**Box-Wilson design modeling of photocatalytic degradation of industrial dye and wastewater in semi-pilot solar photoreactor**

Mohammed Kheir-eddine Bouchareb, Mohammed Berkani, Slimane Merouani and Mohamed Bouhelassa

**ABSTRACT**

This work focuses on the treatment of a dye solution, C.I. Basic Blue 41 (BB41), and industrial wastewater by UV/TiO₂ photocatalytic process using aqueous catalyst suspensions of titanium dioxide (TiO₂), Degussa P25. The procedures were carried out in a semi-pilot scale prototype solar photoreactor under solar radiation. Response surface methodology (RSM) based on Box-Wilson design was applied to assess individual effects of the five main independent parameters: initial dye concentration ([BB41]), TiO₂ concentration ([TiO₂]), flow rate (Q) initial pH and accumulated solar energy (Qvn) on the decolorization efficiency and to optimise the UV/TiO₂ process. Photocatalytic mineralisation was carried out at the optimal conditions found by RSM and results were evaluated by total organic carbon (TOC) abatement for BB41 solution and industrial wastewater. The optimal conditions found by RSM were: 0.4 g/L, 14.04 mg/L, 1,479.6 L/h, 5.52 and 80 KJ/L for TiO₂ concentration, initial dye concentration, flow rate, initial pH and accumulated solar energy, respectively. Photocatalytic mineralisation results show that for accumulated visible solar energy equal to 377.714 kJ/L (after 6 hours of irradiation), under these conditions, the percentage of the initial TOC reduction is about 88% and 85.5% for industrial waste and BB41 solution, respectively.

**Key words** Box-Wilson design, industrial wastewater treatment, photocatalytic process, POA, RSM, solar photoreactor

**HIGHLIGHTS**

- Photocatalytic efficiencies of TiO₂/solar UV in semi-pilot scale prototype solar photoreactor were examined.
- The photocatalytic degradation of an industrial textile dye BB41 in semi-pilot scale prototype solar photoreactor was examined.
- Box-Wilson design was used to optimize the operational parameters of the solar reactor and photocatalytic process.
- RSM was used as a powerful statistical tool to study the photodecolorization yield behavior versus several aquatic factors.
- The results of experiments were expressed as a function of accumulated solar energy QVₙ received by the reactor per unit volume of solution to be treated (Equation (4)), this dimension makes possible the comparison of degradation kinetics for different operating conditions regardless of the weather conditions and the resulting solar irradiation.

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INTRODUCTION

The dyes in waste water are part of the organic pollutants and often require specific treatment. Progress in chemical wastewater treatment has driven the development of a number of chemical technologies, called advanced oxidation processes (AOPs) (Salari et al. 2009).

Hydroxyl radicals are the main oxidizing species produced by AOPs, these being non-selective and highly reactive (Andreozzi et al. 1999). AOPs can be classified by the way in which they generate -OH radicals to chemical and catalytic, photochemical and photocatalytic, mechanical and electrical processes (Koprivanac & Kusic 2009).

Heterogeneous photocatalysis represents a promising alternative technology for the degradation of organic pollutants (Herrmann et al. 1993). It offers a unique advantage over other alternative treatment methods because it presents a ‘green’ treatment approach, since toxic organic pollutants are converted into carbon dioxide (CO2), water and mineral acids (Koprivanac & Kusic 2009).

Heterogeneous photocatalytic process is based on the photonic excitation of a semiconductor by ultraviolet light (wavelengths shorter than 400 nm) in contact with water and in the presence of oxygen to ensure the production of hydroxyl radicals (Galindo & Kalt 1999). The term ‘heterogeneous’ refers to the fact that contaminants are present in the aqueous phase, while the semiconductor catalyst is in the solid phase. The most commonly used catalyst is titanium dioxide (TiO2) because it is chemically and biologically inert, non-toxic, cheap, abundant and has generally been demonstrated to be the most active semiconductor (Malato et al. 2009). Solar photocatalysis consists of using the ultraviolet (UV) share, which represents 5% of the solar spectrum, in order to activate the catalyst, this technique is considered as a durable developmental perspective based on a renewable energy and very promising especially for a country with high levels of sunshine such as Algeria.

