Photolysis of bromophenol blue in aqueous solution under UV-irradiation: optimization of the parameters influencing the kinetics of degradation

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ABSTRACT

Although water purification technologies have advanced considerably, they still come up against certain recalcitrant molecules that are difficult to degrade, such as pesticides, dyes and other industrial or agricultural residues. The degradation by photolysis of bromophenol blue (BPB), a textile dye, is studied under UV irradiation in the absence of the catalyst. Various parameters which influence the kinetics of degradation have been studied, of which we can cite the pH, photonic intensity, BPB concentration and irradiation time. This study shows that the change in the chemical oxygen demand (COD) as a function of irradiation time and the mineralization of the solution occurs slowly. 4 h of irradiation are necessary to observe 20% of COD which is determined by K₂Cr₂O₇ oxidation in the presence of Ag⁺ as a catalyst, 96% of the organic compounds are oxidized under these conditions. The results show that the apparent rate constants of the BPB degradation augment linearly with the light flux. The discoloration rate of BPB solution augments with increasing pH until an optimum pH of 12, the degradation kinetics shows that the Langmuir–Hinshelwood model gives a better correlation. A total disappearance of BPB was observed after 150 min of irradiation, indicating the effectiveness of direct photolysis in eliminating the dye. The apparent rate constants are determined for the different parameters to confirm the validity of the model. The measurement of COD is a determination of organic matter which characterizes the amount of chemically oxidized substances present in water. The results show that the apparent rate constants of the BPB degradation increase linearly with the photonic flux applied in the field of study.

Keywords: Photolysis; Pollutant; Bromophenol blue; UV irradiation; Modeling; Kinetics; Langmuir–Hinshelwood

1. Introduction

Dyes are used in many industries like paper mills, cosmetics, food processing, textiles, and pharmaceuticals as well as in medical diagnostics. Our earth needs urgent actions to save the environment from all pollutants, including metals, pesticides, drugs and dyes, generated by heavy manufacturing industries and complex technological activities. These environmental pollutants represent a serious toxic risk to microorganisms and a real threat to aquatic life and human beings. The heterogeneous photocatalysis has been an area of rapidly growing interest over the last 10 y [1]. The photodegradation of organic compounds is an important branch of the broader subject of photocatalysis, including electrochemistry and surface chemistry. The advanced oxidation process (AOP) method has been used for the degradation of dangerous chemical substances present in water. The use of a photocatalyst under UV-vis irradiation, which is a type of AOP, is one of the most interesting and useful approaches for the degradation of many organic substances (such as phenols and mineral acids). Additionally, compared to other methods involving
biological processes, photocatalytic oxidation is relatively faster because of the absence of transfer from one phase to another and because product disposal is not necessary.

The photocatalysis, increasingly used in effluent treatment, is an efficient, powerful, clean and safe method for the water treatment and the conversion of hazardous chemicals into less harmful forms. The photocatalysis is a newly developed AOP process, which can be conveniently applied for the degradation of dyes. The photocatalysts commonly used are TiO$_2$, ZnO, WO$_3$, CdS, ZnS, SrTiO$_3$ and Fe$_2$O$_3$. TiO$_2$ being the most popular and active in organic degradation. In the water treatment processes involving semiconductors, the non-toxicity and insolubility. Therefore, the use of semiconductor particles as photocatalysts for the initiation of redox chemical reactions continues to be an active area of investigation [2]. In the early literature on this subject [3], the emphasis has been mainly on the solar energy conversion like the water photo-splitting or the photo-reduction of carbon dioxide respectively for energy and environmental issues. Treatment technologies for the remediation of metals-bearing wastewaters include membrane filtration, ultrafiltration, ion exchange, co-precipitation, electrolytic methods, and adsorption [4]. However, these techniques are not capable of efficiently reducing metals concentration below the tolerable limits [5]. They also suffer from economic and technological drawbacks, such as intensive operation, energy-expensiveness, high processing/operational cost, high chemical consumption and the generation of a colossal amount of secondary pollutants [6]. Most conventional techniques are therefore not profitable at an industrial-scale for the elimination of heavy metals from aqueous medium [7]. In an effort to enhance the removal efficiency, considerable research efforts have been focused on addressing the shortcomings associated with conventional treatment options, predominantly via adsorption. The use of adsorbents of natural origin has emerged in recent years as one of the most viable options to established pollutant management strategies [8]. The literature has reported the use of various agricultural wastes and byproducts such as apricot stone [9,10], sawdust [11] pomegranate peels [12], activated carbon [13–15]. The objective of this study is to study the effect of direct photolysis of the bromophenol blue (BPB) dye in the presence of UV irradiation and the influence of parameters on the kinetics of photolysis. The use of typical catalysts for the photodegradation of the dye constitutes the logical continuation of this work.

