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Degradation and mineralization of Direct Blue 71 in a circulating upflow reactor by UV/TiO$_2$ process and employing a new method in kinetic study

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Abstract

Direct Blue 71 ($C_{40}H_{23}N_7Na_4O_{13}S_4$), an azo dye with a high worldwide consumption and providing toxic effluents, can be highly degraded using TiO$_2$ catalyst suspension and irradiation with a UV-C lamp in a circulating upflow photo-reactor with no dead zone. An initial concentration of 50 mg L^{-1} of dye, within the range of typical concentration in textile wastewaters, was used. The influence of catalyst concentration, pH and temperature were investigated. The results showed that degradation of this dye can be conducted in the both processes of only UV irradiation and UV/TiO$_2$; but with the aim of mineralization, the later process provides significantly better results.

Accordingly, a degradation of more than 97% of dye was achieved by applying the optimal operational parameters with 40 mg L^{-1} of catalyst, natural pH and 45 °C, during 120 min irradiation. A removal of about 50% of COD could also be obtained at the same time.

In kinetic investigations, the effect of catalyst particles' turbidity was taken into account and the rate of degradation of the dye, under mild conditions, was expressed as the sum of the rates of individual photolysis and photocatalysis process branches, with mainly influence of the bulk hydroxyl radicals.

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1. Introduction

It has been documented that between 1–20% of the total world production of azo dyes is lost during the dyeing processes and providing major wastewater pollution in wastewaters. There are aromatic rings in the azo dye molecular structures which cause these effluents to be toxic and mostly non-biodegradable; therefore, becoming an important source of environmental pollution [1]. The presence of even small amounts of dyes (below 1 mg L^{-1}) is clearly visible and influences the water quality considerably [2,3].

To perform the wastewater treatment; unfortunately, the conventional chemical and physical methods are not destructive, but only transfer the pollutant from one phase to another; therefore, a new and different kind of pollution is faced and further treatments are required [4].

In this regard and in recent years, advanced oxidation processes (AOPs) have been described as efficient procedures for obtaining high oxidation yields from several kinds of organic compounds. These methods are based on the generation of very reactive agents such as hydroxyl radicals (OH) that are extremely reactive and strong oxidizing agent ($E^o = 2.8$ V), capable of mineralizing organic pollutants [5].

Among these methods, photocatalysis has become a hot topic, because it can completely degrade the organic pollutants into harmless inorganic substances such as CO$_2$ and H$_2$O under moderate conditions and would not bring with any serious secondary pollutions. The photocatalysis has been tested on many different compounds and in many different processes [6,7].

It is well known that TiO$_2$ is one of the suitable semiconductors for photocatalysis and has been applied into various photocatalytic reactions [8]. 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 stable

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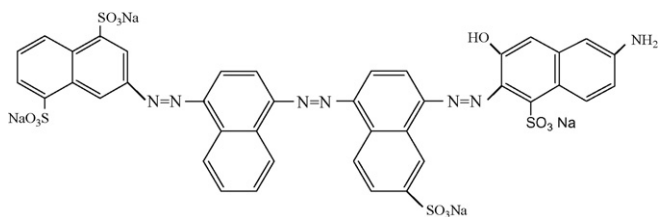
Fig. 1. Chemical structure of Direct Blue 71.

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; (5) the process offers great potential as an industrial technology to detoxify wastewaters [9].

The aim of the present work is to investigate the influence of various parameters on photocatalytic degradation of a three azo dye, called "Direct Blue 71 (DB71)" in the presence of TiO_2 particles and irradiated by the UV-C light in a suspended and circulated reactor. DB71 is a water soluble substantive dye and has a vast amount of application in cotton, cellulose, polyester, silk, leather and paper dyeing.

2. Experimental

2.1. Reagents

All reagents were used as received, without further purification. The three azo dye DB71, $C_{40}H_{23}N_7Na_4O_{13}S_4$ (C.I. no.: 34140, CAS no.: 4399-55-7, MW = 1029.9) was provided from Alvan Sabet company (Iran) with purity of more than 99%. Fig. 1 displays the structure of this dye. TiO_2 catalyst was Merck product and it was in the anatase form (99%); BET surface area of $14.68\,m^2\,g^{-1}$ and the average particle diameter of $27.6\,\mu m$ [10]. Sulfuric acid and sodium hydroxide, used to adjust the pH of solutions, and ethanol, used to quench the hydroxyl radicals in kinetic investigations, were Merck products. Distilled water was used to prepare the solutions.

