

Degradation and kinetic study of Reactive blue BF-5G and Remazol red RB 133% dyes using Fenton and photo-Fenton process

Degradação e estudo cinético dos corantes Azul reativo BF-5G e Remazol vermelho RB 133% empregando processos Fenton e foto-Fenton

¹Rayany Magali da Rocha Santana, ²Graziele Elisandra do Nascimento, ²Daniella Carla Napoleão e ²Marta Maria Menezes Bezerra Duarte

¹Centro Universitário Maurício de Nassau, Brasil
rayanymagalirocha@gmail.com

²Universidade Federal de Pernambuco, Brasil
grazieleen@yahoo.com.br; danicarlan@gmail.com; mmmmbduarte@gmail.com

Abstract

The textile industry is responsible for the generation of highly colored effluents, which need adequate treatment. Thus, the advanced oxidative processes (AOP) have been used to degrade the dye and convert organic matter. In the present study, the degradation of the reactive blue dyes BF-5G and red remazol RB 133% were evaluated through Fenton and photo-Fenton processes (solar and sunlight). To determine the best working condition, the pH, peroxide concentration, iron concentration and time variables were evaluated by performing a kinetic study in this condition. From a preliminary study, it was verified that the Fenton and photo-Fenton processes, using different radiations, presented similar results, reaching a degradation of more than 98% for each dye. The factorial design indicated better results for a concentration of H₂O₂ of 10 mg · L⁻¹, iron concentration of 5 mg · L⁻¹ and time of 15 min, obtaining degradation above 88% for the studied dyes. A good kinetic adjustment was verified for a pseudo first order kinetic model (R² = 0.9921 and 0.9867 for blue and red dyes, respectively). Ultimately, the study of chemical oxygen demand indicated a conversion of 75.98% for the Fenton process, 86.63% photo-Fenton solar and 87.02% photo-Fenton sunlight.

Keywords: Textile dyes; Chemical oxygen demand; Photo-Fenton

Resumo

A indústria têxtil é responsável pela geração de efluentes com alta coloração, que precisam de tratamento adequado. Nesse sentido, os processos oxidativos avançados (POA) têm sido empregados para degradar o corante e converter a matéria orgânica. No presente trabalho avaliou-se a degradação dos corantes azul reativo BF-5G e remazol vermelho RB 133% via processos Fenton, foto-Fenton (solar e sunlight). Para identificação da melhor condição de trabalho foram avaliadas as variáveis pH, concentração de peróxido, concentração de ferro e tempo; sendo realizado estudo cinético nesta condição. A partir de um estudo preliminar verificou-se que os processos Fenton e foto-Fenton, empregando diferentes radiações, apresentaram resultados semelhantes, alcançando uma degradação superior a 98% para cada corante. O planejamento fatorial indicou melhores resultados para uma concentração de H₂O₂ de 10 mg·L⁻¹, concentração de ferro de 5 mg·L⁻¹ e tempo de 15 min, obtendo degradação acima de 88% para os corantes estudados. Um bom ajuste cinético foi verificado para um modelo cinético de pseudo primeira ordem (R² = 0,9921 e 0,9867 para os corantes azul e vermelho, respectivamente). Por fim, o estudo da demanda química de oxigênio indicou uma conversão de 75,98% para o processo Fenton, 86,63% foto-Fenton solar e 87,02% foto-Fenton sunlight.

Palavras-chave: Corantes têxteis; Demanda química de oxigênio; Foto-Fenton

INTRODUCTION

Since 21st century, the development of industrial activities became increasingly more evident, with the textile industry being the main generator of such growth (BAËTA et al, 2012). Nevertheless, alongside its beneficial contribution to modern life, this industrial process is also characterised as a considerable responsible agent of environmental contamination (CERQUEIRA; RUSSO; MARQUES, 2009).

Textile effluent presents a heterogeneous composition, with high concentrations of toxic material, mainly organic compounds in the form of dyes. Accordingly, this type of effluent is characterised for its low biodegradability and relative toxicity (ALI; HAMEED, AHMED, 2009).

Dyes play an important role in the textile industries, being the source of colour in the tinging process, which can either ensure the commercial success or failure of the industrial business (GUARATINI; ZANONI, 2000). Among the different types of dyes used in this field, it is important to highlight the reactive used for colouring fabrics such as jeans, increasing its luster, solidity and uniformity throughout the application process (CERVELIN, 2010).

However, such tinging process is considered as responsible for generating large volumes of effluents, consisting of high amounts of organic matter and pigments. These adverse effects have been solved by using different methodologies, namely: coagulation, flocculation, enzymatic catalysis and nanofiltration (KHOUNI et al, 2011). Conversely, due to the chemical structure of dyes used in the industry, the conventional processes, as well as the processes mentioned, are not always seen as effective in the treatment of matrices containing such substances, leading to an ongoing search for the development of effective and economical alternatives (LIMA; ALMEIDA; PAULA, 2016).

Therefore, the efficiency of the advanced oxidation processes (AOPs) has been further evaluated. These processes are considered capable of promoting the degradation and mineralisation of persistent and refractory pollutants by using an oxidant source and/or catalysts (ARAÚJO; YOKOYAMA; TEIXEIRA, 2006). Among the AOPs employed, are photolysis, Fenton and the photo-Fenton processes, UV/H₂O₂ action and heterogeneous photocatalysis. This treatment technique acts in the degradation of the different class of compounds, such as: pharmaceuticals (NAPOLEÃO et al, 2015; SERPONE et al, 2017), dyes (SALGADO et al, 2009; BILÍNSKA; GMUREK; LEDAKOWICZ, 2017), phenolic compounds (ZAIDAN et al, 2016), polycyclic aromatic hydrocarbons (ROCHA et al, 2014), among others.

Although the POAs use different reaction systems, the processes involve the generation of hydroperoxyl radicals (HO₂•), superoxide radicals (O₂•-) and, mainly, hydroxylic radicals (HO•), the latter being highly oxidizing and non-selective (2.80 V). In order to ensure the release of the last radical, a strong oxidizing agent is used in the various POAs, being the most used the hydrogen peroxide (H₂O₂). Under UV radiation, the H₂O₂ molecule breaks down, generating hydroxyl radicals capable of promoting oxidation of the organic pollutant, whose decomposition is described in Equation 1 (KATSUMATA, 2014; VILAR et al, 2017). For a better comprehension of the UV radiation effect on a hydrogen peroxide decomposition, the Haber-Weiss mechanism must be understood, which is described by Equations 2 to 7 (OPPENLÄNDER, 2003 apud KATSUMATA, 2014).