2. Materials and methods

The irradiations were carried out at a wavelength 365 nm using a device equipped with one, two, three or four 125 W lamps (Philips HPW 125, USA), surrounded by a cylindrical mirror and placed on a stirring plate. These lamps are medium pressure mercury vapor lamps, the emission of which is filtered by a black globe which mainly lets the line pass at 365 nm (approximately 85% of the energy). The Pyrex reactor, equipped with a water cooling jacket, was placed in the axis of the system.

The luminous flux ($\Phi$) emitted by the lamps equipping the various reactors were measured by a radiometer (VLX 3W) equipped with different probes to measure the light intensity at different wavelengths. Wavelengths corresponding to the maximum intensity of the different types of lamps: $\lambda = 254$ nm for UV-C lamps, $\lambda = 365$ nm for UV-A lamps. The spectral width of the detection band of each probe is approximately 2 nm.

BPB also called tetrabromophenol sulfone phthalein (chemical formula $\text{C}_9\text{H}_4\text{Br}_4\text{O}_5\text{S}$) has a chemical structure is illustrated in Fig. 1 while the physical and chemical properties are summarized in Table 1. BPB is a colorful indicator of pH, it is pale yellow for a pH < 3, and blue above pH > 4.6 and can be used as a blue dye in a neutral environment. Its turning zone: in the range (3 < pH < 4.6) it has a green. BPB is also used as a colored marker in order to verify the progress of electrophoresis on polyacrylamide gel or electrophoresis on an agarose gel.

A quantity of BPB powder is accurately weighed and diluted in ultrapure water, in a volumetric flask, of volume relative to the concentration which one wishes to prepare 100 mg L$^{-1}$). This preparation is followed by homogenization, on a magnetic stir plate. The initial pH of the BPB aqueous solution is modified, in order to study the effect of this parameter on the rate of discoloration of the colored solution, by adding a few drops of H$_2$SO$_4$ or NaOH. The pH was measured with a digital HANNA pH meter (Woonsocket, Rhode Island, USA) (Model HI 8521). The measurement of chemical oxygen demand (COD) is a determination of the organic matter in water based on its oxidation by K$_2$Cr$_2$O$_7$. The COD value characterizes the amount of chemically oxidizable substances

![Fig. 1. Developed bromophenol blue dye formula.](image)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>$\text{C}_9\text{H}_4\text{Br}_4\text{O}_5\text{S}$</td>
</tr>
<tr>
<td>Molar mass (g L$^{-1}$)</td>
<td>669.96</td>
</tr>
<tr>
<td>$\lambda$ (max)</td>
<td>592 nm</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Bromophenol blue</td>
</tr>
<tr>
<td>Name</td>
<td>Tetrabromophenol sulfonephthalein</td>
</tr>
<tr>
<td>Purity</td>
<td>99.99%</td>
</tr>
<tr>
<td>Pale yellow</td>
<td>For a pH &lt; 3</td>
</tr>
<tr>
<td>Blue</td>
<td>For a pH &gt; 4.6</td>
</tr>
<tr>
<td>Green color</td>
<td>Turn area 3 &lt; pH &lt; 4.6</td>
</tr>
</tbody>
</table>
present in water. This is the amount of oxygen needed to primarily oxidize the organic compounds in the water.

3. Results and discussion

3.1. UV-Visible spectrum of BPB

The absorption of BPB at different pHs indicates that at pH 6.3, the spectrum shows two bands in the UV region (308 and 380 nm) and one band in the visible region (592 nm); the basic pH does not affect the absorption spectrum of this dye. On the other hand, in an acid medium (pH 3), a hypsochromic displacement of the main band is observed, with a significant decrease in the intensity of the spectral band. The appearance of a new band in the visible region (λ = 440 nm), is due to the transition $\pi \rightarrow \pi^*$ within the bonds C=C–C=O and C=C–C=C.