2.2. The reactor

An annular and symmetric vertical reactor with a conic body shape (Fig. 2) and capacity of about 1 L was used. The UV lamp was positioned centrally in the reactor, inside a quartz tube, surrounded by the dye solution. The lamp was totally immersed in the reactor and therefore the maximum light utilization was achieved. Diameter of the quartz tube was the minimum to hold the lamp and thus the absorption of light photons by oxygen molecules in the air around the lamp was minimized. Quartz is transparent in the range: 160–600 nm. A pump, located below the reactor, provides an adjustable batch circulating and upflow system, receiving the solution from top of the reactor and delivering to bottom, just below the lamp, without catalyst separation. In this way, both the well mixing (the circulating pump delivers a flow-rate of about $5200\,mL\,min^{-1}$) and fluidizing of catalyst particles were provided around the quartz tube, with no dead space in the reactor. The reactor was equipped with a water-flow
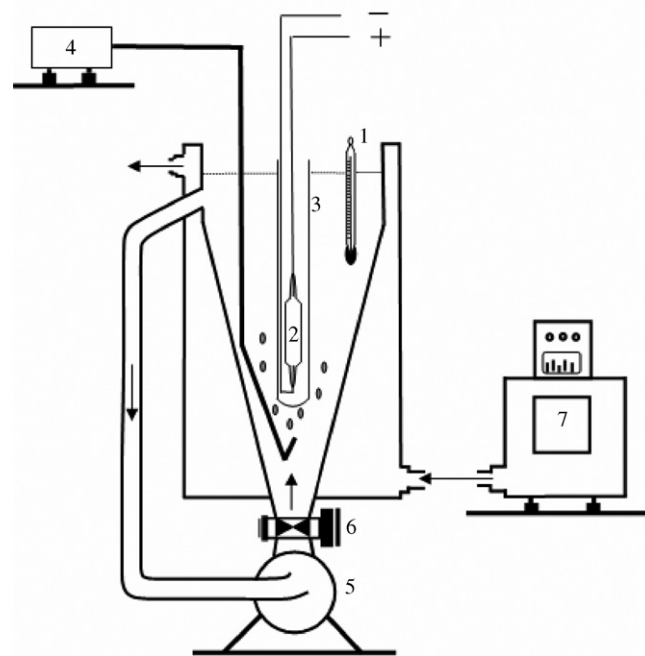

Fig. 2. The schematic view of photo-reactor: 1, thermometer; 2, UV lamp; 3, quartz tube; 4, micro-air compressor; 5, circulating pump; 6, valve; 7, thermostat.

jacket for regulating the temperature by means of an external circulating flow of a thermostat bath (OPTIMA-740, Japan) with an accuracy of $\pm 0.1\,°C$. The UV lamp (66 mm length) was mercury 150 W (UV-C, medium pressure, manufactured by ARDA, French). 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. The whole reactor body was covered with an aluminum thin layer to prevent UV emission around it.

2.3. Procedure

In order to perform the experiments, the appropriate solution, containing $50\,mg\,L^{-1}$ of dye (about $5 \times 10^{-5}\,M$) which is within the range of typical concentration in textile wastewaters [11,12] and a known amount of TiO_2 concentration was prepared. The pH was adjusted to the desired value by means of a pH meter (Denver, UB-10) using dilute H_2SO_4 or NaOH solutions. The solution was then transferred to the reactor and after adjusting temperature, the lamp was switched on to initiate the irradiation. 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 the separation of TiO_2 particles from the samples. The operative conditions of experiments are given in Table 1.

The concentration of the dye in each sample was analyzed with a UV–vis spectrophotometer (Perkin-Elmer, 55 OSE), measuring the absorbance at $\lambda_{max} = 584\,nm$ and using the appropriate calibration curve (Fig. 3). It is notable that the maximum wavelength and the molar absorption coefficient of DB71 were not much dependent on the pH of solution within the range of

Table 1
The operative conditions of experiments

Parameter	Value
DB71 initial concentration ($mg\,L^{-1}$)	50
TiO$_2$ amount ($mg\,L^{-1}$)	0–80
pH	2–10
Temperature (°C)	15–45
Irradiation time	up to 120 min

4–10; however, a considerably different maximum wavelength (571 nm) was observed at pH value of 2.

Using this method, the degradation efficiency or conversion (X) of DB71 at any time, with respect to its initial concentration can be obtained. This parameter is commonly used in the degradation study.

