



RESEARCH ARTICLE

INDIGO BLUE DEGRADATION: PROBABLE PRESENCE OF DYE ADSORBED BY IRON HYDROXIDE DURING FENTON PROCESS

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Abstract

A chemical method using FeSO_4 and H_2O_2 was selected for indigo blue (IB) degradation in aqueous medium. The initial experiments demonstrated that high concentrations of hydrogen peroxide (H_2O_2) and iron sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were capable of total degradation of IB (approximately 100%). Controlled tests, varying the concentrations of both reagents, revealed that the mixture containing approximately 350 mg/L (v/v) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.57% (v/v) of H_2O_2 was considerably efficient in the degradation of IB (1,000 mg/L). The decay kinetics revealed rapid IB degradation and possible IB adsorption on iron (III) hydroxide precipitate $[\text{Fe}(\text{OH})_3] \downarrow$. However, the adsorbed IB also subsequently, leaves the residue of $[\text{Fe}(\text{OH})_3] \downarrow$, which suggests the occurrence of not only chemical degradation of IB but also its possible adsorption by $\text{Fe}(\text{OH})_3$ precipitate.

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Introduction:-

Textile industries are among the most polluting industries in the world. During the dyeing process, most dyes are not completely fixed to the types of fabrics [1]. As a result, these dyes and their chemical additives are discarded in large quantities, without adequate treatment, in the aquatic environment [2]. The presence of textile dyes, such as indigo blue (IB), in this environment, causes great environmental impact and harm to human health [3]. Therefore, utilizing efficient and low-cost techniques for treating contaminated effluents with textile dye is essential. Among methodologies such as bioremediation, electro-flocculation, photo chemo-degradation, adsorption, and chemo-degradation are very investigated [4].

Chemical degradation is one of the most common techniques that employ chemical agents capable of generating reactive oxygen species (ROS) to degrade dyes and other pollutants. Among the best-known reactive species is the hydroxyl radical (OH^\bullet) generated from the reaction between hydrogen peroxide (H_2O_2) and iron (II) sulfate (FeSO_4). The OH^\bullet reacts with different pollutants, including dyes [5]. The reaction is often capable of completely degrading the dye, thus avoiding the production of more waste, as occurs, for example, with adsorption, where the adsorbent containing the adsorbed dye needs to be stored for later incineration, which leads to higher costs for effluent treatment. Therefore, this work aimed to use mixtures of H_2O_2 and FeSO_4 to degrade the high concentration of the textile IB [5].

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Material and Methods:-

Material:-

The reactants ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and hydrogen peroxide 35 % (v/v) (H_2O_2) were obtained from NEON (Suzano-SP, Brazil). The IB was obtained from Tupy Industry (SaoPaulo-SP, Brazil). The following laboratory types of equipment were utilized: analytical balance (Shimadzu AY 220 model, Japan), pH-meter (PHTEK, Labitec, Londrina-PR, Brazil), magnetic stirrer (Warmnest, 78HW-1 model, Brazil), UV/Vis spectrophotometer (EVEN IL-562 Model, Brazil), water-purification system (Quimis, Q241-22 model, Diadema-SP, Brazil), microcentrifuge (EVLAB EV206, Londrina-PR, Brazil). A program from Origin Lab Corporation, Northampton, MA 01060, US, for data treatment was utilized.

Methods:-

Initial test:-

This initial test was performed to plan subsequent IB chemical degradation tests. For this purpose, four types of aqueous solutions were prepared in triplicate: 1) solution containing only IB 1,000 mg/L (pH 6.8, T: 298.15 K; 25 mL), 2) IB 4,000 mg/L + $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 11 mg/L, 3) IB 1,000 mg/L + H_2O_2 0.57% (v/v), and 4) IB 1,000 mg/L + H_2O_2 0.57% (v/v) + $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 11 g/L. After 30.0 seconds of reaction in a volumetric flask, the different solutions (1,2,3, and 4) were transferred to a 50 mL beaker and stirred at 600 RPM for 8.0 minutes to remove gas bubbles. It was then filtered through qualitative filter paper to remove the yellow precipitate $[\text{Fe}(\text{OH})_3]$. To remove the suspended solids, the supernatant was centrifuged at 13,000 RPM/5.0 min. This second supernatant was analyzed at 573 nm (λ maximum for IB) in a UV/Vis spectrophotometer to verify the absorbance of IB.