3.2. Assessment of photochemical activity by UV energy

The UV irradiation of BPB solution (10 mg L$^{-1}$) with a lamp emitting mainly at 254 nm, under the operating conditions of natural pH and temperature, leads to a decrease in the BPB concentration (Fig. 2) and the results show that the irradiation led to a faster discoloration. A disappearance total of BPB was observed after 150 min. of irradiation, indicating the effectiveness of direct photolysis in removing this dye. Indeed, the absorption coefficient of a compound is not the only determining parameter on its degradation capacity by UV irradiation, the quantum yield of the compound is also determined. These results agree with the literature on several points on the degradation of different organic compounds by direct photolysis at 254 nm. This result can also be explained by the presence of halogens in the chemical structure of triphenylmethane dyes, according to Svetlichnyi et al. [16], the degradation by photolysis of compounds containing a halogen (Br in our case) is faster compared to those not containing halogen. On the other hand, the BPB discoloration is clearly significant, because of the high number of bromide substituents in the BPB structures (=4).

3.3. Rate of photolytic mineralization of BPB

The direct photolysis of compounds in water by UV irradiation plays a major role. However, sufficient absorption by these substances is necessary so that they can be selectively destroyed under appropriate conditions. In the perspective of showing the photocatalytic efficiency, it is essential to verify the extent to which direct photolysis contributes to the degradation of the selected dyes BPB under our operating conditions. The evolution of COD as a function of the irradiation time was followed for an initial BPB concentration of 10 mg L$^{-1}$ under UV irradiation (254 nm). The COD evolution over time measured for the dye BPB is shown in Fig. 3. The results show that the mineralization of the solution occurs but in a slow manner; 4h of irradiation was required to observe 20% of COD. It should be noted that the COD variation measured as a function of the irradiation time is very small, and this means that direct photolysis at 254 nm is not effective for the mineralization of BPB and such results are in agreement with the literature [17]. In most cases, the mineralization by photolysis remains partial, and in some cases metabolites are formed which may be more toxic and/or persistent than the starting substances (parent compounds) themselves; in most cases, the nature of these metabolites is largely unknown. Direct photolysis of organic dye has therefore proven difficult in the natural environment because the rate of degradation is highly dependent on the reactivity of the dye and its photosensitivity. Commercial dyes are generally designed to be resistant to light [18].

3.4. COD measurement

The COD measurement is a determination of the matter organic in water based on its oxidation by K$_2$Cr$_2$O$_7$. It corresponds to the amount of oxygen needed to primarily...
oxidize the organic compounds in water. The organic substances are chemically treated under severe oxidation conditions, in order to evaluate those that are difficult to degrade biologically, such as chlorinated organic compounds. For COD measurements, molecular oxygen \( \text{O}_2 \) is not used as an oxidant, because its oxidation capacity is low, and the determination of \( \text{O}_2 \) consumption is relatively difficult. The determination of COD is essentially done by oxidation with \( \text{K}_2\text{Cr}_2\text{O}_7 \) (1.52 V NHE) in a boiling \( \text{H}_2\text{SO}_4 \) solution, at reflux for 2 h at 148°C, in the presence of \( \text{Ag}^+ \) as catalyst and \( \text{Hg}^+ \) to complex the \( \text{Cl}^- \) ions. In these conditions, 95% to 97% of organic compounds are oxidized; in a simplified way, we can describe this oxidation by the reaction:

\[
\text{Organic Compound} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Cr}^{3+} \quad \text{(I)}
\]

In general, the BPB mineralization by the photocatalytic process can be summarized by the reaction:

\[
\text{C}_{19}\text{H}_{10}\text{Br}_4\text{O}_5\text{S} + (41/2) \text{O}_2 \rightarrow 19\text{CO}_2 + \text{SO}_4^{2-} + 2\text{H}^+ + 4\text{H}_2\text{O} + 4\text{Br}^- \quad \text{(II)}
\]

As in the case of UV-visible spectrophotometry, the evaluation of COD of an organic compound in solution requires the establishment of a calibration graph, which relates the absorbance at the dye concentration in an aqueous solution. The COD measurement was carried out on samples taken during the irradiation of BPB solutions, during the photolytic process. After filtration through microfilters (Millipore, India, with a diameter equal to 0.45 μm), 2 mL of each sample were removed and subjected to the same protocol as that of establishing the calibration curve, which represents the micro-COD protocol.

### 3.5. Influence of photon flux (\( \Phi \))

The variation of the luminous flux (\( \Phi \)) was carried out by varying the number of lamps (1–3 lamps), in the \( \Phi \) range (0.04–0.12 mW cm\(^{-2}\)) for a BPB concentration (10 mg L\(^{-1}\)).

