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Low-cost flow photoreactor for degradation of Reactive Black 5 dye by UV/H_2O_2, Fenton and photo-Fenton processes: a performance comparison

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ABSTRACT

In this work, a flow photoreactor was designed and set up using low-cost and recyclable parts to develop chemical treatments based on advanced oxidation processes (AOP) of highly colored textile wastewater. To evaluate this sustainable system´s efficiency, we investigated and compared the performance of three types of destructive methods (UV/H_2O_2, Fenton, and photo-Fenton) on the decolorization of aqueous solutions of Reactive Black 5 dye (RB5). We also analyzed the effect of the oxidant and dye concentrations on the rate of color removal in each one of the three methods. The results showed that, regardless of the initial operating conditions, the photo-Fenton process achieved the highest degradation rates, particularly when the highest ratio between the oxidant and dye concentrations was used ($[H_2O_2]$: [RB5] = 24.5 mg L^{-1}: 25 mg L^{-1}), leading to complete color removal within only 10 minutes of reaction. With the same initial condition, the Fenton and UV/H_2O_2 processes were also capable of removing the color entirely, even though they demanded more extended runs of 25 min. and 45 min., respectively. The effect of pH on the decolorization by the photo-Fenton process was also investigated, showing the same high performance at pHs 3 and 4. The degradation profile achieved by the photo-Fenton treatment was appropriately fitted by a pseudo-first-order kinetic. The non-expensive photoreactor proved to be quite useful for the degradation of the RB5, mainly when this azo dye underwent the photo-Fenton process.

Keywords: advanced oxidation process, color removal, Reactive Black 5 dye, textile pollutants.

Fotorreator contínuo de baixo custo para degradação do corante Reactive Black 5 pelos processos UV/H_2O_2, Fenton e foto-Fenton: uma comparação de performances

RESUMO

Neste trabalho, um fotorreator contínuo foi projetado e montado, usando peças recicláveis e de baixo custo, para desenvolver tratamentos químicos, baseados em processos oxidativos avançados (AOP), de efluentes têxteis altamente coloridos por azo-compostos. A fim de avaliar a eficiência deste sistema reacional sustentável, foi investigada a performance de três tratamentos destrutivos (UV/H_2O_2, Fenton e foto-Fenton) sobre a remoção de cor de soluções aquosas do corante denominado Reactive Black 5 (RB5). O efeito da concentração de oxidante (H_2O_2) e da carga inicial de corante sobre a taxa de remoção de cor foi também analisado. Os resultados mostraram que, independentemente das condições operacionais iniciais, o processo foto-Fenton alcançou as taxas mais elevadas de degradação, especialmente quando a maior razão entre as concentrações do oxidante e do corante foi empregada ($[H_2O_2]$: [RB5] = 24.5 mg L^{-1}: 25 mg L^{-1}), com a completa remoção de cor em apenas 10 minutos de experimento. Usando-se as mesmas condições iniciais, os processos Fenton e UV/H_2O_2 foram também capazes de descolorir completamente o poluente têxtil, entretanto precisando de 25 minutos e 45 minutos de reação, respectivamente. O efeito do pH sobre a descoloração pelo processo foto-Fenton foi também investigado, mostrando a mesma elevada performance nos pHs 3 e 4. O perfil de degradação obtido no tratamento foto-Fenton foi devidamente modelado pela cinética de pseudo-primeira ordem. O fotorreator contínuo de baixo custo mostrou-se bastante útil na degradação do corante RB5, principalmente quando o processo foto-Fenton foi empregado.

Palavras-chave: corante Reactive Black 5, poluentes têxteis, processos oxidativos avançados, remoção de cor.

1. INTRODUCTION

The textile industry is one of the essential socio-economic activities in Brazil. According to the Brazilian Association of the Textile Industry and Confection (ABIT), this type of sector accounts for more than 1 million tons of fabric annually, making this industrial segment stand out as the second-most important in respect of job generation nationwide.

Although this activity significantly contributes to wealth creation and social inclusion, inevitably, environmental impacts may be caused, especially when there is inappropriate disposal of the effluents from the fabric dyeing process. These effluents typically have a high organic load of synthetic dyes, particularly azo dyes, which combine high toxicity with low biodegradability (Bali and Karagözoglu, 2007; Liu *et al.*, 2011; Silva *et al.*, 2009). Azo dyes are molecules bearing the functional group diazenyl (R – N = N – R´), where R and R´ usually are aromatic groups, which makes them a highly conjugated and stable system. Figure 1 shows the structure of azo dye Reactive Black 5 (RB5 dye) studied in the present work.

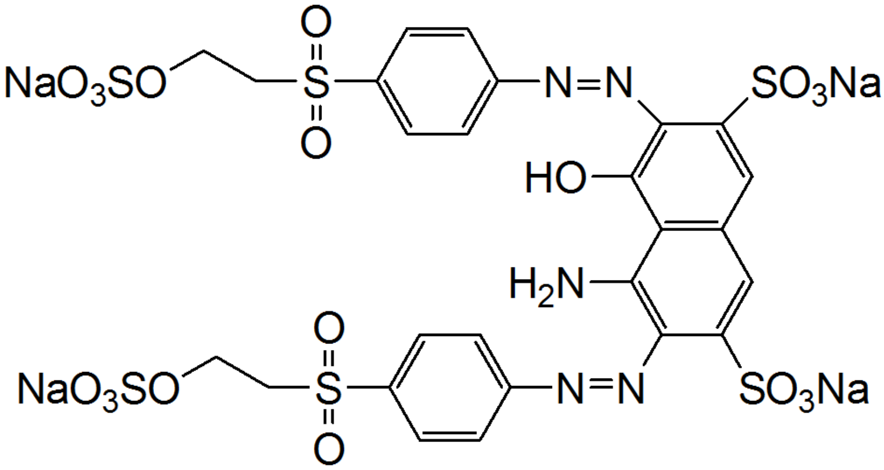


Figure 1. Structural formula of the Reactive Black 5 dye (RB5).