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

3. Results and discussion

3.1. UV–vis spectra

In a precedent study the UV–vis absorption spectra of DB71 were studied at different times of irradiation. As it is presented in Fig. 4, the bands relating to different molecular parts in this dye are decreased with respect to time.

DB71 is a three azo dye in which the chromophore part of molecular structure contains azo linkage and shows a strong absorbance in the visible region, while the absorbance peaks of the benzene and naphthalene rings are appeared in the UV region. The absorbance peaks at UV region and at 584 nm are respectively attributed to these aromatic rings and azo linkage [14].

The decrease of absorption peaks at $\lambda_{max} = 584$ nm in Fig. 4 indicates a rapid degradation of azo dye from the –N=N– double bond of the azo dye as the most active site for the oxidation attack [15]. The nearly perfect disappearance of the band at 584 nm reveals that DB71 is eliminated in the presence of TiO$_2$ suspension after about 120 min.
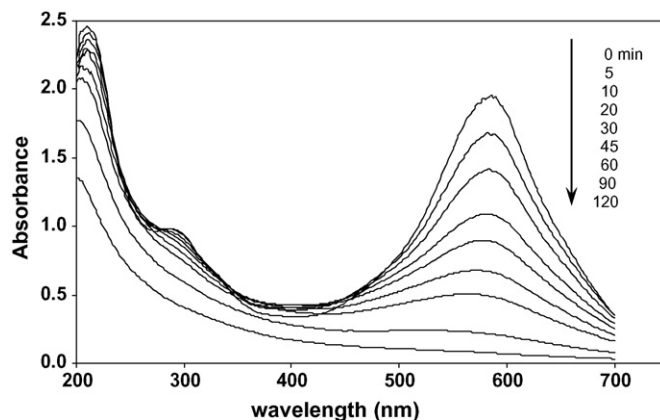

Fig. 4. UV–vis spectra changes of DB71 in the aqueous suspension at different times; [TiO$_2$] = 40 mg L^{-1}, pH 6.22 and $T = 25$ °C.

3.2. The role of TiO$_2$ photocatalyst

Fig. 5 demonstrates the enhancement of DB71 photodegradation in the presence of TiO$_2$ particles. In the presence of TiO$_2$, about 93% of dye degrades in an irradiation time of 120 min; under its natural pH (6.22) and at temperature of 25 °C. This efficiency decreases to about 83% at the same conditions and for the only UV irradiation (photolysis). The degradation is therefore significantly achieved when UV light is assisted with TiO$_2$ particles; however, light (UV-C) alone 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. Fig. 5 also shows that there was no change in dye concentration, when TiO$_2$ particles were used in darkness; i.e. no physical adsorption of the dye is occurred by the catalyst particles.

The more activity of the UV/TiO$_2$ process is due to the well-known electron promotion from the valance band to the conduction band of the semi-conducting oxide to give electron–hole pairs [16,17]. The valance band hole (h_{VB}^{+}) potential is positive enough to generate hydroxyl radicals at the surface. Also, the conduction band electron (e_{CB}^{-}) is negative enough to reduce the oxygen molecules, present in the solution.
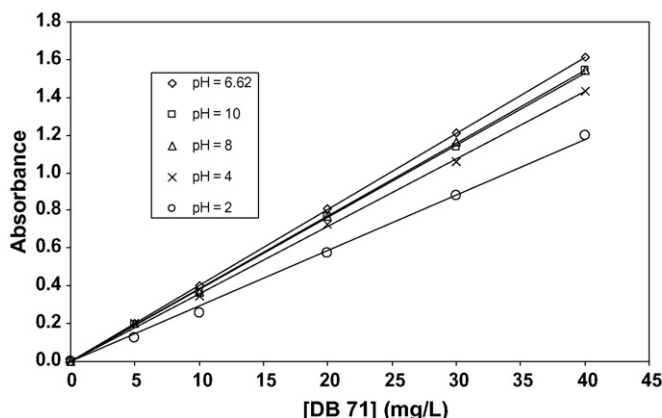

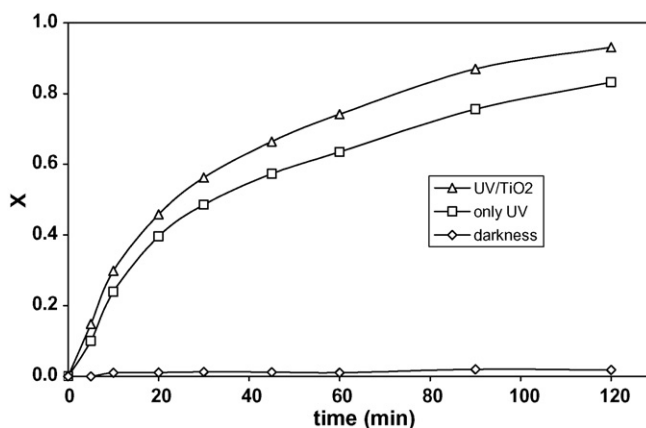Fig. 3. The calibration chart for measuring DB71 concentration at different pH values and $T = 25$ °C.