![Fig. 4](image1.png)  
**Fig. 4.** Influence of photon flux \( \Phi \) on the rate of degradation ([BPB] = 10 mg L\(^{-1}\); \( \text{pH} = 6.1; T = 20^\circ\text{C}; I = 0.04-0.12 \text{mW cm}^{-2} \)).

Fig. 4 shows the evolution of the apparent kinetic constant of the BPB discoloration that augments linearly with \( \Phi \). Such a result is expected because the increased intensity is synonymous with a greater contribution of the number of incident photons and therefore, an acceleration of the BPB photodegradation.

Studies reported elsewhere Ollis et al. [19] on the effect of light intensity on the kinetics of the photocatalytic process shows that:

- At low light intensities (0–20 mW cm\(^{-2}\)), the rate increases almost linearly with increasing light intensity (first-order);
- At intermediate light intensities above a certain value (25 mW cm\(^{-2}\)) [20], the rate depends on the square root of the light intensity (\( \Phi^{1/2} \));
- At higher light intensities the rate becomes independent of light intensity.

### 3.6. Influence of pH

\( \text{pH} \) is one of the physicochemical parameters of the reaction medium having the most impact on the photochemical process. Its effect on the BPB photodegradation was studied in the \( \text{pH} \) range (1–12). The \( \text{pH} \) was adjusted by the addition of \( \text{NaOH} \) for basic media and \( \text{H}_2\text{SO}_4 \) for acidic media. The experiments were carried out with an initial concentration (10 mg L\(^{-1}\)) under a constant flux (\( \Phi = 0.04 \text{ mW cm}^{-2} \)). Fig. 5 reports a comparison between the evaluations as a function of \( \text{pH} \) of the apparent discoloration constant. BPB behaves differently during the \( \text{pH} \) variation, the discoloration rate of BPB solution increases with increasing \( \text{pH} \) until reaching an optimal \( \text{pH} \) 12. These variations can be explained by the changes in the specification of the dye, represented by its protonation or deprotonation, which can change the characteristics of the photochemical activity. The effects of \( \text{pH} \) on the dye's photodegradation have been studied by many researchers [21,22]. Interpreting the effects of \( \text{pH} \) on the efficiency of the dye
photodegradation is a very difficult task because of its multiple roles. The first one is related to the state of ionization of the surface and that of the functional groups of the dyes [23].

3.7. Determination of the kinetic order of the dye discoloration reaction

To describe the kinetics of BPB degradation, we were inspired by the results reported elsewhere [24–28]. In most cases, the pseudo-first-order of the Langmuir–Hinshelwood model describes the photodegradation kinetics of many organic molecules. Previous studies showed that the pollutant degradation by heterogeneous photocatalysis follows rather the Langmuir–Hinshelwood model, where the degradation rate is proportional to the fraction of the catalyst surface covered by the substrate molecules; the model is given by the following equation:

\[
V = \frac{-dC}{dt} = K_r \cdot K \cdot C
\]

For low concentrations (\(C < 10^{-3}\) M), the term \(K_r \cdot C\) is negligible in front of 1. Therefore, the reaction follows pseudo-first-order kinetics and Eq. (1) becomes as follows:

\[
V = \frac{-dC}{dt} = K_r \cdot K \cdot C = K_{app} \cdot C
\]

The integration of Eq. (2) gives:

\[
\ln \left( \frac{C_0}{C} \right) = K_{app} \cdot t
\]

The initial rate \((r_0)\) is given by:

\[
V_0 = \frac{K_r \cdot K \cdot C}{1 + K_r \cdot C} = K_{app} \cdot C_0
\]

where \(V\) is the photodegradation rate (mg L\(^{-1}\) min\(^{-1}\)), \(V_0\) the initial rate (mg L\(^{-1}\) min\(^{-1}\)), \(C\) the pollutant concentration at time \(t\) (mg L\(^{-1}\)), \(K_r\) the constant of the adsorption equilibrium (mg L\(^{-1}\) min\(^{-1}\)), \(K\) the kinetic constant of Langmuir–Hinshelwood (L mg\(^{-1}\)) and \(K_{app} = K_r \cdot K\) the apparent rate constant (min\(^{-1}\)), that is affected by the initial concentration \(C_0\). The plots \(\ln(C_0/C)\) vs. \(t\) for different initial concentrations \(C_0\) of BPB are shown in Fig. 6. The photodegradation follows perfectly the pseudo-first-order kinetic for \(C_0\) value of 10 mg L\(^{-1}\), the constants \(K_{app}\) (Table 2). Fig. 6 indicates that the discoloration rate increases with raising \(C_0\) which corresponds to Langmuir–Hinshelwood adsorption model. A linear expression can be occasionally obtained from Eq. (4) by plotting the reciprocal initial rate constant against \(C_0\). The plot of \(1/K_{app}\) against \(C_0\) (Fig. 7 Inset) gives a linear relationship.