Therefore, to reduce potential impacts in the environment, the development and application of efficient techniques are crucial for removal or degradation of that type of dye from textile industry effluents.

Countless published studies have demonstrated promising aspects of advanced oxidation processes (AOP) for the degradation of organics pollutants (Fragoso *et al.*, 2009; Guimarães *et al.*, 2012; Vedrenne *et al.*, 2012; Basturk *et al.*, 2015; Abhilasha *et al.*, 2016; Leite *et al.*, 2016; Starling *et al.*, 2017; Manaa *et al.*, 2019; Mittersteiner *et al.*, 2020). In that technique, the organic molecule undergoes successive oxidative breakings through a chain reaction initiated with highly reactive radicals, particularly the hydroxyl (·OH) and hydroperoxyl (·OOH). These radicals are promoted by the direct action of solar light or artificial source of UV radiation on the hydrogen peroxide (H_2O_2), a process known as UV-induced peroxidation (UV/H_2O_2). Another way to induce those radicals is to use iron ions (Fe^{2+}, Fe^{3+}) as initiating species, a process, in this case, known as Fenton. The following equations describe an overview of the reactions mentioned (Hsueh *et al.*, 2005; Ioannou *et al.*, 2015; Mofrad *et al.*, 2015; Pouran *et al.*, 2015; Gutierrez-Mata *et al.*, 2017; Vorontsov, 2019).

H_2O_2 photolysis (Equation 1):

$$\mathrm{H_2O_2 + h\nu \rightarrow \cdot OH\ + \cdot OH} \tag{1}$$

Fenton Equations 2 and 3:

$$\mathrm{Fe^{2+}\ +\ H_2O_2\ \rightarrow\ Fe^{3+}\ +\ OH^- + \cdot OH} \qquad \mathrm{k_1\ =\ 76\,Ms^{-1}} \tag{2}$$

$$\mathrm{Fe^{3+}\ +\ H_2O_2\ \rightarrow\ Fe^{2+}\ + \cdot OOH\ +\ H^+} \qquad \mathrm{k_2\ =\ 0.001 - 0.01\,Ms^{-1}} \tag{3}$$

Upon comparing the reaction rate constants (k_1, k_2), it becomes evident that the Fe^{2+} ion is remarkably more active than the Fe^{3+} ion, as a radical promoter of the oxidation process, a fact that unexpectedly brings about a technical drawback. As can be seen in Equation 3, the Fe^{2+} ion is regenerated from the reduction of Fe^{3+} ion. Unfortunately, since $k_2 << k_1$, the regeneration of the most active iron ion is much slower than its consumption rate, leading to a gradual reduction in the Fenton process efficiency over time. Additionally, the pH increase (Equation 2), along with the Fe^{3+} accumulation, might lead to coagulated ferric complexes (Neyens and Baeyens, 2003), which requires na extra solid-liquid separation step or a pH adjustment to the efluente treatment process.

Combination of UV irradiation and the Fenton process (photo-Fenton) is considered a promising alternative to the drawbacks aforementioned, since the radiation allows the direct photolysis of the H_2O_2, as well as na increase in the Fe^{2+} regeneration rates, according to Equation 4, enhancing the overall production rate of hydroxyl radicals.

$$\mathrm{Fe^{3+}\ +\ H_2O\ +\ h\nu\ \rightarrow\ Fe^{2+}\ + \cdot OH\ +\ } H^+ \tag{4}$$

The high reactivity of the radicals from H_2O_2, especially the hydroxyl (·OH), turn them into non-selective and strong oxidants (Gligorovski *et al.*, 2015; Miao *et al.*, 2018), which considerably broadens the application spectrum of the Fenton process and photo-Fenton process. Thus, they are capable of efficiently degrading countless types of organic pollutants, such as pharmaceutical residues (Trovó *et al.*, 2012; Dúran *et al.*, 2013; Ahmed and Chiron, 2014), agricultural defensives (Farré *et al.*, 2006; Zhang and Pagilla, 2010; Monteagudo *et al.*, 2011) and the azo dyes themselves (Barka *et al.*, 2010; Sun *et al.*, 2013; Yu *et al.*, 2010; Mehrdad *et al.*, 2011; Khataee *et al.*, 2016; Leite *et al.*, 2016; Guo *et al.*, 2018; Rubeena *et al.*, 2018). Several of those applications highlight the photo-Fenton capability to obtain high mineralization rates of pollutants, according to Equation 5 (Sun *et al.*, 2009; Idel-aouad *et al.*, 2011; Guimarães *et al.*, 2012; Monteagudo *et al.*, 2014). This vital outcome significantly reduces the environmental impacts from the effluents with a high organic load.

$$\mathrm{R-H\ (org.)} + \cdot\mathrm{OH} \rightarrow \mathrm{H_2O} + \cdot\mathrm{R} \rightarrow \text{further oxidation} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} + \text{mineralization products} \quad (5)$$

As the Fenton process is usually performed in mild conditions and needs simple and low-cost chemicals, it can lead to economically feasible industrial applications. According to the work of Starling *et al.* (2017), the processing cost is estimated somewhere between US$ 0.90 and 2.20 per cubic meter of treated effluent, including the energy costs.