Fig. 5. Effect of TiO$_2$ particles on degradation of DB71 at different conditions; [TiO$_2$] = 40 mg L^{-1}, natural pH and $T = 25$ °C.

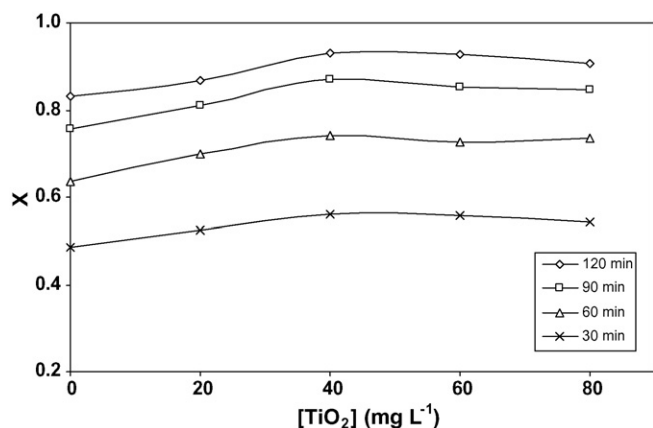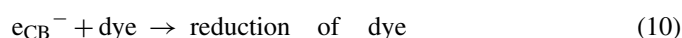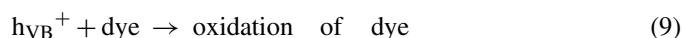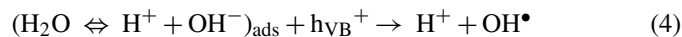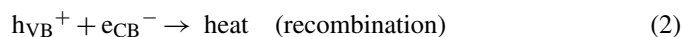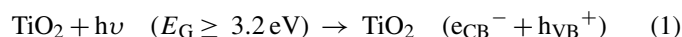Fig. 6. The effect of the amount of TiO_2 on degradation of DB71 at different irradiation times; natural pH and $T = 25\,^\circ C$.

The generated hydroxyl radicals are powerful oxidizing agents and attack organic pollutants, present at the surface of TiO_2 or near it (within $500\,\mu m$) and of course the reaction rate of hydroxyl radicals with pollutants decreases as the distance from surface increases [18]. These functions cause the degradation of dye according to the following reactions [8,19,20]:

$$TiO_2 + h\upsilon \quad (E_G \geq 3.2\,eV) \rightarrow TiO_2 \quad (e_{CB}^- + h_{VB}^+) \quad (1)$$

$$h_{VB}^+ + e_{CB}^- \rightarrow \text{heat} \quad (\text{recombination}) \quad (2)$$

$$O_{2(ads)} + e_{CB}^- \rightarrow O_2^{\bullet-} \quad (3)$$

$$(H_2O \Leftrightarrow H^+ + OH^-)_{ads} + h_{VB}^+ \rightarrow H^+ + OH^\bullet \quad (4)$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \quad (5)$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (6)$$

$$H_2O_2 + e_{CB}^- \rightarrow OH^\bullet + OH^- \quad (7)$$

$$Dye + OH^\bullet \rightarrow \text{degradation of dye} \quad (8)$$

$$h_{VB}^+ + dye \rightarrow \text{oxidation of dye} \quad (9)$$

$$e_{CB}^- + dye \rightarrow \text{reduction of dye} \quad (10)$$

The influence of TiO_2 concentration on the degradation is shown in Fig. 6. The photodegradation efficiency increases with increase in the amount of photocatalyst until about $40\,mg\,L^{-1}$ and then decreases moderately. The reason of this observation is thought to be due to the fact that when enough TiO_2 is present in the suspension for adsorbing dye molecules, the additional higher quantities of TiO_2 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 TiO_2 particles [21].