\[
\frac{1}{K_{app}} = \frac{1}{K_r \cdot C_0} + \frac{1}{K_r \cdot K}
\]

From the slope \((1/K_r)\) and the intercept \((1/K \cdot K)\), the constants \(K_r\) and \(K\) for the BPB photocatalytic are computed. The use of TiO\(_2\) and SnO\(_2\) catalysts under irradiation constitutes the objective of our next work for the comparative study. The results are satisfactory and will be reported very soon.

3.8. Bibliographical summary on BPB discoloration

The photocatalytic activity of “Thioglycerol capped and uncapped” ZnS nanoparticles was investigated for the decoloration of BPB, crystal violet and reactive red by Sharma et al. [29]. All three dyes were decolorized after 3 h of UV irradiation. However, solar irradiations were more effective for the discoloration and mineralization of these dyes.
showed that the mineralization of the solution occurs in a slow manner; 4 h of irradiation was required to observe 20% of COD.

The determination of COD was essentially done by oxidation \( K_2Cr_2O_7 \) in the presence of \( Ag^+ \) as catalyst oxidation and \( Hg^+ \) as complexing agent the \( Cl^- \) ions. In these conditions, 95%–97% of organic compounds were oxidized. The results also indicated that the apparent rate constants of the dye degradation augment linearly with the flux \( \Phi \). The discoloration rate of BPB solution increases with increasing pH and peaks at pH 12.

The kinetic obeys the theoretical model of Langmuir–Hinshelwood and the economic cost of this study shows that direct photolysis in the absence of the catalyst gave satisfactory results. A quasi total degradation in the presence of a catalyst and in a short time constituted the objective of the next study.

4. Conclusion

The elimination of an aqueous solution of bromophenol blue, an organic dye used in the textile industry was carried out by photocatalysis. The AOP has been used for the degradation of dangerous chemical substances present as pollutants in water. The process involves the active degradation of dangerous chemical substances present as pollutants in water. The process involves the active degradation of dangerous chemical substances present as pollutants in water. The process involves the active degradation of dangerous chemical substances present as pollutants in water. The process involves the active degradation of dangerous chemical substances present as pollutants in water. The process involves the active degradation of dangerous chemical substances present as pollutants in water. The process involves the active degradation of dangerous chemical substances present as pollutants in water.

Fig. 7. Influence of the bromophenol blue concentration on the photolysis rate (photolysis at 254 nm; ([BPB] = 5–30 mg L\(^{-1}\); pH = 6.1; \( T = 20^\circ C; I = 0.04 \text{ mW cm}^{-2}\)).

Djepang et al. [30], used photocatalytic methods coupled with humid air plasma for the degradation of bromophenol blue; Moist air plasma was applied for its oxidation in an aqueous medium. Plasma treatment was coupled with TiO\(_2\) as a photocatalyst with and without oyster shell powder for acidity control. The degradation kinetics was studied under different conditions such as the treatment time, dye concentration type and dose of the catalyst. The discoloration was carried out with and without the TiO\(_2\) and the oyster shell: a maximum degradation was reached after 20 min of treatment at pH 2.4 for TiO\(_2\) concentration of 3 g L\(^{-1}\) (61.21%) and oyster shell 0.4 g L\(^{-1}\) (28.48%).

Chairin et al. [31], used a lactase enzyme, purified from Trametes polyzona, as a biocatalyst for the degradation of synthetic dyes. All of the synthetic dyes used in this experiment: bromophenol blue, Remazol Brilliant Blue R, Methyl Orange, Remazol Brilliant Blue R, Methyl Orange, Relative Black 5, Congo Red, and Acidine Orange were decolorized. This study showed that Trametes polyzona lactase is an effective enzyme with a high potential for the environmental detoxification and fading of synthetic dyes.

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Declaration of conflicting interests

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