Degradation of ‘‘ Bromocresol Green’’ by direct UV photolysis, Acetone/UV and advanced oxidation processes (AOP’s) in homogeneous solution (H$_2$O$_2$ /UV, S$_2$O$_8^{2-}$ /UV). Comparative study.

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Abstract

The aim of this work is to verify the ability of some photochemical processes to eliminate an acidic dye in aqueous medium, used as molecule model: The Bromocresol Green. The obtained results showed that system like: H$_2$O$_2$/UV and S$_2$O$_8^{2-}$/UV were better than direct UV photolysis at 254 nm and acetone/UV at the same wavelength. This improvement seems to be linked to production of OH$^-$ and SO$_4^{2-}$ radicals issued from the photolysis of H$_2$O$_2$ and S$_2$O$_8^{2-}$, always at this same wavelength. The influence of concentration of H$_2$O$_2$ has permitted to find the optimal dose in order to avoid the scavenger effect by H$_2$O$_2$ itself.

The UV spectral change of Bromocresol Green has been also studied for both processes. One can conclude that it was easier to destroy the partial π –π* conjugated system and n-π* bonding related to OH groups. On the other hand, the rate of decolourisation was found to follow first order kinetic in almost cases (except in photolysis). The effect of parameters like: alcohols, oxygen and initial concentration of the dye were also studied. One observes that alcohols inhibit the elimination of the dye in the H$_2$O$_2$/UV case, whereas oxygen has a minor effect on it. About, the third parameters, the initial concentration of the dye affects the decolourisation process: it decreases as its concentration increases.

Keywords: Degradation, BCG, Irradiation, Acetone, H$_2$O$_2$, S$_2$O$_8^{2-}$

1-Introduction

Industrial effluents from textile, tannery and printing activities have often a significant pollutant load dye which is hardly biodegradable. Their decontamination was made by using several techniques to remove these harmful compounds. We can list for example biological method [1-2], ion exchange [3-5] and adsorption on various media [6-7], which is simply a transfer of pollutant from one phase to another, requiring again a costly treatment of wastewaters. They are on the whole ineffective for decontamination. In these latter decades, an alternative way to treat pollution was the use of advanced oxidation processes (AOP’s) [8-9] since they destruct or reduce recalcitrant leads from textile effluents. The effectiveness is linked to the production of highly reactive species: radical OH$^-$. They react rapidly and without specificity with most organic compound [10] leading therefore to mineralization process in term of CO$_2$ and H$_2$O. [11] These techniques will therefore play an important role in the process of decontamination of the environment by providing a means of an advanced mineralization of this process [10].

The purpose of this study is to evaluate and to compare the efficiency of photochemical processes (direct photolysis, acetone/UV and POAs such: H$_2$O$_2$/UV and S$_2$O$_8^{2-}$/UV) on the elimination of a dye (Bromocresol Green) in homogeneous phase. In this work, we investigate also the effect of some parameters, as on efficiency like: the dose in H$_2$O$_2$, in acetone, in S$_2$O$_8^{2-}$, in substrate and in oxygen. These investigations will help to situate the effectiveness of these processes during the fading process.
2- Experimental

2.1. Material

Bromocresol Green (abbreviation BCG) was purchased from Fluka chemical company and used without further purification. The hydrogen peroxide (33% Fluka), Sodium persulfate (Na$_2$S$_2$O$_8$, Prolabo) and Acetone (C$_3$H$_6$O d=0.79, Labosi) solutions were prepared with ultra pure water from a Milli pure water (Milli-Q purification unit). The structure of our substrate is represented in figure (1). The concentration of solution the substrate is 6 \times 10^{-5} M, and its natural pH is 4.5. The experiences of degassing BCG solutions were performed with nitrogen gas.

![Molecule structure of Bromocresol Green (BCG).](image)

2.2. Photoreactor and source light

Aqueous solutions were irradiated at 254 nm in cylindrical reactor quartz (100 cm of length and 2 cm in diameter), located on one of the principal axis of the assembly and equipped with three symmetrical externals low-pressure mercury lamps (germicide lamp, Philips TUV 15 W) emitting mainly at 254 nm [12]. The reactor is surrounded symmetrically by these lamps. The temperature of the reactor is maintained between 18 and 20 °C by the use of an air flow provided by a ventilator. The entire system is placed in a cylindrical enclosure. The mean value of flux intensity measured with a radiometer type VLX3W [13].

