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LED Light Integrated Reactors: Study of the Methylene Blue Chemical Oxidation Process

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Abstract: The contamination of water by organic dyes, such as methylene blue, is a risk factor for the environment, since all aquatic fauna and flora are immensely affected due to the reduction of the amount of dissolved oxygen and the passage of light, affecting the photosynthesis. The main source of contamination comes from the textile industry, so it is necessary to study efficient techniques for treating effluent without the cogeneration impact. In the present work, a study was developed to evaluate the best combination of factors of a batch treatment to be applied in a continuous treatment system. The removal of methylene blue by chemical oxidation was evaluated using sodium persulfate as an oxidizing agent. A complete experimental design 2^3 was devised to evaluate the effects of the activation of the oxidizing agent by iron sulfate (II) and visible light (LED), these being the factors. After this batch step, the tests that were efficient in degrading the contaminant were carried out in the continuous reactor. The degradation results showed that, in batch, the oxidation with activation of sodium persulfate by iron sulfate (II) is more efficient, removing 91.2% of the dye in 20 minutes. In the continuous reactor, activation with a visible light source showed greater conversion due to its greater contact surface with water contaminated with dye, removing 59.2% over 15 meters from the reactor and residence time of 109 seconds.

Keywords: Advanced Oxidative Process, Visible Light, LED, Persulfate, Methylene Blue, Continuous Process, Experimental design

Adherence to the BJEDIS' scope: This article presents a study based on the use of a 2^3 experimental design of a batch system for the analysis of variables that can be used alone and together for its application in a continuous reactor for the treatment of water contaminated with methylene blue and it is inserted in the category Biotechnology, biopolymers, biocatalysts, bioremediation, and ecotoxicology, covering all fields of environmental chemistry, environmental toxicology, and risk assessment.

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1. INTRODUCTION

In Brazil, the textile industry is part of the country's history and technological evolution, with factories that have been in operation for more than 200 years and that have all stages of the production process, from cotton production to the production of fabrics and final finishing. The textile industry is responsible for 3.5% of Brazil's Gross Domestic Product (PIB). There are around 27,500 formal companies in this activity, employing 1.5 million people directly and 8 million indirectly [1].

With economic growth, the environmental impact generated by the textile sector also grows regardless of the country [2,3]. The effluent from the textile industries is rich in organic matter and dye, when released into water bodies, its high organic load causes a reduction in the amount of dissolved oxygen, which harms the aquatic ecosystem [4]. Another aggravating factor is that water containing dyes reduces the passage of sunlight, which results in decreased oxygen production by microorganisms and algae, as they cannot perform photosynthesis [5].

In Brazil, the Ministry of Health with Ordinance No. 2,914 / 2011 requires that the maximum value for apparent color of the effluent be 15 uH (Hazen unit), therefore, studies on treatments to minimize environmental impacts and comply with regulations are needed [6]. There are several forms of treatment for the reduction of water color, such as advanced oxidative processes (AOP), ion exchange, adsorption, biological, chemical and physical treatments [7]. Oxidation processes are being extensively studied, as they are capable of converting various contaminants into inert compounds in a short time [8], such as, for example, organic dyes, pollutants from the pharmaceutical industry, surfactants, hydrocarbons and pesticides [9-13].

One of the oxidants that has stood out in the most recent studies is sodium persulfate (SP), mainly because it does not show significant changes in pH changes to assist activation with iron ions, as well as having a half-life longer [14,15]. As already mentioned, normally this oxidant is activated in the presence of Fe^{2+} (Fe(II)), but, in order for the sulfate radicals to be produced, it is necessary that the medium be at acidic pH. However, if an acidic effluent is discharged into aquatic bodies, water fauna and flora can be affected. Thus, an additional stage of neutralization of the medium must be carried out [16]. Another form of activation is through light, a range of works shows the use of ultraviolet light and visible light, which is more interesting because it allows the use of sunlight [17].

The activation of persulfate through iron ions for the degradation of methylene blue (MB) in batches is efficient [18]. However, tests in a continuous process and with other more efficient forms for the reality of the persulfate activation region, such as light activation, are more interesting to be studied, due to the ease of implementation of such a system in an industry that operates continuously [19].

This work aims to treat a synthetic effluent contaminated by methylene blue dye through chemical oxidation, using persulfate activated with iron and visible light in a continuous regime, evaluating the individual influence of the reagents as forms of activation, as well as they combined.

