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## Treatment of Bromocresol Purple Dye by Several Photochemical Processes in Aqueous Medium: A Comparative Study

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### ABSTRACT

Pollution of aquatic water became one serious environmental problem. However photochemical processes have been widely used in water decontamination process whether coupled or not with Ultraviolet (UV) light. The aim of the following study is to test the ability of some photochemical processes (photolysis at 254 nm and some Advanced Oxidation Technics (AOTs) in absence of light (Fenton) and in its presence (photo-Fenton) to eliminate the Bromocresol Purple (BCP, anionic structure) in aqueous solution. The obtained results showed that the best conditions were found to be pH of 3, hydrogen peroxide-to-iron (II) molar ratio of 10:1 and artificial light (254 nm and 365 nm). Influence of some parameters was also studied like: pH, concentration of H<sub>2</sub>O<sub>2</sub> and the irradiation wavelength. The efficiency of the processes studied decreases in the following order: Photo-Fenton 254 nm > Fenton > photolysis 254 nm.

**Keywords:** Advanced oxidation processes, Bromocresol Purple (BCP), Fenton, Photolysis, Ultraviolet

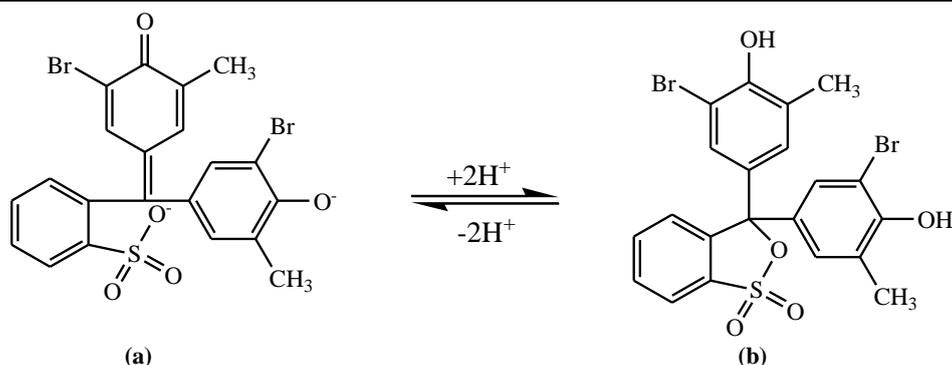
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### INTRODUCTION

Dyes can give various products beautiful colors, and therefore they are widely used in many fields such as textiles, paper, plastic, food, painting, and medicine [1]. Dyeing industry wastewater is one of the major environmental problems, because they consume dissolved oxygen and their color inhibits sunlight penetration into the stream and reduces photosynthetic action [2,3]. Moreover, most of them are carcinogenic and mutagenic and they can seriously harm human health [4]. Dyes have a synthetic origin and complex aromatic molecular structures which make them stable to biological degradation. Due to low biodegradability of dyes, a conventional biological wastewater treatment process is not very efficient in treating dye wastewater. In these later decades, photochemical systems, mainly, the Advanced Oxidation Processes (AOPs), are innovative and alternative techniques for wastewater treatment. This effectiveness is related to the production of highly reactive species: the radical's <sup>•</sup>OH they may react rapidly with a high rate constant (10<sup>7</sup>–1, 010 M<sup>-1</sup>s<sup>-1</sup>) and non-selectively with a broad range of organic pollutants [5]. Thus, a process of oxidation takes place until the final stage of mineralization which is characterized by the production of CO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. AOPs include several processes in homogeneous medium: Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>, Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>/U and in heterogeneous medium: UV/Semi-conductors [6-13]. The purpose of this study is to evaluate and to compare the efficiency of photochemical processes (direct photolysis and POAs such: Fenton, Photo-Fenton at 254 nm and photo-Fenton at 365 nm) on the elimination of a dye (Bromocresol purple) in homogeneous phase.

