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Optimization of Photo-fentom like process for the remediation of sodium diclofenac residues in water samples

Otimização do processo foto-fentom para a remediação de resíduos de diclofenaco de sódio em amostras de água

Optimización del proceso foto-fentom para la remediación de residuos de diclofenaco sódico en muestras de agua

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Abstract
Worldwide, there is an increasing incidence of contaminants in aqueous matrices, among them, antibiotics, pesticides and pharmaceutical products. This problem, coupled with the occurrence of these pollutants at trace levels, creates unique challenges for the analytical detection and performance evaluation of the removal of these contaminants from water. The purpose of this experiment was to optimize the operational conditions of the Photo-fentom like process of sodium diclofenac residues by Response Surface Methodology (RSM), based on analysis in aqueous solution. The drug was determined via UV-Vis spectrophotometry using a 2^3 factorial design with a central point to evaluate the degradation of the sodium diclofenac. The design was composed of two levels and three factors: (X_1) Irradiation time, ranging from 2 to 4 h; (X_2) Hydrogen peroxide content, ranging from 1 to 7%; and (X_3) Fe^{2+} concentration, ranging

from 25 to 100 mg L^{-1}. According to the levels defined for each parameter, the optimized methodology showed that the best degradation of the drug was achieved by combining 2 h of irradiation, 1% Hydrogen peroxide solution and 25 mg L^{-1} of solution containing Fe^{2+}, where 97.04% of drug degradation was achieved. From ANOVA it could be inferred that the concentration of Fe^{2+} (p = 0.13044) and the interaction irradiation time with Fe^{2+} concentration (X_1X_3) (p = 0.0439) had the highest significance in the degradation process. The experimental planning was useful to indicate the region of maximum degradation, therefore, the methodology was suitable for degradation of residues of this drug in water samples.
Keywords: Advanced oxidative process; Diclofenac sodium; Environmental contamination; Spectrophotometry; Water.

Resumo
Mundialmente, há uma incidência crescente de contaminantes em matrizes aquosas, entre eles, antibióticos, pesticidas e produtos farmacêuticos. Este problema, juntamente com a ocorrência destes poluentes em níveis traços, cria desafios únicos para a detecção analítica e avaliação do desempenho da remoção destes contaminantes da água. O objetivo deste experimento foi otimizar as condições experimentais de um processo oxidativo avançado para resíduos de diclofenaco de sódio em solução aquosa. O fármaco foi determinado por espectrofotometria UV-Vis usando um planejamento experimental com ponto central para avaliar a degradação do diclofenaco de sódio. O planejamento foi composto de dois níveis e três fatores: (X_1) Tempo de irradiação, variando de 2 a 4 h; (X_2) Teor de peróxido de hidrogênio, variando de 1 a 7%; e (X_3) Concentração de Fe^{2+}, variando de 25 a 100 mg L^{-1}. De acordo com os níveis definidos para cada parâmetro, a metodologia otimizada de degradação do fármaco foi obtida pela combinação de 2 h de irradiação, 1% de solução de peróxido de hidrogênio e 25 mg L^{-1} de solução contendo Fe^{2+}, onde 97,04% da degradação do diclofenaco de sódio foi alcançado. A partir da ANOVA pôde-se inferir que a concentração de Fe^{2+} (p = 0,13044) e, a interação tempo de irradiação com a concentração de Fe^{2+} (X_1X_3) (p = 0,0439) foram os fatores mais significativos no processo de degradação. O planejamento experimental foi útil para indicar a região de degradação máxima, portanto, a metodologia foi adequada para a degradação dos resíduos deste medicamento em amostras de água.
Palavras-chave: Processo oxidativo avançado; Diclofenaco de sódio; Contaminação ambiental; Espectrofotometria; Água.