2. MATERIALS AND METHOD

The materials and reagents used in this work were Methylene Blue P.A.; formula: $C_{16}H_{18}ClN_3S.3H_2O$; molar mass: 373.90 $g.mol^{-1}$; brand: Dinâmica Química Contemporânea Ltda.; Sodium Persulfate 99%; formula: $Na_2S_2O_8$; molar mass: 238.11 $g.mol^{-1}$; brand: LABSYNTH Produtos para Laboratórios Ltda.; Iron Sulfate II (OSO) P.A.; formula: $FeSO_4.7H_2O$; molar mass: 278.01 $g.mol^{-1}$; brand: Dinâmica Química Contemporânea Ltda.; Sodium Thiosulfate P.A; formula: $Na_2S_2O_3.5H_2O$; molar mass: 248.18 $g.mol^{-1}$; brand: ISOFAR Indústria e Comércio de Produtos Químicos Ltda.; Genesys 10 UV-Vis spectrophotometer. The experiments were carried out in a unit built in such a way that both batch and continuous experiments were carried out in the unit. Figure 1 shows the diagram of the continuous reactor unit.

Solutions of 50 ppm methylene blue, 0.5 $g.L^{-1}$ sodium persulfate, 0.15 $g.L^{-1}$ iron sulfate II and 400 mM sodium thiosulfate were prepared. The sodium persulfate solution were subsequently diluted to carry out all the experiments as well as the iron sulfate II solution. The sodium thiosulfate solution was necessary to stop the degradation reaction for its analysis in the spectrophotometer [20].

EXPERIMENTAL

Initially, batch experiments were carried out to identify the action of the different activators (catalysts) on the degradation of the contaminant. That is, the variables studied were sodium persulfate (as oxidizer), iron sulfate (II) and visible light, as shown in Table [1].

Table [1]. Variables of the complete experimental design and their levels.

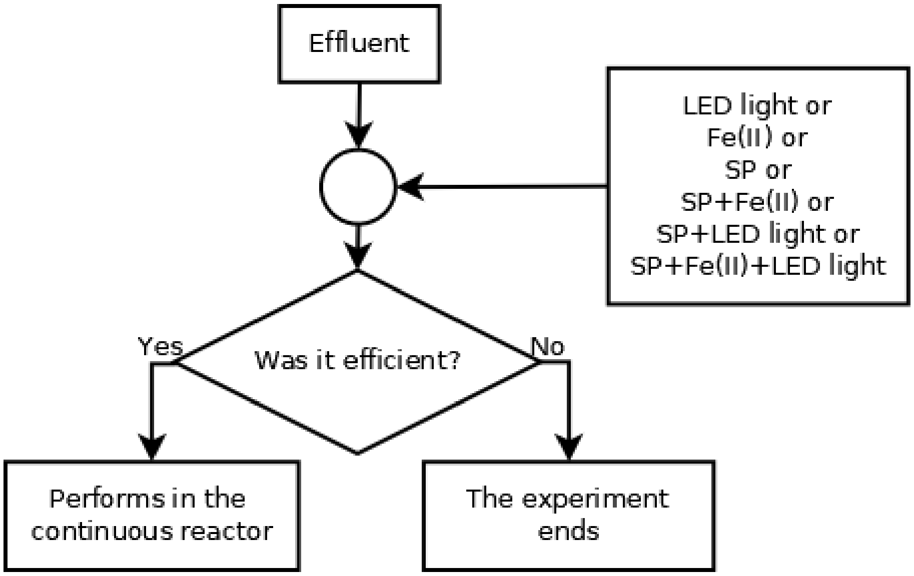
Independent Variables X_i	**Levels**		
	-1	**0**	**+1**
X_1, Sodium Persulfate Concentration ($g.L^{-1}$)	0.00	0.25	0.50
X_2, Iron Sulfate (II) Concentration ($g.L^{-1}$)	0.00	0.07	0.15
X_3, Visible Light	Off	Flashing	On

For the study of the factors, a complete planning was carried out 2^3, with the response of the experiments to degradation of methylene blue calculated through its final concentration value divided by the initial value (C/C_0). It was analyzed how the degradation occurred over time in each case, this was made possible by samples being taken as time progressed and the reaction being stopped with the aid of sodium thiosulfate solution.

The concentration value was obtained through an absorbance and concentration calibration curve found for the mixture of methylene blue and water with the aid of a spectrophotometer. All tests were performed in duplicate.

After the batch experiments, the catalysts that showed the most promising degradation results were repeated in the continuous reactor as shown in the flowchart in Figure 1.