Global reaction



The process that combines the Fenton reaction with UV radiation is named photo-Fenton, occurring a photochemical decomposition of H_2O_2 . The photo-Fenton is one of the most used technique to generate hydroxyl radicals, once the photochemical regeneration of Fe^{2+} ions through the reduction of Fe^{3+} ions, resulting in an increase of organic compounds degradation capacity, as can be verified in Equation 8 (MELO et al., 2009, KATSUMATA, 2014).



The degradation of organic compounds via Fenton reaction occurs through the hydrogen peroxide decomposition into hydroxyl radicals in acidic environment with the presence of Fe^{2+} , according Equation 9. In this process, the hydrogen peroxide induces the oxidation of ferrous ion to ferric ion caused by its decomposition.



In this case, the organic substances present in the pollutant load will be oxidized by reacting with hydroxyl radicals formed. The description of this step of the process can be described according the Equation 10.



The UV/ H_2O_2 action and photo-Fenton processes have been notable for their combination of ultraviolet radiation (UV) and hydrogen peroxide in the presence/absence of iron ions. On the other hand, the Fenton process is considered more economically viable, as it does not use UV radiation. Regarding the efficiency of the AOPs in the degradation of aqueous dyes, various studies have been carried out. When analysing indigo carmine and combo red azo, researchers achieved a discolouration rate of 99% using the Fenton and UV/ H_2O_2 processes (SALGADO et al, 2009), as well as for Drimarene Blue XGN-150 and Drimarene Red X-6BN 150, reaching a degradation rate higher than 99% (ZAIDAN et al, 2016). Regarding the Reactive Blue BF-5G dye, a discoloration rate higher above 91% was noted (LIMA; ALMEIDA; PAULA, 2016), also when using UV/ H_2O_2 action; finally, for the Remazol black B, a 99.92% degradation rate was observed when using the Fenton process (SILVA; BARROS NETO; SILVA, 2009).

Experimental design techniques have been used in order to evaluate the best operating conditions of different processes, either in the degradation or removal of contaminants. Fernandes et al (2016) in this study an experimental design was used for evaluating the adsorption process of blue methylene dye when using nut coal, while Napoleão et al (2015) using design of experiments tools for evaluating the variables that directly influence the degradation of the Paracetamol pharmaceutical when employing advanced oxidation processes.

Thus, this present work was aimed at evaluating the degradation of an aqueous solution of Reactive Blue BF-5G and Remazol Red RB 133% textile dyes, using advanced oxidation processes: photolysis, UV/ H_2O_2 , Fenton and photo-Fenton processes; therefore, defining the best operating conditions for the levels studied, monitoring the process by using ultraviolet-visible and chemical oxygen demand analyses.

MATERIAL AND METHODS

WORKING SOLUTION

The matrix used in this study consists of an aqueous solution containing Reactive Blue BF-5G and Remazol Red RB 133% textile dyes (Figure 1a and 1b), at a concentration of approximately 50mg.L⁻¹ each. Both have in their structure the azo chromophore, from the class of reactive dyes, having been supplied by the company DyStar.

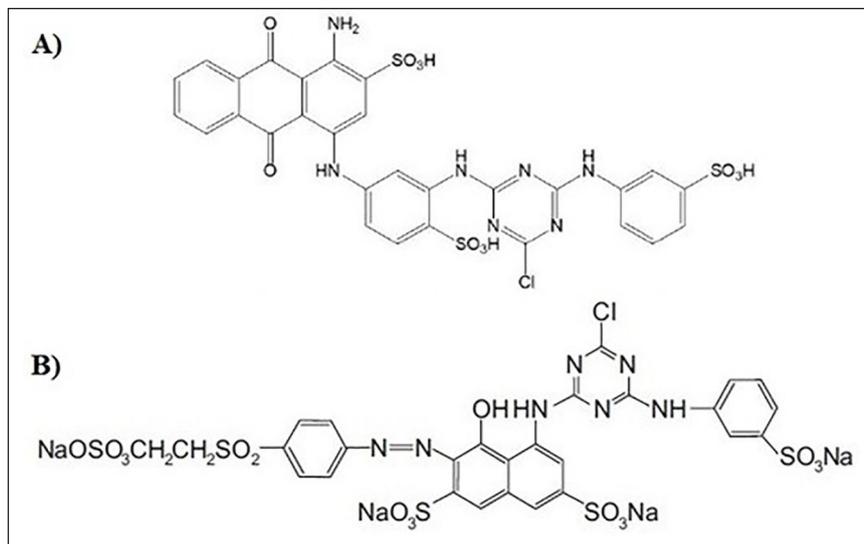


Figure 1 - Structures of dyes a) blue reactive BF-5G and b) remazol red 133%.
Source: FIORENTIN (2010); CATANHO; MALPASS; MOTHEO (2006).

For determining the wavelength of maximum absorbance for each of the two dyes used, an ultraviolet-visible spectrophotometer equipment (Thermoscientific, Genesys 10S model) for a wavelength range between 190 and 1100 nm was used. The quantification of the compounds before and after the degradation process was carried by drawing analytic curves, with a linear concentration range from 2 to 100 mg.L⁻¹, with a stock solution of 100 mg.L⁻¹.

PRELIMINARY STUDY

The preliminary study trials were carried out under the following conditions: iron concentration ([Iron]) = 5 mg.L⁻¹; hydrogen peroxide concentration ([H₂O₂]) = 150 mg.L⁻¹ (according to stoichiometry determination), with no pH adjustments (between 5 and 6) and a time of 20mins. In order to identify the best process to be employed, different types of advanced oxidation processes (AOPs) were tested: photolysis, Fenton and photo-Fenton processes and UV/H₂O₂ action. For the degradation trials of the aqueous solution containing the dyes, the samples were submitted to solar radiation and to a sunlight system. This system consisted of an UV lamp (300W) in a wooden-box reactor, as observed from Figure 2. For each case, the photon emission was measured using a radiometer (Empóronet)

In order to ensure that no interference of H₂O₂ and iron in the analysis carried out in the UV-Vis spectrophotometer, sweeps were performed in the wavelength range of 190 to 900 nm, considering the possible interferents (water, water/H₂O₂/Fe (in form of ferrous sulfate heptahydrate)), as well as the solution containing the dyes and the latter containing reactants.