However, it is essential to consider the usually high initial costs with the project and assembly of the reactor. In a global scenario of financial limitations, the first step to achieving an industrial system of effluent treatment that is technically and economically feasible consists of building a versatile and low-cost lab-scale apparatus to research the operating conditions that optimize the pollutant degradation.

In most reported studies, the AOP experiments have been developed in batch systems, usually by adapting glass beakers or Erlenmeyer flasks as reactors (Farré *et al.*, 2006; Bali *et al.*, 2007; Fragoso *et al.*, 2009; Silva *et al.*, 2009; Guimarães *et al.*, 2012; Módenes *et al.*, 2012; Khataee *et al.*, 2016; Starling *et al.,* 2017; Guo *et al.*, 2018; Rubeena *et al.*, 2018; Manaa *et al.*, 2019; Mittersteiner *et al.*, 2020;). Although this alternative is capable of providing essential data for the optimization of operating conditions, the batch reactor is rare when it comes to industrial applications, where processes with flowing streams are much more common. Thus, the advantage of employing a flow photo-reactor in lab experiments is undeniable, even with refluxing streams, since it allows not only an assessment on variables that directly affect the reaction rates but also the hydrodynamic conditions, which can speed up an industrial scale-up.

Hence, primarily focusing on a sustainable and cost-effective approach, the present study had as a first step the design and setup of a continuous annular photo-reactor, employing recyclable materials and adapting low-cost parts, available on the local market. With this reactional apparatus, experiments with three types of advanced oxidation process (UV/H_2O_2, Fenton and photo-Fenton) were carried out in order to compare their effectiveness of decolorizing RB5 dye solutions. Additionally, the chemical kinetics was studied, assessing the effect of the oxidant dosage and dye concentration on degradation rates.

2. MATERIAL AND METHODS

2.1. Chemicals

Reactive Black 5 (RB5, color index 20505, CAS number 17095-24-8) was used in this study as the model of azo textile dye without any further purification process. Its molecular formula is $C_{26}H_{21}O_{19}N_5S_6Na_4$, a molecular weight of 991,82 g mol^{-1}, maximum absorbance wavelength of 597 nm, and water solubility of 200 g L^{-1} at 20°C.

To make the Fenton´s reagent, hydrogen peroxide (H_2O_2, 30% m/m) was used as oxidant agent, purchased from Êxodo Científica (Brazil), and, as the source of ferrous ions (Fe^{2+}), ferrous sulfate heptahydrate ($FeSO_4.7H_2O$, purity 99%) was acquired from Vetec (Brazil). For any pH adjustments, sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) was used as needed.

2.2. Photoreactor Setup

The experimental apparatus was almost entirely designed and constructed in our lab and basically consisted of an annular flow photoreactor (Figure 2, left). This reactor was set up by mounting a UV-C germicidal Hg-lamp (power 30 W) in the center of a cylindrical glass tube 1 m long, a configuration that left a total working volume of 334 mL. The glass tube was externally wrapped with an aluminum foil to prevent the technicians from being exposed to the harmful UV irradiation.

The bottom of two recyclable PET bottles (volume of 2 L each) was transversally cut off to turn them into reservoirs (Figure 2, right), one for the aqueous dye solution and the other one for cooling water. The cooling system is composed of two Liebig condensers with a series connection, working as heat exchangers to maintain temperature during the reaction.

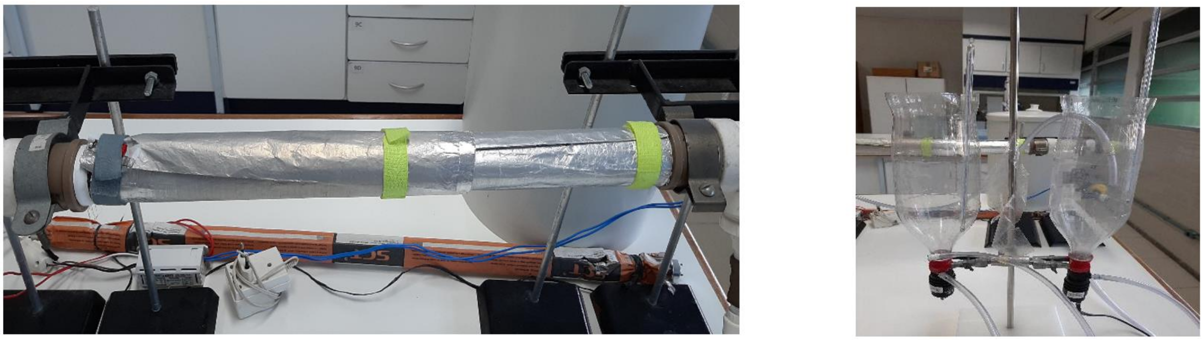


Figure 2. Annular flow photoreactor with the aluminum foil (left) and reservoirs for the dye solution and cooling water (right).

Two windshield washer pumps were purchased from a local auto parts store and adapted to the reservoir outlets to pump the dye solution through the photoreactor and the cooling water through the heat exchangers. A digital power supply (MedTec, Model PS-4000) was used to set the voltage and current appropriately to operate the pumps at a constant volumetric flow rate of $1.5\ 10^{-5}\ m^3\ s^{-1}$.

2.3. Advanced oxidation experiments: efficiency analysis

Before the AOP experiments themselves, various standard RB5 solutions (2 ,4, 10, 20, 50, 80, 100 and 150 mg L^{-1}) were prepared to build the calibration curve that depicts the relationship between the dye concentration and maximum absorbance of its chromophore group, which occurs at the wavelength of 547 nm. A UV-visible spectrophotometer (THERMOSCIENTIFIC, Model EVO 60) was used to measure the absorbances.