Resumen
En todo el mundo hay una creciente incidencia de contaminantes en las matrices acuosas, incluidos los antibióticos, los pesticidas y los productos farmacéuticos. Este problema, junto con la presencia de estos contaminantes a niveles de trazas, crea desafíos únicos para la detección analítica y la evaluación del rendimiento de la eliminación de estos contaminantes del agua. El objetivo de este experimento fue optimizar las condiciones experimentales de un proceso oxidativo avanzado para residuos de diclofenaco sódico en solución acuosa. El fármaco se determinó por espectrofotometría UV-Vis utilizando una planificación experimental de punto central para evaluar la degradación del diclofenaco sódico. La planificación estaba compuesta por dos niveles y tres factores: (X_1) Tiempo de irradiación, que va de 2 a 4 h; (X_2) Contenido de peróxido de hidrógeno, que va de 1 a 7%; y (X_3) Concentración de Fe^{2+}, que va de 25 a 100 mg L^{-1}. De acuerdo con los niveles definidos para cada parámetro, la metodología optimizada de degradación del fármaco se obtuvo mediante la combinación de 2 h de irradiación, solución de peróxido de hidrógeno al 1% y 25 mg L^{-1} de solución que contenía Fe^{2+}, donde se logró el 97,04% de la degradación del diclofenaco sódico. A partir del ANOVA se pudo inferir que la concentración de Fe^{2+} (p = 0,13044) y, la interacción tiempo de irradiación con la concentración de Fe^{2+} (X_1X_3) (p = 0,0439) fueron los factores más significativos en el proceso de degradación. La planificación experimental sirvió para indicar la región de máxima degradación, por lo que la metodología fue adecuada para la degradación de residuos de este fármaco en muestras de agua.
Palabras clave: Proceso oxidativo avanzado; Diclofenaco sódico; Contaminación ambiental; Espectrofotometría; Agua.

1. Introduction

Diclofenac sodium (DCF) is another one of several anti-inflammatory drugs used to treat inflammatory diseases, and various types of pain (Tiwari, 2015). The annual consumption of DCF has reached over 60 tons in many countries (Lonappan et al, 2016). However, DCF waste is poorly treated and reaches water treatment plants, resulting in the residue of DCF in surface and groundwater. In addition, DCF at low concentration can cause cytological changes in animals in aquatic environment (Li et al, 2021, Acuña et al., 2015), which can cause a risk to aquatic ecosystems. Thus, DCF exposed to the natural environment needs to be removed urgently. Sodium diclofenac is available on the drugstores as a free salt, sodium salt, or potassium salt. The latter salt is more soluble, promoting a higher rate of absorption and thus a faster analgesic effect compared to the other orally administered forms. Sodium diclofenac sodium, a non-steroidal drug, acts in the body by decreasing the production of prostaglandins, which play an important role in causing inflammation, pain, and fever. The unbridled consumption of this drug linked to a wide diversity of applications, which does not restrict its purchase in drugstores, consequently contributes to the contamination of effluents when it comes to the issue of disposal and waste production (Li et al., 2021; Lima et al., 2015; Santos & Bergold, 2007).

The pharmaceutical industry is established as one of the most prominent industrial sectors, which works with the conservation of human health over time, promoting an increase in both quality and life expectancy of the world population. Every year, large quantities of pharmaceutical products are produced with application in the most diverse areas of human and animal health, and most of the active ingredients used are biologically active organic compounds. The pharmaceutical sector presents a definition as the branch of economy that incorporates the set of activities involved in the production, commercialization and transportation of pharmochemicals, drugs and pharmaceutical preparations (Vieira & Santos, 2020; Alygizakis et al., 2016).

The use of chemical treatments as an alternative technological resource for the treatment of industrial effluents has attracted considerable attention, showing advantageous characteristics such as ease of automation and a reduction in physical space, among which are included the oxidative and photo-oxidative processes, in the set called Advanced Oxidative Processes (AOP). The AOP are processes based on the generation of free radicals, mainly the hydroxyl radical (HO-), and present high efficiency in the removal of non-biodegradable pollutants or of high persistence, for which, the conventional effluent treatments (sedimentation, coagulation/flocculation, biological filters, among others) are not effective. These processes are characterized by facilitating the transformation of various organic contaminants into less complex chemical species (inorganic anions, water or carbon dioxide) (Araújo et al., 2016; Sun et al., 2016; Tong et al., 2019; Carra et al., 2015; Cihanoglu, Gunduz & Dukkanci, 2015). The reduction in the use of chemicals is a great benefit, since the electron is the main reactant in the process, and the estimate of reuse of the coproducts generated, shows an excellent initiative within the current global scenario of sustainability. These technologies submerge reactive oxygen species (ROS), which makes possible the degradation of organic pollutants with various chemical structures and functional groups to fewer toxic substances. The correct management, recycling and treatment of these wastes should be performed, in order to ensure that the emission of substances of high concern and contamination is avoided, ensuring environmental protection of human health (Hahladakis et al., 2018; Li et al., 2021; Hu, Zhai and Zhu, 2021).