EVALUATION OF THE CONCENTRATION OF HYDROGEN PEROXIDE

Previous studies carried out by the research group from Laboratório de Engenharia Ambiental e da Qualidade (LEAQ/UFPE) indicated that the [H₂O₂] established by the stoichiometry of the reaction was in surplus for the AOPs studied. Thus, further trials were carried out in order to determine the ideal concentration of H₂O₂ to be used, setting [Iron] (5 mg.L⁻¹), time (20 min) and pH (natural solution, between 5 and 6). The 30% hydrogen peroxide v/v (Química Moderna) used in this study was properly standardised.

RESULTS AND DISCUSSION

WORKING SOLUTION

For the identification of the dyes in study, the wavelengths of maximum absorbance were determined, having been verified: a) $\lambda = 621$ nm for the Reactive Blue BF-5G and b) $\lambda = 515$ nm for the Remazol Red RB 133%. According Lima et al. (2016) these two wavelength correspond to azo groups, typical of this type of dye. In Figure 3 can be observed the peaks for each of the dyes analyzed, considering the absorbance (Figure 3a) and its logarithm (Figure 3b).

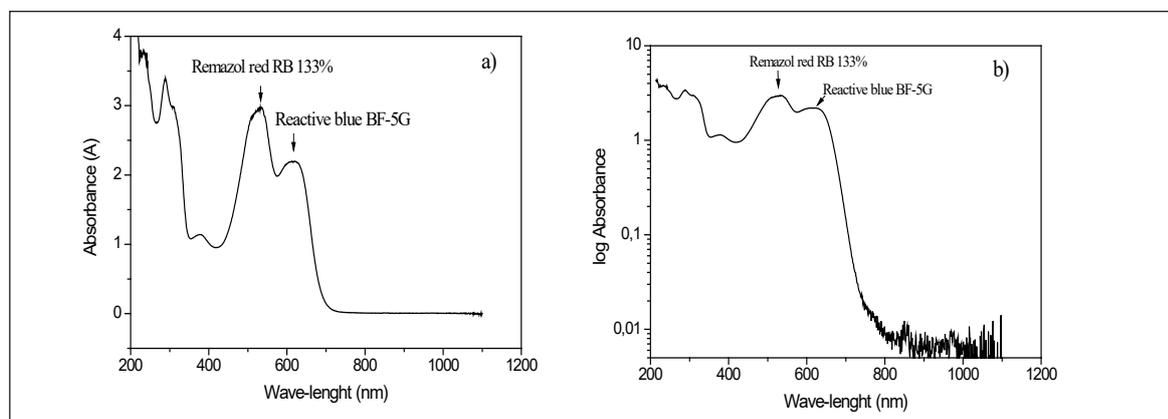


Figure 3 – UV-Spectrum of dyes. a) absorbance versus wave-length and b) log absorbance versus wave-length

Afterwards, analytic curves were drawn (2 to 100 mg·L⁻¹), determining the equation for the curve in each case: reactive blue BF-5G (Equation 11) and remazol red RB 133% (Equation 12).

$$y = 0,0226249 \cdot x \quad (11)$$

$$y = 0,0275194 \cdot x \quad (12)$$

Based on the equations of the curves, the linear correlation coefficient (r) was determined, being equal to 0.999 for both dyes. These values indicate a linearity of the curve, as r should be higher than 0.995 (INMETRO 2011). Subsequently, the limit of detection (LOD) was determined for each of the curves, based on the reading of ten times the lowest point in the curve, according to Equation 13, and the limit of quantification (LOQ), according to Equation 14.

$$LD = X_m + t(n-1, 1-\alpha) \cdot S \quad (13)$$

$$LQ = X_m + 10s \quad (14)$$

In which X_m is the average between the values of the sample banks, t is the Student distribution dependant on the sample size and the confidence level, and s is the standard deviation estimation of the blank assays. Thus, a value of 0.03 for the LOD was observed for both dyes. As for LOQ, the results were of 0.16 and 0.15 for the reactive blue and BF-5G and remazol red RB 133% dyes, respectively.

PRELIMINARY STUDY

A preliminary study was subsequently carried out, employing the conditions mentioned in item 2.2. It is worth mentioning that the sunlight reactor presented a photo emission rate of 4×10^6 W·m⁻², while for the process using solar radiation, the emission rate varied from 2.06×10^4 to 12.16×10^4 W·m⁻². Thus, it was possible to evaluate the efficiency of the different oxidative processes employed, as a function of the percentage of degradation of the dyes studied. It was verified that the photolysis process, using both solar radiation and sunlight reactor, did not promote the degradation of any of the dyes. However, the UV/H₂O₂ process degraded only 6.1% of the blue dye, also failed to degrade the red dye.

The best results were observed for those processes employing iron (Fenton and photo-Fenton), which presented similar values of degradation percentages: Fenton (99.4% for blue and 99.2% for red); solar photo-Fenton (99.6% for blue and 99.7% for red) and sunlight photo-Fenton (98.3% for blue and 99.1% for red).

This is due to the fact that concentrations of the dyes after being submitted to the AOP were below the LOD; with a more detailed study being therefore carried out for both processes. It was also observed that the reagents used in the AOP do not interfere with the analyses performed on the UV-Vis spectrophotometer as can be observed in Figure 4.