To evaluate the effectiveness of the photoreactor towards the color removal of the azo dye RB5, several assays of three types of homogeneous advanced oxidation process were performed: UV-induced peroxidation, Fenton and photo-Fenton process. Photolysis experiments without any oxidant agent were carried out as well.

For all the assays aforementioned, dye solutions 50 mg L^{-1} were prepared by dissolving the RB5 in distilled water. The effect on the color removal of two different concentrations of the hydrogen peroxide (2.45 mg L^{-1} and 24.50 mg L^{-1}) was analyzed. For the Fenton and photo-Fenton experiments, the ferrous sulfate heptahydrate 15.00 mg L^{-1} was dissolved in the dye samples. Their pH was adjusted to 3, by using a solution of H_2SO_4 0.50 mol L^{-1} previously prepared, in order to avoid the coagulation of ferric ions (Fe^{3+}) with the hydroxyl ions (Pignatello *et al.*, 2006).

The UV-induced peroxidation (UV/H_2O_2) was performed at neutral pH. Each one of AOP runs was performed in the photoreactor, keeping the volumetric flow rate at $1.50\ 10^{-5}\ m^3\ s^{-1}$, with the UV-C lamp turned on, except for the Fenton process. Afterwards, all the samples were taken to the UV-visible spectrophotometer to read the absorbance at the characteristic wavelength (547 nm), then the final concentrations were obtained by using the calibration curve.

The efficiency of each treatment on color removal was calculated as follows (Equation 6), where C_0 and C denote, respectively, the initial azo dye concentration and its concentration at a given time.

$$Efficiency\ (\%) = \frac{(C_0 - C)}{C_0}\ x\ 100 \tag{6}$$

The AOP at the highest ratio [oxidant]:[RB5] that led to the most efficient color removal was chosen to investigate the residual hydrogen peroxide, by using permanganate titration in acidic medium (Tzanov *et al.*, 2002). Moreover, the acidity effect on the dye degradation profile was evaluated at two different pHs, one slightly lower (pH=2) and the other higher (pH=4) than the value set for all experiments.

2.4. Kinetics analysis of AOPs

The kinetic profiles of the color removal were obtained for the Fenton, photo-Fenton, and UV/H_2O_2 processes, performing experiments with the following initial azo dye concentrations: 25, 50 and 100 mg L^{-1}.

For each run, the effluent reservoir was loaded with 1 L of the dye solution and enough oxidant solution to provide 24.5 mg of H_2O_2 ($[H_2O_2]$ = 0.720 mM). Moreover, 15 mg $FeSO_4.7H_2O$ was dissolved for the Fenton and photo-Fenton assays, corresponding to a concentration of 0.054 mM for the ferrous ion (Fe^{2+}). The UV lamp and pumps were turned on simultaneously, allowing the dye solution to be exposed to the UV irradiation, except for the Fenton process, which takes place in a completely dark environment. During the reaction, effluent aliquots were collected from the reservoir, at predefined time intervals, then their absorbances were immediately measured by the UV-vis spectrophotometer.

The pseudo-first-order and pseudo-second-order kinetic models (Equations 7 and 8) were employed to check, through linear regression, which one better fits the actual degradation profiles of the dye over the reaction time. In Equations 7 and 8, C_0, C and k denote the initial concentration of the dye, its concentration at a given time t, and the apparent rate constant, respectively.

$$Ln\left(\frac{C_0}{C}\right) = kt \qquad (pseudo - first - order\ model) \tag{7}$$

$$\frac{1}{C} - \frac{1}{C_0} = kt \qquad (pseudo - second - order\ model) \tag{8}$$

3. RESULTS AND DISCUSSIONS

In this study, a low-cost annular photoreactor was built to develop and study several degradation processes of the RB5 azo dye. The efficiencies of four techniques were investigated (UV photolysis, UV/H_2O_2, Fenton, and photo-Fenton), using three initial concentrations of dye (25, 50, 100 mg L^{-1}). Two different dosages of H_2O_2 were used (2.45 mg L^{-1} and 24.5 mg L^{-1}) to investigate the oxidant effect on the advanced oxidation processes. The kinetic modeling of the RB5 decolorization by Fenton and photo-Fenton treatments was also studied and reported.

3.1. Efficiency comparison between UV/H_2O_2 and photolysis

First, to bring up an overview on the role played by the presence of the oxidant on the degradation of the dye, the efficiency of the lone action of the UV irradiation (photolysis) was compared to the combination of UV with H_2O_2 (UV-induced peroxidation), performing the experiments with a specific set of initial concentrations ([RB5] = 50 mg L^{-1}, $[H_2O_2]$ = 24.5 mg L^{-1}) at neutral pH.

As can be seen in Figure 3, after a long 90-min. run, the dye degradation by photolysis was quite low, roughly 22%, an expected result (Lizama *et al.*, 2002; Elmorsi *et al.*, 2010), since no oxidant nor catalyst was employed. The degradation rate notably improves with the H_2O_2, as this oxidant generates highly reactive radicals (·OH) under the action of UV photons. As a result, those species promote fast successive bond breakings, generating other intermediate radicals through a complex mechanism that can lead to the mineralization of most organic fragments (Shu and Chang, 2005; Elmorsi *et al.*, 2010). Figure 3 shows the complete removal of the dye color by the UV/H_2O_2 process after the same 90-min. run. Although this time interval seems long, it is important to highlight that the UV/H_2O_2 process required approximately 30 min. to bleach more than 90% of the dye.

