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Discoloration of a red cationic dye by supported TiO_2 photocatalysis

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Abstract

The degradation under UV, visible and sunlight irradiation of C.I. Basic Red 46 (BR 46) dye used for acrylic fibers dyeing has been studied in a lab-scale continuous system with two different immobilized TiO_2 systems. Catalyst I was based on TiO_2 particles deposited on cellulose fibers; Catalyst II combined TiO_2 particles deposited on a layer of cellulose fibers (as in Catalyst I) with a layer of carbon fibers and finally a layer of cellulose fibers. The treatment of aqueous dye solutions and industrial wastewater contaminated with the same dye has been evaluated in terms of color removal and chemical oxygen demand (COD) decrease. With UV light, aqueous solutions containing dye were decolorized slightly more rapidly with Catalyst II than with Catalyst I. Sunlight was also very effective and experiments involving sunlight irradiation showed Catalyst II to be the more efficient, giving more than 90% discoloration after 20 min of treatment. Comparing the discoloration yield by adsorption or under visible light for both catalysts, it was observed that the difference between them is below 5%. The adsorption kinetics was found to follow a second-order rate law for Catalyst I and a first-order rate law for Catalyst II. The kinetics of photocatalytic degradation under UV or sunlight were found to follow a first-order rate law for both catalytic systems. Under sunlight the COD removal yield for textile wastewater reaches 33% with Catalyst I against 93% with Catalyst II.

Keywords: Activated carbon; Sunlight; Titanium dioxide; UV radiation; Visible light

1. Introduction

Textile industry is a large consumer of dyes, using them in conjunction with a wide range of auxiliary chemicals for various dyeing and finishing processes [1]. The major environmental concern associated with the use of dyes is their loss during the dyeing process [2,3]. Consequently, textile wastewaters are characterized by a high chemical oxygen demand (COD), a low biodegradability, a high salt content and color. If discharged in environment without any treatment, they are highly harmful [4].

Because of the complexity and the variety of dyes employed in the dyeing processes, it is difficult to find a unique treatment that insures complete elimination of all types of dyes. Biological processes, in the presence or absence of oxygen, have proven to be adequate but dyes can inhibit bacterial development [5–8], reducing their efficiency. Physical methods of discoloration include different coagulation methods [9–12], adsorption on activated carbon [10], coal [13,14] and natural inexpensive materials [15] such as sawdust [16], chitin [17] or fruit debris [18,19]. Membrane processes have also been advocated [10,20–22] in order to obtain a particle-free reusable effluent. The main drawback of these methods is that they operate by transfer of the pollutants to another phase or by concentrating them rather than destroying them.

Among the new oxidation methods or "advanced oxidation processes" (AOPs) heterogeneous photocatalysis [23] has become very popular as an alternative or a complement to the conventional water and wastewater treatment methods. In many cases, the efficiency of photocatalytic degradation has been demonstrated on azo or reactive dyes [1–3]. However fewer studies have been devoted to cationic dyes such as methylene blue [3,24] as they perform poorly on natural fibers; they

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do, however, work very well on acrylic fiber which is widely used in manufacturing of blankets, carpets, knitting, goods, decorative fabrics, paper, and leather products. These dyes are characterized by their very strong tinctorial power, outstanding brightness, and excellent fastness properties.