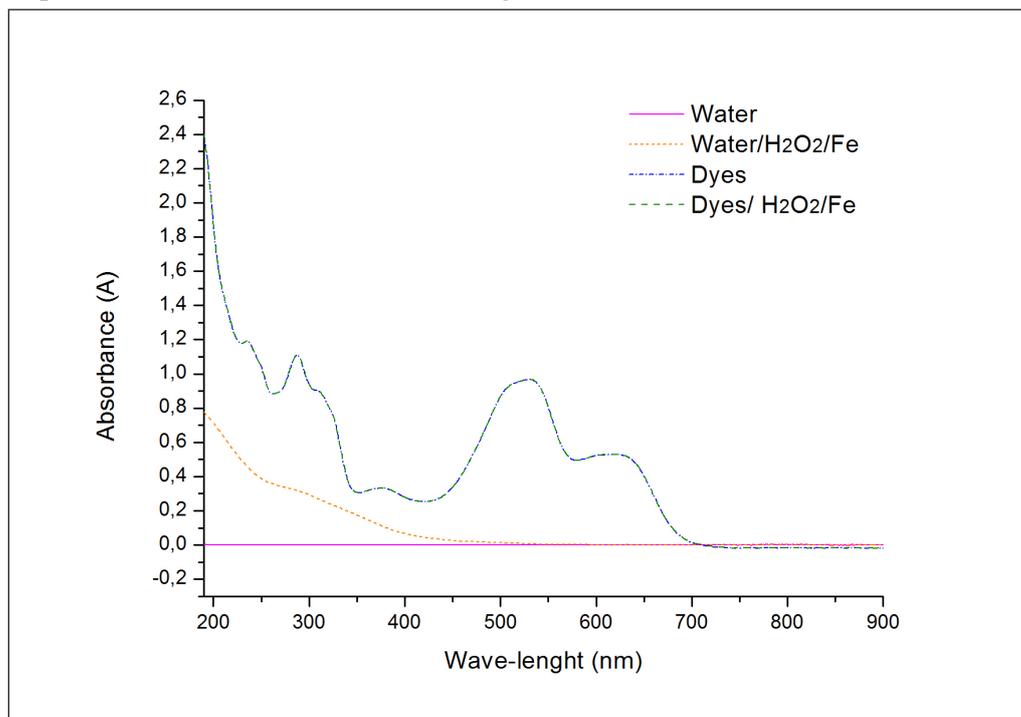


Figure 4 - UV-spectra in different conditions: in water, in water/H₂O₂/Fe, dyes and dyes/ H₂O₂/Fe.

EVALUATION OF THE CONCENTRATION OF HYDROGEN PEROXIDE

In this study step, the Fenton process was used to evaluate the influence of the H₂O₂ concentration ([H₂O₂]) on the percentage of degradation of the analyzed dyes. Thus, the following [H₂O₂] were used: 40, 60, 80, 100, 120 and 150 mg·L⁻¹, noting that for both dyes little variation was observed with respect to percentages of degradation, which varied between 99.2% and 99.8% and are within the experimental error.

Since no influence of [H₂O₂] over the results was verified, the working concentration chosen was 40 mg·L⁻¹. This concentration was used in the pH study as well as in the determination of residual peroxide. The analyses of residual peroxide were carried out taking into account the associated cost of hydrogen peroxide, as well as the fact that it tends to stay in the solution for long periods of time.

STUDY OF pH AND MEASUREMENT OF RESIDUAL PEROXIDE

The evaluation of pH interference in the UV/Vis spectrum showed that none of the maximum absorbance peaks were displaced for the two dyes studied, indicating that there is no significance of the pH for the present study. These results can be seen in Figure 5.

For the trials that were aimed at analysing the influence of pH on the solution, the Fenton process was carried out with [Iron] = 5 mg·L⁻¹, [H₂O₂] = 40 mg·L⁻¹ and a time of 20mins. The results showed that the pH had little influence on degrading Reactive Blue BF-5G and Remazol Red RB 133% dyes, since for the analyzed pH ranges the following percentages of degradation were obtained: 1) pH between 3 and 4 (99, 3% for blue and 98.8% for red); 2) pH between 4 and 5 (99.6% for blue and 99.7% for red) and 3) pH between 5 and 6 (natural solution) (99.5% for blue and 99.1% to red).

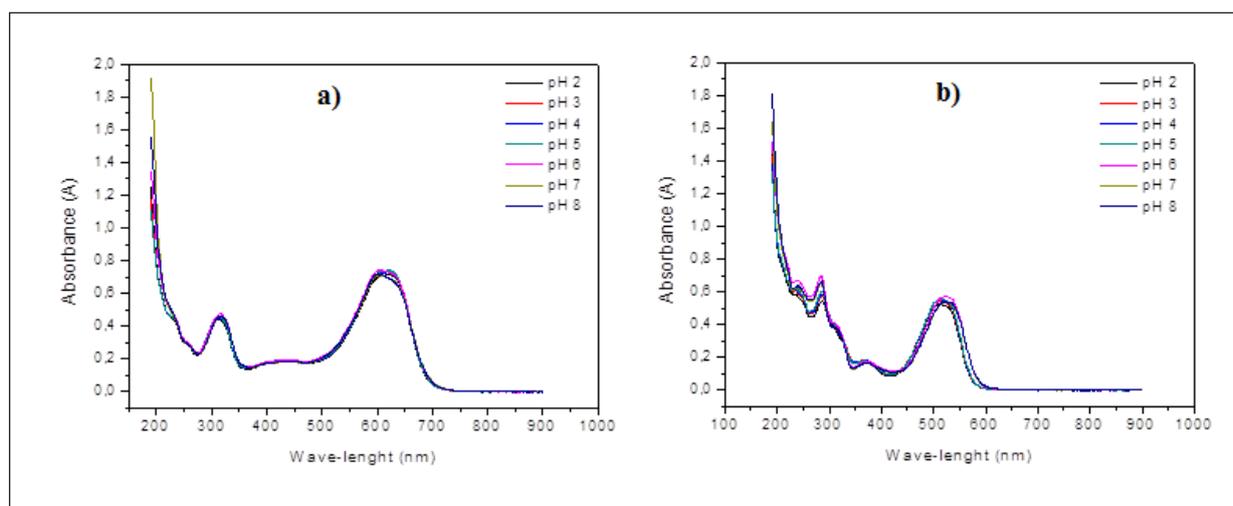


Figure 5 - Absorbance spectrum for pH variation of dyes: a) reactive blue BF-5G and b) remazol red RB 133%

Therefore, for the conditions studied, the range of pH used has little influence on the degradation of the solution containing Reactive Blue BF-5G and Remazol Red RB 133% dyes. Therefore, in order to minimise operation costs, it was decided to continue the studies with the natural pH of the solution, as previously reported in another study investigating pharmaceutical compounds (NAPOLEÃO et al, 2013).