### MATERIALS AND METHODS

Bromocresol purple (BCP) was purchased from Fluka chemical company and used without further purification. The hydrogen peroxide solution (33% Fluka), salts of iron (II) ((NH<sub>4</sub>)<sub>3</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, Labosi 99%), were prepared from ultrapure water from a Milipore unit and at pH=3.0, to prevent formation and precipitation of hydroxyls. Besides, the pH was adjusted with NaOH or HCl to reach the desired value. The structure of our both substrates is represented in Figure 1. We notice that initial concentration is 25 mg. L<sup>-1</sup> and the natural pH is equal to 4.5.



**Figure 1: Molecule structure of BCP. The BCP exists under equilibrium state between two forms: (a) and (b). In our experimental conditions (pH 4.5), the dominant form is the species “b”**

#### Photo reactor and source light

Different aqueous solutions are irradiated at 254 nm in cylindrical reactor in 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 external low-pressure mercury lamps (germicide lamp, Philips TUV 15 W) emitting mainly at 254 nm. 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 [14].

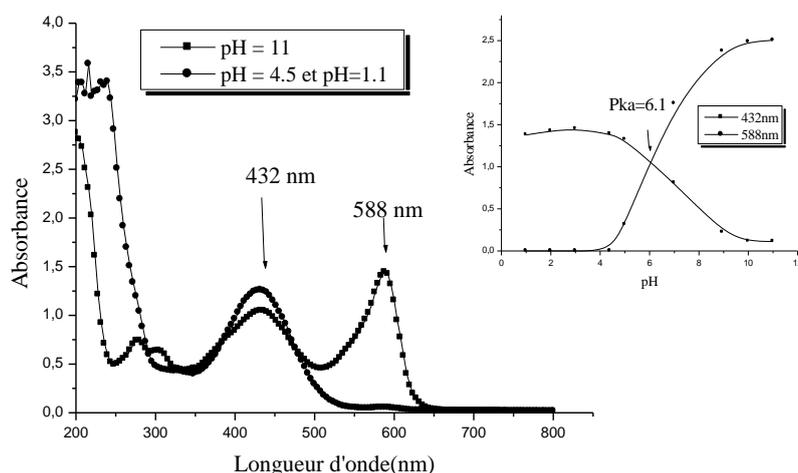
### RESULTS AND DISCUSSION

#### Analysis method

The irradiation experiments were carried out with 100 ml of solution with 25 mg L<sup>-1</sup> of BCP. The UV-Visible absorption spectrum was recorded from 200 to 800 nm using Unicam Helios "α" a UV-Visible spectrophotometer at λ<sub>max</sub>=432 nm. The residual concentrations of the substrate at different times were obtained at λ<sub>max</sub>=432 nm using a calibration curve.

#### UV-Vis spectrum of BCP

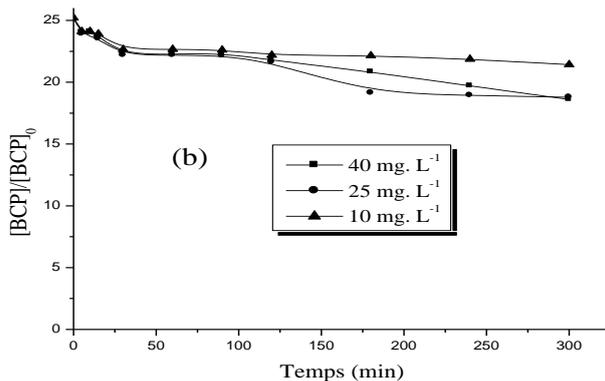
The UV-Vis spectrum of BCP is presented in Figure 2. It is clear that BCP (pH 4.5) absorbs light in the range of wavelength: 200-700 nm and shows an intense band located around 432 nm (ε=28,246 L mol<sup>-1</sup> cm<sup>-1</sup>). It can be seen that pH affects spectrum of dye. Thus, in basic solution (pH 11.00), for BCP, a shift to a higher wavelength occurs for the band positioned at 432 nm. This shift is equal to 588 nm and involves a bathochromic effect, with a color change (turning into violet). In acidic solution (pH 2.00), the most intense band increases. Additionally, no shift and no color change are observed for substrate. According to these conditions, we may determine the pKa of acid/Base couple of this dye where its magnitude of order is about 6.1.