Photocatalytic degradation efficiency is dependent on a number of parameters such as the reactor configuration, initial dye concentration, catalyst concentration, flow rate, reaction time and pH. In the conventional methods used to determine the influence of operational parameters, experiments were carried out systematically varying the studied parameter and keeping the others constant. This should be repeated for all the influencing parameters, resulting in an unreliable number of experiments. To optimize the effective parameters with the minimum number of experiments, the application of experimental design methodologies can be useful. Response surface methodology (RSM) (Gunaraj & Murugan 1999), is an experimental strategy for seeking the optimum conditions for a multivariable system, and an efficient technique for optimization. It has been successfully applied to different processes to achieve its optimization using experimental designs, which include TiO2-coated/UV oxidation (Jiang et al. 2013), TiO2 slurry/UV oxidation (Calza et al. 2013; Yang et al. 2013), O3 oxidation and electrochemical oxidation (Chen 2000; Li et al. 2011). In the present work we developed a simulation model using response surface methodology (RSM) based on Box-Wilson design, also called central composite design (CCD) (Montgomery 2012), in order to assess individual and interactive effects of the four main independent parameters, namely catalyst concentration (X1), initial dye concentration (X2), flow rate (X3), initial pH (X4) and the accumulated visible energy incident on the reactor $Q_{V,n}$ (X5) on the decolorization efficiency ($Y_\%$) of an cationic azo dye, C.I. Basic Blue (BB41), using TiO2 aqueous suspension in a semi-pilot solar photoreactor equipped with compound parabolic collectors (CPCs) and under solar radiation.

METHODS

Materials

The textile dye, C.I. Basic Blue 41 (molecular formula $= \text{C}_{20}\text{H}_{26}\text{N}_4\text{O}_8\text{S}_2$, color index number $= 11,105$, $\lambda_{\text{max}} = 608 \text{ nm, Mw } = 483 \text{ g mol}^{-1}$, single azo class) and real effluent were obtained from Aurassienne Spinning and Blankets (SAFILCO) Company, Algeria. Titanium dioxide powder used was TiO2 Degussa P-25 with greater than 99.5% purity (average primary particle size: $21 \text{ nm, BET surface area: } 50 \pm 15 \text{ m}^2 \text{ g}^{-1}$). Initial pH of the aqueous solutions was adjusted by sulfuric acid and sodium hydroxide (see Table 1).

Experimental solar setup

The solar photocatalytic reactor used in our study was a tubular reactor CPC type (Figure 1(a)) and the volume of wastewater to be treated in each experiment was 10 L. The solar reactor operating in batch mode (Figure 1(c)) was made up of five UV-transparent borosilicate glass tubes (length: 1 m, external diameter: 30 mm, thickness: 1.4 mm) made in Germany (Schott–Rohrglas GmbH Company) and
delivered by SOMIVER (E.N.A.V.A) Company, Algeria. These tubes were connected in series to a storage tank (40 liter capacity) by plastic joints and mounted on CPC-type aluminium reflectors (Figure 1(b)), ensuring that the light reaching the surface of the tubes was homogeneous (Malato et al. 2015). The volume effectively irradiated was 3.2 L and the volume of colored water to be treated was 10 L. A stirrer inside the tank ensures a homogeneous concentration of particles in the solution. The effluent was circulated by a centrifugal pump. A flow meter, fitted with a calibration curve, was placed between the pump outlet and the reactor inlet. The reactor was oriented southward and inclined at an angle of 36° (latitude at Constantine, Algeria) with respect to the horizontal; with this position, the annual collection of solar energy is maximized (Rodríguez et al. 2004).

Table 1 | Characteristics of Basic Blue 41

<table>
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<tr>
<th>Name and color index (C.I)</th>
<th>Structure</th>
<th>λ_{max} (nm)</th>
<th>Mw (g mol⁻¹)</th>
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<td>483</td>
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Analytical procedures

All the samples collected from the experiments were centrifuged at 4,000 rpm for 25 min using a centrifuge (sigma 2–16) to remove the TiO₂. Color removal of the dye BB41 was determined by UV absorption at λ_{max} = 608 nm using a UV-vis spectrophotometer (Shimadzu UV-160A) and calibration curve. The percentage decolorization rate (Y%) was expressed as the percentage ratio of decolorized dye concentration to that of the initial concentration. TOC was determined with a Sievers InnovOx analyser equipped with manual injector, according to the total carbon method (TC), two measurements are made and the average is retained, TOC is equal to the difference between total carbon and carbon in inorganic form.
Solar radiation (400–720 nm) was measured by light-meter Lutron (LX-107) mounted next to the CPCs (Figure 1(b)).