The amount of residual H_2O_2 was subsequently determined, having obtained for the Fenton process after 20 minutes: $1 \text{ mg}\cdot\text{L}^{-1} < [H_2O_2] < 2 \text{ mg}\cdot\text{L}^{-1}$. In order to obtain the best results regarding the determination of residual peroxide, the same analysis was carried out for the photo-Fenton process. The latter was evaluated using solar radiation and beams from the sunlight UV-system over the same period of time, having verified that the $[H_2O_2]$ was lower than $1 \text{ mg}\cdot\text{L}^{-1}$ in both cases. Since for $[H_2O_2] = 40 \text{ mg}\cdot\text{L}^{-1}$ the presence of the reagent had not yet been detected, it was decided that in the subsequent step the percentages of degradation in relation to the variations in the concentration of peroxide would be evaluated for values lower than $40 \text{ mg}\cdot\text{L}^{-1}$.

FACTORIAL DESIGN

A statistical analysis was carried out based on the factorial design described in the methodology in order to find the best operating conditions for each of the processes in study. Figure 6 exhibits the Pareto charts for the degradation of the Reactive Blue BF-5G and Remazol Red RB 133% dyes, using the photo-Fenton sunlight process.

By analysing the Pareto charts, it was possible to verify that for the Reactive Blue BF-5G (Figure 6a) dye, all the main effects $[H_2O_2]$, $[\text{Iron}]$ and time were statistically significant for a 95% confidence level, as well as the effect of the interaction $[\text{Iron}]$ -time. For the Remazol Red RB 133% dye (Figure 6b), besides these effects, the interaction between H_2O_2 - $[\text{Iron}]$ and the interaction between the three factors were also seen as significant. For better understanding the best operating conditions and the effects of each of the variables study, surface graphs were plotted (Figure 7).

The analysis of Figures 7a and 7b indicates that when combining the highest level of $[\text{Iron}]$ with the highest amount of time, higher degradation levels of the dyes are reached. A similar result is obtained when analysing Figure 7c, when combining higher levels of $[H_2O_2]$ with a higher amount of time. Thus, a higher degradation level of the dyes could be observed for the higher levels of all the variables studied, in accordance with positive values observed in the Pareto chart for the three main effects. Subsequently, Pareto charts were drawn for the degradation of the dyes by using the Fenton process, as can be seen in Figure 8.

When analysing the Pareto charts, it was possible to verify that for the Reactive Blue BF-5G (Figure 8a) dye, only the main effect $[\text{Iron}]$ and time were considered as being statistically significant for a 95% confidence level. On the other hand, for the Red RB 133% dye (Figure 8b), besides these two effects, the interaction between $[\text{Iron}]$ -time was also seen as significant. In order to better understand the

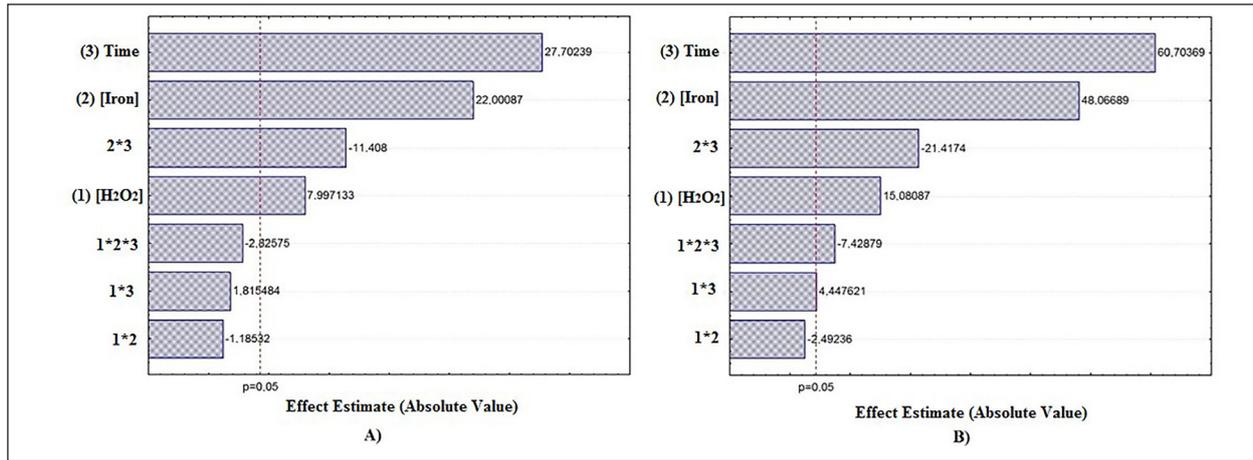


Figure 6 - Pareto chart for degradation of dyes using photo-Fenton process with sunlight radiation: A) reactive blue BF-5G and B) remazol red RB 133%