Among the tested photocatalysts [25,26], titanium dioxide is the most used one due to its large photocatalytic activity, high stability, non-environmental impact and low cost. TiO_2 can be applied as a powder suspended in slurry or be immobilized on various supports, such as cellulose, glass, quartz or stainless steel. Pelton et al. [27] have recently reviewed the use and performance of photocatalytic paper, which is flexible and easy to replace. Furthermore pure cellulose exhibits a good photostability [28]. When a suspension of catalyst is used, the photocatalytic degradation efficiency is high. But the fine catalyst particles have to be separated from the treated water after treatment. This difficulty can be overcome by combination with another process such as coagulation [29] and is solved in the case of catalyst immobilization. In most cases, the degradation is conducted for dissolved compounds in water with combination of UV irradiation and catalysts. To achieve high degradation efficiency a relatively long illumination time with UV irradiation is required. This is unfavorable from the economical point of view. To solve this problem a low-cost irradiation source can be used or the catalyst activity can be increased. Addition of a low percentage of metallic ions such as Fe^{3+}, Cr^{3+}, Mn^{2+}, . . . is beneficial [30,31]. Another option is to use TiO_2-coated carbon [32] or metal-coated TiO_2 [33]. Other work has been aimed at the use of natural sunlight which reduces significantly the electrical power requirements and operating cost [34–40].

Unfortunately, only 5% of the solar energy reaching the Earth's surface can be absorbed by a typical photocatalyst such as titanium dioxide. However, in countries such as Morocco where sunlight is very abundant and textile industries represent an important economical activity, sun-based photocatalysis can be considered in order to treat in an efficient manner and at low cost, dye-contaminated wastewater.

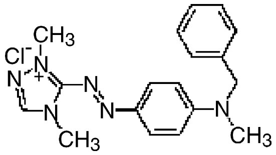
In this study, we have examined the practical usefulness of sunlight radiation for color removal and chemical oxygen demand (COD) decrease in textile wastewater. The dye studied in this work is the basic red (BR 46) used for dyeing acrylic fiber in a local textile company. This dye has been found to cause skin problems and therefore to be harmful for humans [41].

Experiments were run using aqueous solutions of the pure dye and industrial wastewater on titanium dioxide immobilized on cellulose fibers (Catalyst I) or in combination with carbon fibers (Catalyst II) under different radiation sources (UV and visible artificial lights and sunlight).

2. Materials and methods

Basic Red 46 (BR 46) was provided by SDI textile company (Safi, Morocco). Table 1 summarizes its properties. The pure solutions were prepared with de-ionized water and contained 10 and 25 mg/L of dye at pH = 5 (adjusted with acetic acid), which corresponds to the pH of the industrial wastewater. A wastewater sample was collected at the exit of the dye bath and contained the red dye as well as dyeing additives (cationic leveling agent, non-ionic dispersing agent and acetic acid). The sample was kept at 4 °C. Before the experiment, an aliquot was taken out of the cold room and brought back to ambient temperature (24 °C).

Table 1
Properties of Basic Red BR 46

Color index	Basic Red 46
Molecular structure	
Structure type	Cationic
Sulphonic group	None
Azo group	One
λ_{max}	530 nm
pH range	2–12
Molecular weight (g/mol)	357.5

The catalysts, based on flexible mats of fibers, were donated by Ahlstrom (Pont-Evêque, France). Catalyst I is made of TiO_2 particles deposited on cellulose fibers. Catalyst II is a three-layer system: a layer of cellulose fibers with deposited TiO_2 particles (such as in Catalyst I), a layer of carbon fibers and finally a layer of cellulose fibers. Both catalysts were rinsed for 12 h by deionised water prior to use, to eliminate any particle which could have detached due to cutting to size.

A schematic representation of the reactor, made of aluminum, except for the cover glass, is shown in Fig. 1. The reactor interior is coated with PTFE to prevent corrosion. The circulation of the liquid is provided by a peristaltic pump at a constant flow (40 ml/min). Tubes are made out of PTFE. The reservoir is open to air. The support presents an inclination of 30° with the horizontal in order to optimize the sunlight irradiation as well as the flow distribution on the catalyst support.