**Experimental design**

In the present study, RSM based on the Box-Wilson design was applied for optimization of the photocatalytic decolorization process. Based on the literature and operating conditions (Tanaka Padermpole & Hisanaga 2000; Malato et al. 2009; Khataee et al. 2010), five main factors, namely catalyst concentration (0.1–1.1 g L⁻¹) (X₁), initial dye concentration (10–50 mg L⁻¹) (X₂), flow rate (300–1,500 L h⁻¹) (X₃), initial pH (2–12) (X₄) and accumulated solar energy (0–80 KJ L⁻¹) (X₅) were considered as the system variables in order to evaluate their influences on the photocatalytic decolorization efficiency of BB41.

A total of 47 experiments were employed in this work, including 2³ = 32 cube points, 5 replications at the center point and 10 axial points. Experimental data were analyzed using Minitab 16 software. The test factors were coded according to the following equation:

\[ x_i = \frac{X_i - X_{i0}}{\Delta X} \]  

where \( x_i \) is the coded value of the \( i^{th} \) independent variable, \( X_i \) is the natural value of the \( i^{th} \) independent variable, \( X_{i0} \) is the natural value of the \( i^{th} \) independent variable at the center point, and \( \Delta X \) is the step change value (Cho & Zoh 2007). The experimental results of the Box-Wilson design were fitted with a second-order polynomial equation by a multiple regression technique as follows:

\[ Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_5X_5 + a_6X_1X_2 + a_7X_1X_3 + a_8X_1X_5 + a_9X_2X_3 + a_{10}X_2X_4 + a_{11}X_3X_4 + a_{12}X_3X_5 + a_{13}X_4X_5 + a_{14}X_1^2 + a_{15}X_2^2 + a_{16}X_3^2 + a_{17}X_4^2 + a_{18}X_5^2 \]  

where \( Y \) is a response variable of decolorization efficiency. The \( a_i \) are regression coefficients for linear effects; \( a_{ir} \) the regression coefficients for quadratic effects and \( X_i \) are coded experimental levels of the variables. The experimental ranges and the levels of the independent variables for BB41 removal are given in Table 2.

The results of experiments are expressed as a function of accumulated solar energy \( Q_{V,n} \) (KJ L⁻¹) received by the reactor per unit volume of solution to be treated (Equation (3)).

\[ Q_{V,n} = Q_{V,n-1} + \Delta n V_{G,n} \tag{3} \]

\[ \Delta n = t_n - t_{n-1} \]

where \( Q_{V,n} \) is the accumulated solar energy incident on the reactor (KJ L⁻¹), \( t_n \) is the experimental time of each sample, \( V_{G,n} \) the solar radiation intensity (W m⁻²) measured by the lightmeter, \( A_r \) the collectors surface (m²) and \( V_r \) volume of solution to be treated (L). This dimension makes possible the comparison of degradation kinetics for different operating conditions regardless of the weather conditions and the resulting solar irradiation (Bouchareb et al. 2014).

**RESULTS AND DISCUSSION**

**Box-Wilson design model and statistical analysis**

The Box-Wilson design matrix and experimental results obtained in the photocatalytic decolorization runs are presented in Table 3. Based on these results, an empirical relationship between the response and independent variables was attained and expressed by the following second-order polynomial equation:

\[ Y = 71.4923 + 3.4605x_1 - 4.991x_2 + 3.0245x_3 - 1.5245x_4 + 23.908x_5 + 0.661875x_1x_2 - 0.223750x_1x_3 + 5.75375x_1x_4 - 0.1875x_1x_5 + 2.07321x_2x_3 + 2.88562x_2x_4 + 1.01438x_2x_5 - 0.5425x_3x_4 - 0.2125x_3x_5 - 0.3225x_4x_5 + 9.54922x_1^2 + 2.43828x_2^2 + 0.720781x_3^2 - 3.24922x_4^2 - 6.41547x_5^2 \]  

Photocatalytic decolorization efficiencies (Y (%)) have been predicted by Equation (4) and presented in Table 3.
Table 3 | Box-Wilson design matrix in coded units along with the observed and predicted responses

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<th>pH</th>
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(continued)
These results indicated good agreements between the experimental and predicted values of decolorization efficiency.