The Fenton process can be understood as a system involving a set of cyclic reactions in an acidic medium, where the hydroxyl radical (an oxidizing agent used in the degradation of organic material) can be generated as a product of hydrogen peroxide decomposition in the presence of Fe^{2+} or Fe^{3+} ions (Aydin et al., 2018; Baloyi, Ntho & Moma, 2018; Ameta et al., 2018). In the photo-Fenton process, radiation is used to increase the speed of oxidation reactions in the sample. The incidence of radiation promotes electron transfer from the ligands of the hydroxylated Fe^{2+} and Fe^{3+} species to the metal, providing, the formation of the hydroxyl radical and the regeneration of the Fe ion (Faust & Hoigné, 1990; Ammar et al., 2016; Bel Hadjltaief et al., 2014).

In view of the above, this research aims to study to optimize the application of the photo-Fenton process in the treatment of solution containing the active ingredient sodium diclofenac.

2. Materials and Methods

2.1 Chemicals

Methanol, iron sulfate and hydrogen peroxide were all purchased from Sigma-Aldrich (Milan, Italy). A stock solution of 100 mg mL^{-1} of diclofenac sodium was prepared by dissolution in methanol. Working solutions with concentrations of 0.01;

0.50; 1.00; 2.00; 5.00 and 10 mg mL^{-1} were prepared from the dilution of the stock solution.

2.2 Instruments

UV analysis was performed by an UV spectrophotometer Spectroquant Prove 600 (Merck, Darmstadt, Germany).

2.3 UV analysis

For the UV analysis, the samples filtered after the degradation assays were used. All tests were performed in triplicate, at a wavelength of 330 nm, in order to verify the decrease in the concentration of the analyte before and after the oxidative process.

2.4 Experimental Design

To evaluate the efficiency of the degradation process of the drug, a 2^3 factorial design with central point was performed. Factors were: (1) Irradiation time, 2 to 4 h; (2) Hydrogen peroxide content, 1 to 7%; and, (3) Fe^{2+} concentration, 25 to 100 mg.L^{-1}. The concentration of sodium diclofenac was used as the response variable. All optimization experiments were performed under constant stirring and fixed pH (pH = 3). A 0.01 mol L^{-1} sulfuric acid solution was used to adjust the pH. The experimental design is shown in Table 2. Origin pro 8.5 and Minitab 17.3.1 software was used to process the data and obtain the response surfaces. A two-way interaction linear model was adjusted to the experimental data (Equation 1), where yˆ is the predicted value (the yield of the extracted compound, ferulic acid), β's are the model coefficients and 1,2,3 the encoded factors.

$$\hat{y} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (1)$$

2.5 Photodegradation experiments

To perform each experiment, initially, the beaker was washed with distilled water. First, adequate volumes of H_2O_2 and $FeSO_4.7H_2O$ (according to the experimental design) and diclofenac sodium solution were mixed in a 600 mL beaker to obtain 200 mL of a 10 mg mL^{-1} solution of the drug, as well as in the experiments performed by Davididou et al., (2017); Carra et al., (2015). Photodegradation experiments were conducted with a black light fluorescent lamp FoxLux® with irradiation power of 27 W and frequency of 60 Hz. After the predefined irradiation times, the sample was filtered and analyzed in a spectrophotometer to evaluate the degradation of the analyte.

3. Results and Discussion

3.1 Factorial Design Performed

Initially, the effect of Fe^{2+} concentration, irradiation time and H_2O_2 content on the degradation capacity of the photo-Fenton system was investigated by a factorial planning system of experiments, using sodium diclofenac solution. In these studies (results shown in Table 1) a strong combined effect between both variables was verified, as well as a maximized degradation efficiency under experimental conditions represented by: irradiation time: 2 h; Fe^{2+}: 25 mg L^{-1}; H_2O_2: 1 %. Under these conditions, the minimum Fe^{2+} concentration (25 mg L^{-1}) was sufficient for maximum hydroxyl radical (-OH) production from the H_2O_2 content (1%).