3.3. Effect of pH

pH is one of the factors influencing the rate of degradation of some organic compounds in the photocatalytic process [22]. In wastewater treatments, it is also an important operational parameter. Fig. 7 demonstrates the photocatalytic degradation of DB71 at different pH values. The degradation efficiency does
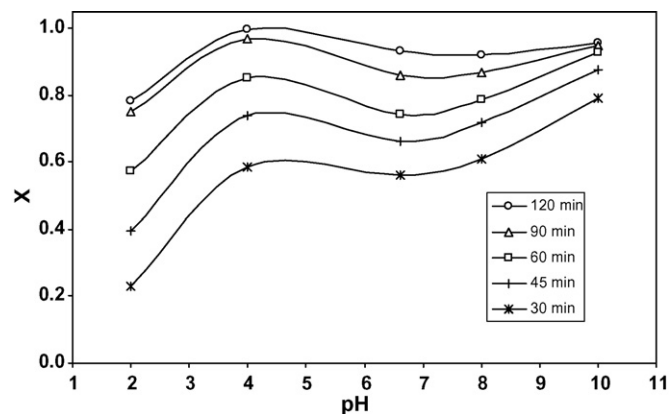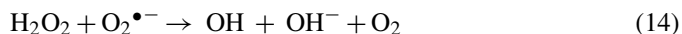

Fig. 7. Effect of pH on degradation of DB71 at different irradiation times; $[TiO_2] = 40\,mg\,L^{-1}$ and $T = 25\,^\circ C$.

not change too much at pH values between 4 and 8, but the degradation at pH value of 2 is significantly lower than those appropriate values. Our observations show that the dye finds low solubility in water at this pH.

The significant increase in degradation efficiency from pH value of 8–10 at most irradiation times could be commented by the significant abundance of OH^- in the medium and near the surface of the catalyst that leads to the generation of hydroxyl radicals (Eq. (4)) which has an important role in the degradation.

The reason for the higher degradation efficiency at pH value of 4 is that according to the pH of zero point of charge of TiO_2 which is 6.25 [20], its surface is presumably positively charged [23] and since the dye has negative charge sulfuric groups, the acidic solution favors the adsorption of dye onto catalyst surface or at least causing to find closer position to it and thus providing enhancement in degradation (Eqs. (9) and (10)). The formation of $OH^\bullet$ radicals in acidic solution can also be another reason, as it can be inferred from the following reactions [24]:

$$e_{CB}^- + O_{2(ads)} \rightarrow O_2^{\bullet-} \quad (11)$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \quad (12)$$

$$2HO_2^\bullet \rightarrow O_2 + H_2O_2 \quad (13)$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow OH + OH^- + O_2 \quad (14)$$

Because the maximum difference between the degradation efficiency of DB71 in the acidic solution with pH value of 4 and in its natural solution (pH 6.22) amounts to only about 6%, the natural pH was chosen as a moderate and optimum pH value and the experiments was followed under this pH, having the advantage that there is no need to add extra agents in order to regulate the pH of solution.

3.4. Effect of temperature

In the range of 15–$45\,^\circ C$, a low enhancement (about 7%) in the dye degradation efficiency was observed (Fig. 8) which must be due to the low activation energy of photocatalytic reaction [25,26]; however, an increase in temperature helps the reaction to compete more effectively with e_{CB}^-–h_{VB}^+ recombination (Eq.
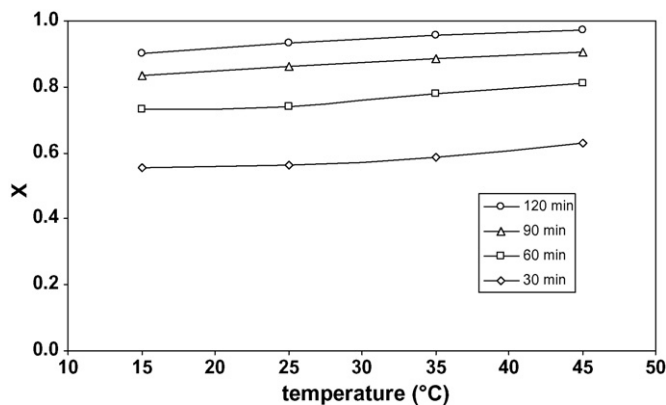
Fig. 8. Effect of temperature on degradation of DB71 at different irradiation times; $[TiO_2] = 40\,mg\,L^{-1}$ and pH 6.22.