The quality of fitting the second-order equation was expressed by the coefficient of determination $R^2$. The $R^2$-values provide a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions (Zarei et al. 2019). It was found that the predicted values matched the experimental values reasonably well with $R^2 = 0.9905$. This implies that 99.05% of the variations for percent color removal are explained by the independent variables.

Adjusted $R^2$ (Adj-$R^2$) is also a measure of goodness of fit, but it is more suitable for comparing models with different numbers of independent variables. It corrects $R^2$-value for the sample size and the number of terms in the model by using the degrees of freedom on its computations. If there are many terms in a model and not a very large sample size, Adj-$R^2$ may be visibly smaller than $R^2$ (Zarei et al. 2010). Here, the Adj-$R^2$ value (0.9831) was close to the corresponding $R^2$ value (see Table 4).

Table 4 indicates the results of the quadratic response surface model fitting in the form of analysis of variance (ANOVA). ANOVA is required to test the significance and adequacy of the model. The ANOVA test is made by the Fisher value (F value), which is the ratio between the mean square of the model and the residual error (Aleboyeh Daneshvar & Kasiri 2008; Santos & Boaventura 2008), the value F must be greater than the tabulated value of F to say that the model is a good predictor of the experimental results. The F-value obtained, 135.09, is clearly greater than the tabulated F (1.99 at 95% significance) which confirms the adequacy of the model fit.

The Student’s $t$ distribution and the corresponding values, along with the parameter estimate, are given in Table 5. The probability value (P values) was used to check the meaning of each of the coefficients. The greater the amplitude of Student’s $t$ test and the smaller the P value, the more significant the corresponding coefficient (Liu & Chiou 2005).

It is clear from Table 5 that the main significant reaction parameters were (most to least significant): Accumulated solar energy, second-order effect of catalyst concentration, second-order effect of solar energy, interaction between the catalyst concentration and initial pH, effect of initial dye concentration and effect of catalyst concentration.

### Response surface and contour plots

The contour plots and response surface shown in Figures 2, 4–6 provide the results of interaction between factors and accumulated solar energy and Figure 3 shows the response surface and contour plots of photocatalytic decolorization efficiency (Y %) as a function of initial pH and catalyst concentration (g L$^{-1}$).

Figure 2 illustrate the effects of initial pH and accumulated solar energy on photocatalytic decolorization efficiency (Y %) for initial dye concentration of 30 mg L$^{-1}$, flow rate of 900 L h$^{-1}$ and catalyst concentration of 0.6 g L$^{-1}$. As can be seen in the figure, both of alkaline...
and acidic conditions of the solution provided good results (Y > 80% when Qvn > 50 KJ/L). The pH-effect is related to the point of zero charge (pzc). The point of zero charge of the TiO₂ (Degussa P25) is at pH 6.2 (Chou & Liao 2005).

Thus, the TiO₂ surface is positively charged in acidic media (pH < 6.2), whereas it is negatively charged under alkaline conditions (pH > 6.2) (Jiang et al. 2008). These variations in pH can influence adsorption of dye molecules onto the TiO₂ surfaces. Since C.I. Basic Blue 41 is a cationic dye, in an acidic medium the repulsive force inhibits the adsorption of dye molecule at the catalyst surface but the formation of hydroxyl radicals remains possible, which react with the dye molecules. An alkaline condition favors adsorption of the cationic dye on the catalyst surface (Neppolian et al. 2002; Toor et al. 2006), which results for both cases (alkaline and acidic conditions) in high decolorization efficiency, as we can see in Figure 3.

Figure 4 shows the effect of initial dye concentration as a function of accumulated solar energy on photocatalytic decolorization efficiency (Y%) for initial pH of 7, flow rate of 900 L h⁻¹ and catalyst concentration of 0.6 g L⁻¹. It is clearly that with decreasing initial dye concentration the photocatalytic decolorization provides very significant results (Y > 80% when Qvn > 50 KJ/L and [BB41] < 20 mg/L).