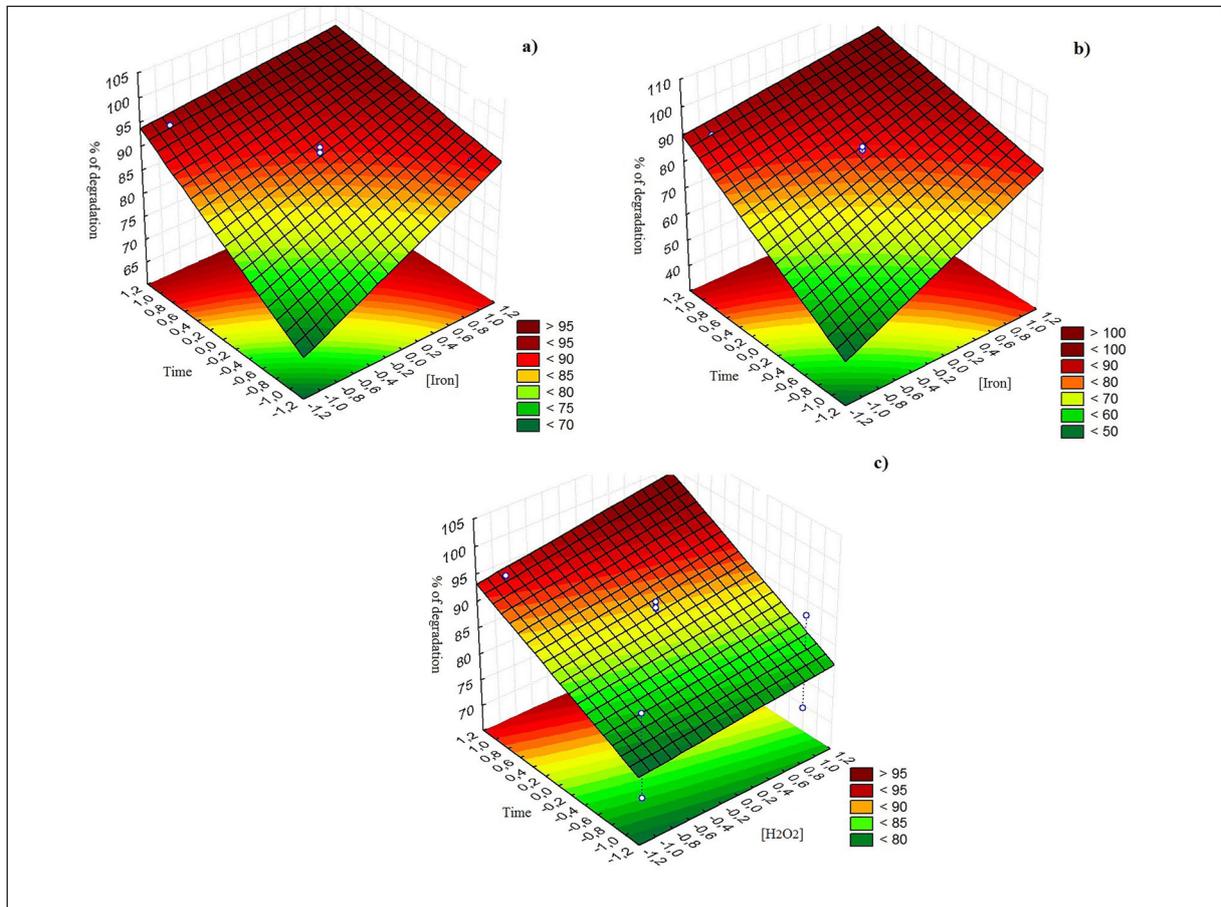


Figure 7 - Response surfaces of the interaction [Iron] - time for the dyes a) reactive blue BF-5G and b) remazol red 133% and c) interaction [H2O2] - time for the red remazol dye 133%, using photo-Fenton process sunlight

effects of the interactions, response surfaces (Figure 9) were also drawn for the photo-Fenton process. Figures 9a and 9b indicate that when combining higher levels of the factors studied ([Iron] and time), higher degradation percentages of the dyes were obtained. Accordingly, it can be observed that higher levels of degradation of both dyes (1- Fenton: 93.45 and 91.22, for the blue and red dyes, respectively; 2- Photo-Fenton sunlight: 97.86 and 97.29, for the blue and red dyes, respectively) could be verified at the highest concentration levels studied: [H2O2] = 40 mg·L⁻¹, [Iron] = 5 mg·L⁻¹ and time of 15 minutes.

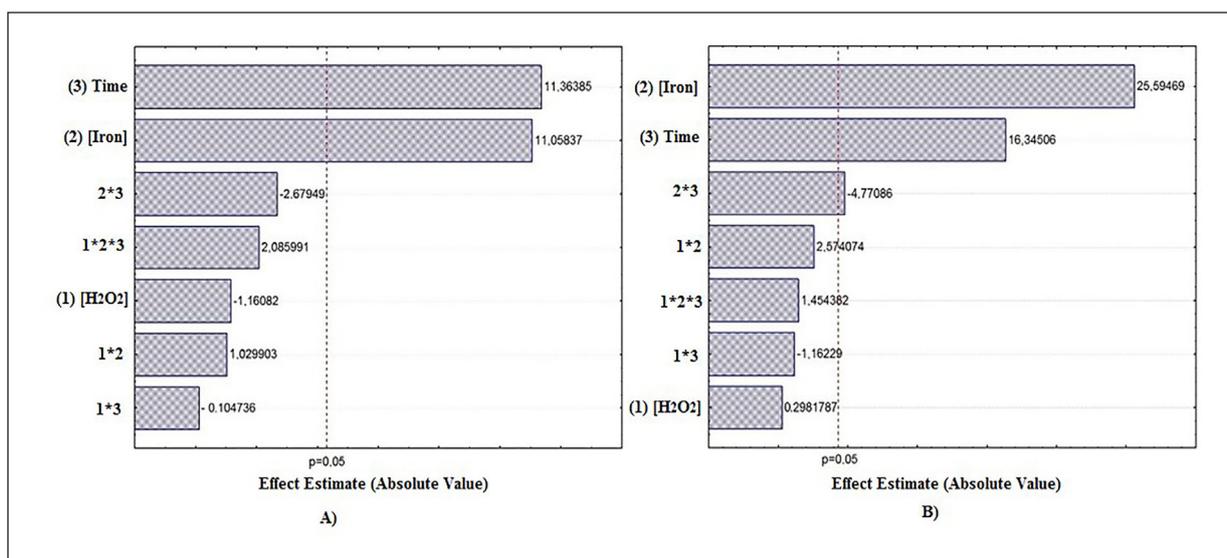


Figure 8 - Pareto chart for degradation of dyes employing Fenton process: A) reactive blue BF-5G and B) remazol red RB 133%