**Figure 2: UV-Vis spectrum of BCP, [dye]<sub>0</sub>=25 mg L<sup>-1</sup>. Influence of pH; evolution of pKa**

#### Direct photolysis of BC

Figure 3 present typical data obtained from the photolysis of BCP ([BCP]<sub>0</sub>=25 mg L<sup>-1</sup>) in aerated medium, in a tubular reactor and under UV irradiation at 254 nm. The experimental results show that the BCP removal reaches 25.8% after a long reaction time: 240 min. These results depicted show that the decolorization process decreases as the initial concentration increases. Indeed, the results obtained for this process are: 25.8% (10 mg L<sup>-1</sup>), 25.6 % (25 mg L<sup>-1</sup>) and 16.6% (40 mg L<sup>-1</sup>). This behavior may be explained by a less participation of the photons emitted by the source as the solution becomes more colored or more concentrated.

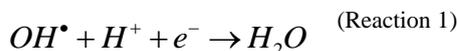


**Figure 3: Decolourization of BCP by direct photolysis at 254 nm and different initial concentrations**

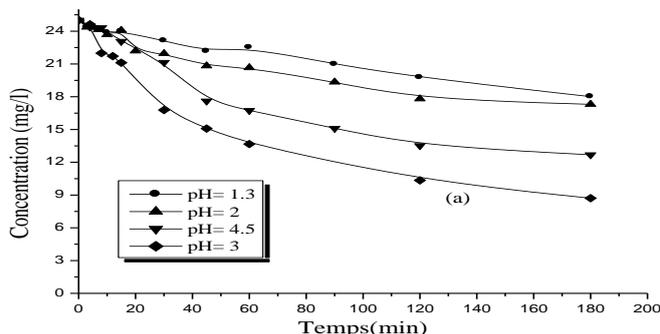
**Degradation of BCP by the Fenton and photo-Fenton systems**

*Absence of light*

The effect of pH in the bleaching process of the dye (25 mg. L<sup>-1</sup>), was investigated too and reported in Figure 4 for Fenton system. Was carried out between pH 1.3 and 4.5 Thus, by considering this figure we observed that: In very acidic medium (pH<2) the efficiency was low due to a feeble participation of radical OH<sup>•</sup> which are scavenged by this medium (Reaction 1).



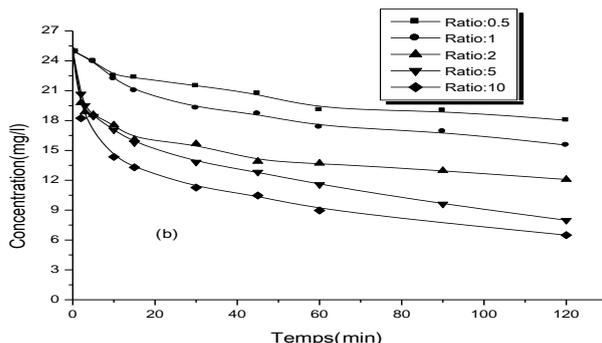
In basic medium, we observed also a sensitive diminution of the efficiency linked to the formation and precipitation of iron Fe(OH)<sub>3</sub>, stopping the formation of radicals OH<sup>•</sup>.



**Figure 4: Effect of pH on decolorization process of BCP in aqueous medium by Fenton. Initial conditions: C<sub>0</sub> (dye)=25 mg.L<sup>-1</sup>. C<sub>0</sub> (Fe<sup>2+</sup>)=10<sup>-4</sup> M. C<sub>0</sub> (H<sub>2</sub>O<sub>2</sub>)=10<sup>-3</sup> M and pH=3.0**

*Effect of concentration of H<sub>2</sub>O<sub>2</sub>*

It is well known that Fenton reaction is effective at pH=3.0 [15]. Taking into account this value, a set of experiments was performed to obtain best color removal from the related ratio: H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>. As recommended by the literature, ratio ranged generally from 10:1 to 40:1 [16-18]. Therefore, this best efficiency was achieved for 10:1 (Figure 3). As it can be seen on figure, we observed a decolourization process reaching a color removal of 74% for Fenton for a reaction time of 120 min. This could be attributed to an effective participation of OH<sup>•</sup> to the oxidation of the dye.