Fe^{++} influence:-

In this step, aqueous solutions containing IB 4,000 mg/L (m/v), H_2O_2 0.57% (v/v) (pH 6.8, V: 25.0 mL, and T: 298.15 K), and different concentrations of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (v/v) (0, 80, 160, 200, 240, 350, and 720 mg/L) were prepared. After $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ addition, each solution reacted for 15.0 minutes. After this time, the solution was magnetically stirred at 600 RPM for 8.0 minutes to eradicate oxygen gas bubbles. Each solution and remove the precipitate. Part of the supernatant (3.0 mL) was transferred to a plastic microtube and centrifuged at 13,000 RPM/5.0 min. to remove possible solids. After solutions centrifugation, two procedures were performed: a) visually forming a possible in the microtube and b) the absorbance measurement of the supernatant at 573 nm.

H_2O_2 influence:-

Aqueous solution containing IB 4,000 mg/L (v/v) (pH 6.8; v: 25.0 mL, and T: 298.15 K), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 350 mg/L (optimized in the previous step), and different concentrations of H_2O_2 (0.00 - 0.6 %) (v/v) were prepared. After adding H_2O_2 , each solution reacted for 15.0 minutes. After the reaction, each solution was magnetically stirred at 600 RPM for 8.0 minutes to eradicate oxygen gas bubbles. Then, the solutions were filtered using qualitative filter paper to recover the supernatant and remove the solid formed. Part of the supernatant (3.0 mL) was transferred to a plastic microtube and centrifuged at 13,000 RPM/5.0 min. to remove possible solids in suspension. After centrifugation of these solutions containing different concentrations of H_2O_2 (v/v), two procedures were performed: a) visual monitoring of possible precipitate formation at the microtube's-bottom and b) absorbance measurement of the supernatant at 573 nm to determine the IB amount (%) degraded after the oxidative process. Subsequently, the filter paper was rested for approximately 30 minutes to verify the stability of the solid purple color.

Kinetics:-

Aqueous solutions containing IB 4,000 mg/L (v/v) (pH 6.7, v: 25.0 mL, and T: 298.15 K), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 350 mg/L, and two different concentrations of H_2O_2 (0.08 and 0.57%) (v/v) were prepared. After adding H_2O_2 , each solution was left to react for 6.0 minutes. After each minute of reaction, a certain amount of the reagent solution was removed and vacuum filtered through quantitative filter paper, for maximum removal of possible suspended solids. After filtration, the filtrate was stirred on a magnetic stirrer for 2.0 minutes at 600 RPM to remove as many bubbles as possible and centrifuged. The absorbance of the centrifuged liquid was measured at 573 nm. The following equation was used to determine the decay rate constant:

$$\ln(\text{Abs}_f/\text{Abs}_0) = k_t \text{ (equation 1)}$$

where \ln is the Napierian logarithm, Abs_f is the absorbance of IB after a certain reaction time, Abs_0 is IB's initial absorbance, and k_t is the decay kinetic constant of IB absorbance in minutes⁻¹.

Results and Discussion:-

Initial test:-

Many works on chemical photodegradation and chemical degradation have already been published in the scientific literature [6] [7]. For example, in a certain study, the total degradation of the Red M5B was observed in the presence of Fe^{++} and H_2O_2 at pH 3.0 [6]. This kind of reaction is called a Fenton reaction [6]. This process can also be carried out using ultraviolet light (Photo-Fenton Reaction), making it more efficient [8]. In another study using the Fenton and Photo-Fenton processes, considerable percentages of degradation of the IB were observed [9]. In this work, in the initial test, we used high concentrations of FeSO_4 and H_2O_2 to verify whether the commercial IB could be degraded with complete discoloration of the blue color. In the presence of only FeSO_4 or H_2O_2 , the IB solution didn't discolor (Figure 1).