For the treatment under UV, two lamps (emission wavelength = 365 nm, power of one lamp = 15 W) (ref A89013, Bioblock, Illkirch, France) were used. For the treatment under visible light, they were replaced by Sylvania F15W/GRO lamps (ref 0000708) (SLI Lichtsysteme GmbH, Erlangen, Germany), whose emission spectrum is given in Fig. 2. For the treatment

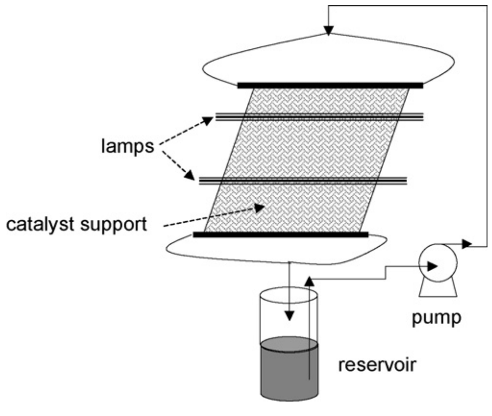


Fig. 1. Schematic representation of the photocatalytic reactor.

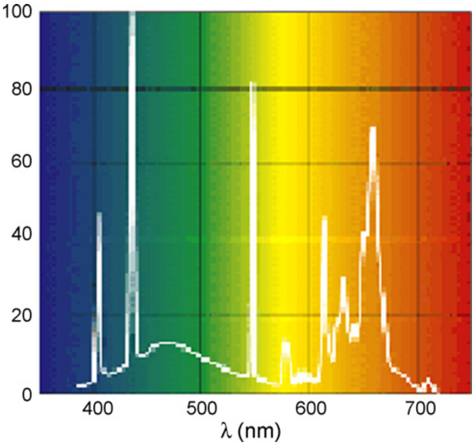


Fig. 2. Emission spectrum of visible light lamps.

under sunlight, all the experiments were run in Safi (Morocco) between 12 p.m. and 15 p.m. by fine weather conditions in order to achieve the same conditions of luminosity. The intensity of the solar light was measured with a luxmeter (Gossen Metrawatt, Nuremberg, Germany) and varied between 120,500 and 130,000 lux (corresponding to a solar irradiation intensity between 180 and 190 W/m^2) during the experiments.

Chemical oxygen demand (COD) was assessed by the dichromate standard method. The dye concentrations were determined from their absorbance characteristics in the UV–vis range (Fig. 3). An Anthélie Light (Secomam, Domont, France) spectrophotometer was used for experiments run in France and a GBC (Ajax, Ontario) UV/VIS 911 spectrophotometer for experiments run in Morocco. In both cases the devices were connected to a PC for data collection. Quartz cuvettes (path length = 1 cm) and de-ionized water (blank) were used. A linear correlation was established between the dye concentration and the absorbance at $\lambda_m = 530$ nm, in the range $c_{dye} = 0$–35 mg BR 46 L^{-1} with a coefficient of correlation $r^2 = 1$:

$$c_{\text{dye}} = 11.86A_{530}(\text{cm}^{-1})$$

where A_{530} is the absorbance at $\lambda_m = 530$ nm.

The discoloration yield is calculated as:

$$Y = 100\left(\frac{1 - A_{530}(t)}{A_{530}(0)}\right)$$

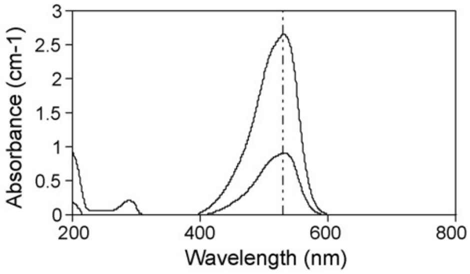


Fig. 3. UV–vis spectra of Basic Red 46 (thin line = 10 mg/L, thick line = 25 mg/L).

3. Results

It should be stated that, during all the experiments, no particle detachment or degradation of paper fibers was observed.

3.1. Photocatalytic degradation using Catalyst I

As shown in Fig. 4, for 10 and 25 mg BR 46 L^{-1}, the discoloration by adsorption (i.e. without any radiation) on Catalyst I reached 20% after only 10 min and increased to 30% after 3 h of treatment. The difference between discoloration by adsorption or under visible irradiation was below 5%.