2.3. Procedure and analysis

The irradiation experiments were carried out with 100 ml of solution at 6 \times 10^{-5} M of BCG. The UV-Visible spectra absorption was recorded from 200 to 800 nm by Unicam Helios "α" a UV-Visible spectrophotometer. The residual concentrations of the substrate in the reaction mixture at different time was obtained at $\lambda_{\text{max}}$ = 444 nm from a calibration curve.

3. Results and discussion

3.1. UV–vis spectrum of BCG

The UV–vis spectra of BCG is reported in figure (2). One observed mainly three absorption bands, each characterized by a molar absorption coefficient $\varepsilon$ and located at 280nm ($\varepsilon$=9165 l mol$^{-1}$cm$^{-1}$), at 444nm ($\varepsilon$=16545 l mol$^{-1}$ cm$^{-1}$ being the most intense) and at 616 nm ($\varepsilon$=7490 l mol$^{-1}$ cm$^{-1}$) respectively.

The pH influences the behavior of the substrate. Thus, in acid medium (pH< 4.5), one observes a color change (turning into yellow) but without a shift of all bands whereas in basic medium (pH≥ 8) one observes a color change (turning into blue) again, but with a displacement of the most intense band (616 nm). This allowed the determination of the pKa where Its magnitude order was 5.1. (Inserted figure 2)

The results are well represented in figure (2) where we observe an isosbestic point. In this point the basic and acid form have the same unit absorbance and wavelength (515 nm). In these conditions, the pH would not have an impact on the measurement of BCG concentrations. In our case, the pH is not changing at the end of the oxidation process that is why all measurement were made at 444 nm.
3.2. Direct photolysis of BCG

Direct UV photolysis experiments were carried out in static tubular reactor in dilute medium in the presence and absence of oxygen. The photodegradation was followed by spectrophotometer at different irradiation time. The results obtained show that this compound undergoes very slow photolysis for the purpose concentration in aerated medium $10^{-5}$ M (18.4%), $10^{-5}$ M (20.6%), $10^{-5}$ M (21 %). This could be attributed on one part to the size of the molecules present in the solution, preventing the exposure of certain of them to light and on the other part on absence of radicals OH which are generated by $\text{H}_2\text{O}_2$. Therfore, the efficiency was not significant (figure 3.).

3-3 Degradation of BCG by acetone /UV, $\text{H}_2\text{O}_2$/UV and $\text{S}_2\text{O}_8^2$/UV

3-3-1 Sensitivity of BCG in presence of $\text{H}_2\text{O}_2$, $\text{S}_2\text{O}_8^2$, acetone in absence of light

In this work, we have considered the highest and the lowest concentrations of the products which were $10^{-1}$ M and $10^{-4}$ M respectively. Thus, for $\text{H}_2\text{O}_2$ and $\text{S}_2\text{O}_8^2$ taken at same doses and added separately to the dye (6 $10^{-5}$M) in absence of light, we remarked no reaction for a time of 180 minutes, but only an addition of spectra between both products (BCG /acetone, BCG /$\text{H}_2\text{O}_2$ and BCG /$\text{S}_2\text{O}_8^2$). Same result has been obtained with acetone (figure 4. a, b and c)
Fig. 4. Sensibility of BCG in presence of \( \text{H}_2\text{O}_2 \), \( \text{S}_2\text{O}_8^{2-} \), acetone in absence of light [dye]_o = 6 \times 10^{-5} \text{M}, (a): BCG/acetone, (b):BCG/H\(_2\text{O}_2\), (c): BCG/S\(_2\text{O}_8^{2-}\).

