PHOTO-FENTON AND ADSORPTION COMBINED PROCESS FOR DEGRADATION AND REMOVING OF COOMASSIE BRILLIANT BLUE DYE FROM AQUEOUS SOLUTION

A. M. D. CANTELI¹, D. CARPINE¹, G. DONÁ¹, T. A. TAKASHINA¹, A. de P. SCHEER¹, L. IGARASHI-MAFRA¹

¹ Universidade Federal do Paraná, Departamento de Engenharia Química
E-mail para contato: andersonmdcanteli@gmail.com

RESUME – Coomassie Brilliant Blue (CBB) is a commonly dye present in the waste of the textile industry. Its use produces waste which must be treated before being discharged into rivers or sewage. Combined processes have been used with efficiency for wastewater treatment. This study aims to evaluate the combined process of photo-Fenton and adsorption for the degradation and removal of the dye CBB in aqueous solution. Initially, the CBB was submitted to photo-Fenton oxidation. Photo-Fenton oxidation degraded 76.9% of the initial CBB concentration, which was not enough to satisfies the Brazilian legislation. The fixed-bed adsorption was conducted for 13 hours, and during all this period the outlet concentration was always lower than the breakpoint, being this concentration in compliance with the legislation. The combined photo-Fenton/Fixed-bed adsorption was effective in the CBB removing (at least 95.9%).

Keywords: Fixed bed; granular activated carbon; waste treatment; combined treatment; oxidation.

1. INTRODUCTION

Coomassie Brilliant Blue (CBB) is a non-azo dye commonly present in the waste of the textile industry and also widely used as a reagent for determining protein concentration (e.g. Bradford protein assay). Its continuous dumping into rivers may cause several problems to the ecosystem, such as the inhibit of the sunlight penetration into the water (which reduces the photosynthesis) and unsightly appearance of the water (Wang et al., 2012; Han et al., 2009).

The Brazilian legislation (CONAMA Nº 430/2011) does not establishes a maximum color values to an effluent can be discharged into receiving bodies. However defines that the effluent should be virtually absent color (which is not noticeable by sight) (Conama, 2014). In this context, is necessary to implement a treatment that can minimize environmental damages.

Some techniques have been studied for CBB removal and/or degradation, such as batch adsorption (Sales et al., 2013; Rauf et al., 2008), photolytic oxidation with H₂O₂ (Rauf et al., 2005); photocatalytic decoloration with titanium oxide (Bukallah et al., 2007) and photo-Fenton (Caixeta et al., 2013). None of these papers have reported completed discoloration of the CBB.

Photo-Fenton oxidation is a process that uses hydrogen peroxide and ferrous ion (as a catalyst) in the presence of the light in order to generate hydroxyl radicals (HO*) which can destroy organic compounds (Lucas and Peres, 2006). This hydroxyl radical can be formed in tree
distinct reactions (Equations 1, 2 and 3):

\[ H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^* \]

\[ H_2O_2 + UV \rightarrow HO^* + HO^* \]

\[ Fe^{3+} + H_2O + UV \rightarrow HO^* + Fe^{2+} + H^+ \]

Adsorption is a technique that removes a compound (adsorbate) from the solution to the adsorbent, which usually is an activated carbon. The fixed bed column is an effective process, which uses the concentration difference as the driving force for the process. It allows an efficient adsorbent utilization and results in an effluent with a low adsorbate concentration. The fixed-bed process offers several advantages, such as simplified operation, construction, scale up and process automation and allow the treatment of a large volume of wastewater continuously (Aksu and Gönen, 2004).

Hybrid process, such as photo-Fenton followed by adsorption, has been reported efficiently for the complete removal and/or degradation of some wastewater compounds, such as the leather tanning agent syntan (Thankappan et al., 2014); methyl orange (Saldaña-Robles et al., 2014); organic compounds in landfill leachates (Ramírez-Sosa et al., 2013); methyl methacrylate (Almazán-Sánchez et al., 2014).