After the first ten minutes, the discoloration yields under UV and under sunlight were both equal to 30%. Later, the discoloration yield under UV became larger than the one under sunlight but the discoloration rate decreased. The difference between the yields reached 20% after 2 h: for the 10 mg/L sample the discoloration yield reached 85% under UV against 65% under sunlight and for the 25 mg/L it reaches 65% under UV against 45% under sunlight. By adsorption or under the various types of irradiation, the yields decreased when the dye concentration increased.

The experiment with wastewater was carried out only under sunlight. According to the calibration curve between absorbance at 530 nm and the dye concentration, the dye concentration in the wastewater was estimated to be about 12.5 mg/L, which justifies the dye concentration range selected for the experiments with aqueous solutions. By comparing the variations of the discoloration yield (Fig. 5) it can be observed that during the experiment, the discoloration yield was lower for wastewater than for the pure solutions. After 3 h of treatment, it reached 45% for wastewater against 77% for the 10 mg/L solution and 53% for the 25 mg/L solution. It can be assumed that the various

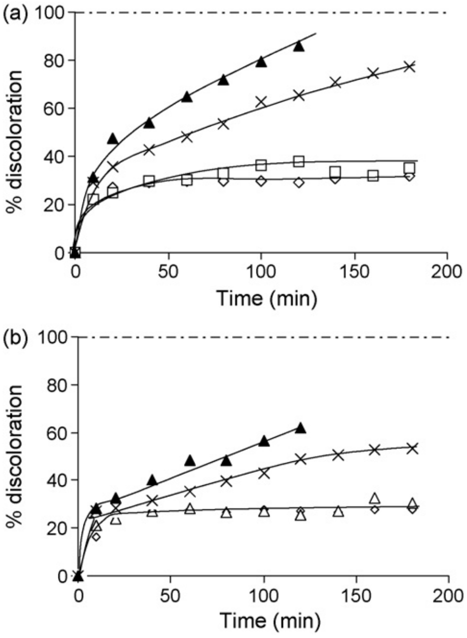


Fig. 4. Discoloration of BR46 (a, 10 mg/L; b, 25 mg/L) on Catalyst I by adsorption (◊), under UV light (▲), visible light (△) and sunlight (×).

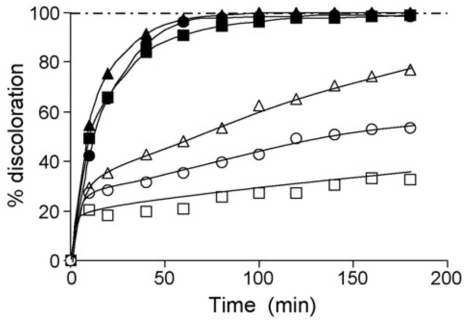


Fig. 5. Discoloration of wastewater (■, □) compared to the 10 mg/L (▲, △), and 25 mg/L (●, ○) solutions under sunlight using Catalyst I (open symbols) and Catalyst II (closed symbols).

additives contained in the wastewater decreased the efficiency of the photocatalytic process. In terms of COD, the initial COD of the wastewater sample was 2000 mg O_2/l. It decreased to 1333 mg O_2/l at the end of the test (3 h), giving a COD removal yield of 33%.

3.2. Photocatalytic discoloration using Catalyst II

As for Catalyst I, the discoloration of pure solutions was investigated for the aqueous solutions concentrations and under the effect of adsorption and of the different irradiation sources. As shown on Fig. 6, for both concentrations, discoloration by adsorption and under visible light was similar: the visible irradiation had no influence. The discoloration by adsorption was very significant as it reached 70% after the first hour of treatment. The discoloration under solar and UV irradiation exhibited faster rates during the first hour. The yields levelled off then but they reached already ≈90% under UV irradiation and ≈100% under sunlight irradiation. The rates were slightly larger when the dye concentration was lower. It can be observed that, with the lower dye concentration, a discoloration yield of 90% can be reached after 2 h just by adsorption on the catalyst.