3-3-2 - Photoxydation of Bromocresol green

I. Acetone /UV process

Direct UV photolysis of BCG is not very effective. For this reason, we combined UV and acetone at different concentration to enhance removal efficiency of the BCG. It is well known that acetone when excited by UV radiation (254 nm, could led to a triplet state: acetone* (79-82 Kcal/mole). As a result, we observe a rapid decolourization process of the dye after a collision between our substrate and this excited form of the acetone (acetone*), mainly, at high concentration [14-15]:

\[
\text{Acetone} + h\nu \rightarrow \text{Acetone}^* \\
\text{BCG} + \text{Acetone}^* \rightarrow \text{BCG}^* + \text{Acetone} \\
\text{BCG}^* \rightarrow \text{Decolourization}
\]
At the end of the energy transfers, we constate that acetone is regenerated as indicated in equation (2) figure (5).

The results obtained from the solutions of the BCG (6 × 10^{-5} M) and acetone (1 M, 10^{-1} M, 10^{-2} M et 10^{-4} M) in ultra pure water show that (figure 6.a):

- The presence of acetone increases the rate of photodegradation of BCG.
- The efficiency of this oxidation process (acetone / UV) increases with increasing dose in acetone.

This enhancement of the disappearance of BCG observed in the presence of acetone concentrations mainly 1 M, 10^{-1} M et 10^{-2} M can be described by an apparent first-order kinetics law 1 (figure 6.b). The values of rate are summarized in table (I).
2- UV/H₂O₂ process
As seen before, direct UV photolysis was not efficient (at most 18.6% removal) whereas the process UV/acetone led to good improvement (99.8% and 96.7% removal for acetone 1M and 10⁻³M respectively) for a reaction time of 120 minutes. A better result was observed when combining hydrogen peroxide with radiation light at 254 nm. Indeed, this combination facilitates the decomposition of H₂O₂ into radicals OH⁻ which are capable of reacting without any discrimination with the majority of organic compounds with a rate constant of 10⁻²M⁻¹s⁻¹ [10]. To verify this efficiency, irradiation experiments, at 254 nm were carried out with various concentrations in H₂O₂.

<table>
<thead>
<tr>
<th>[Acetone] mol/l</th>
<th>rate %</th>
<th>t₅₀%(min)</th>
<th>R²</th>
<th>Apparent rate constants (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99.8</td>
<td>53</td>
<td>0.9474</td>
<td>6.64 x 10⁻²</td>
</tr>
<tr>
<td>10⁻¹</td>
<td>96.7</td>
<td>63</td>
<td>0.9376</td>
<td>2.21 x 10⁻²</td>
</tr>
<tr>
<td>10⁻²</td>
<td>53.3</td>
<td>150</td>
<td>0.9941</td>
<td>4.31 x 10⁻¹</td>
</tr>
<tr>
<td>10⁻³</td>
<td>19.6</td>
<td>not reached</td>
<td>0.9197</td>
<td>1.21 x 10⁻³</td>
</tr>
</tbody>
</table>

**Fig. 7.** Decolourization process of the dye [dye]₀ = 6 x 10⁻⁵ M, λₐₚ = 254 nm.
(a): in presence of H₂O₂ at various concentrations. (b): Kinetics of BCG decolourization (linear transform Ln (C₀/Cₜ) vs t) in UV/H₂O₂ process.

The figure (7.a) illustrates well this process. Thus, the bleaching was obtained in a short time compared to the direct photolysis and UV/acetone. Indeed, the 92% of the decolourization was reached at 50 minutes. If we compare with UV/acetone system, the rate of the decolourization was improved by a factor of 18.8. The measure of same parameters like: the rate of photodecomposition, the rate constant (k) and the use of various concentrations in hydrogen peroxide to a certain limit, illustrate well the efficiency. Nevertheless, for the highest concentration H₂O₂ (5 x 10⁻¹ M), we have found a decrease in the fading rate. This anomaly could be attributed to an scavenging effect of radical OH⁻ by excess H₂O₂ according to the reaction [16-18].

\[
OH^* + H₂O₂ → OH₂^* + H₂O \quad k_{H₂O₂} = 2.7 x 10^7 M^{-1} s^{-1} \quad (4)
\]

In all experiments, this process is well described by a first order kinetics law with regard of the used concentrations. Initial decolourization rate constants has been computed from the slope of Ln C₀/Cₜ vs t (minutes), where C₀ and Cₜ are dye concentrations at instant t=0 and t respectively (figure 7.b). Also, to get better knowledge of this bleaching process, one can calculate graphically the useful time to reduce to 50%
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(t_{50\%} called also a half time t_{1/2}), the initial dose of the substrate. Results are recapitulated in table (II).