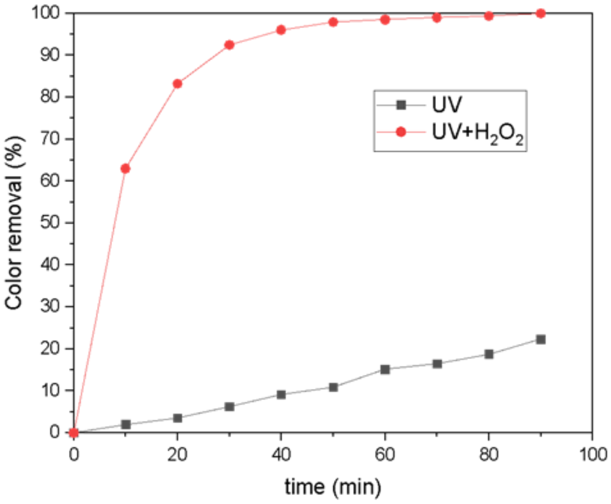


Figure 3. Color removal of the RB5 dye by the UV photolysis and UV/H_2O_2. Initial concentrations: [RB5] = 50 mg L^{-1}, [H_2O_2] = 24.5 mg L^{-1}.

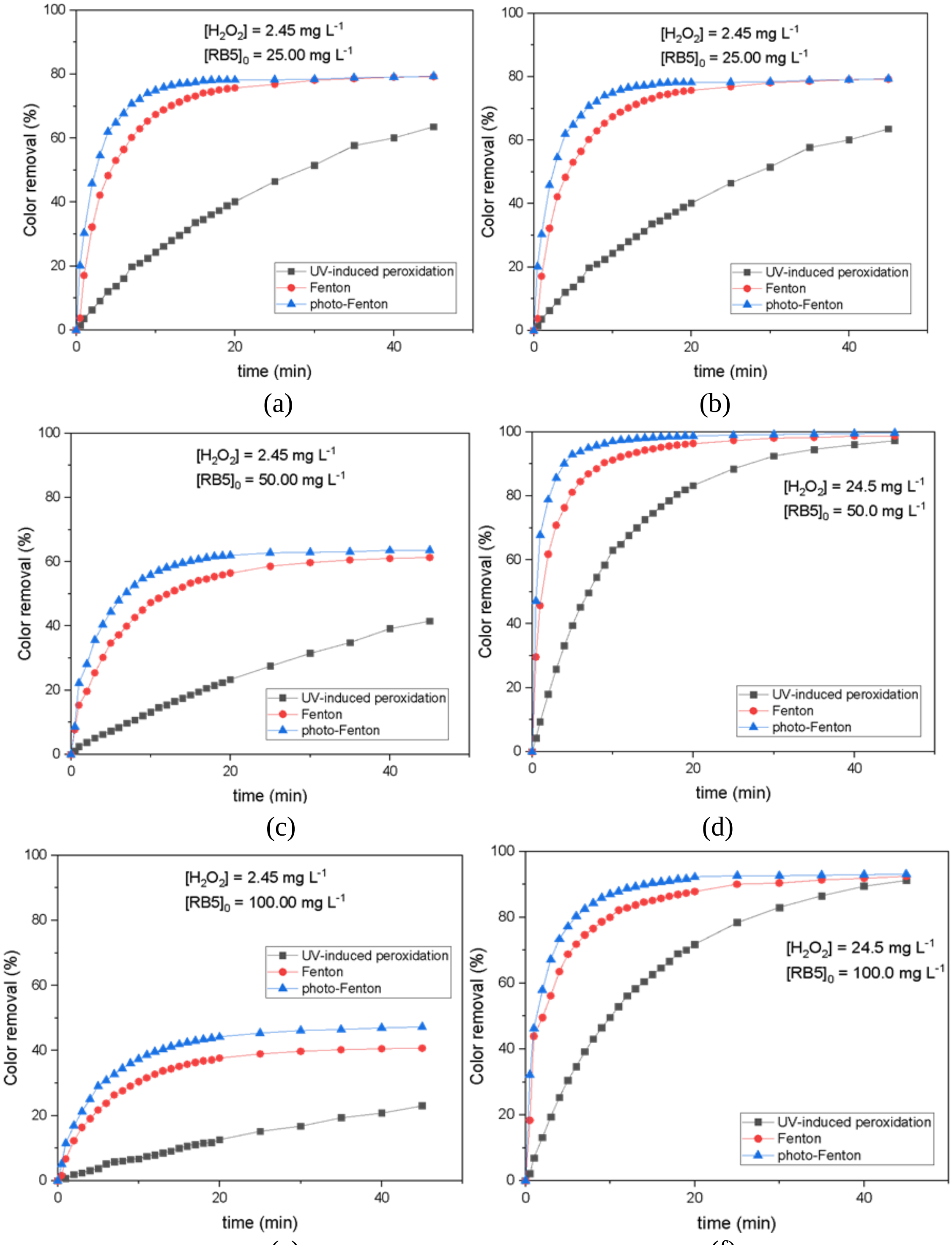
3.2. Efficiency of the advanced oxidation processes

The results of the three advanced oxidation processes on the decolorization of RB5 are depicted in Figure 4. The effect of the initial concentrations of dye and oxidant dosages on the degradation profile can also be analyzed. Upon a quick comparison between the three processes, it becomes evident, as expected, that the photo-Fenton turns out to be the most efficient and fastest on the color removal of RB5 in all initial operating conditions employed in this study.