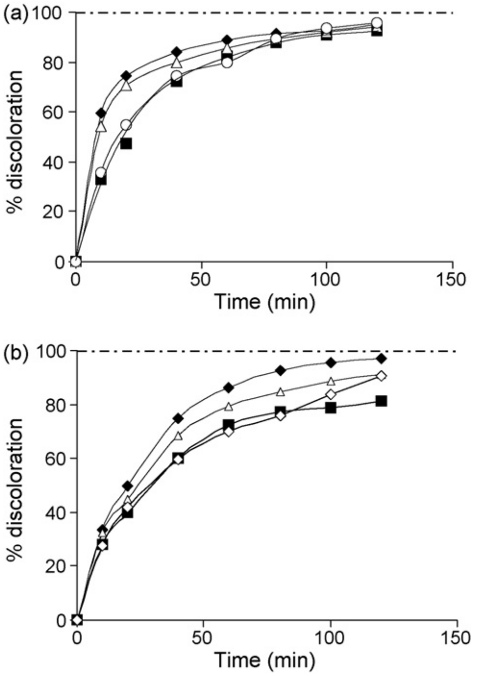


Fig. 6. Discoloration of BR46 (a, 10 mg/L; b 25 mg/L) on Catalyst II by adsorption (■), under UV light (△), visible light (◇) and sunlight (◆).

The wastewater sample was treated with Catalyst II under sunlight (Fig. 5). The discoloration yield reached 86% after one hour of treatment. During the first 10 minutes, the discoloration yield was similar for three solutions. For larger irradiation times the yield was lower for wastewater than for the pure solutions. In terms of COD, it decreased to 133 mg O_2/l at the end of the test (3 h), giving a COD removal yield of 93%.

4. Discussion

4.1. Removal by adsorption

Since the photodegradation of dye occurs predominantly on TiO_2 surface, the adsorption of dye molecules from aqueous solution particularly on TiO_2 surface is very important.

Various kinetic models have been proposed [42]. In the present work two models were tested to explain the data presented in Fig. 7: a pseudo-first-order model and a pseudo-second-order model.

The pseudo-first-order model equation is given by

$$\mathrm{Log}(q_e - q(t)) = \mathrm{Log}(q_e) - \frac{K_{\mathrm{ads},1}}{2.303}t$$

where q_e and $q(t)$ are the amounts of the dye adsorbed at equilibrium and at time t, in mg, and $K_{\mathrm{ads},1}$ is the pseudo-first-order rate constant.

The pseudo-second-order model is given by

$$\frac{t}{q(t)} = \frac{1}{K_{\mathrm{ads},2}\, q_e^2} + \frac{t}{q_e}$$

where $K_{\mathrm{ads},2}$ is the pseudo second-order rate constant.

The agreement between experimental data and model predicted values was expressed by the correlation coefficient (r^2). Adsorption tests with regular sampling of the liquid phase were carried out in absence of light in order to evaluate the equilibrium constants. Equilibrium was reached after 120 min for both catalysts.

The results are reported in Table 2 (for the pseudo-first-order model) and in Table 3 (for the pseudo-second-order model). For Catalyst II, the higher values of $r^2 > 0.99$ and the good agreement between the experimental and predicted equilibrium sorption

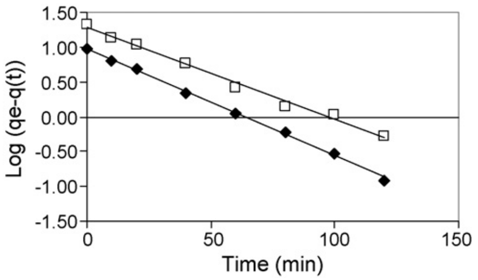


Fig. 7. Pseudo-first-order model for adsorption of Basic red 46 on Catalyst II (□) = 25 mg/L, (◆) = 10 mg/L.

