as a result of excess of TiO₂ particles [18].

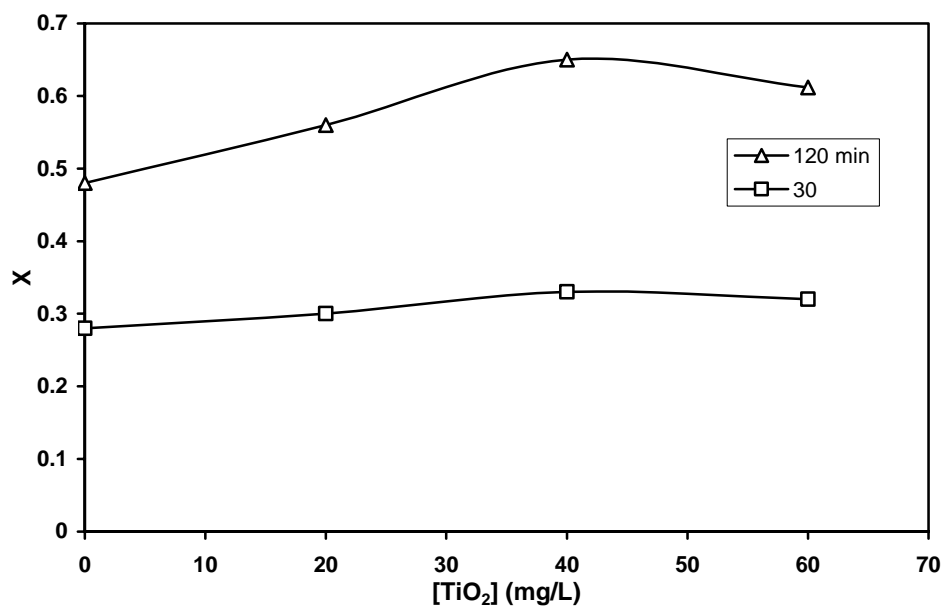


Fig.5. The effect of the amount of TiO₂ on degradation of DB86 at two typical irradiation times; natural pH (6.38) and $T=20^{\circ}\text{C}$.

3. 4. Effect of pH

pH is one of the factors influencing the rate of degradation of some organic compounds in the photocatalytic process [19, 20]s also an important operational parameter in wastewater treatments. Fig. 6 demonstrates the significant variation in degradation of DB86 as a function of pH. The degradation efficiency does not change too much at pH values between 6 and 10 for most irradiation times, but the degradation at pH value of 2 is significantly lower than those appropriate values. The reason for this case is due to our observations that the dye finds lower solubility at pH value of 2 and therefore, the probability of dye adsorption on the surface of catalyst will be decreased.

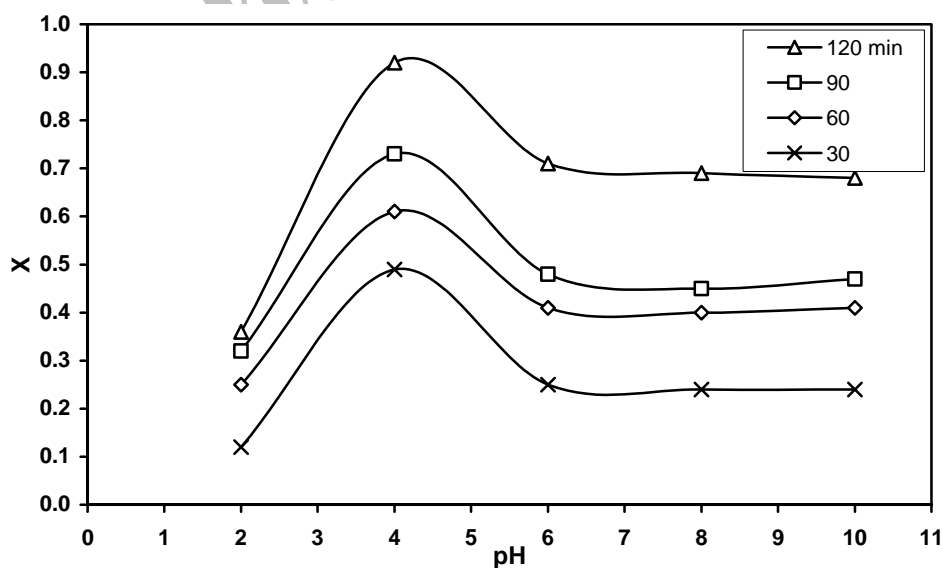


Fig.6. Effect of pH on degradation of DB86 at different irradiation times; [TiO₂]=40 mg/L and $T=20^{\circ}\text{C}$.