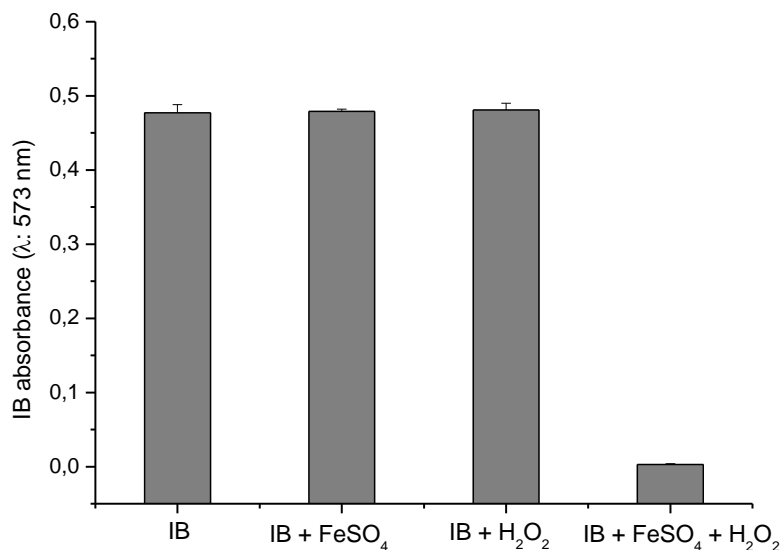


Figure 1:-Initial test for IB degradation in the presence of FeSO_4 and H_2O_2

Figure 2 summarizes the laboratory process, revealing the discoloration of IB, formation of $\text{Fe}(\text{OH})_3$ in suspension, the release of O_2 , filtration to collect the $\text{Fe}(\text{OH})_3$, centrifugation (13,000 RMP) of the gasless filtrate, and formation of a small yellow $\text{Fe}(\text{OH})_3$ in a microtube.

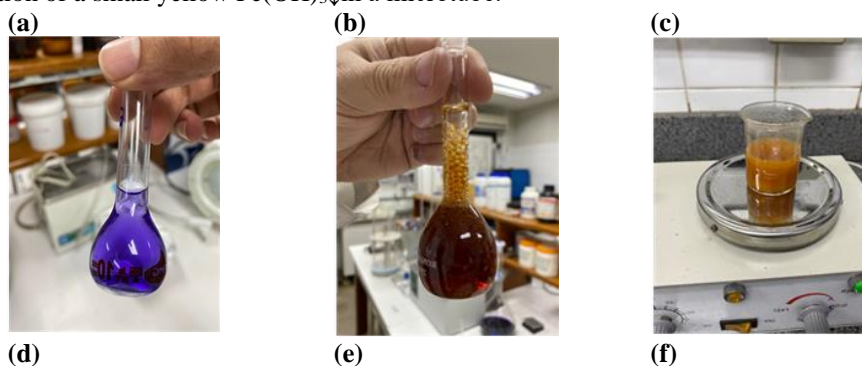




Figure 2:- IB solution before FeSO_4 and H_2O_2 addition (a), after addition (b), the release of O_2 (c), after filtration to collect the $\text{Fe}(\text{OH})_3\downarrow$ (d), solution after filtration (e), and after centrifugation at 13,000 RPM/5 min. (f).

Chemical reactions 1 and 2 (Figure 3) only summarize the process. The literature cites other important intermediary chemical reactions that provoke, for example, the H^+ generation [10].

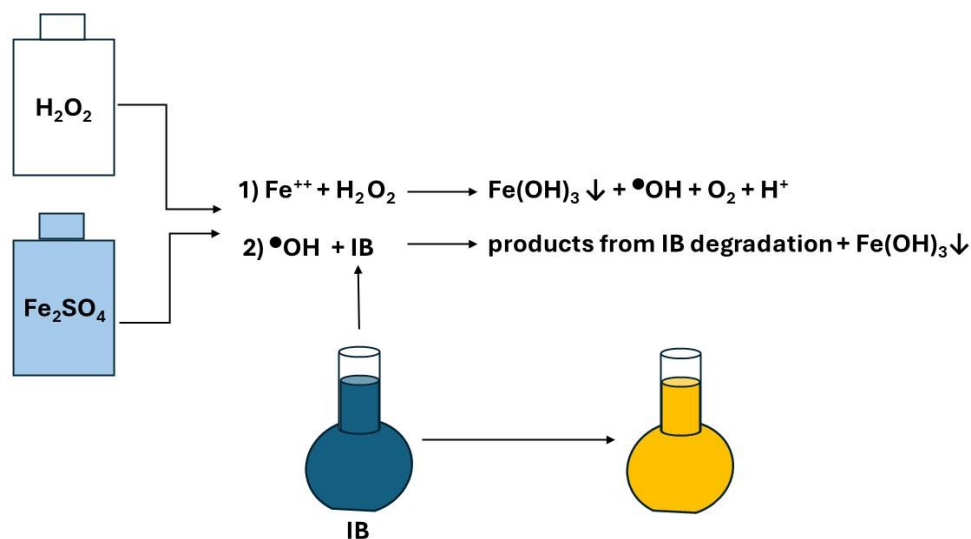


Figure 3:- Chemical reactions 1 and 2 for IB degradation by hydroxyl radical.