Table 2
Pseudo-first-order model constants for adsorption process

Initial concentration	Catalyst I				Catalyst II			
	$K_{ads,1}$ (min^{-1})	q_e (mod) (mg)	q_e (exp) (mg)	r^2	$K_{ads,1}$ (min^{-1})	q_e (mod) (mg)	q_e (exp) (mg)	r^2
10 mg/L	0.019	1.3	2.7	0.8081	0.035	9.4	9.5	0.9983
25 mg/L	0.023	1.8	6.8	0.6423	0.03	19.	21	0.9928

Table 3
Pseudo-second-order constants for adsorption process

Initial concentration	Catalyst I			
	$K_{ads,2}$ (mg^{-1} min^{-1})	q_e (mod) (mg)	q_e (exp) (mg)	r^2
10 mg/L	0.068	2.66	2.7	0.9945
25 mg/L	0.048	6.8	6.8	0.9978

capacities ($q_{e,exp}$ and $q_{e,mod}$) confirm that the pseudo-first-order model describes correctly the adsorption kinetics. Contrary, for Catalyst I, the lower values of r^2 suggest that the pseudo-first-order model fails to describe adequately the adsorption kinetics. The high values of r^2 for Catalyst II and the agreement between predicted and experimental equilibrium sorption capacities suggest that the pseudo second-order model describes its adsorption kinetics very well (Fig. 8). $K_{ads,1}$ and $K_{ads,2}$ decrease when the dye initial concentration increases for Catalyst I and Catalyst II, respectively. The rate constant is a measure of the initial discoloration and with increasing dye concentration, a lower number of photons reaches the photocatalyst surface resulting in slower production of $OH^{\bullet}$, e^{-} and h^{+}. A lower photocatalyst activation results in fewer electrons available for direct reduction and fewer holes (h^{+}) available for direct oxidation of the dye, limiting therefore the degradation.

4.2. Photocatalytic degradation by visible radiation

As shown on Figs. 4 and 6, it can be noticed that for both catalysts and both initial concentrations of BR 46, the photocatalytic degradation under visible light radiation was similar to degradation by adsorption (<5%) and slightly less than under UV.

It has been reported that the mechanism of photocatalytic degradation under visible radiation is different from the one under UV illumination [36,43,44]: under UV irradiation, TiO_2 excites an electron from valence band to the conduction band, and these electron and hole participate in a redox reaction with chemicals (usually in water, oxygen is reduced to super-oxide radical and hydroxyl ion is oxidized to hydroxyl radical). However, under visible light irradiation conditions, TiO_2 functions also by dye-sensitization. The process of photosensitization involves initial excitation of dye molecules rather than TiO_2 particles. Charge is then transferred from the excited states of the dye into the conduction band of the semi-conductor particle whereas the dye is converted to its cationic radical. The transferred electron can reduce surface chemisorbed oxidants, usually O_2, to yield the oxidizing species ($O_2^{\bullet -}$, $H_2O^{\bullet}$, and $OH^{\bullet}$ radicals) which can cause photodegradation. Experimental results obtained by photocatalytic degradation under visible light suggest that the process of photosensitization was not able to excite the dye molecules and that the photocatalytic degradation of dye was induced solely by excitation of TiO_2 under UV radiation.

4.3. Photocatalytic degradation under UV radiation

The degradation curves of the BR46 dye by UV radiation (Figs. 4 and 6) show that the color removal was more important with the Catalyst II than with Catalyst I. Degradation curves also suggest that a first-order homogeneous reaction model can be taken in consideration for describing the kinetic behavior. The kinetic equation that describes this process is

$$\mathrm{Ln}(C) = \mathrm{Ln}(C_0) - K_{UV}t$$

with K_{UV} the first-order rate constant and C the concentration of BR46 at time t.