Figure 5 shows the photocatalytic decolorization efficiency as a function of flow rate and accumulated solar energy at catalyst concentration of 0.6 g L⁻¹, initial dye concentration of 30 mg L⁻¹, flow rate of 900 L h⁻¹ and catalyst concentration of 0.6 g L⁻¹. The response surface and contour plots of photocatalytic decolorization efficiency (Y%) as a function of initial pH and accumulated solar energy (KJ L⁻¹) for initial dye concentration of 30 mg L⁻¹, flow rate of 900 L h⁻¹ and catalyst concentration of 0.6 g L⁻¹.

Table 5: Regression results from the data of central composite design experiments

<table>
<thead>
<tr>
<th>Term</th>
<th>Parameter estimate</th>
<th>t-Value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>71.4923</td>
<td>49.077</td>
<td>0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.4605</td>
<td>6.506</td>
<td>0</td>
</tr>
<tr>
<td>BB41</td>
<td>-4.991</td>
<td>9.383</td>
<td>0</td>
</tr>
<tr>
<td>FLOW</td>
<td>3.0245</td>
<td>5.686</td>
<td>0</td>
</tr>
<tr>
<td>pH</td>
<td>-1.5245</td>
<td>2.866</td>
<td>0.008</td>
</tr>
<tr>
<td>Qvn</td>
<td>23.908</td>
<td>44.946</td>
<td>0</td>
</tr>
<tr>
<td>TiO₂ × TiO₂</td>
<td>-9.5492</td>
<td>15.353</td>
<td>0</td>
</tr>
<tr>
<td>BB41 × BB41</td>
<td>2.4383</td>
<td>3.92</td>
<td>0.001</td>
</tr>
<tr>
<td>FLOW × FLOW</td>
<td>0.7208</td>
<td>1.159</td>
<td>0.257</td>
</tr>
<tr>
<td>pH × pH</td>
<td>-3.2492</td>
<td>5.224</td>
<td>0</td>
</tr>
<tr>
<td>Qvn × Qvn</td>
<td>-6.4155</td>
<td>10.315</td>
<td>0</td>
</tr>
<tr>
<td>TiO₂ × BB41</td>
<td>0.6619</td>
<td>1.113</td>
<td>0.276</td>
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<tr>
<td>TiO₂ × FLOW</td>
<td>-0.2237</td>
<td>0.376</td>
<td>0.71</td>
</tr>
<tr>
<td>TiO₂ × pH</td>
<td>5.7538</td>
<td>9.675</td>
<td>0</td>
</tr>
<tr>
<td>TiO₂ × Qvn</td>
<td>-0.1875</td>
<td>0.315</td>
<td>0.755</td>
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<tr>
<td>BB41 × FLOW</td>
<td>2.0731</td>
<td>3.486</td>
<td>0.002</td>
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<tr>
<td>BB41 × pH</td>
<td>2.8856</td>
<td>4.852</td>
<td>0</td>
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<tr>
<td>BB41 × Qvn</td>
<td>1.0144</td>
<td>1.706</td>
<td>0.1</td>
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<tr>
<td>FLOW × pH</td>
<td>-0.5425</td>
<td>0.912</td>
<td>0.37</td>
</tr>
<tr>
<td>FLOW × Qvn</td>
<td>-0.2125</td>
<td>0.357</td>
<td>0.724</td>
</tr>
<tr>
<td>pH × Qvn</td>
<td>-0.3225</td>
<td>0.542</td>
<td>0.592</td>
</tr>
</tbody>
</table>

Figure 2: The response surface and contour plots of photocatalytic decolorization efficiency (Y%) as a function of initial pH and accumulated solar energy (KJ L⁻¹) for initial dye concentration of 30 mg L⁻¹, flow rate of 900 L h⁻¹ and catalyst concentration of 0.6 g L⁻¹.
Figure 6 illustrates the effects of catalyst concentration as a function of accumulated solar energy for a flow rate of 900 L h$^{-1}$, initial dye concentration of 30 mg L$^{-1}$ and initial pH of 7. It can be seen from the figure that at high levels of dye TiO$_2$ loading, the decolorization efficiency of the dye decreases as the concentration increase ([TiO$_2$] > 0.9 g/L); in this case the photons are intercepted before they reach the active-catalyst surface, which decreases the color removal of BB41. Likewise at very low concentration of catalyst ([TiO$_2$] < 0.35 g/L), the response surface and contour do not present a very significant photodegradation due to the adherence of catalyst particles to the system walls, including to some non-illuminated sections (Lasa et al. 2005). In addition, the optimum catalyst loading for photodegradation varies, and mainly depends on the dimension of the photoreactor (Chong et al. 2010).