The reason for the significantly higher degradation at pH of 4 is that according to the zero point of charge of TiO_2 with pH 6.25^[5], its surface is presumably positively charged^[21, 22] since the dye has negative charge sulfite groups in its structure, the acidic solution favors the adsorption of dye onto photocatalyst surface or at least causing to find closer position to it and thus providing enhancement in degradation (Eqs. (7), (8)). The formation of $\cdot\text{OH}$ radicals in acidic solution can be enhanced, as it can be inferred from the following reactions^[23]:



3. 5. Effect of temperature

In the range of 20-40 °C, a low enhancement in the dye degradation efficiency was observed (Fig. 7) which must be belonging to low activation energy of photocatalytic reaction [24,25] and the photocatalysis with TiO_2 is not very temperature dependent in this case; however, an increase in temperature helps the reaction to compete more efficiency with $e_{\text{CB}}^- - h_{\text{VB}}^+$ recombination (Eq. (3)). On the other hand, an increase in temperature decreases the solubility of oxygen in water which is not desirable. The maximum temperature of 40 °C can be applied as the optimum available temperature at which a degradation efficiency of about 96% of dye is achieved in 120 min. Higher temperatures will cause significant evaporation of the solution during the experiments.

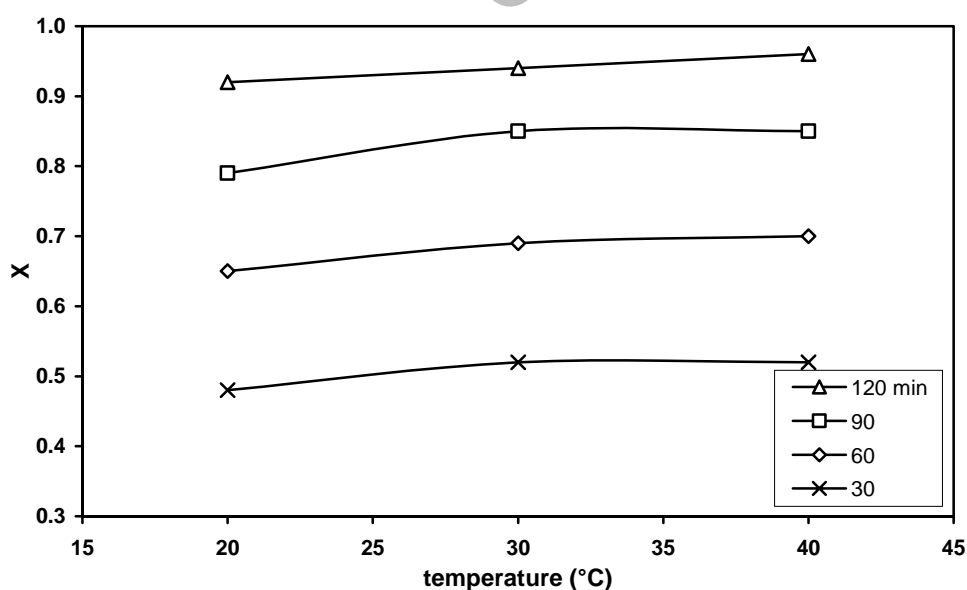


Fig. 7. Effect of temperature on degradation of DB86 at different times; $[\text{TiO}_2] = 40 \text{ mg/L}$ and $\text{pH} = 4$.

Applying the above found, optimum operating conditions ($[\text{TiO}_2] = 40 \text{ mg/L}$, $\text{pH} = 4$ and $T = 20 \text{ }^\circ\text{C}$) provides a degradation of dye which is represented in Fig. 8. The degradation tends to reach perfect degradation for irradiation times more than 120 min. The degradation efficiency is still significant for the lower times of the order 30 min; after which about 50% of degradation can be obtained; however, the tendency decreases after about 45 min. The reason

could be due to the more stable intermediates and the complicate interactions under the operating conditions.