The generation of hydroxyl radical ($\bullet\text{OH}$) through the reaction between Fe^{++} and H_2O_2 is well-known (reaction 1) [11] and has been extensively studied in the degradation of organic compounds [10] [12]. The formation of $\text{Fe}(\text{OH})_3\downarrow$ (reaction 1) can be explained by the low value of its solubility product constant (K_{sp} : 2.64×10^{-39}) [13]. This initial test, combining Fe^{++} with H_2O_2 , revealed a good potential for decolorizing water contaminated with IB. In addition, it stimulated more detailed studies, the results of which are described and discussed in the following items.

Fe^{++} influence:-

The increase of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration (mg/L) in the presence of 0.57% (v/v) H_2O_2 caused a considerable decrease in the IB concentration (mg/L) (Figure 4). From 200 mg/L of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, the formation of a purple solid in suspension was observed in the beakers where the reactions occurred (Figure 5), and it remained until the end of the process, that is, until the concentration of 720 mg/L of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Figure 4). After filtration, this solid could also be seen on the filter paper (Figure 5). Part of this precipitate passed through the filter paper and was observed in the microtubes subjected to centrifugation at 13,000 RPM/5.0 min. (Figure 5). The spectrophotometry measurements (573 nm) of the post-centrifugation supernatant revealed that the dye concentration went from 4,000 mg/L to close to 0.000 mg/L (Figure 4).

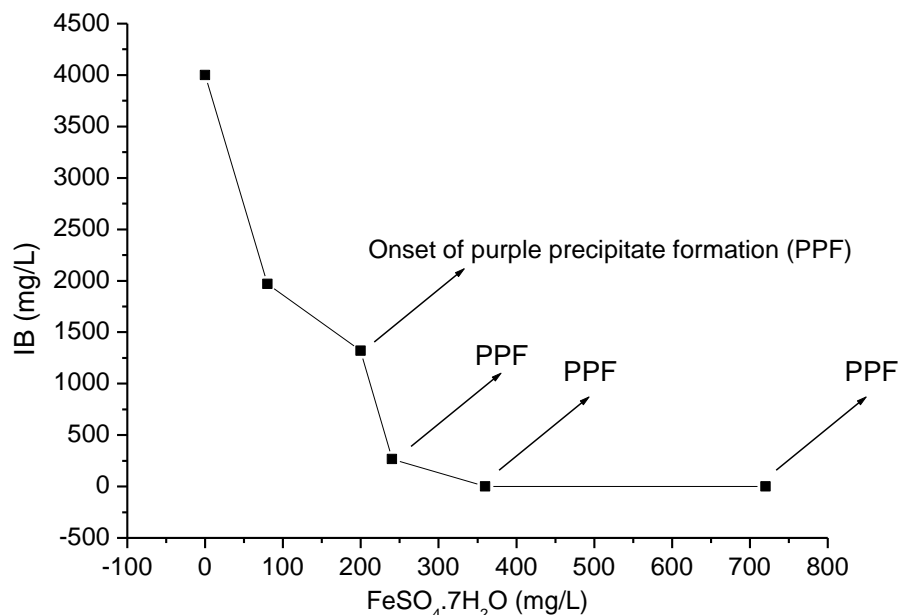


Figure 4:- IB concentrations (mg/L) as a function of increasing FeSO₄.7H₂O concentrations (mg/L) in the presence of H₂O₂ 0.57% (v/v). Results obtained post-centrifugation process (13,000 RPM/5.0 min.).