(2)). On the other hand, an increase in temperature decreases the solubility of oxygen in water which is not desirable. The maximum temperature of 45 °C can be applied as the optimum available temperature at which a degradation efficiency of about 97% of dye is achieved in 120 min. Higher temperatures will cause significant evaporation of the solution during the experiments.

3.5. COD measurements

COD values have been related to the total concentration of organics in the solutions [5]. Using this criterion, the mineralization of DB71 was investigated under the process of photolysis and UV/TiO₂. For the initial concentration of $50\,mg\,L^{-1}$ of dye and under the optimum conditions, the COD values were measured and the appropriate efficiencies were calculated with respect to its initial value, before the UV irradiation (similar to the degradation efficiency). The results are presented in Fig. 9. Using UV/TiO₂ process, after 90 and 120 min irradiation, for instance, 32% and 50% of COD removal efficiency were achieved; however, these values are reduced to 12% and 14%, respectively, when using photolysis; i.e. significantly less than the case when photocatalyst is used.
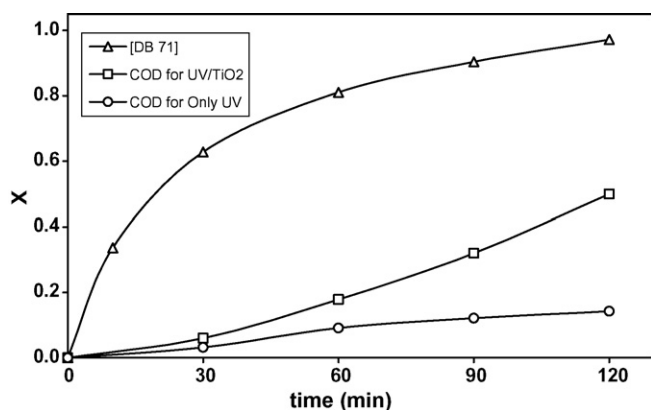

Fig. 9. Comparison between the efficiencies based on dye concentration and COD values; $[TiO_2] = 40\,mg\,L^{-1}$, natural pH and $T = 45$ °C.

From the trend of the COD efficiency variation, it is also observed that for degradation times longer than 120 min, higher COD removal can be expected for the UV/TiO₂ process; however, for the case of photolysis the changes is not considerable. The reason could be due to the stable intermediates which are not more degradable by photolysis. The presence of TiO₂ is vital for an effective mineralization of DB71, especially for short times of irradiation.

The difference between the efficiencies based on COD removal and dye removal, both in the presence of photocatalyst (Fig. 9) is due to the point that decolorization and mineralization (as the result of complete degradation) are not simultaneous. These parameters tend to reach each other, as the irradiation time increases.

3.6. Kinetic studies

Due to the practical applications, the degradation kinetics of DB71 was investigated under the mild conditions of $40\,mg\,L^{-1}$ of TiO₂, natural pH and 25 °C.

From the experiments (Section 3.2), it becomes clear that the difference between degradation when using UV alone and when UV is assisted with TiO₂ particles is considerable (about 10%). The degradation reaction progress is therefore the influence of two parallel branches of photolysis and photocatalysis:

$$R = -\frac{d[DB71]}{dt} = R_1 + R_2 \tag{15}$$

where R, R_1 and R_2 are the net degradation, the photolysis and the photocatalysis rates, respectively. The difference between the net and photolysis rates can be expected as the photocatalysis branch rate.

An important point to be mentioned is that the TiO₂ particles have to play two different roles: (1) having a positive catalytic activity leading to the generation of hydroxyl radicals (as mentioned above) and (2) causing the turbidity in the solution that leads to unfavorable weakening of the light efficiency, compared with the case when this processes is carried out with UV light alone. Hence, the difference between the rates (with and without catalyst) is not a perfect representation of the photocatalysis rate.

To investigate this case, the comparison was made between the a solution, containing $40\,mg\,L^{-1}$ of TiO₂ and another containing inert particles of BaSO₄, having the same turbidity of the first solution (2.286 NTU, measured by turbidimeter, HACH, 2100). BaSO₄ particles were prepared by the precipitation reaction of BaCl₂ (Merck) and H₂SO₄. Each of the solutions was added by $50\,mg\,L^{-1}$ of dye and the irradiation was imposed. The results are presented in Fig. 10. Using BaSO₄ particles have caused the UV efficiency to find an absolute reduction of about 4%. This means that actually the role of catalyst in degradation reaches to about 14%. The difference between these two appropriate rates was referred to as the portion rate due to photocatalytic degradation.