The lowest oxidant dosage (2.45 mg L^{-1}) appears inadequate to bleach the dye dissolved completely in the studied solutions (25, 50, 100 mg L^{-1}). In this case, naturally, the best result occurs with the highest ratio [H_2O_2]:[RB5], where a maximum degradation of 79% is reached by the Fenton and photo-Fenton treatments, and 63% by UV/H_2O_2 process (Figure 4 (a)).

By observing all the graphics in Figure 4, the slope of the curves clearly demonstrates that the higher [H_2O_2]:[RB5] ratio, the higher degradation rate of the azo dye, regardless of the type of treatment used. The best scenario for the dye degradation emerges, as shown in Figure 5 (b), when the highest oxidant dosage (24.5 mg L^{-1}) and lowest dye concentration (25 mg L^{-1}) are used. With this initial set of concentrations, the most efficient treatment, photo-Fenton, was capable of a complete color removal after only 10 min. The dark Fenton and UV/H_2O_2 treatments were less efficient, requiring approximately 25-min. and 45-min. run, respectively, to bleach the solution entirely. Furthermore, higher dye loads make its degradation even lower, an outcome that can be explained by the shallow penetration of the UV photons into the solution with high intense color (Behnajady *et al.*, 2004).

In each one of the graphics (Figure 4), a comparison between the three treatments demonstrated that the degradation promoted by the UV/H_2O_2 is clearly slower than the one achieved by the Fenton and photo-Fenton processes, which suggests that the ferrous ions play an essential role in the generation of H_2O_2-derived radicals. As expected, the highest degradation rate of the azo dye occurs when the ferrous ions are combined with the UV irradiation, since it increases the generation of those radicals (Neamtu *et al.*, 2003).



(a) (b)

(c) (d)

(e) (f)

Figure 4. Decolorization profile of the RB5 dye by UV/H_2O_2, Fenton and photo-Fenton treatments with respect to initial dye concentration and oxidant dosage.

For comparison purposes, Table 1 presents an overview of the AOP performances on the dye color removal at some reaction times, using the highest oxidant dosage ($[H_2O_2] = 24.5$ mg L^{-1}).

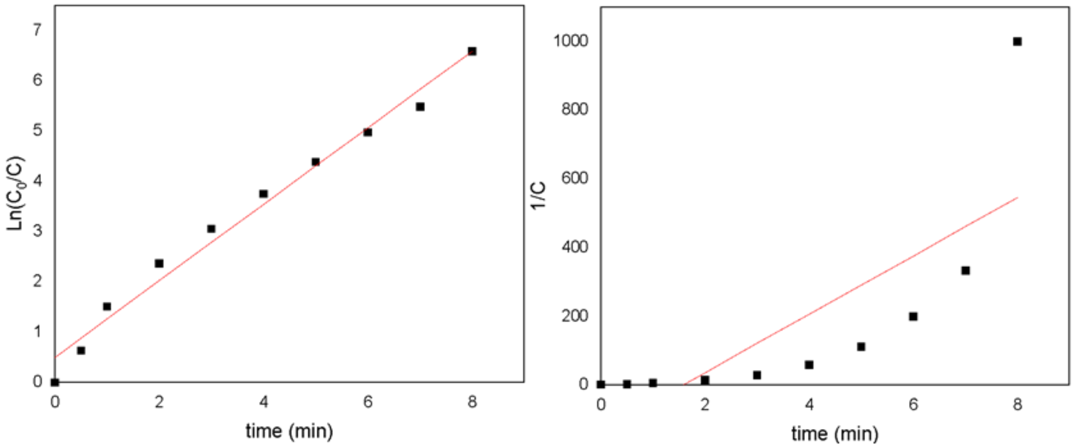


Figure 5. Kinetic profile of the RB5 degradation by the photo-Fenton treatment ($[H_2O_2]$ = 24.5 mg L^{-1}, [RB5] = 25 mg L^{-1}). Pseudo-first-order fitting (left) and Pseudo-second-order fitting (right).

Table 1. RB5 color removal by the UV/H_2O_2, Fenton and photo-Fenton processes using the initial oxidant dosage of 24.5 mg L^{-1}.

[RB5] (mg L^{-1})	Dye color removal (%)			
	Reaction time (min)	UV/H_2O_2	Fenton process	Photo-Fenton process
25	5	47.2	92.2	98.7
	10	76.6	97.8	100
	30	98.8	99.8	100
50	5	39.4	81.1	92.4
	10	63.0	91.2	
	30	92.5	98.0	99.2
100	5	30.5	68.8	77.2
	10	49.6	79.9	87.0
	30	83.0	90.4	92.7

The results described in some similar previous studies found in the literature can corroborate the promising aspects of the continuous photo-reactor developed in the presented work. For instance, Silva *et al.* (2009) carried out several photo-Fenton experiments to degrade the RB5 in a batch reactor, testing out, among other operational conditions, three different reaction times (40 min., 50 min., 60 min.). In the shortest run (40 min.), complete dye removal was only reached when the concentration ratio was $[H_2O_2]$:[RB5] = 150 mg L^{-1}:100 mg L^{-1}, slightly higher than the best concentration set used in our work ($[H_2O_2]$:[RB5] = 24.5 mg L^{-1}:25 mg L^{-1}). In another AOP work, now using a flow photo-reactor, Leite *et al.* (2016) developed studies of degradation of the dispersed red 1 (DR1) dye, also by the UV-Fenton process. In this work, a 45-min. run was required to reduce the dye concentration from 23 mg L^{-1} to 0.4 mg L^{-1} (98.2% removal) with a high oxidant concentration of 170 mg L^{-1}. In the Miao *et al.* (2018) study, a heterogeneous photo-Fenton system, with α-FeOOH as the catalyst, was used to study Orange II dye color removal. With the initial concentrations of the oxidant and dye set at 340 mg L^{-1} and 70 mg L^{-1}, respectively, color removal of 99.7% was obtained in 30-min. reaction. In comparison to the instances above and other previous works (Barka *et al.*, 2010; Belayachi *et al.*, 2019), the results presented in Table 1 demonstrate more rapid dye degradation rates, particularly by the photo-Fenton process, despite using a lower ratio [oxidant]:[dye] than the ones set in those works. This comparison suggests that the continuous photo-reactor, set-up and used in our work, notably allowed an improvement in color removal efficiency and, thus, this low-cost apparatus can be considered as a promising alternative towards a feasible treatment of textile pollutants.