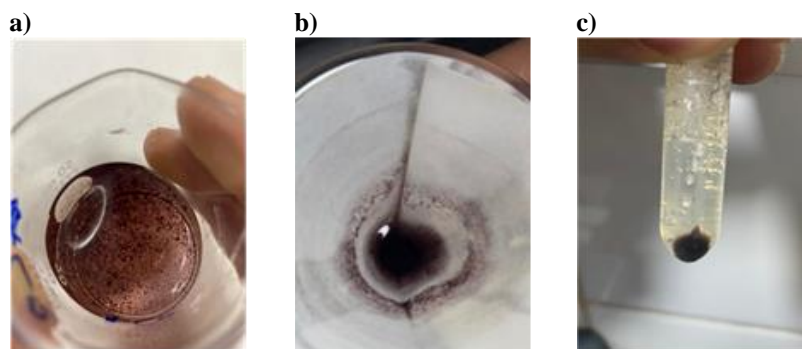


Figure 5:- Purple solid (PS) in suspension observed in the beakers (a). PS on the filter paper after filtration (b). PS in the microtube subjected to centrifugation at 13,000 RPM (c).

According to the literature, the purple solid may result from the chemical adsorption of IB monomers or IB aggregates, which have not yet been degraded in reaction 2 in the Fe(OH)₃↓ precipitate. We suggest that this event would form an IB-Fe(OH)₃↓ precipitate [14] [15]. Other authors who studied the Congo Red (CR) dye removal in an aqueous medium observed this dye adsorption by iron hydroxide [15]. In another study, the adsorption of dyes was also observed using granulated iron hydroxide [14]. Another possible explanation is that in addition to the formation of IB-Fe(OH)₃↓, insoluble IB may have occurred, generally present in a very acidic medium [16]. In this same test, the pH was also measured. The results revealed that the pH dropped from approximately 6.8 to 3.0. An acidic pH is compatible with the presence of insoluble IB [17]. We also suggest forming IB deposits on the iron hydroxide precipitate (Figure 5).

H₂O₂ influence:-

The increase of H₂O₂ provoked an increase in IB degradation (%). The best result was obtained with H₂O₂ 0.57 % which degraded approximately 98.31% of IB (Figure 6). This was evidenced by the color of the water before and after filtration (Figure 7). In another study, the authors evaluated the degradation of dyes in the presence of FeSO₄ and H₂O₂. The results reveal complete success in the degradation of Red M5B and Blue MR prepared in aqueous solutions [6].

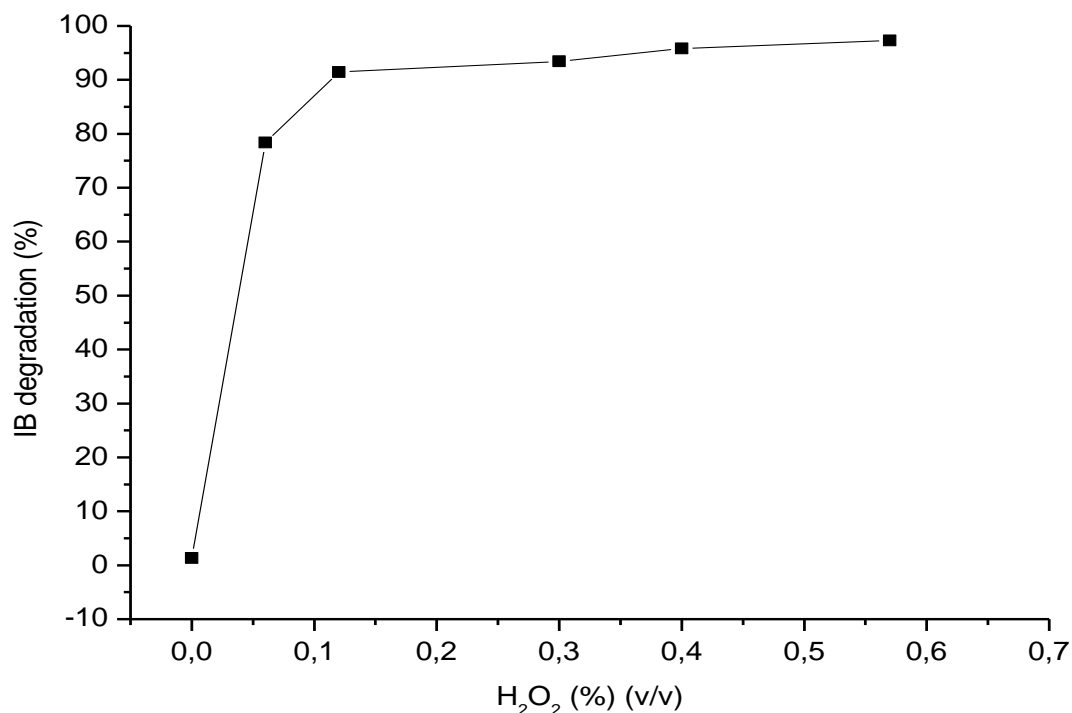


Figure 6:-The increase of H₂O₂ provoked an increase in IB degradation (%)