Table 1 - Experimental design: Actual (and encoded) levels of factors and observed responses.

Factors			**Efficiency (%)***
(X_1) Irradiation time (h)	**(X_2) H_2O_2 (%)**	**(X_3) Fe^{2+} (mg L^{-1})**	
3 (0)	3 (0)	50 (0)	91.74
4 (1)	1 (-1)	100 (1)	91.13
2 (-1)	7 (+1)	100 (1)	88.65
2 (-1)	1 (-1)	100 (1)	86.66
2 (-1)	7 (+1)	25 (-1)	93.04
2 (-1)	**1 (-1)**	**25 (-1)**	**97.04**
4 (1)	7 (+1)	25 (-1)	93.44
4 (1)	1 (-1)	25 (-1)	94.16
4 (1)	7 (+1)	100 (1)	85.09

*(n=3). Bold numbers indicate the best conditions for 97% efficiency in the photo-Fenton process. Source: Research data.

3.2 Estimated Model

The adjustment of the statistical model of factorial planning is verified by the coefficient of determination (R^2). From the data in Table 3, the coefficient found was: $R^2 = 0.9992$ ($R^2_{adj} = 0.9987$) indicating that the model was adequate. From the ANOVA (Table 2) the F and p values are presented, showing the significance of the factors in the degradation process studied.

Table 2 - Analysis of variance (ANOVA) for the experiments results.

Source	Sum of square	Degree of freedom	Mean of square	F-value	*p*-value
Model	2.95562	8	0.36945	12.86198	5.14097E-6
X_1	0.01832	2	0.00916	0.06364	0.9385
X_2	0.29794	2	0.14897	1.12615	0.34082
X_3	2.56715	2	1.28357	**34.02037**	9.88037E-8
X_1X_2	0.1676	4	0.0419	0.25174	0.90482
X_1X_3	0.3507	4	0.08768	**3.05231**	0.0439
X_2X_3	0.17503	4	0.04376	1.82897	0.16723
Error	0.51704	18	0.02872		
Cor. Total	3.47266	26			
	$R^2 = 0,9992$	$R^2_{adj.} = 0,9987$			

X_1 = irradiation time, X_2 = H_2O_2 content and X_3 = Fe^{2+} concentration. Bold numbers indicate significant factors as identified by the analysis of variance at the 95 % confidence level. Source: Research data.

From the result of the ANOVA of the linear model fit, we have that higher F values associated with low *p* values (<0.05) demonstrate that the generated model is statistically significant (Karabegovic et al., 2013).

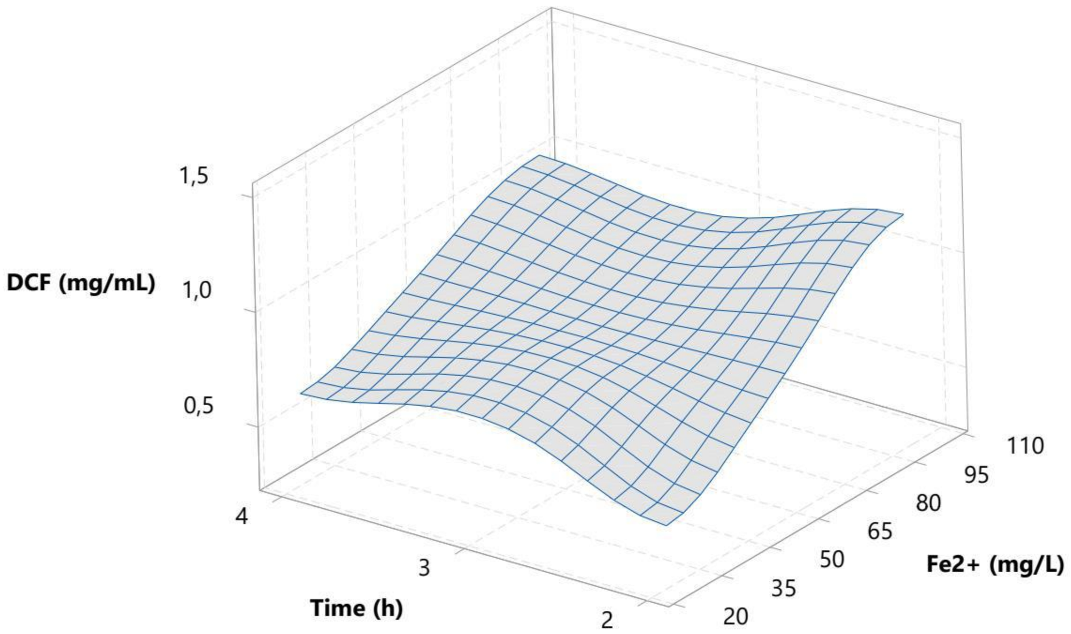
P values are used to confirm the significance of each coefficient, i.e., the lowest p value is at the highest effect (Zhao et al., 2011). According to the F and *p* values (Table 3), the factor with the largest effect is on Fe^{2+} concentration (X_3, $p = 9.88.10^{-8}$); however, this analysis indicates that only the irradiation time x Fe^{2+} concentration interaction (X_1X_3) was significant ($p = 0.0439$).