**Figure 4: Effect of ratio [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>] on the decolorization of BCP during Fenton process. Initial conditions: (C<sub>0</sub> (dye)=25 mg L<sup>-1</sup>. C<sub>0</sub> (Fe<sup>2+</sup>)=10<sup>-4</sup> M, (Ph=3.0)**

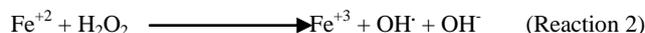
From observation of the effects of pH on the decay kinetics of BCP, it can be concluded that the Fenton process is more efficient at pH 3.0, because hydrogen peroxide and ferrous iron are more stable at this pH.

### Presence of light

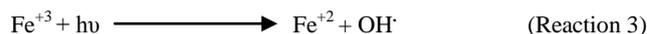
#### Photo-Fenton process

Although the Fenton reagent is an efficient oxidant, its oxidation power is enhanced by light that promotes the regeneration of iron (II) from iron (III). The regenerated iron (II) will then react with the hydrogen peroxide to produce hydroxyl radicals thus regenerating the iron (III) in the medium.

### Reaction of Fenton



### Photo-reduction of iron (III)



The efficiency of the photo-Fenton process depends strongly on the ratio of the  $[\text{H}_2\text{O}_2]_0/[\text{Fe}^{2+}]$  concentrations present in the solution but also the pH of the solution (Reactions 2 and 3) [7].

### Effect of artificial light (254 nm and 365 nm)

Oxidation of the dye was greatly improved by light for the system. In this case, the total decolorization was reached in 120 min and the best degradation ratio was always 10 for the photo-Fenton process at 254 nm and 365 nm. Consequently, it appears that this route is faster than that obtained by Fenton. This improvement could be attributed to the large production of radical OH from different sources such as: The reaction between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  with  $\text{H}_2\text{O}_2$ . The photolysis of  $\text{H}_2\text{O}_2$  at 254 nm. The results illustrated in the Figure 5a and 5b [19,20].

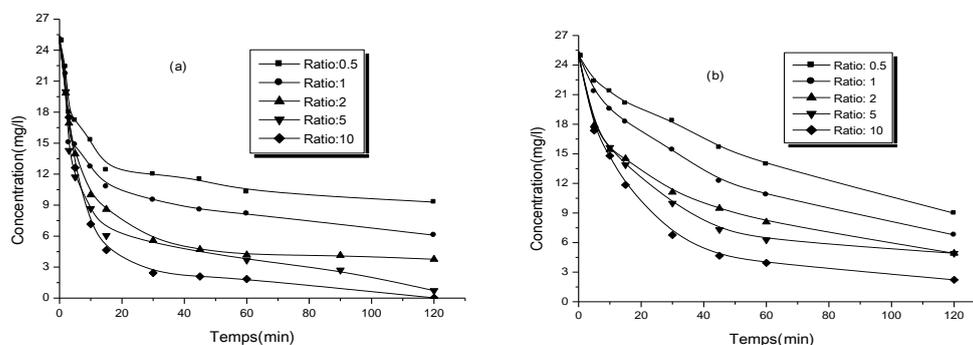


Figure 5: Effect of light on the degradation of BCP. ( $C_0$  (dye)=25 mg L<sup>-1</sup>.  $C_0$  ( $\text{Fe}^{2+}$ )=10<sup>-4</sup> M.  $C_0$  ( $\text{H}_2\text{O}_2$ )=10<sup>-3</sup> M (pH=3), (a)  $\lambda=254$  nm; (b).  $\lambda=365$  nm

### Mineralization of BCP by the Fenton and Photo-Fenton processes

The evolution of the Chemical Oxygen Demand (COD) as a function of the irradiation time was followed for the BCP for an initial concentration of 25 mg. L<sup>-1</sup>, at a pH of 3, in the presence of  $\text{H}_2\text{O}_2$  at 10<sup>-3</sup> M, in the dark and under irradiation successively. The values of the COD measured for each process as a function of time and the curves representing the variation thereof as a function of time are plotted in Figure 6a and 6b). It is clear that BCP mineralized more slowly than its discoloration. Under these conditions the mineralization process is reached after a time of 240 min where the removal rates are 94.02% for the Fenton process and 100% for photo-Fenton.