The aim of this article was to evaluate the non-azo dye Coomassie Brilliant Blue present in aqueous synthetic solution. A hybrid process composed by photo-Fenton oxidation followed by activated carbon fixed bed adsorption was used to this purpose.

2. MATERIAL AND METHODS

2.1 Material

Coomassie Brilliant Blue G-250 (CAS: 6104-58-1; chemical formula: C_{45}H_{44}N_{3}NaO_{7}S_{2}; molecular weight: 825.99) was supplied by Isofar Ind. e Com. Produtos Químicos LTDA (Duque de Caxias, RJ, Brazil). The chemistry structure of this dye is show by Figure 1. CBB concentration was determined by measuring the absorbance of the aqueous solution (\( \lambda_{max} = 554 \text{ nm} \)) using a UV spectrophotometer (Shimadzu 1800) and quartz cuvettes in both photo-Fenton and fixed-bed adsorption experiments. The CBB aqueous solution was prepared in distilled and deionized water.
The higher concentration which the blue color of the CBB cannot be seen (which is not perceptible by sight) was determinate being $1.0 \text{ mg L}^{-1}$. Then this concentration was defined as the breakthrough concentration.

**Activated carbon:** The adsorbent utilized in this work was a granular activated carbon derived by coal, named TOG 12x50, produced by Calgon Carbon.

### 2.2 Methods

**Photo-Fenton:** The photo-Fenton reaction was conducted in a laboratorial system as shown by Figure 2, according to the methodology described by Igarashi-Mafra *et al.* (2007). The is composed by a mixing vessel (500 mL); a magnetic stirrer (model 114, Nova Ética); a peristaltic pump (model Pump drive PD 5002 – Heidolph); UV lamp (15 W; $\lambda = 380 \text{ nm}$) of 435 mm in length and 26 mm in diameter and a spiral glass of 9.0 mm in diameter.

![Figure 2 – photo-Fenton experimental unity (Igarashi-Mafra *et al.*, 2007).](image2.jpg)
The initial concentration of the synthetic CBB aqueous solution used was 7.9 mg L\(^{-1}\). Initially, the pH of the solution was adjusted to 3.0 (H\(_2\)SO\(_4\) 0.1M L\(^{-1}\)). Then, 1.24 mL of ferrous sulfate heptahydrate solution (FeSO\(_4\) \(\cdot\) 7H\(_2\)O, 10 g L\(^{-1}\), which provided 5 mg L\(^{-1}\) of Fe\(^{2+}\) to the system) and 1.25 mL of hydrogen peroxide (H\(_2\)O\(_2\), 20 g L\(^{-1}\), which provided 50 mg L\(^{-1}\) of H\(_2\)O\(_2\) to the system) was added to the solution. This solution circulated through the glass spiral contained in the photo reactor, at a rate of 200 mL min\(^{-1}\), during 60 minutes. The CBB concentration was monitored at regular intervals, and determined by spectrophotometry (\(\lambda = 554\) nm). After the 60 minutes of the reaction, the pH of the solution was adjusted to 7.0 (NaOH 0.1 M L\(^{-1}\)) in order to inhibit the reaction. The experiments were conducted at room temperature (298 ± 1 K).

**Fixed-bed:** The fixed-bed experiments were conducted in 250-mm-long glass columns with inner diameter of 9.2 mm. Glass spheres (3 mm in diameter) were added to the base of the column to promote uniform flow through the bed. Glass wool was then fixed (5 mm in height) in the column to provide support to the adsorbent. The column was filled with type II water, and activated carbon was added to the column (5.5 g) which provided a 171 mm to the bed depth. At the top of the column, glass wool was added (5 mm in height) to avoid fluidization of the activated carbon during the experiment. The column was fed with the CBB solution (after pH adjustment to 7.0) obtained after being treated with photo-Fenton oxidation using a peristaltic pump (Masterflex® L/S Digital Drive) employing an upward flow and feed flow rate of 5 mL min\(^{-1}\). Samples were collected at regular intervals. The experiments were conducted for 13 hours. A thermostatic bath was used to maintain the temperature of the system at 299 ± 0.5 K. Figure 3 shows the diagram of the experimental set up.