Meanwhile, the branch of photocatalysis is also constituted of two paths: (1) bulk degradation by hydroxyl radicals and (2) degradation of dye by h_{VB}^+ during the adsorption of dye on TiO₂
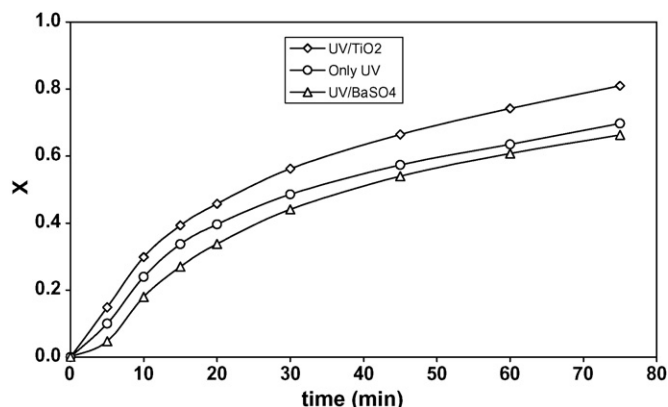
Fig. 10. Variation of the degradation of DB71 vs. time for different conditions; $[TiO_2] = 40 \, mg \, L^{-1}$, natural pH and $T = 25 \, ^\circ C$.

surface particles. The importance of these two paths depends on the substrate structure and operational parameters, such as pH.

In order to evaluate these two paths, experiments were performed by adding different amounts of ethanol to the solution. Alcohols such as ethanol are commonly used to quench hydroxyl radicals [27]. The results are presented in Fig. 11. The rate constant of reaction between hydroxyl radicals and ethanol is $1.9 \times 10^9 \, M^{-1} \, s^{-1}$ which is significantly high [27]. As it is observed from this figure, adding small amounts of ethanol, up to 0.1% (v/v), decreases the degradation efficiency of DB71 to about 10% which is in agreement with the percentage for degradation enhancement by catalyst (Section 3.2), i.e. hydroxyl radicals have the major role in photocatalytic process and no effective interaction is occurred between the valance band holes (h_{VB}^+) and dye molecules. This matter has been pointed out by Khodja et al. [27].

From Fig. 11, it is also obvious that higher ethanol additions would provide increase in the degradation of dye. The possible formation of ethoxy radicals ($C_2H_5O^\bullet$) from direct photocatalytic oxidation of ethanol in addition to the formation of hydroxyl radicals, produced from water, can provide further degradation. It is also notable that the ethanol molecules can produce hydroxyl radicals in direct photolysis, with respect to the C–O energy bond [28].
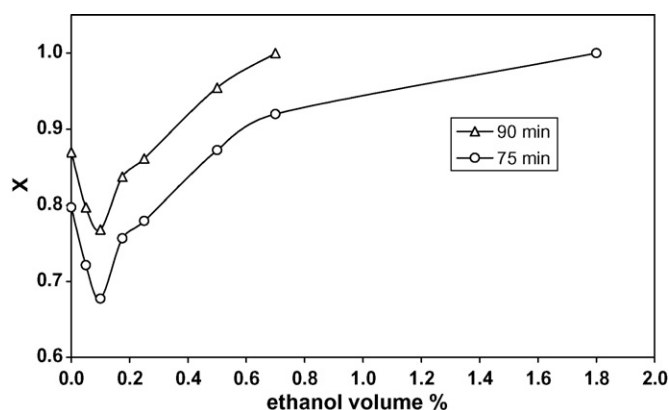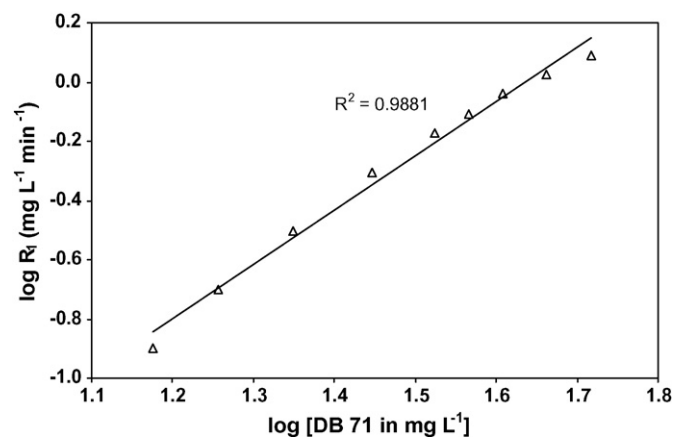

Fig. 12. The variation of DB71 degradation rate vs. its concentration for the only photolysis; natural pH and $T = 25 \, ^\circ C$.