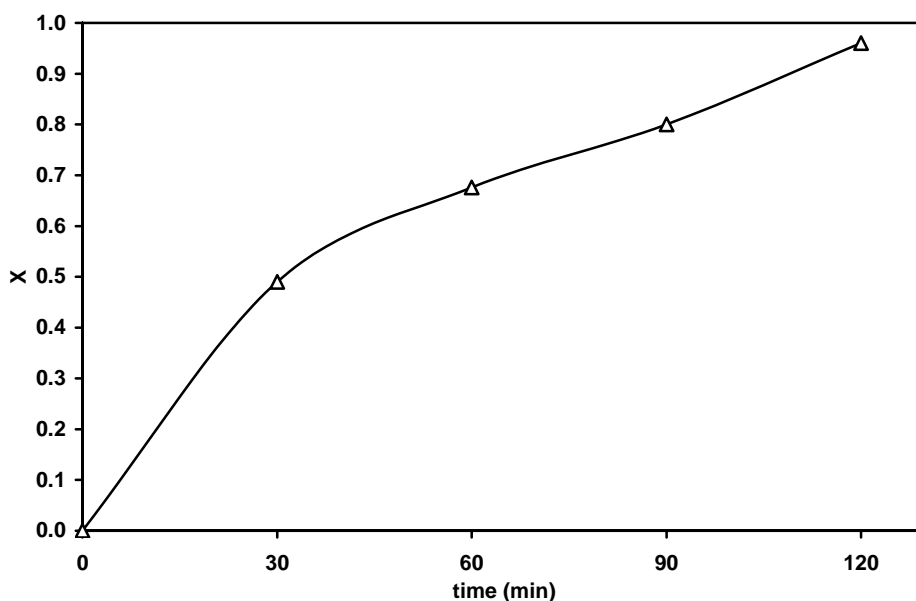


Fig.8. Degradation conversion versus time under optimum conditions.

3.6. Investigation on mineralization of DB 86

COD values have been related to the total concentration of organics in the solution [4]. Using this criterion, the mineralization of DB86 was investigated under the process of photocatalyst degradation under optimum operating conditions. For the initial concentration of 50 mg/L of dye and under the optimum conditions, the COD values were measured at different times and the appropriate conversion was calculated using Eq. (1), in which the COD values were applied. The results are presented in Fig. 9. Using photocatalysis process and after 120 min COD decrease from 38 mg/L to about 5 mg/L, equivalent of about 87% efficiency that is quite useful for an effective mineralization of DB 86 and also that for the shorter times of process, to about 60 min, the process is quite efficient.

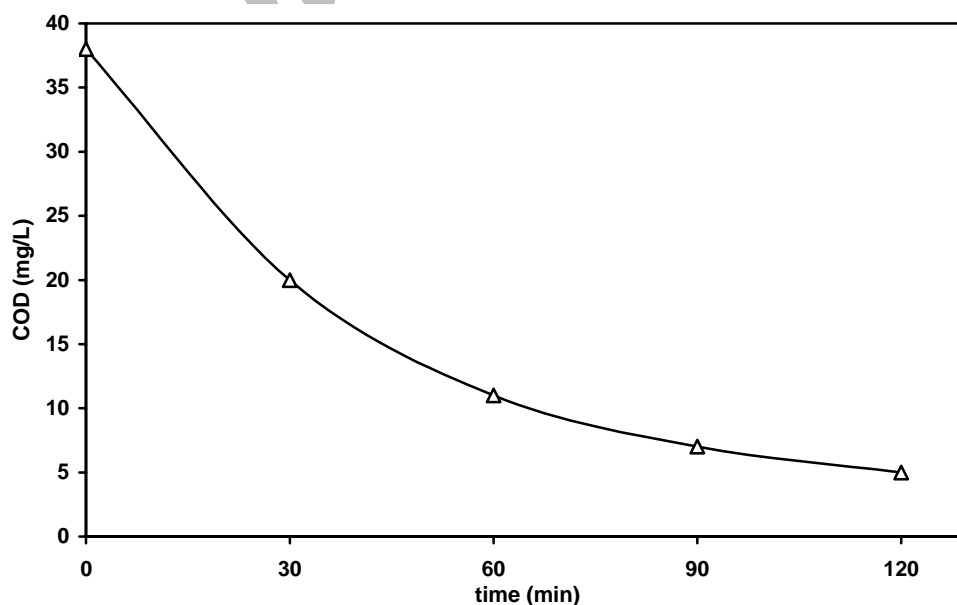


Fig. 9. Variation of COD of the solution of DB86 vs. time, under optimum conditions.

4. Conclusions

The results show that UV/TiO₂ process can efficiently be used to degrade the Direct Blue 86 dye in aqueous solutions. Degradation was high in the both cases of photolysis and photocatalysis and was negligible in the presence of TiO₂ without UV irradiation

For the initial concentration of 50 mg/L of DB86, as a representative concentration in industrial wastewaters, the pH of solution has the most obvious influence due to the simultaneous effect of hydroxyl radicals and the structure of molecule. Meanwhile the temperature, within the investigated range of 20-40 °C leads to enhance the progress, but with minor influence. The moderate obtained optimum conditions are: catalyst concentration of 40 mg/L; pH of 4 and temperature of 40 °C. Applying these conditions, can decolorize the substrate to about 96% and mineralize it to about 87% during about only 120 min irradiation. Significant mineralization is still provided for shorter times about 60 min.

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