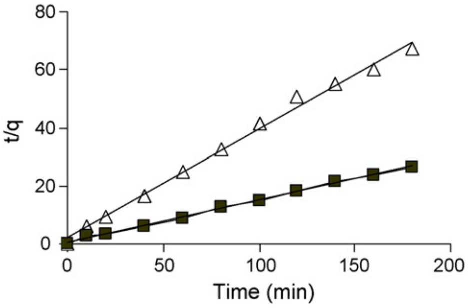


Fig. 8. Pseudo-second-order model for adsorption of Basic red 46 on Catalyst I (■) = 25 mg/L, (Δ) = 10 mg/L.

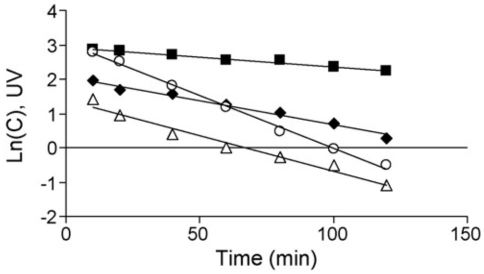


Fig. 9. First-order model for photocatalytic degradation under UV of Basic Red 46 on Catalyst I: (■) = 25 mg/L, (♦) = 10 mg/L and on Catalyst II: (○) = 25 mg/L, (Δ) = 10 mg/L.

Table 4
First-order model constants for photocatalytic process under UV

Initial concentration	Catalyst I				Catalyst II			
	K_{UV} (min^{-1})	C_{0model} (mg/L)	$C_{0corrected}$ (mg/L)	r^2	K_{UV} (min^{-1})	C_{0model} (mg/L)	$C_{0corrected}$ (mg/L)	r^2
10 mg/L	0.0142	8	8.4	0.9837	0.0321	5.69	6.8	0.9955
25 mg/L	0.0056	18.54	21.4	0.9795	0.0291	17.69	17.7	0.9955

Table 5
First-order model constants for photocatalytic process under sunlight

Initial concentration	Catalyst I				Catalyst II			
	$K_{sunlight}$ (min^{-1})	C_{0model} (mg/L)	$C_{0corrected}$ (mg/L)	r^2	$K_{sunlight}$ (min^{-1})	C_{0model} (mg/L)	$C_{0corrected}$ (mg/L)	r^2
10 mg/L	0.0069	7.12	8.4	0.9958	0.0726	9.98	10	0.9925
25 mg/L	0.0029	20.085	21.4	0.9816	0.0557	25.44	25	0.9979

Fig. 9 represents the variations of Ln(C) versus t, respectively, for both catalysts. It can be shown in Table 4 that the values of the correlation coefficient r^2 are reasonably high and the intercept gives values of C_{0model}. Since the adsorption process occurs predominantly at the beginning of the experience, $C_{0measured}$ was corrected by removing the amount of dye adsorbed on catalyst for the first 10 min. It can be observed that C_{0model} are reasonably close to $C_{0corrected}$. The observed decrease on K_{UV} as the initial concentration of dye increases can be explained in terms of the reduced availability of photons as the color of the solution gets more intense.

4.4. Photocatalytic degradation by sunlight radiation

As shown in Figs. 4–6, the color removal under sunlight was higher with Catalyst II than Catalyst I: the discoloration yield reached 100% for Catalyst II as opposed to 70% for Catalyst I. It can be also observed that, for both catalysts, the discoloration yield of the wastewater sample was lower than for the pure solutions. This behavior can be explained by the additional cations introduced to the sample by the leveling agent and which enter in competition with dye cations, decreasing the efficiency of the photocatalytic process. It was reported that the presence of additional cations such as Fe^{3+}, favorable on the photocatalytic degradation of dissolved azo dyes in aqueous TiO_2 suspensions is unfavorable in case of cationic dyes [29].