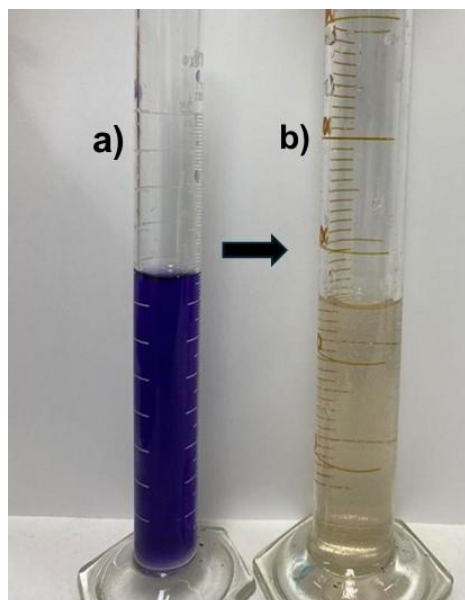


Figure 7:-Aqueous solution of IB before (a) and after (b) chemical degradation.

As expected, it was also noted that the increase in the percentage of hydrogen peroxide favored the appearance of a purple residue (Figure 8) and a considerable drop in the pH of the aqueous medium (Figure 9) due to the H⁺ presence, as demonstrated in reaction 1. The precipitate mass increased significantly between 0.12 and 0.57 % peroxide (Figure 10). However, the purple color disappeared almost completely after 30 minutes on the filter paper, giving way to a yellowish color of iron hydroxide (Figure 11). The suggestion for this event is that the moistened filter paper could still contain a small amount of hydroxyl radical capable of decolorizing the adsorbed purple precipitate. In another investigation, the authors demonstrated the phenol decomposition by the Fenton reaction and phenol adsorption/precipitation on the iron surface [18].



Figure 8:- Purple residue formation during IB degradation.

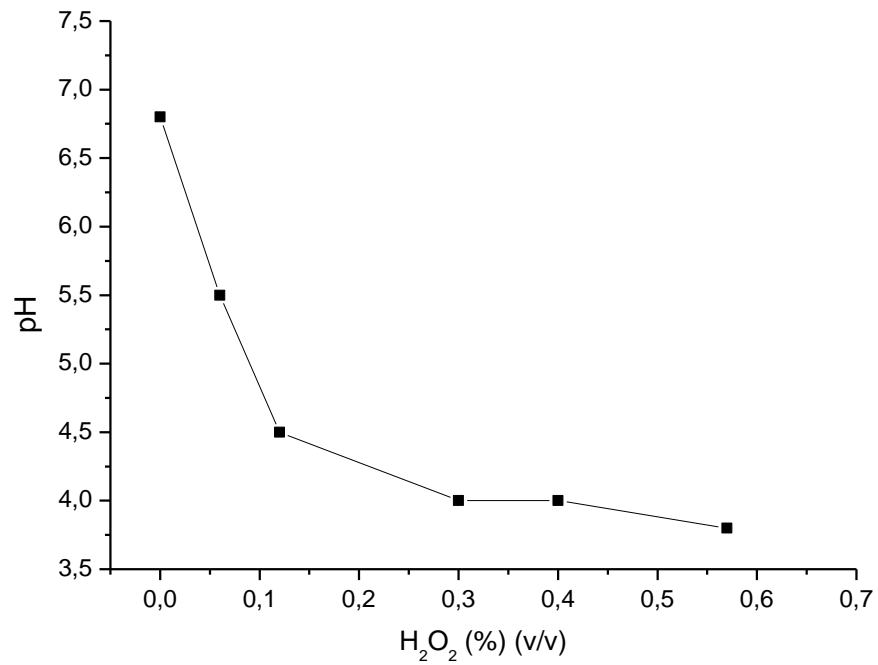


Figure 9:- pH variation depending on the peroxide amount (%).