At the end of the oxidation process the pH has changed slightly

**Table (II):** Apparent constants obtained in the process H$_2$O$_2$ / UV at 254 nm.

<table>
<thead>
<tr>
<th>[H$_2$O$_2$] mol/l</th>
<th>rate %</th>
<th>t_{50%}(min)</th>
<th>R$^2$</th>
<th>Apparent rate constants (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 $\times$ 10$^{-1}$</td>
<td>90.3</td>
<td>36.5</td>
<td>0.9936</td>
<td>2.24 $\times$ 10$^{-2}$</td>
</tr>
<tr>
<td>10$^{-1}$</td>
<td>99.8</td>
<td>12.1</td>
<td>0.98579</td>
<td>4.30 $\times$ 10$^{-2}$</td>
</tr>
<tr>
<td>10$^{-2}$</td>
<td>99.2</td>
<td>16.9</td>
<td>0.97552</td>
<td>3.70 $\times$ 10$^{-2}$</td>
</tr>
<tr>
<td>10$^{-3}$</td>
<td>88.5</td>
<td>54.3</td>
<td>0.99323</td>
<td>1.22 $\times$ 10$^{-2}$</td>
</tr>
<tr>
<td>10$^{-4}$</td>
<td>21.7</td>
<td>not reached</td>
<td>0.98564</td>
<td>1.32 $\times$ 10$^{-3}$</td>
</tr>
</tbody>
</table>

2.1. **Spectral Evolution of BCG by UV/H$_2$O$_2$**

The variation of the absorption spectra of BCG was recorded previously between 200 and 800 nm (figure 8). As it can be seen, we observed two bands in the visible region at 444 nm and 616 nm and one band in the ultraviolet region located at 280 nm. During its treatment by UV/H$_2$O$_2$ and according to our experimental condition (10$^{-2}$ M H$_2$O$_2$ and 6 $\times$ 10$^{-5}$ M BCG), we observed a decolourization of the solution due to the disappearance of the following peaks: $\pi-\pi^*$ transition related to benzenic ring and n- $\pi^*$ transition related to OH groups. Moreover, we noticed that the decolourization is due mainly to destruction of the partial conjugated $\pi-\pi^*$ systems by radical OH$^\cdot$.

![Fig.8. Spectral Evolution of BCG by UV/H$_2$O$_2$, [dye]$_o$ = 6 $\times$ 10$^{-5}$ M, pH$_o$ = 4.5, $\lambda_{irr}$=254 nm,[H$_2$O$_2$]$_o$ = 10$^{-2}$ M](image)

2.2. **Optimal value of the dose of H$_2$O$_2$**

Considering the evolution of the concentration of H$_2$O$_2$ during the course of the BCG photoxydation, optimum value of hydrogen peroxide was determined. Referring to Figure (9), one observed an increase in the initial rate of the substrate to a maximum of [H$_2$O$_2$] at 5 $\times$ 10$^{-2}$ M and a decrease from this value to (5 $\times$ 10$^{-1}$ M),
2.3. Influence of oxygen on the process UV/\textsubscript{2}O\textsubscript{2}/254 nm

The degradation of the dye by UV/\textsubscript{2}O\textsubscript{2} was followed also in absence of oxygen (bubbling the solution with nitrogen gas) and in the same experimental conditions. In comparing rates in both media, we can deduce a slight diminution of the decolourization rate in absence of oxygen. Thus results shows us that production of OH\textsuperscript{-} was not affected figure(10.a). A simple kinetic modeling demonstrated that this process followed also order one (1) (figure 10 b).