Figure 1. Flowchart with the summary of the experimental steps.



The tests in the continuous reactor were performed in duplicate following the description of Table [2] with respect to the independent variables and their values. The water contaminated with methylene blue was inserted into the reactor with the aid of a submerged pump (Pump 1 in Figure 2), while the oxidant or the oxidant+catalyst mixture was mixed and pumped with a choke pump (Pump 2). Both currents were mixed with the aid of a T connection just before entering the reactor. The LED light was inserted in the upper part of the box, which was black inside, and as the pipes were made of borosilicate it was possible to penetrate the inserted solution. The samplers were purposely inserted along the reactor in the lengths of 347.5 cm and 677.5 cm and the outlet of the system was in a length of 1115 cm, thus, it was possible to calculate residence time, since the flow rates of both pumps were controlled by an Arduino. The state of the LED light was also controlled by the Arduino. Therefore, it was possible to identify the best conditions to implement the continuous treatment system in an industry.

Figure 2. Scheme of the continuous reactor with the samplers and pumps used.

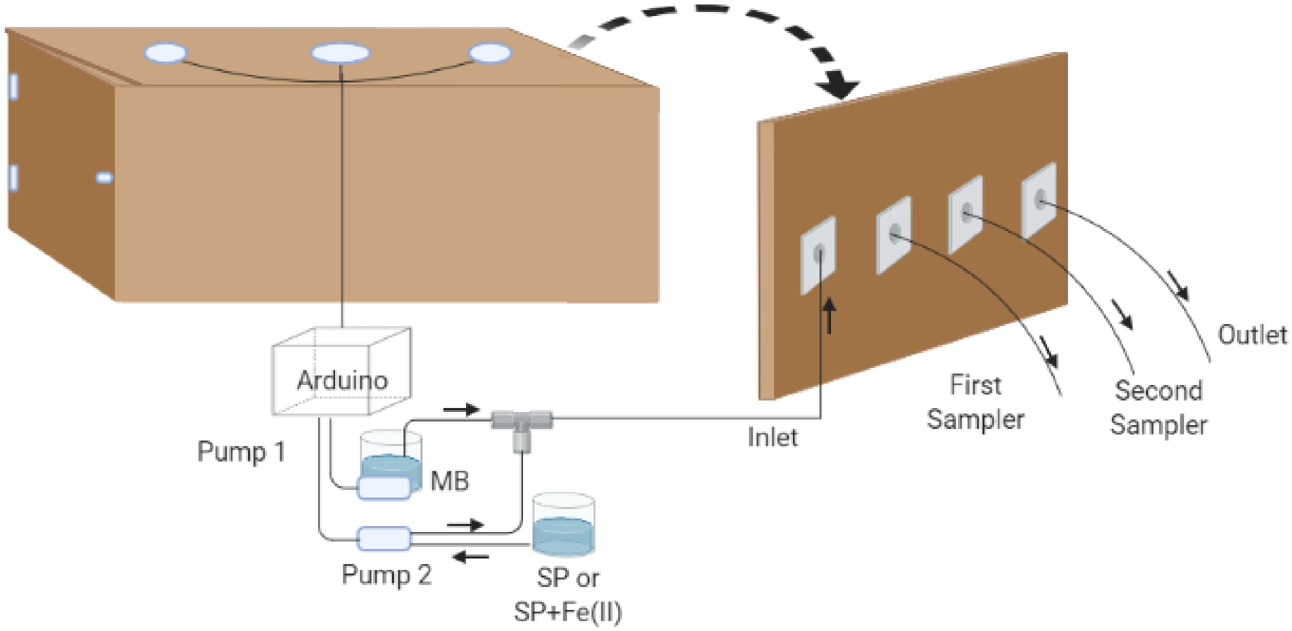


Table [2]. Experimental tests for oxidation of methylene blue (MB) in a continuous reactor.

Runs	SP (g.L^{-1})	Fe(II) (g.L^{-1})	LED Light
I	0.5	0.15	On
II	0.5	0.00	On
III	0.5	0.15	Off

3. RESULTS AND DISCUSSION

The degradation of methylene blue was initially studied through control tests done individually with Fe(II) and light in a batch reactor. Table [3] presents the average of the results of degradation of the dye for planning 2^3.

Table [3]. Experimental design 2^3 used for oxidation of methylene blue (MB) in a batch reactor and the results.