Fig. 10 represents Ln(C) versus t, respectively, for Catalyst I and Catalyst II. The obtained plots suggest that a first-order model can describe the kinetic behavior: for Catalyst I. The values of the correlation coefficient r^2 are reasonably high for the pure solutions (>0.98) (Table 5), but for wastewater, r^2 is lower (<0.94). For Catalyst II, the values of the correlation coefficient r^2 are high for both the pure solutions and the wastewater sample (>0.99). As observed previously, an increase in the initial concentration of the dye leads to a decrease on the rate constant.

Comparing the kinetic behaviors of the photocatalytic processes under UV and sunlight radiations, we can observe that for Catalyst I, photocatalytic process under UV is more efficient than under sunlight radiations which leads to an increase on the rate constant when using UV radiations ($K_{UV} = 0.0142$ against $K_{sunlight} = 0.0069$ for initial dye concentration of 10 mg/L and $K_{UV} = 0.0056$ against $K_{sunlight} = 0.0029$ for initial dye concentration of 25 mg/L). By using Catalyst II, we observe that the photocatalytic process under sunlight radiations is more efficient than under UV radiations ($K_{UV} = 0.0321$ against $K_{sunlight} = 0.0726$ for initial dye concentration of 10 mg/L and $K_{UV} = 0.0291$ against $K_{sunlight} = 0.0557$ for initial dye concentration of 25 mg/L). This behavior can be explained by an increase in the adsorption of the BR46 dye on activated carbon due to the increase of temperature. It was reported by other researchers for aqueous phase adsorption that adsorption increases with the increase of temperature [45–47]. Catalyst II was also more efficient in terms of COD removal, with a yield of 93% against 33% for Catalyst I.

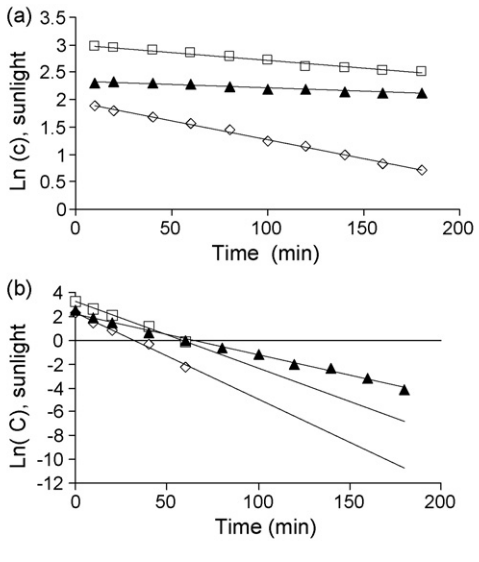


Fig. 10. First-order model for photocatalytic degradation under sunlight of Basic Red 46 on Catalyst I (a) and Catalyst II (b): (□) = 25 mg/L, (◇) = 10 mg/L, (▲) = wastewater.

5. Conclusions

This study shows that photocatalysis under UV or sunlight radiation, in conjunction with TiO_2 immobilized on a mat of cellulose fibers, is a very promising method for degrading textile wastewater at temperature and pH of actual industrial wastewater, avoiding any adjustment. The main advantage is the formulation of the catalyst, as the immobilization avoids the costly step of separation before treated water discharge or polishing. The rate of degradation of the color varies according to catalyst and the irradiation used: Catalyst I shows a higher yield of discoloration under UV than under sunlight. The difference between them reaches 20% after 2 h of treatment. Catalyst II, which combines TiO_2 particles and carbon fibers, exhibits a very important yield of discoloration under sunlight. It reaches 99% at the end of 2 h of sunlight irradiation. Photocatalysis under sunlight with Catalyst II is very promising for the treatment of textile wastewater due to its clean technology, ease of use and low operating cost. Further work is evaluating the degree of mineralization and the coupling with a biological wastewater treatment process.

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