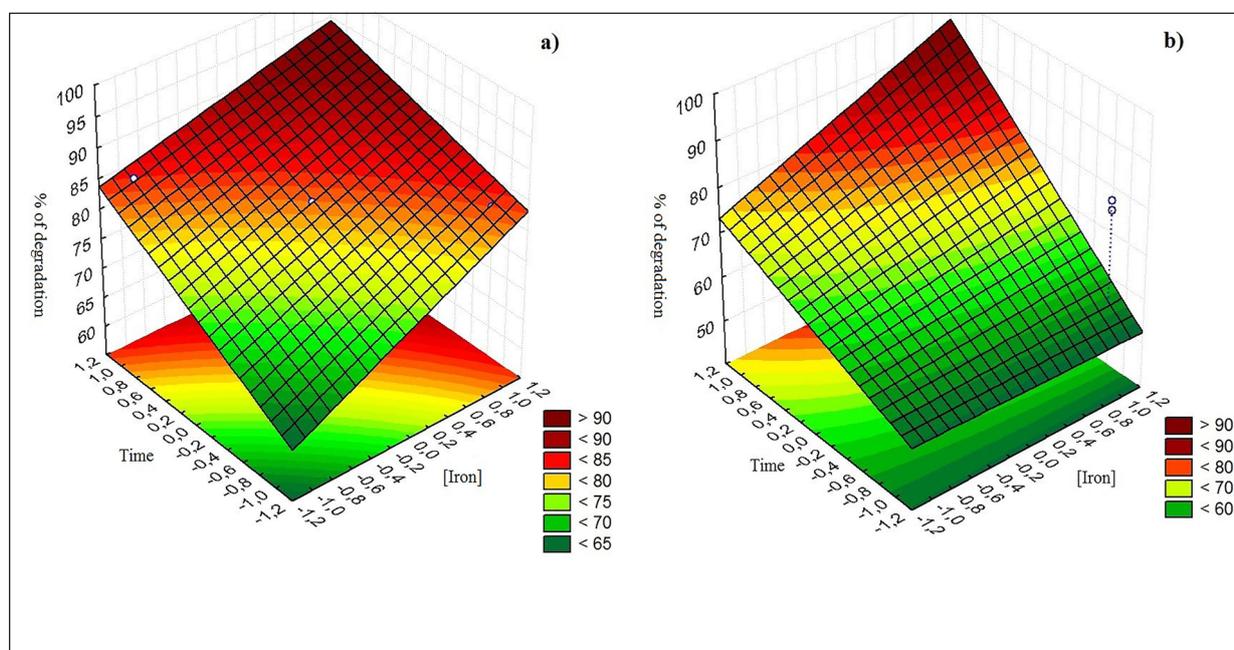


Figure 9- Response surfaces of the interaction [Iron] - time for dyes employing Fenton process: a) BF-5G Reactive Blue and b) Remazol Red 133%

However, an analogous result (difference < 4% of degradation) was obtained in an experiment using a lower concentration of hydrogen peroxide (10 mg·L⁻¹), indicating the possibility of working with the photo-Fenton process using only a minimum concentration of H₂O₂. Therefore reducing the residual levels of this compound, as well as the possibility of obtaining the same degradation levels by extrapolating the submission time to the AOPs. Based on this consideration and optimisation of the process, a kinetic study was carried out.

KINETIC STUDY

Having determined the best operating conditions (\equiv 10 mg·L⁻¹, [Iron] = 5 mg·L⁻¹), and maintaining the solution natural pH (between 5 and 6), the kinetic study was carried out by monitoring the degradation of the dyes at the time periods of: 0.5; 1.0; 1.5; 2.0; 2.5; 3.0; 4.0; 5.0; 6.0; 7.0; 8.0; 9.0 and 10.0 minutes. Figure 10 contains the kinetic adjustment regarding the evolution of degradation of the compounds, according to the plotting of the ln(C/C₀) versus time graph. It is important to note that in this study only time periods of until 10 mins were used, as in higher periods of time the concentrations obtained were lower than the quantification limit of the method employed.

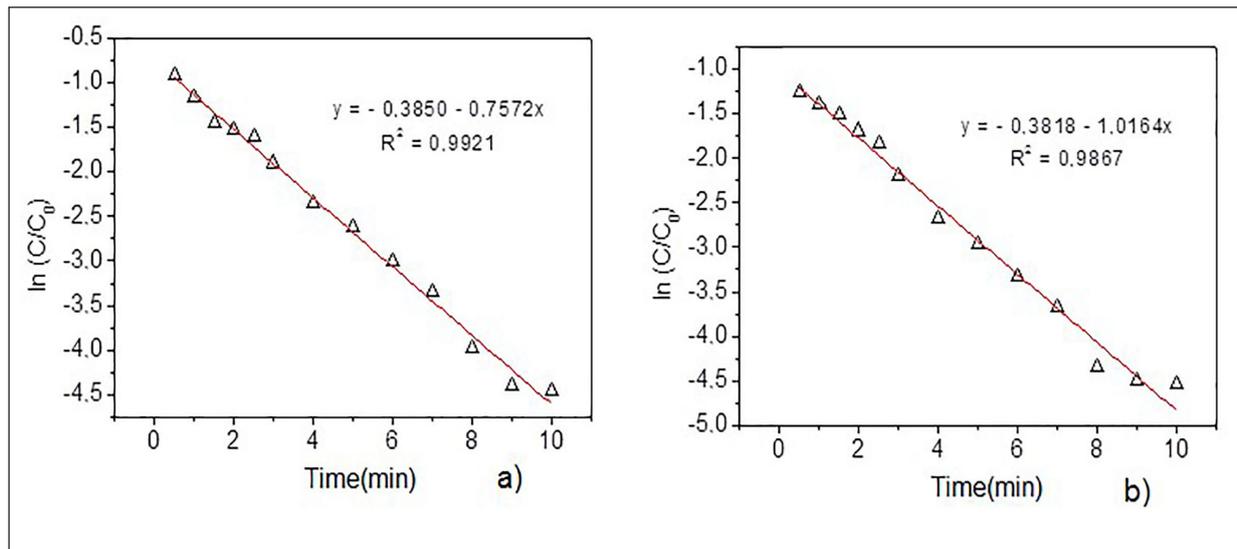


Figure 10 - Kinetic adjustment of dye degradation using process: a) Fenton and b) photo-Fenton using solar radiation

By analysing Figure 10, it is possible to notice that the photo-Fenton solar process for the degradation of the aqueous solution containing the Reactive Blue BF-5G and Remazol Red 133% dyes presented a good adjustment to the pseudo first order kinetic model. It was possible to observe from the analysis of Figure 10 that the two processes can be used together, once they presented equivalent kinetic behavior, making possible the alternation of the treatments in a real effluent treatment plant.

This could be noted from the results for the linear regression coefficients (R^2): 0.9921 (blue - a) and 0.9867 (red - b). Thus, the kinetics of the degradation of the dyes can be described according to Equation 15.

$$-dC_A / dt = kC_A C_{OH} \quad (15)$$

In which C_A is the concentration of azo dyes, C_{OH} is the concentration of the hydroxyl radical and k is the second order kinetic constant. According as described in item 3.4, the residual hydrogen peroxide was monitored by identification strips of this compound (Merck). It was verified that the final amount of the reagent present in solution was negligible.