From these Figures 2, 4–6 we can obtain areas for the optimal conditions with the maximum rate of photocatalytic degradation of BB41: from Figure 6 the optimal area for [TiO$_2$] is between 0.45 and 0.75 g/L, lower than 30 mg/L for [BB41] (Figure 4), greater than 1,300 L h$^{-1}$ for the flow rate (Figure 5), and between 2 and 10 for pH (Figure 2). As can be seen; the photocatalytic degradation rate rises with increasing accumulated solar energy. Minitab 16 allows us to obtain the optimum values for a rate equal to 100% and which are: 0.4 g/L, 14.04 mg/L, 1,479.6 L/h, 5.52 and 80 KJ/L for concentration of TiO$_2$, initial dye concentration, flow rate, pH and accumulated solar energy, respectively. The predicted and observed Y (%) was 100% and 97.8%, respectively. After verifying by a further experimental test with the predicted values, the result indicates that the maximal decolorization efficiency was obtained when the values of each parameter were set at the optimum values, which is in good agreement with the predicted value from the regression model.

**Photocatalytic mineralisation**

With optimal conditions previously determined two photocatalytic experiments in the solar reactor were performed to evaluate the mineralization rate of organic matter contained
in the dye solution and industrial wastewater of the textile industry, Algerian SAFILCO Company. The sample was filtered before use. Knowing that the initial concentration of BB41 in wastewater effluent was 5.6 mg/L. The solar photocatalysis mineralization of effluent was followed in this perspective by measuring total organic carbon (TOC) as a function of accumulated solar energy. The results are given in Figure 7. This figure shows that the use of these operating conditions provides high mineralization for BB41 solution and also industrial waste. In fact, for a cumulated solar energy equal to 377.714 kJ/L (after 6 hours of irradiation), the percentage of the initial TOC reduction is about 88% and 85.5% for industrial waste and BB41 solution, respectively. The results also indicate that the efficiency of the mineralization increased with accumulated solar energy.

**CONCLUSION**

In this study, we realized the photocatalytic decolorization of the textile dye C.I. Basic Blue 41 in a semi-pilot scale prototype solar photocatalytic decolorization reactor, using an aqueous suspension of TiO_2-P25 and under solar irradiation. The effect of operational parameters (catalyst concentration (X_1), initial dye concentration (X_2), flow rate (X_3), initial pH (X_4) and the accumulated visible energy incident on the reactor Q_{vn} (X_5)) on the decolorization efficiency of BB41 was optimized by response surface methodology based on Box-Wilson design. The process optimum values for the maximum decolorization efficiency determined in this study by RSM were: 0.4 g/L, 14.04 mg/L, 1,479.6 L/h, 5.52 and 80 KJ/L for TiO_2 concentration, initial dye concentration, flow rate, initial pH and accumulated solar energy, respectively. At these optimum values, the predicted and observed Y (%) was 100% and 97.8%, respectively. A further experimental test was carried out at the optimal conditions to study the mineralization of BB41 by evaluating the total organic carbon (TOC) abatement, the percentage of the initial TOC reduction is about 88% and 85.5% for industrial waste and BB41 solution, respectively.
DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


Figure 7 | Photocatalytic mineralisation of real effluent (experimental conditions: 0.6 g/L for TiO2, 5.6 mg/L for BB41, 1,479.6 L/h for flow rate and 5.5 for pH) and dye solution of BB41 (experimental conditions: 0.6 g/L for TiO2, 14.04 mg/L for BB41, 1,479.6 L/h for flow rate and 5.5 for pH).
Degradation of wastewater in semi-pilot solar photoreactor

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