2.4. Influence of alcohol on the process UV/\textsubscript{2}O\textsubscript{2}/254 nm

BCG solution was irradiated in the presence of tertiobutanol (5%) in order to evaluate the participation of OH\textsuperscript{-} radicals during photoxydation of the BCG. Figure (11) shows that this process is inhibited at the amount of 35.4% after 180 minutes. It can be calculated by the following relation

\[
\text{Inhibition percentage } \% = \frac{(V_0)_{\text{max}} - (V_0)_{\text{min}}}{(V_0)_{\text{max}}} \times 100
\]

\[(V_0)_{\text{max}} : \text{Maximum initial rate (0% tertiobutanol)}
(V_0)_{\text{min}} : \text{Minimum initial rate (5% tertiobutanol)}\]
The percentage of degradation by UV/H$_2$O$_2$ in absence of tertiobutanol, is about 99.2% after a reaction time of 120 minute which is less than that obtained in the presence of this scavenger, at the same time (60.2% after 120 minute). Thus, these results confirm well the participation of OH $^-$ radical to this process.

![Graph showing degradation rate with and without tertiobutanol](image)

**Fig. 11.** Effect of alcohol on the degradation of BCG by UV/H$_2$O$_2$ process. [dye]$_o$ = 6 $10^{-5}$ M, $\lambda_{irr}$ =254 nm, [H$_2$O$_2$]$_o$ = $10^{-2}$ M.

### 3. UV/S$_2$O$_8^{2-}$ process

The photolysis of S$_2$O$_8^{2-}$ alone at 254 nm in aqueous solution is represented in figure (12). The optical absorption of the alone compound shows a band with a maximum around 212 nm and an absorption coefficient an magnitude order of 235 M$^{-1}$cm$^{-1}$. These results corroborated with those find in the literature ($\lambda_{max}$=215 nm) and $\varepsilon$=220 M$^{-1}$ cm$^{-1}$ [19] At the 254 nm which is the excited wavelength, the value of the absorption coefficient is equal to 45.47 M$^{-1}$cm$^{-1}$.

![Absorption spectrum of S$_2$O$_8^{2-}$](image)

**Fig. 12.** Photolysis at 254 nm of the Na$_2$S$_2$O$_8$ alone. [S$_2$O$_8^{2-}$]= $10^{-2}$ M
In this condition and according to some data found in the literature, the persulfate photolysis gives a radical anion $SO_4^{•-}$ which has a band with a maximum at 455 nm and with an absorption coefficient equal to the 1600 $M^{-1}cm^{-1}$. [19]

Sulfate radicals produced by photolysis at 254 nm may initiate a series of radical chain reactions where the substrate could be degraded (5)(6)(7)(8) (9)(10) and (11) [20].

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{•-} \quad (5)$$
$$SO_4^{•-} + H_2O \rightarrow OH^{•} + HSO_4^{-} \quad (6)$$
$$SO_4^{•-} + M \rightarrow M + Products \quad (7)$$
$$OH^{•} + M \rightarrow M + Products \quad (8)$$
$$SO_4^{•-} + M \rightarrow Chain\err\mination \quad (9)$$
$$2OH^{•} + M \rightarrow Chain\err\mination \quad (10)$$
$$2SO_4^{•-} \rightarrow Chain\err\mination \quad (11)$$

The formation of hydroxyl radical and the sulfate anion which are powerful oxidants can degrade dye molecules at faster rate. As with radicals $OH^{•}$ and $SO_4^{•-}$ have the unique nature of attacking the dye molecule at same positions, hence, leading to a rapid fragmentation of dye molecules [21]. (Eqs. 12 and 13).

$$SO_4^{•-} + $dye$ \rightarrow SO_4^{2-} + $dye$^{•-} \quad (intermediates) \quad (12)$$
$$SO_4^{•-} + $dye$^{•-} (int\err\erm\ediate) \rightarrow SO_4^{2-} + CO_2 + HNO_3 + other – inorganics \quad (13)$$

The effect of different concentrations of $S_2O_8^{2-}$ on the kinetics of disappearance of BCG by UV /$S_2O_8^{2-}$ (254 nm) process is shown in figure (13.a). By considering the good results obtained for the decolourization process, we can conclude that the produced $SO_4^{•-}$ has reacted totally in the presence of pollutants; then, the risk of interference has been minimized.