Figure 3 – Schematic diagram of the experimental set up. (1) Column support; (2) glass spheres; (3) glass wool; and (4) activated carbon.
3. RESULTS AND DISCUSSION

3.1 Photo-Fenton

Figure 4a shows the CBB degradation caused by photo-Fenton reaction. The break line was always above the degradation points, which indicates that the effluent was colored. As can be seen, in the first 15 experimental minutes, the degradation has occurred rapidly, being degraded 65.2% of the initial dye concentration. After this time, the CBB degradation rate decreased reaching 76.9% degradation after 60 min of reaction.

![Figure 4a](image)

Figure 4a – CBB degradation (%) by photo-Fenton oxidation.

This reduction in the reaction rate becomes evident when seen in Figure 4b, where is represented the CBB degradation in each period evaluated. In the first period (0-15 minutes) takes place the majority of the dye degradation, however, the degradation reduces over the next periods, being only 2.1% in the last period studied (45-60 minutes). Extend the reaction for a longer time would cause greater dye degradation; however to this degradation be significant, this time should be very large, which would reduce the efficiency of the process. Caixeta et al. (2013), studied the CBB alcoholic solution degradation using photo-Fenton reaction, removing ~70% in 60 minutes and ~80% in 120 minutes of the color, which corroborates to the discussion above.

The study of CBB degradation using the photo-Fenton oxidation degraded the CBB in 76.9%. However, with the experimental conditions used in this process, has not been possible attend the requirements of the Brazilian legislation, which requires that the effluent be absent of color (in which degradation should reach at least 86.6% in our study). Therefore, to obtain an effluent absentee in color it was proposed the use of a fixed-bed column filled with activated carbon in order to remove the residual dye obtained after photo-Fenton degradation.

3.2 Fixed-bed adsorption

Figure 5 shows the breakthrough curve for the effluent obtained after photo-Fenton oxidation (where \( C_0 \) is the CBB concentration before the photo-Fenton oxidation and C the outlet concentration). From Figure 5 can be seen that the outlet concentration was very low during all the 13 hours of experimental time. \( C/C_0 \) was always lower than 0.04, which indicates high CBB removing (95.9%). This percentage removal was similar to those found in studies where the hybrid photo-Fenton/adsorption process (Ramírez-Sosa et al., 2013; Almazán-Sánchez et al.,...
A breakthrough curve usually presents a characteristic S shape, due to the mass transfer forces. In the breakthrough curve obtained in this study, the characteristic S form was not achieved. This is because the activated carbon was not saturated. Even the breakthrough point \( C/C_0 = 0.14 \) was not achieved. This indicates that the bed depth used was high to obtain the complete breakthrough curve.

With the experimental conditions employed, the breakthrough \( (C/C_0 = 0.14) \) was not achieved (as shown by the break line). This indicates that during the 13 hours of operation time, the solution were always color absent. Then, the effluent obtained after fixed-bed column can be considered absent color, and therefore satisfies the Brazilian legislation.

5. CONCLUSIONS

The hybrid process of photo-Fenton followed by fixed-bed adsorption was investigated in the degradation of a synthetic Coomassie Brillant Blue aqueous solution in order to remove the blue color and meet Brazilian legal requirements (effluent absent of color). With the photo-Fenton oxidation, 76.9% of the initial CBB concentration were degraded, which was not enough to achieve the maximum concentration that is color absent. The photo-Fenton effluent was fed into a fixed-bed adsorption filled with activated carbon during 13 hours, being its effluent always color absent, removing at least 95.9% of the initial CBB concentration.
So, the hybrid process photo-Fenton/Fixed-bed adsorption proposed in this study, showed to be efficient to remove the blue color originated by the Coomassie Brilliant Blue.

6. REFERENCES