The results of the residual hydrogen peroxide for the best treatment (photo-Fenton) and ratio [H_2O_2]:[RB5] = 24.5 mg L^{-1}:25 mg L^{-1} are presented in Table 2.

Table 2. Residual hydrogen peroxide for the photo-Fenton process with ratio [H_2O_2]:[RB5] = 24.5 mg L^{-1}:25 mg L^{-1}.

Reaction time (min.)	[H_2O_2] (mg L^{-1})	Residual percentage
0	24.5	100.0
45	3.4	13.9
90	2.0	8.2

The residual concentration of hydrogen peroxide, higher than 10%, even after 45 min. of photo-Fenton reaction, indicates that a much lower oxidant dosage would have been needed if the only goal of the treatment was the RB5 color removal. Actually, it is well known that the color of a dye emerges from a structure based on the resonance of highly conjugated π-electrons, and, therefore, a simple cleavage of the azo bonds (- N = N -), turning the RB5 into smaller fragments, would cease this extended resonance and accomplish the effluent decolorization. However, besides the color removal, other issues are likewise crucial for appropriate effluent treatment, such as the aromatic chemicals´ degradation. The slight drop of the hydrogen peroxide concentration, from 3.4 mg L^{-1} to 2.0 mg L^{-1}, between 45 min. and 90 min. of reaction, significantly later than the complete color removal (10 min.), demonstrates few oxidable organic compounds remained in the system after 45 min. However, further analysis should be essential to corroborate this outcome, such as total organic chemical (TOC) analysis.

3.3. Kinetic modelling

Graphics of - $ln(C_0/C)$ and $1/C$ versus time were plotted, and their linearization coefficients (R^2) were calculated to compare the ability of pseudo-first-order and pseudo-second-order kinetic models in fitting the experimental results of dye degradation. The most efficient operating condition, which was the photo-Fenton process with the highest ratio [H_2O_2]/[RB5] ([H_2O_2] = 24.5 mg L^{-1}; [RB5] = 25 mg L^{-1}), was chosen to analyze the kinetic modelling of the degradation profile. The temperature was kept constant at 20°C.

As shown in Figure 5, the pseudo-first-order kinetic fits the RB5 degradation appropriately, which can be confirmed by its high linearization coefficient ($R^2 = 0.98$). The rate constant and half-life are shown in the Table 3 for this pseudo-first-order degradation. The same conclusion is reported by several other studies in the literature (Shuai *et al.*, 2018; Manaa *et al.*, 2019). On the other hand, the pseudo-second-order kinetic is remarkably inadequate to fit the experimental results ($R^2 = 0.54$).

Table 3. Kinetic parameters of the pseudo-first-order modelling for the dye degradation by the photo-Fenton treatment ([H_2O_2] = 24.5 mg L^{-1}; [RB5] = 25 mg L^{-1}).

Parameter	Value
Rate constant (k)	0.76 min^{-1}
Half-life ($t_{1/2}$)	0.91 min

3.4. Effect of the initial pH

Three different acidic pHs (2, 3, and 4) were chosen to investigate its effect on color removal of the photo-Fenton treatment. Higher pHs can bring about the complexation of insoluble ferric hydroxides, which hinders the crucial reaction between ferrous ions (Fe^{2+}) and H_2O_2. As a result, the concentration of hydroxyl radicals is reduced (Sun *et al.*, 2009). Furthermore, this coagulation is likely to clog the pumps, which decreases the flow rate and eventually damages them. Figure 6 depicts the decolorization efficiency at 3 min., 5 min., and 10 min. of reaction for the three chosen pHs. All the experiments were carried out with the highest ratio [oxidant]:[RB5].

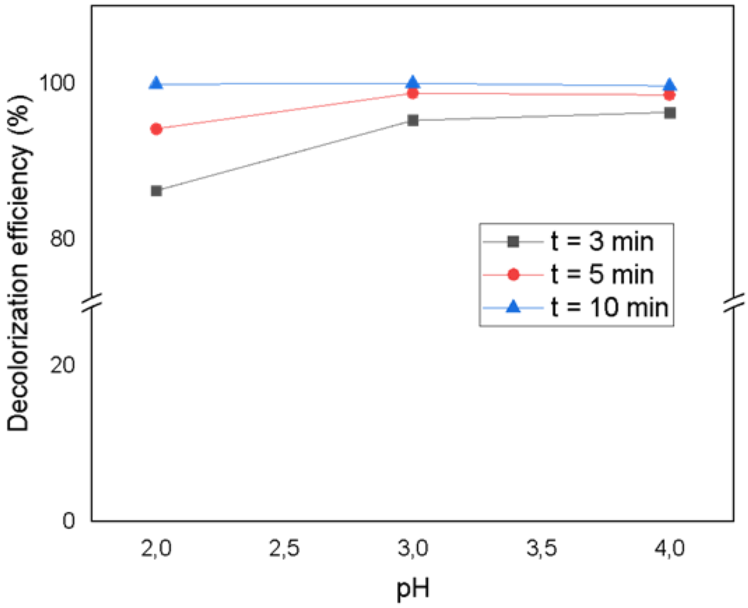


Figure 6. Effect of initial pH on the color removal of RB5 by photo-Fenton process. $[H_2O_2]$:[RB5] = 24.5 mg L^{-1}: 25 mg L^{-1}.