Thus, in view of the results obtained for kinetic monitoring of the process, it was not possible to perform the radical mechanism of the solution, which has been criticized in the past, since it depends on the stereospecificity of the oxidation process of certain compounds. Nevertheless, when it comes to the advanced oxidative processes, high-oxidizing agents are used, which do not produce stereospecificity, making it possible to simplify the proposed kinetic adjustment

Therefore, it can be utilized the following consideration: $C_{OH} \gg C_A$, which makes an approximation of C_{OH} equal to 1. Thus, an Equation 15 can be simplified by obtaining Equation 16.

$$-dC_A / dt = k' C_A \quad (16)$$

In which k' is the pseudo first order kinetic constant. In order to guarantee that the process employed was efficient, a quantitative analysis with a scan between 190 and 1100 nm was carried out on an ultraviolet/visible equipment for the Fenton and photo-Fenton processes, using solar radiations and sunlight beams (Figure 11). The scanning analysis was performed under the conditions of the kinetic study at a final time of 15 minutes.

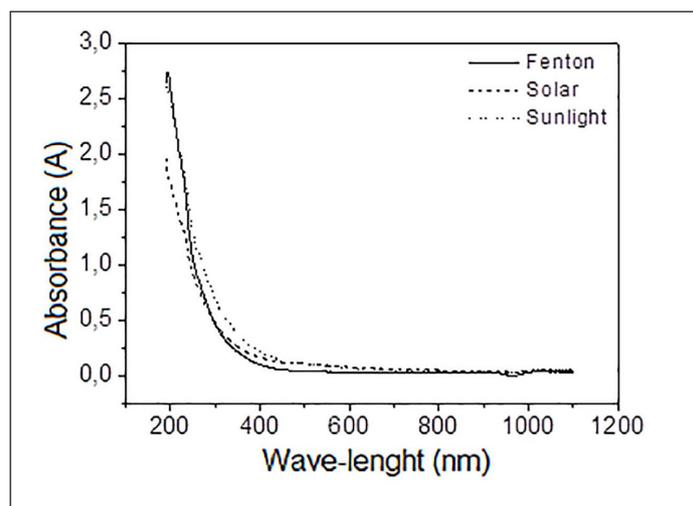


Figure 11 - Scanning analysis (190 to 1100 nm) for aqueous water containing reactive blue dyes BF-5G and red remazol 133% after different POAs.

By analysing Figure 11, it can be noted a lack of intermediaries in the formation process, for the wavelength range studied. Thus, a study regarding the concentrations of organic matter was carried out in order to corroborate the efficiency of the degradation process.

BEHAVIOR OF CHEMICAL OXYGEN DEMAND

As reported in the literature, the removal of colour is directly associated to the breaking of the N≡N bond, more commonly known as the azo bond (ARAÚJO; YOKOYAMA; TEIXEIRA, 2006). For ensuring that besides discolouration, the degradation of the dyes also took place, COD analyses were carried out for the Fenton, photo-Fenton (solar) and photo-Fenton (sunlight system) processes. The results obtained for the removal levels of COD are presented in Figure 12. It is thus worth noting that the value of COD for the solution before the treatment was of 132.80 mg·L⁻¹. It is important to mention that the standart deviation between the tests performed were less than 4%.

When analysing Figure 12, it can be observed that although the processes using ultraviolet radiation presented better results regarding the percentage of conversion of COD, reducing the amount of organic matter by more than 87%, the Fenton process can be used in combination with the photo-Fenton solar process, complementing the treatment in the period of absence of sun radiation.

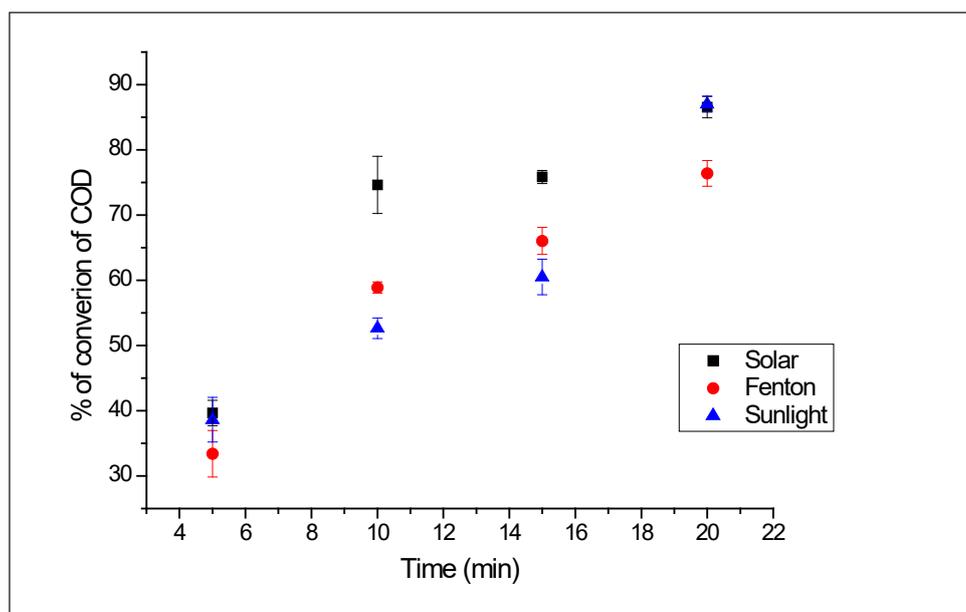


Figure 12 - Follow-up of the kinetics percentage of COD conversion for different AOP.

Therefore, it can be concluded that the alternation between the photo-Fenton solar (for the period of sun radiation exposure) and the Fenton processes (night-time period – no sun radiation exposure) favours the application of such operating conditions in wastewater treatment plants, ensuring favourable degradation levels of the dyes and of COD conversion.

CONCLUSION

The present study verify that the advanced oxidative processes applied (Fenton and photo-Fenton) were efficient in the study of the aqueous solution containing the reactive blue dyes BF-5G and remazol red RB 133%, degrading them in values higher than 98% in a relatively short time (20 min). A very similar efficiency could be observed for the same period of time when using sunlight and solar radiation (<1% for dye degradation and COD conversion). It was found that the hydrogen peroxide concentration and pH ranges evaluated were not significant for the percentages of degradation obtained for the dyes. The pseudo first order model was a good adjustment to degradation evaluated, with R² values equal to 0.9921 for blue dye and 0.9867 for red dye. Therefore, it can be verified that the use of Fenton and photo-Fenton solar processes are efficient to degrade the dyes used in the present study and can be used in samples of textile effluents, promoting the cost reduction, once the treatment can be applied also with the absence of light, as well as in different seasons.

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