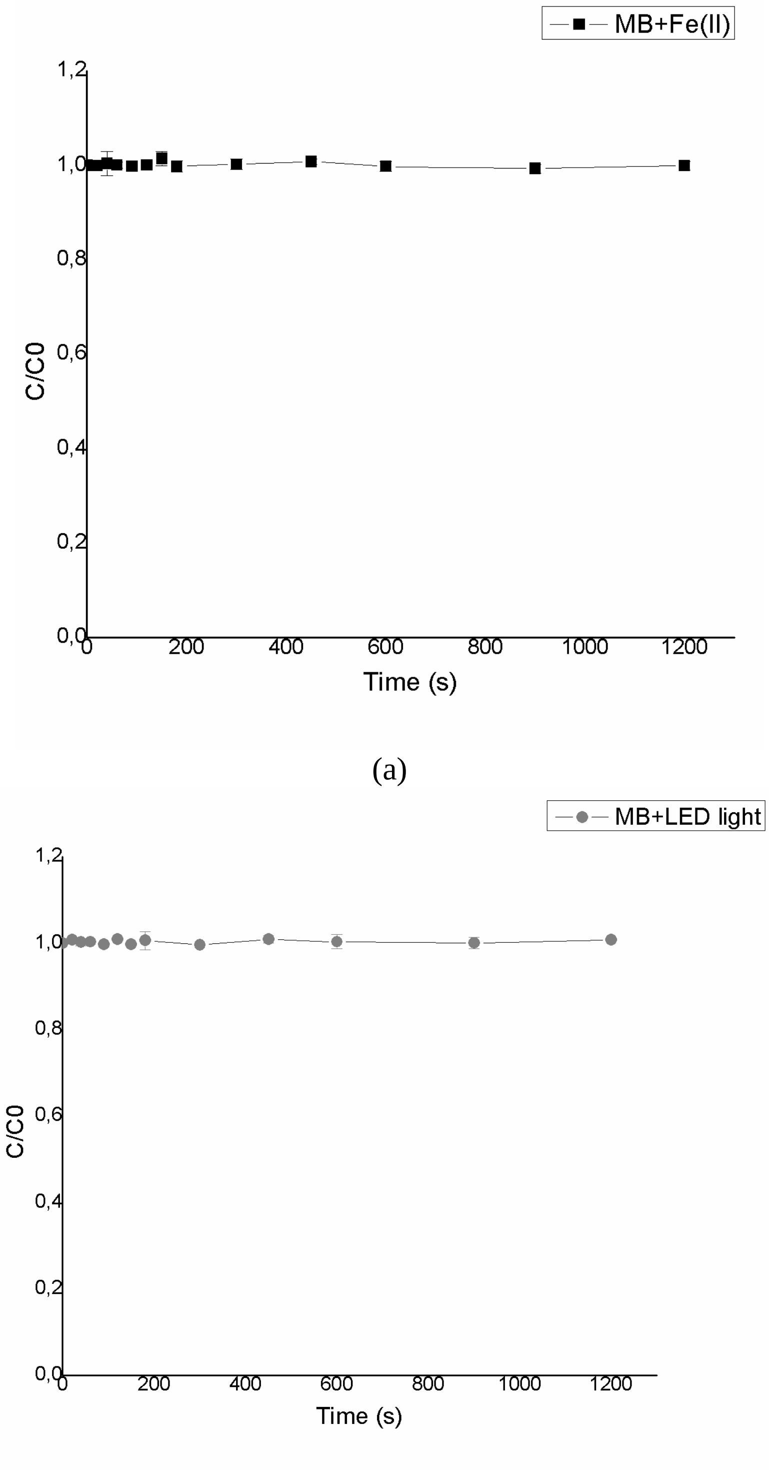
Runs	**Levels**			**Degradation of methylene blue (C/C_0)**
	X_1	X_2	X_3	
I	-	-	-	1
II	-	-	+	1
III	-	+	-	1
IV	-	+	+	1
V	+	-	-	0.810
VI	+	-	+	0.604
VII	+	+	-	0.240
VIII	+	+	+	0.574
IX	0	0	0	0.533
X	0	0	0	0.492
XI	0	0	0	0.638

It is possible to state from Table [3] and Figure 3 that, alone, both light and Fe(II) do not have the ability to degrade methylene blue. That is, there is no photolysis of the pollutant, and Fe(II) does not have individual collaboration to remove the dye.

The literature shows that sodium persulfate in solution forms the sulfate anion, which is only able to partially degrade the pollutant. Thus, it is necessary to activate the oxidant and convert it to its radical form (radical sulfate), either by the action of light, transition metal (iron) or a combination of both. Figures 4a - 4d show the results of the control tests with the effect of persulfate alone and, with the combined effects between persulfate with Fe(II), persulfate with light and persulfate with Fe(II) and light, respectively.