![Graph](a)
![Graph](b)

**Fig.13.** Decolourization process of the dye $[dye]_0 = 6 \times 10^{-5}$ M, $\lambda_{irr} = 254$ nm.
(a): in presence of $S_2O_8^{2-}$ at various concentrations.
(b): Kinetics of BCG decolourization (linear transform $\ln (C_0/C_t)$ vs t) in UV/$S_2O_8^{2-}$ process.

Moreover, the bleaching process of BCG by UV /$S_2O_8^{2-}$ is described correctly by an apparent kinetics law of order 1 (figure.13.b). In other hand, the measure of a half time for each curve ($t_{1/2}$) allowed us to compare the
performance of this process: \( t_{1/2} (10^{-2} \text{ M}) < t_{1/2} (10^{-3} \text{ M}) < t_{1/2} (5 \times 10^{-4} \text{ M}) < t_{1/2} (10^{-4} \text{ M}) \) (a short half time mean a rapid rate of decolourization). The calculated rate and \( t_{50\%} \) are recapitulated in table (III).

Table (III): Apparent constants obtained in the UV /S\(_2\)O\(_8^2\) process.

<table>
<thead>
<tr>
<th>[S(_2)O(_8^2)] (\text{mol/l})</th>
<th>rate %</th>
<th>( t_{50%} ) (min)</th>
<th>( R^2 )</th>
<th>Apparent rate constants (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{-2})</td>
<td>99.3</td>
<td>6.9</td>
<td>0.98751</td>
<td>4.69 (10^{-2})</td>
</tr>
<tr>
<td>(10^{-3})</td>
<td>92.6</td>
<td>25.4</td>
<td>0.99839</td>
<td>1.44 (10^{-2})</td>
</tr>
<tr>
<td>(5 \times 10^{-4})</td>
<td>73.01</td>
<td>68.9</td>
<td>0.98335</td>
<td>7.38 (10^{-3})</td>
</tr>
<tr>
<td>(10^{-4})</td>
<td>32.49</td>
<td>not reached</td>
<td>0.98887</td>
<td>2.18 (10^{-3})</td>
</tr>
</tbody>
</table>

The spectral evolution in this case is almost identical to that obtained with UV/ H\(_2\)O\(_2\). Indeed, decolourization process is also marked by a slightly more rapid destruction of bands located in the visible (partial conjugated system and \( n- \pi^* \) transition) and in the ultraviolet region (\( \pi - \pi^* \) transition in the benzenic ring) figure.14.

![Fig.14. Spectral Evolution of BCG by UV/ S\(_2\)O\(_8^2\), [dye]\(_o\) = 6 \(10^{-5}\) M, pH\(_o\) = 4.5, \( \lambda_{irr} \) =254 nm.[S\(_2\)O\(_8^2\)]\(_o\) = \(10^{-2}\) M.](image)

**Conclusion**

The objective of this work was to compare efficiency of different processes to eliminate a dye from aqueous and homogeneous medium. Experiments conducted in one hand by direct UV photolysis (254 nm) and the other hand by system like: acetone /UV, UV/H\(_2\)O\(_2\) and UV /S\(_2\)O\(_8^2\).were carried out in similar experimental conditions. In direct photolysis, the results obtained indicate that BCG undergoes to a very feeble percentage of decolourization of the used substrate concentration.

A real improvement of the efficiency has been reached by using system like: acetone /UV, UV/H\(_2\)O\(_2\) and UV/S\(_2\)O\(_8^2\) under these conditions and at \(10^{-3}\)M concentration of H\(_2\)O\(_2\), S\(_2\)O\(_8^2\) and acetone. The reaction speed of the decolourization of the dye at 50 minutes is as follows: direct UV photolysis (4.15%) < acetone/UV (18.2%) < UV/ H\(_2\)O\(_2\) (85.4%) < UV/ S\(_2\)O\(_8^2\) (94.5%). However, before any treatment, we observed no sensitivity of the dye when mixed with H\(_2\)O\(_2\), S\(_2\)O\(_8^2\) and acetone taken each separately.

**Reference**


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