3.3 *Response surface plot analysis*

Response surface plots are very useful to visualize the effects of two factors on the response, as well as the identification of the optimal values, for obtaining the maximum response (Silva, Azevedo and Rezende, 2016).

Response Surface Methodology (RSM) is a statistical method that uses quantitative data from a factorial planning to determine multivariate equations. Unlike conventional empirical methods, RSM generates a mathematical model, taking into account the possible interrelationships between the test variables, minimizing the number of experiments (Song et al., 2011). The effects of the independent variables (factors) and their interactions on the response can be observed in three dimensions by means of response surface analysis (Silva, Landgraf, and Rezende, 2017). Figures 1, 2 and 3 show the main interactions of the process: Fe^{2+} concentration x irradiation time; H_2O_2 content x irradiation time and H_2O_2 content x Fe^{2+} concentration. The graphs were plotted using the z-axis (sodium diclofenac concentration in mg mL^{-1}) against two independent variables.

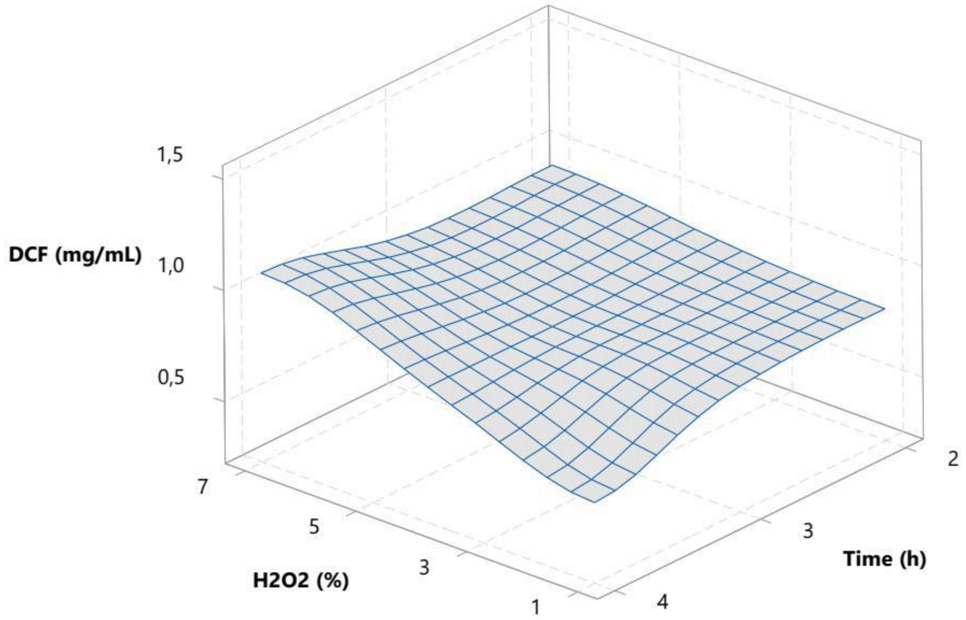
Figure 1 - Response surface plot showing the effects of the variables time (h) x Fe^{2+} concentration (mg L^{-1}) on the response, sodium diclofenac concentration (mg mL^{-1}).



Source: Research data.