The degradation of methylene blue with persulfate was 20% in 500 seconds of reaction time, while that of persulfate with light was 50.5% in a reaction time of 600 seconds, that of persulfate with light and Fe(II) was 65.1% in 1200 seconds, that is, in 20 minutes, highlighting the fact that the regime did not enter a steady state. The degradation of methylene blue using persulfate with Fe(II) was 91.2% in a reaction time of 900 seconds.

Figure 3. Batch system behavior over time to observe the influence: (a) Fe(II), and (b) LED Light.

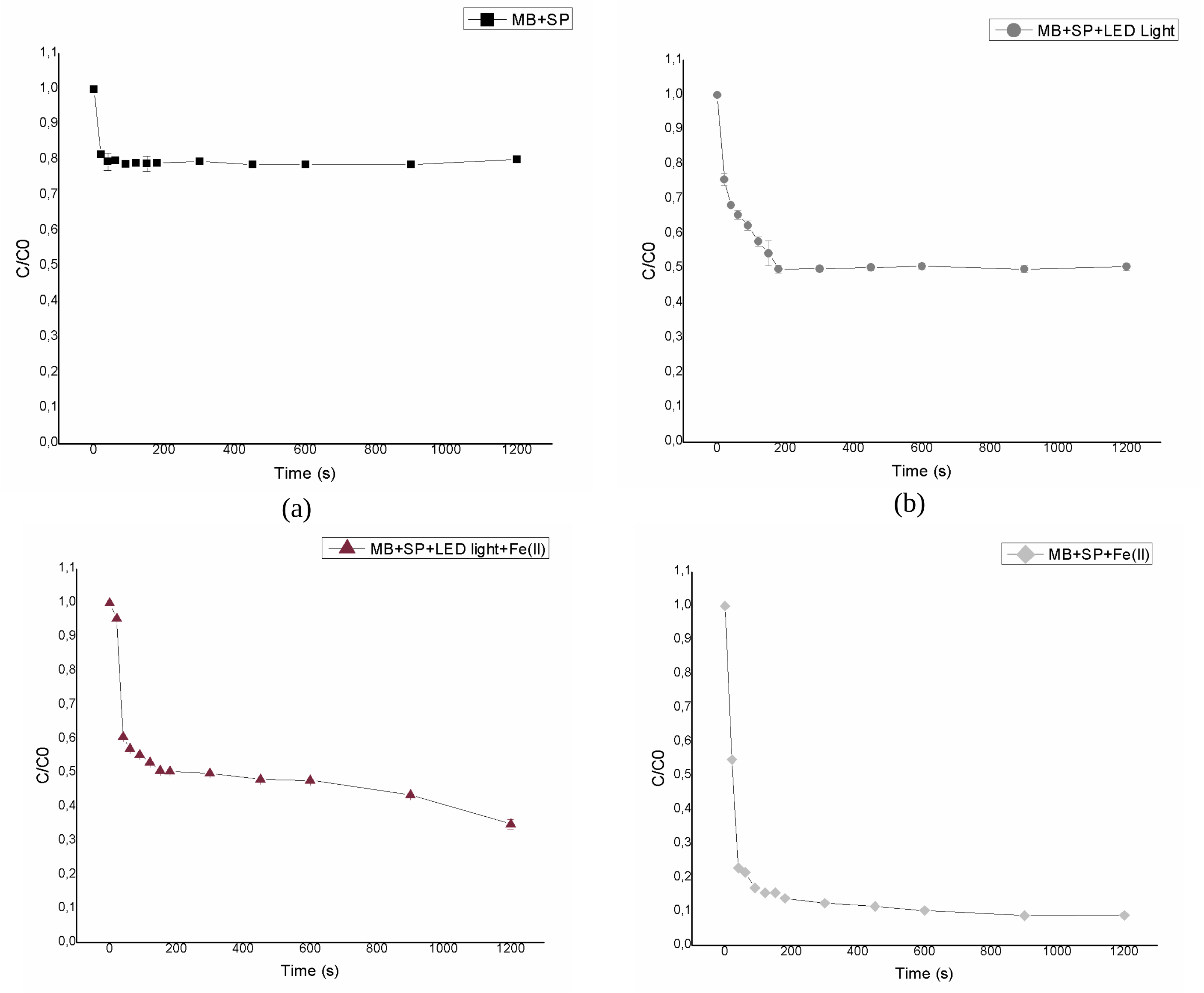


(a)

(b)

As previously mentioned, batch reactions that showed efficiency in the degradation of methylene blue were carried out in the continuous reactor.