The results showed that pH had an insignificant effect on the time required for complete color removal of RB5, which was nearly 10 min. of reaction in the three acidic conditions. The only notable effect of the pH on the decolorization arose within the first 3-min. reaction when the most acidic condition (pH=2) led to 86% efficiency. In contrast, the pHs of 3 and 4 led to higher decolorization degrees, 95% and 96%, respectively. After 5-min. reaction, the decolorization efficiency reached 94% in the most acidic condition, in this case slightly closer to the results at the other studied pHs (99%). Based on similar reported studies (Sun *et al.*, 2009; Elmorsi *et al.*, 2010; Liu *et al.*, 2011), the pH that maximizes the degradation rates ranges between 3 and 4. Moreover, those studies demonstrated the dye degradation appears to slow at very low pHs. According to Xu *et al.* (2004), pH < 2.5 increases the concentration of the ferrous hexaaqua complex, $[Fe(H_2O)_6]^{2+}$, which is less active than the $[Fe(OH)(H_2O)_5]^{+}$ complex towards the hydroxyl radicals generation. Therefore, the overall oxidation is retarded.

3.5. EE/O analysis

In order to estimate the cost-effectiveness with electricity of our oxidative system towards RB5 color removal, the electrical energy per order (EE/O) was calculated for the UV/H_2O_2 and photo-Fenton processes, and the results are presented in Table 4. EE/O is defined as the electric energy required to degrade one order of magnitude of the textile pollutant in one cubic meter of effluent, and it can be calculated according to the following Equation 9 (Nikravesh *et al.*, 2020).

$$\frac{EE}{O} = \frac{P.t.1000}{60.V.log\left(\frac{C_0}{C}\right)} \tag{9}$$

Where P is the power (kW) of UV lamp, V is the volume (L) of effluent, t is reaction time (min), C_0 and C are initial and final concentrations of RB5.

Table 4. EE/O for RB5 color removal by the UV/H_2O_2 and photo-Fenton processes ([H_2O_2] = 24.5 mg L^{-1}).

	EE/O (kWh m^{-3} $order^{-1}$)	
[RB5] (mg L^{-1})	UV/H_2O_2	Photo-Fenton
25	7.5	1.0
50	13.5	2.0
100	21.0	7.5

As expected, the photo-Fenton process with the highest ratio [oxidant]:[RB5] stands out as the most effective treatment in the matter of energy cost, with the lowest EE/O of 1.0 kWh m^{-3} $order^{-1}$. Additionally, Table 4 corroborates the crucial role played by ferrous ions on the degradation rates, since without them, in the UV/H_2O_2 treatment, the cost with electricity might be 7.5 times higher to achieve the same degradation degree, depending on the initial concentrations.

The EE/O was not reported for the experiments with the lowest oxidant dosage ([H_2O_2] = 2.45 mg L^{-1}), because with this initial condition, the processes were unable to reach 90% color removal within the total reaction time, as can be observed in Figure 4.

4. CONCLUSIONS

The presented work aimed to design and build a sustainable experimental apparatus for performing advanced oxidation processes (AOPs), adapting low-cost parts and recyclable materials. Several experiments were performed with this annular flow photo-reactor for color removal of dye RB5, using three types of AOP, namely UV-induced peroxidation, Fenton, and photo-Fenton process. The effect of the dye load and oxidant (H_2O_2) concentration on the degradation efficiency was evaluated. As expected, the combination of Fe^{2+} ions and UV photons to generate more hydroxyl radicals made the photo-Fenton process the most effective treatment, regardless of the set of initial concentrations. For instance, for the highest ratio [H_2O_2]:[RB5] (24.5 mg L^{-1}: 25 mg L^{-1}), the photo-Fenton was capable of bleaching entirely the dye solution within only 10 minutes, whereas the Fenton and UV/H_2O_2 processes required 25 min. and 45 min., respectively.

The pH study showed that the high decolorization efficiency by the photo-Fenton process was not impacted by switching the pH from 3 to 4. The most acidic condition (pH=2) slightly slowed down the degradation rate, although it can be considered high, with 86% of color removal achieved within only a 3 min. reaction. Naturally, from a cost-wise point of view, the pH of 4 should be chosen for further studies with photo-Fenton treatment, since closer pHs to neutral conditions allows lower acid-base consumption for appropriate treatment and disposal of the effluent.

It is crucial to point out that the lower the ratio [H_2O_2]:[RB5], the lower the degradation efficiency in all types of AOPs evaluated in this work. For the lowest ratio ([H_2O_2]:[RB5] = 2.45 mg L^{-1}: 100 mg L^{-1}), none of the treatments were capable of complete color removal. Even the photo-Fenton process only led to a degradation of roughly 47% after 45 minutes.

As long as the adequate oxidant concentration is set for a given pollutant load, those results demonstrated that the non-expensive photo-reactor, built in this work, proved to be a propitious system for textile effluent treatments. Especially when the photo-Fenton process is employed, notable decolorization rates were accomplished.

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