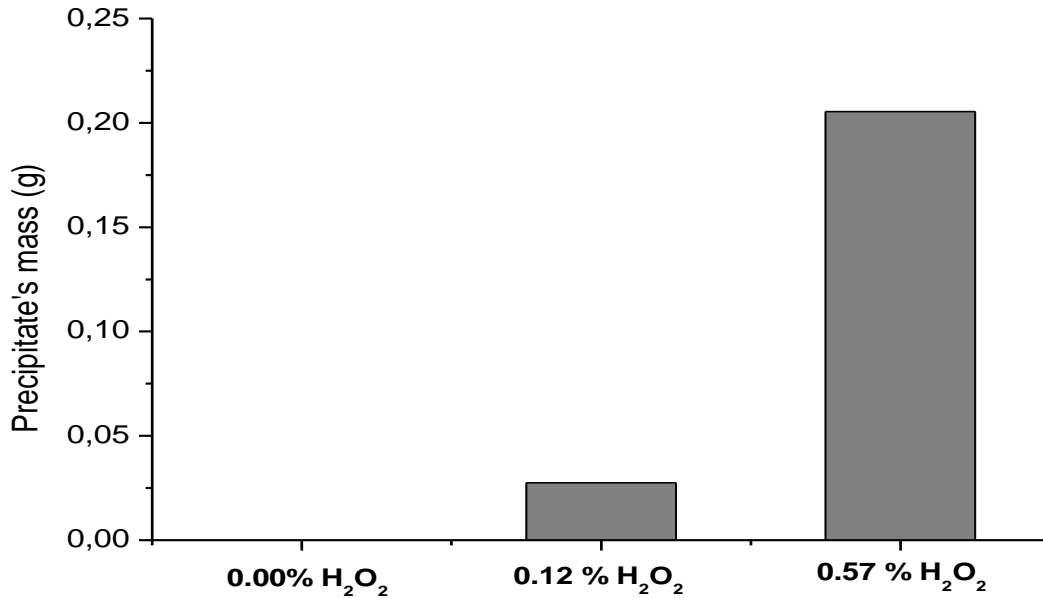


Figure 10:- The precipitate mass formation at 0.12 and 0.57 % peroxide.

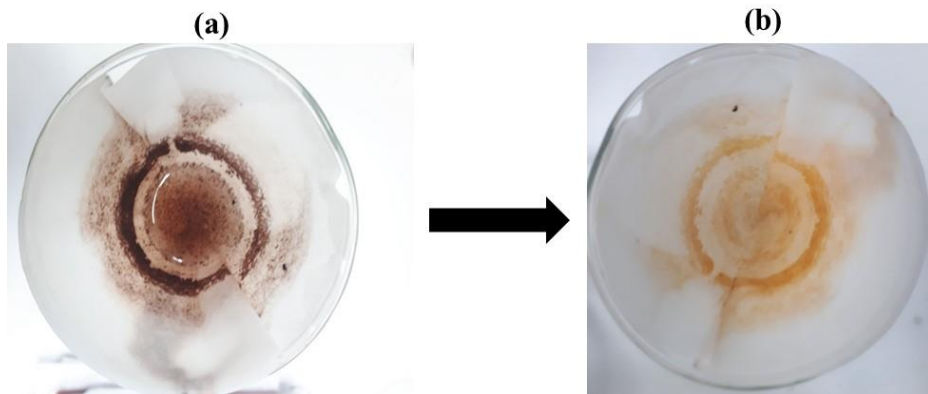


Figure 11:- The purple color (a) disappeared after 30 minutes, giving way to a yellowish color (b).

Kinetics

The decrease in their fluorescence intensity can measure the chemical degradation kinetics of several molecules [19]. Although fluorescence is considered more sensitive than absorbance (Abs), Abs can also be used in this process [20]. Therefore, through equation 2, the decay rate constant (k_t) can be obtained in minutes (min^{-1}) or seconds (s^{-1}). The higher the value of k_t , the greater the density, and the more efficient the molecular degradation process [20]. The result obtained through the linearization (Figure 13), determines that the higher the concentration of H_2O_2 , the higher the decay rate constant of IB absorbance, showing the degradation process to be more efficient. The linearization results are listed in Table 1.