Here, the two appropriate simple power law models were examined for these two competing paths:

$$R = k_1[DB71]^{n_1} + k_2[DB71]^{n_2} \tag{16}$$

where n_1, n_2, k_1 and k_2 are the appropriate orders of reactions and the rate constants. Several kinetic studies in photocatalyst degradation have been concerned in the power law models [29,30].

To obtain the appropriate parameters in Eq. (16), the differential method of data analysis, based on the data of concentration vs. time, with 9 data points at different times, until 75 min, was used. From Eqs. (15) and (16), the following equations are appropriate:

$$\log R_1 = \log k_1 + n_1 \log[DB71] \tag{17}$$

$$\log R_2 = \log k_2 + n_2 \log[DB71] \tag{18}$$

Figs. 12 and 13 present the goodness of fit of the rate Eqs. (17) and (18) to the data. For the experimental results, Table 2 indicates the values of the obtained parameters. The order of reactions of the photolysis and photocatlysis are more than one, indicating a rather complicate degradation mechanism. For decomposition of sodium dodecylbenzene sulfonate solution, for instance, an order of 1.32 has been reported [29].

Fig. 11. Variation of the degradation of DB71 vs. added amounts of ethanol at two irradiation times; $[TiO_2] = 40 \, mg \, L^{-1}$ and $T = 25 \, ^\circ C$.
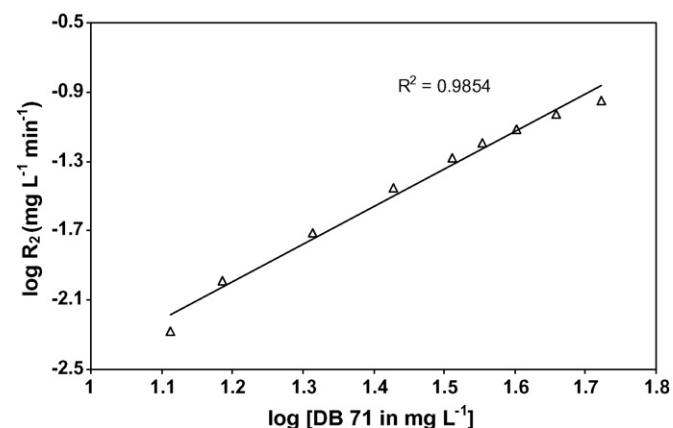

Fig. 13. The variation of DB71 degradation rate vs. its concentration for the photocatalysis; $[TiO_2] = 40 \, mg \, L^{-1}$, natural pH and $T = 25 \, ^\circ C$.

Table 2
Kinetic parameters of DB71 degradation

n_1	1.83
k_1 ($\times 10^{-4}$ (mg L^{-1})$^{-0.83}$ min^{-1})	9.92
n_2	2.16
k_2 ($\times 10^{-5}$ (mg L^{-1})$^{-1.16}$ min^{-1})	2.58

The net rate of degradation of DB71, under conditions used, can therefore be given (in mg L^{-1} min^{-1}) as

$$R = 9.92 \times 10^{-4}[\text{DB71}]^{1.83} + 2.58 \times 10^{-5}[\text{DB71}]^{2.16} \quad (19)$$

4. Conclusions

Effective degradation of the azo dye Direct Blue 71 in water is available in the both cases of UV irradiation and UV/TiO$_2$ processes using a circulated upflow reactor; however, the mineralization of the dye can be obtained effectively by the later process.

The results indicate that efficiency of degradation of DB71 is not much affected by pH and temperature; in this regard and for degradation and mineralization of 50 mg L^{-1} of DB71 (as a representative concentration in wastewaters), the moderate and the most suitable conditions are: catalyst concentration: 40 mg L^{-1}, pH: 6.22 (natural pH) and temperature: 45 °C. Under these conditions, for 97% degradation of dye and for the removal of about 50% of COD, about 120 min irradiation time is required.

It became clear that the bulk degradation by hydroxyl radicals has the major role in the photocatalytic processes compared with the direct degradation of dye molecules on the catalyst surface.

To investigate the kinetics of degradation, a satisfied procedure can be employed to determine the portion of degradation rate in photocatlysis branch while excluding the effect of turbidity in the photolysis branch. The two appropriate models of power law showed the goodness of fitting with experimental data.

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