Optimization of Fenton process by factorial design for gestodene removal

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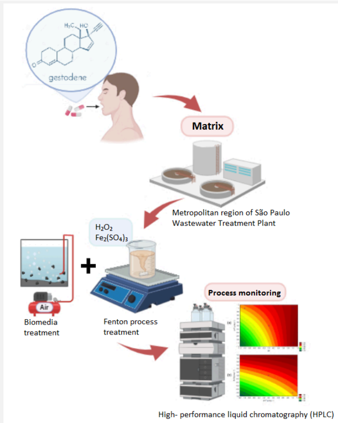
G. S. S. Almeida[1], *J. M. S. Jesus* [a1], *T. A. Costa*[1] *and R. F. Bueno*[1]. *(1) Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas, Universidade Federal do ABC – UFABC, Av. dos Estados, 5001, B. Bangú, Santo André, SP 09070-200, Brazil, julianams.silva@gmail.com*



The effectiveness of the Fenton process mediated by hydroxyl radical for the degradation of the progestin gestodene (GES) was investigated using a 2^3 experimental design. The aim is to evaluate the significance of the operating parameters applied to treated sewage as a tertiary effluent process. The evaluation of hormone removal and kinetic behavior made it possible to verify the effectiveness of the process, obtaining removals of over 90% in 8 min of the advanced oxidation process (AOP).

Introduction

Pharmaceutical compounds in effluents pose a growing challenge due to their potential environmental and public health impacts. Synthetic hormones are particularly concerning due to their persistence and bioaccumulation in aquatic environments [1]. These compounds are considered endocrine disruptors, causing imbalances even at low concentrations in humans [2]. Gestodene (GES), a progestin used in oral contraceptives, is frequently detected in domestic effluents, necessitating effective treatment strategies [3]. The Fenton reaction is a process that involves the generation of highly reactive hydroxyl radicals (•OH) through the reaction of hydrogen peroxide (H_2O_2) with ferrous iron (Fe^{2+}). These hydroxyl radicals are powerful oxidizing agents that can degrade a wide range of organic pollutants in wastewater. The basic steps of the Fenton reaction are:

(i) **Reaction initiation**: Ferrous iron (Fe^{2+}) reacts with hydrogen peroxide (H_2O_2) to produce hydroxyl radicals (•OH) and ferric iron (Fe^{3+}) (**Equation 1**).

(ii) **Propagation**: The hydroxyl radicals react with organic pollutants, leading to their degradation into simpler, less harmful compounds.

(iii) **Regeneration**: Ferric iron (Fe^{3+}) is reduced back to ferrous iron (Fe^{2+}) by reacting with more hydrogen peroxide or other reducing agents in the system, allowing the cycle to continue (**Equation 2**).

In this context, the Fenton process has been recognized as a promising approach for degrading persistent organic compounds in wastewater. This method involves the in-situ generation of highly reactive hydroxyl radicals that oxidize and degrade a wide range of organic pollutants [6,7] .

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^{\cdot}_2 + H^+ \quad (2)$$

In this study, we investigated the application of the Fenton process to degrade gestodene present in wastewater. Optimization of the process conditions aimed to maximize degradation efficiency, considering factors such as pH, Ferrous, and H_2O_2 concentration.

Material and Methods

Reagents. Gestodene (GES,≥ 98.0%) was purchased from Zhejiang Xianju Pharmaceutical Co. Ltd. H2O2 (35% w/w solution), H_2SO_4 (97%) and FeSO4·7H2O were supplied by LabSynth, while Na2S2O8 (PS, ≥ 98.0%) was supplied by Sigma-Aldrich. Methanol (HPLC grade) and acetic acid (LabSynth) were used to prepare the mobile phases used in liquid chromatography. Deionized water (18.2 MΩ cm) was obtained from a Milli-Q Direct-Q system (Millipore).

Factorial design 2^3: Considering the standard order of the factorial design approach, 10 experiments were conducted based on three replications of the central point (CP), and eight factorial points in a random sequence. As an independent variable pH (X_1), Fe(II) concentration (mg L^{-1})(X_2), and [H_2O_2] (mol L^{-1})(X_3) were applied to evaluate the effect on percentage GES removal (Y_1) and kinetic constant (Y_2). The variable's value levels were selected based on previous studies [4,5]. Statistica 7.0 software was used to analyze variance (ANOVA), with a confidence level of 90.0%. A statistical model representing the process was then generated.