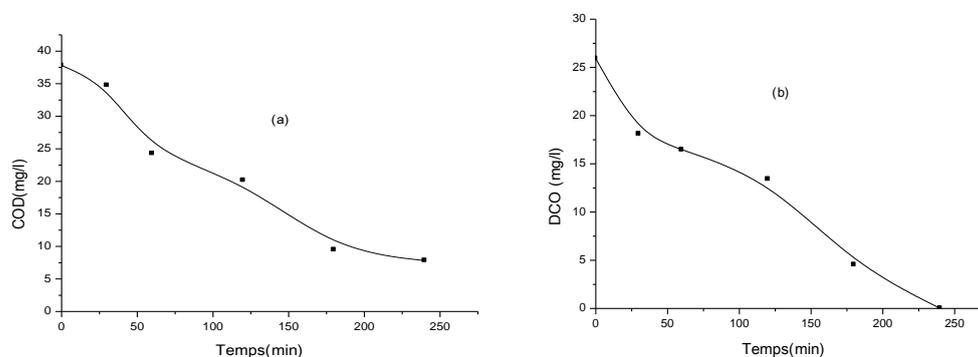


Figure 6: Evolution of COD as a function of irradiation time for different photochemical processes:  $[\text{BCP}]=25$  mg L<sup>-1</sup>,  $[\text{H}_2\text{O}_2]=10^{-3}$  M,  $[\text{Fe(II)}]=10^{-4}$  M, (a): Fenton, (b): Photo-Fenton at 254 nm

### Comparison of Fenton and Photo-Fenton process efficiencies

Figure 7 makes it possible to compare the degradation kinetics of BCP by Fenton and photo-Fenton processes (at 254 nm and 365 nm). To compare these two processes, we have retained the same experimental conditions:

$$- [\text{H}_2\text{O}_2]_0 / [\text{Fe}^{+2}]_0 = 10 \text{ (where } [\text{Fe}^{+2}] = 10^{-4} \text{ M)}$$

The same concentration of BCP (25 mg. L<sup>-1</sup>). The same pH value in acid medium (pH=3).

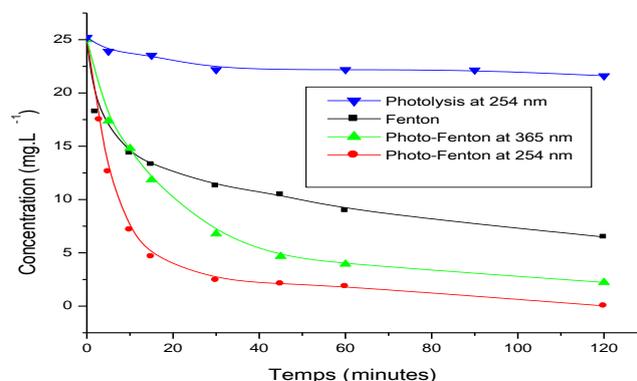


Figure 7: Comparative study between, Fenton, photo-Fenton processes ( $C_0$  (dye)=25 mg L<sup>-1</sup>.  $C_0$  (Fe<sup>2+</sup>)=10<sup>-4</sup> M.  $C_0$  (H<sub>2</sub>O<sub>2</sub>)=10<sup>-3</sup> M, pH=3

The efficiency of the processes studied decreases in the following order

Photo-Fenton 254 nm > Photo-Fenton 365 nm > Fenton > photolysis 254 nm.

### CONCLUSION

According to previous analyses and results: a better efficiency of the degradation of BCP was obtained by Fenton and photo-Fenton processes, the optimal value of pH was equal to 3.0 and the most favorable ratio of H<sub>2</sub>O<sub>2</sub> to iron was 10:1 for oxidation state of iron II. Photo-Fenton process at 254 nm which is more efficient than that used at 365 nm and Fenton.

In general, photo-Fenton and, appeared to be suitable for the degradation of the dye since they reinforce the production of radicals OH. These investigations showed that these processes might be used for the treatment of waste water in industrial scale.

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