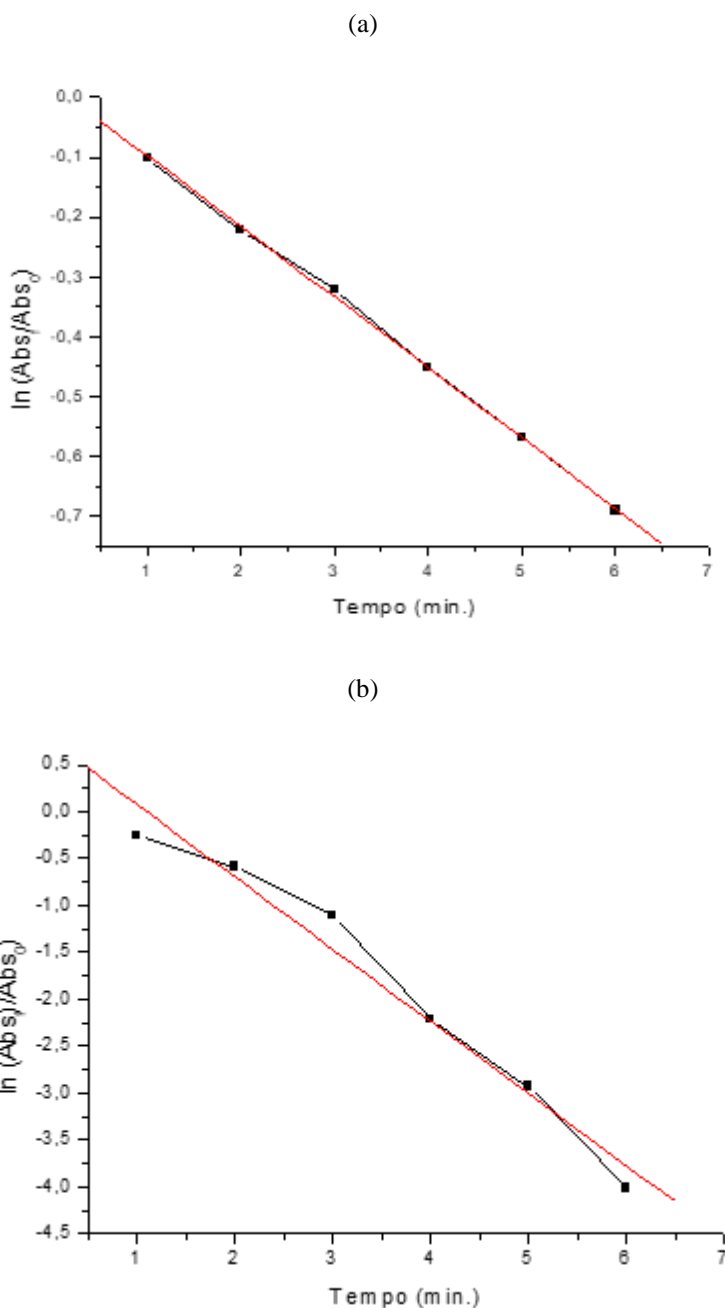


Figure 13:- Decay kinetics of absorbance (573 nm) of IB in the presence of 0.08% (v/v) (a) and 0.57 (v/v) (%) (b) hydrogen peroxide.

Table 1:- Data obtained from linearizing the IB absorbance decay kinetics graphs in the presence of two different H_2O_2 concentrations.

Parameters	H_2O_2 0.08% (v/v)	H_2O_2 0.57% (v/v)
R^2	0.99912	0,98529
k_t (min.^{-1})	- 0.11777	-0.76980

Conclusions:-

The mixture of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with H_2O_2 in high concentrations is capable of significant IB degradation. Furthermore, a yellowish precipitate is formed, probably from $[\text{Fe}(\text{OH})_3] \downarrow$. In addition, a yellowish filtrate is formed, due to the presence of iron ions in the solution. The increase in the concentrations of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 increases the intensity of IB degradation. The control of these concentrations allows the observation of the formation of a suspended solid. Suggests that these solids the IB adsorbed on $[\text{Fe}(\text{OH})_3] \downarrow$. In addition, the pH decreases sharply, making the acidic medium. The purple solid formed undergoes subsequent discoloration, indicating that all remaining IB has been degraded. This is suggested by the fact that the solid, on filter paper, assumes the same yellowish coloration as $[\text{Fe}(\text{OH})_3] \downarrow$ after approximately 30 minutes at room temperature. The reaction kinetics revealed that the higher the H_2O_2 concentration, the greater the intensity of IB degradation. Finally, the results encourage more in-depth studies that include analyses of more parameters such as ΔG , ΔS , gas pressure, detection of possible IB derivatives, and toxicological analysis of these possible derivatives.

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