Analytical methods. GES concentrations were monitored by ultra-fast liquid chromatography (UFLC) using Shimadzu equipment (LC 20AD) equipped with a UV-visible detector (SPD 20A) and C18 column (ACE, 250 mm × 4.60 mm, 5 µm). An isocratic method was applied using 70% methanol and 30% water containing 1% v/v acetic acid as the mobile phase [8]. GES was detected at 244 nm. The sample injection volume, oven temperature, and flow rate were 20 µL, 40 °C, and 1.0 mL min^{-1}, respectively. The calibration curves were obtained by diluting the stock solutions to obtain GES standards from 0.05 to 20.0 mg L^{-1}.

Results and Discussion

Progestin removal: Table 1 presents the run matrix conducted for GES removal by the Fenton process.

Table 1. Run matrix 2^3 applied for GES degradation. Conditions: $[GES]_0$ = 4.1 ± 0.21 mg L^{-1}. Y_1 and Y_2 were determined at 10 min of the experiment.

Runs	X_1	X_2	X_3	Y_1	Y_2
1	3.00	10.00	20.00	71.6	0.1294
2	7.00	10.00	20.00	85.1	0.1756
3	3.00	20.00	20.00	88.1	0.2079
4	7.00	20.00	20.00	86.6	0.2189
5	3.00	10.00	60.00	90.1	0.2164
6	7.00	10.00	60.00	97.8	0.3283
7	3.00	20.00	60.00	86.8	0.1913
8	7.00	20.00	60.00	99.7	0.5255
CP1	5.00	15.00	40.00	99.8	0.8820
CP2	5.00	15.00	40.00	100.0	1.3480
CP3	5.00	15.00	40.00	100.0	1.3360

As presented in Table 1, the Fenton process was feasible to remove 100% of GES when applied to the central point conditions. The pH effect can be observed through the application of high levels improving GES removal (Runs 6 and 8; and central point). From the coefficients of the significant effects observed (coefficients with p-values ≤ 0.1) it was possible to generate the statistical model of the data set (**Equation 3**), with the independent variables coded.

$$\hat{Y}_1 = 88.22 + 5.37X_1 + 2,07X_2 + 4.07X_3 - 2.42X_1X_2 + 1,07X_1X_3 - 1.22X_2X_3 \quad (3)$$

Among the response functions selected, GES removal (%) and specific rate of GES degradation (min^{-1}) only the first one was allowed; the statistical model generated (**Equation 3**) showed R^2 = 0.9375 and adjusted R^2 = 0.7917. As can be seen, all the main variables had a positive effect on hormone degradation, indicating that they should be maintained at high levels. However, two negative interaction effects—between pH and ferrous concentration, and between ferrous concentration and H_2O_2 concentration—suggest that these variables should not exceed certain maximum values.

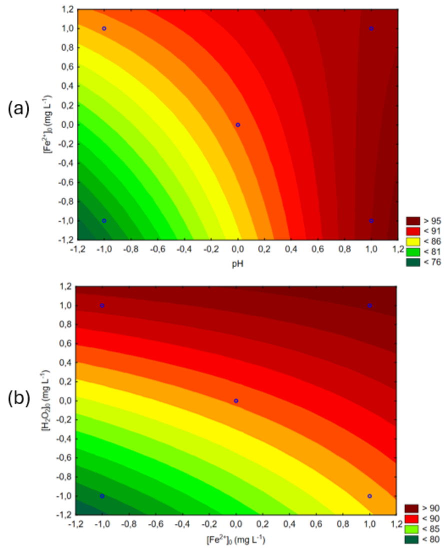


Figure 1. Contour plot of negative interaction effects in central condition for X_1X_2 and X_2X_3.

Figure 1 shows GES maximization removal due to the interactive effect of X_1X_3 (a) and X_2X_3 (b), in which in both cases, one of the variables should be operated at a low level. This result agrees with Pinoargote-Chain *et al.* [9]. findings, who evaluated the efficacy of Photo-Fenton parameters for 17β-estradiol and dye degradation. In the mentioned study the authors verified an excess of [H2O2] attributed to the elimination of •OH (oxidizing species) to form hydroperoxyl radicals, which reduces the target compounds removal.

Conclusions

From the results presented, it can be concluded that the Fenton process is effective in removing GES. The statistical analysis identified the central point as the best condition. Using the regression model generated, it was possible to identify the significant effects of the variables, with pH and $[H_2O_2]_0$ being the most important.

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