Figure 1 shows the interaction between Fe^{2+} concentration and irradiation time on the degradation of sodium diclofenac. Combining the lower concentration of Fe^{2+} photo-Fenton process and running a shorter irradiation time (2 h), the effect on degradation is satisfactory. Evaluating the x-axis (Time) in relation to the z-axis (DCF) it is possible to observe the decrease in the concentration of the analyte, by the extremity of the response surface pointing to the 2 h. In the Fenton process, Fe^{2+} ion initiates and catalyzes the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals, which then promote the degradation of organic compounds.

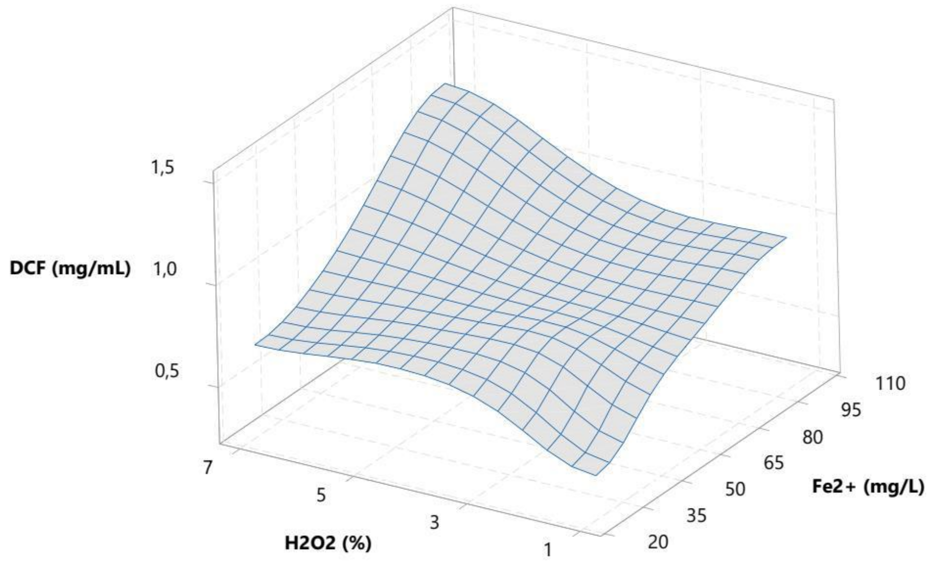
Figure 2 - Response surface plot showing the effects of the variables peroxide content (%) x time (h) on the response, sodium diclofenac concentration (mg mL^{-1}).



Source: Research data.

Figure 2 shows the interaction between H_2O_2 content and irradiation time in the degradation of diclofenac sodium. Combining the lower H_2O_2 content with the shorter irradiation time gives a better yield. Evaluating the x-axis (H_2O_2) in relation to the z-axis (DCF) it is possible to observe the decrease in the concentration of the analyte, by the extremity of the response surface pointing to the 1 % H_2O_2 content.

Figure 3 - Response surface plot showing the effects of the variables peroxide content (%) x Fe^{2+} concentration (mg L^{-1}) on the response, sodium diclofenac concentration (mg mL^{-1}).



Source: Research data.

Figure 3 shows the interaction between H_2O_2 content and Fe^{2+} concentration in the degradation of diclofenac sodium. Evaluating the y-axis (Fe^{2+}) in relation to the z-axis (DCF) it is possible to observe the decrease in the concentration of the analyte, by the extremity of the response surface pointing to the 20 mg L^{-1} Fe^{2+} concentration. According to Martins et al. (2011), it is important to determine the ratio between the reactants $[H_2O_2]$:$[Fe^{2+}]$, as a way to minimize the sequestering effects of hydroxyl radicals, caused in some cases by excess H_2O_2. In our study, it can be inferred that the lower concentration of Fe^{2+} in solution was able to saturate all the H_2O_2 in the process, which possibly promoted the best yield regarding the degradation of the drug.

4. Conclusion

Current studies have shown the need to develop treatments facing the problems arising due to the widespread of emergent contaminants. In this investigation, an optimized methodology for degradation of diclofenac sodium, based on UV-Vis spectrophotometric analysis, was performed, reducing the initial concentration of the drug by approximately 97%. The degradation of diclofenac in the eight experiments was enhanced by the combination of lower peroxide and Fe^{2+} contents.

For future researches, it would be interesting to evaluate the degradation of commercial samples of the drug and to test other types of lamps and/or radiation.

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