Figure 4. Behavior of concentration over time to observe the influence: (a) persulfate, (b) persulfate with light, (c) persulfate with light and Fe(II), and (d) persulfate with Fe(II).



(a) (b)

(c) (d)

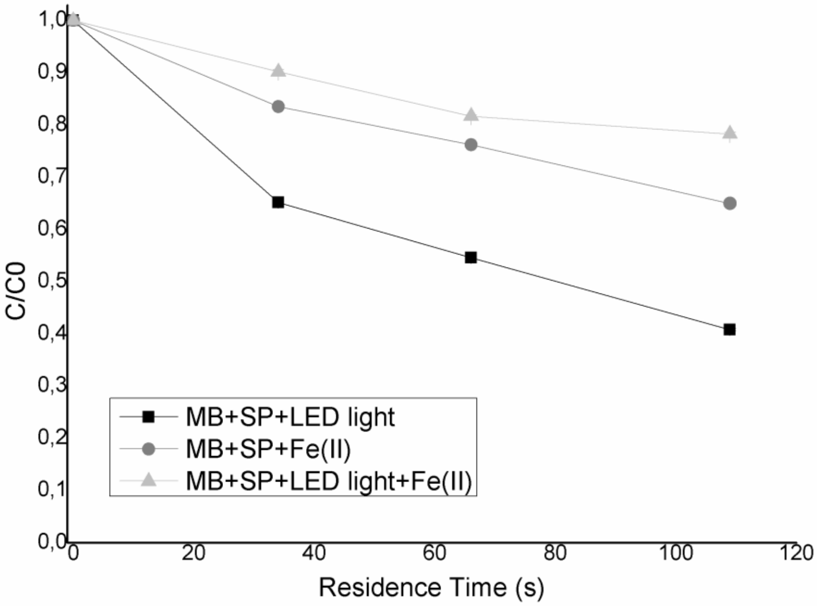
Figure 5 shows the behavior of the concentration at three points of the reactor, when the length is 3.475 meters, 6.775 meters and 11.15 meters, which is where the samplers and the tube reactor outlet are located, resulting in a residence time for the flow used of approximately 34, 66 and 109 seconds. Table [4] explains the final results of the degradations in the continuous reactor.

It was observed, with the experiments carried out, that the methylene blue reaction does not behave in the same way as Rhodamine B [21]. It is believed that the photosensitization characteristic of the reaction that contributes to the degradation of Rhodamine B, is not relevant for the methylene blue solution, that is, the contamination of the two activators for the studied dye will not cause the reaction to have a greater conversion.

It is possible to notice that the reaction of persulfate with light in a tubular reactor operating continuously, unlike the batch reaction, showed a higher degradation conversion of methylene blue, followed by the persulfate reaction with Fe(II) and the persulfate reaction. with Fe(II) and light. This behavior may have happened because in the batch reactor the light reaches only the upper surface of the reactor, while in the continuous one, as the tube has a very small diameter, the light reaches a greater surface area of the solution, which leaves it with a greater efficiency when compared to the solution only with Fe(II).

Another important point to note is that the conversions in the tubular reactor occur in less than 2 minutes (residence time). When compared to the degradation obtained with the batch reaction, the continuous process was different. In the case of the persulfate reaction with light, the degradation in the continuous process was 59.2% while in batch the degradation was 42.2% (for a reaction time of 2 minutes).

Figure 5. Behavior of methylene blue concentrations along the continuous reactor using persulfate and LED light, persulfate and Fe(II) and persulfate, LED light and Fe(II).



Tab*le 4*. The degradation of reactions in the continuous reactor.

Reaction	Degradation (%)
SP + LED light	59.2
SP + Fe(II)	35.0
SP + Fe(II) + LED light	21.7

Conclusions

The treatment of water contaminated by methylene blue dye can be carried out through chemical oxidation, with the activation of sodium persulfate with iron and light. For the batch reactor, the greatest degradation occurred with the activation of persulfate by means of Fe(II), with a conversion of 91.2% (in 20 minutes of reaction). For the continuous reactor, the highest efficiency was achieved with the activation of persulfate by artificial light, highlighting the phenomenon of photosensitization was not observed. In numbers and for the conditions adopted, this degradation was 59.2% in less than 2 minutes of reaction.

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Conflict of interest: None

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