Performance of Fenton process for the removal of recalcitrant organics from landfill leachate after nitrification

Desempenho do processo Fenton para remoção de orgânicos recalcitrantes de lixiviado do aterro sanitário após a nitrificação

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ABSTRACT
The Fenton's process was evaluated for mature leachate treatment, after the biological one, by means of an experimental design divided into three steps: analyzes of the factors separately to establish values ranges; evaluation of significant factors and their interactions by a fractional factorial design; and analyzes of factors by a Central Composite Design (CCD). Performance results were measured by removal efficiency of the chemical organic demand (COD) and color. Four factors were considered: [H₂O₂], [H₂O₂]/[Fe²⁺], pH, and addition mode of reagents. The removal achieved were 88 (COD) and 99% (color) for: [H₂O₂] = 480 mM (6.02 mg H₂O₂ mgCOD⁻¹; [H₂O₂]/[Fe²⁺] = 6 (1.65 mg Fe²⁺ mgCOD⁻¹); pH=3.5, and reagents dosages divided into three stages. For the range evaluated, the [H₂O₂] had the greatest influence in the COD and color removal. The models established for COD and color removal were able to explain 86.7 and 80.3% of the variance around the average. Alkalinity concentration and the characteristics of the leachate used may interfere in the Fenton efficiency, so should be the focus of further research. The addition of the reagents shared in fractions was not significant in the treatment, however, it is recommended for system operation, avoiding foam formation. In the biological treatment for nitrogen removal from landfill leachate, there is high alkalinity consumption, therefore, when one used before Fenton's process, it helps to reduce the pH. This and the possibility of applying Fenton's process at circum-neutral
initial pH demonstrates the potential of association these technologies for the treatment of landfill leachate.

**Keywords:** Landfill Leachate, Advanced Oxidation Processes (AOP), Fenton’s Reagent, Alkalinity, Central Composite Design (CCD).

**RESUMO**

O processo de Fenton foi avaliado para o tratamento do lixiviado estabilizado, após a nitrificação, por meio de um delineamento experimental dividido em três etapas: análise dos fatores separadamente para estabelecer faixas de valores; avaliação de fatores significativos e suas interações por um planejamento fatorial fracionário; e análises de fatores por um Delineamento Composto Central Rotacional (DCCCR). Os resultados de desempenho foram medidos pela eficiência de remoção da demanda química orgânica (DQO) e cor. Quatro fatores foram considerados: [H\textsubscript{2}O\textsubscript{2}], [H\textsubscript{2}O\textsubscript{2}]/[Fe\textsuperscript{2+}], pH e modo de adição dos reagentes. As remoções alcançadas foram de 88 (DQO) e 99% (cor) para: [H\textsubscript{2}O\textsubscript{2}] = 480 mM (6,02 mg H\textsubscript{2}O\textsubscript{2} mgDQO\textsuperscript{-1}); [H\textsubscript{2}O\textsubscript{2}]/[Fe\textsuperscript{2+}] = 6 (1,65 mg Fe\textsuperscript{2+} mgCOD\textsuperscript{-1}); pH = 3,5, e as dosagens dos reagentes divididas em três etapas. Para a faixa avaliada, a [H\textsubscript{2}O\textsubscript{2}] teve maior influência na DQO e na remoção de cor. Os modelos estabelecidos para remoção de DQO e cor foram capazes de explicar 86,7 e 80,3% da variância em torno da média. A concentração de alcalinidade e as características do lixiviado utilizado podem interferir na eficiência de Fenton, por isso deve ser foco de novas pesquisas. A adição dos reagentes dividida em frações não foi significativa no tratamento, porém é recomendada para operação do sistema, evitando a formação de espuma. No tratamento biológico para retirada do nitrogênio do lixiviado do aterro, há alto consumo de alcalinidade, portanto, quando utilizado antes do processo de Fenton, ajuda a reduzir o pH. Isso e a possibilidade de aplicação do reagente de Fenton em pH inicial próximo ao neutro demonstram o potencial de associação dessas tecnologias para o tratamento de lixiviado de aterro.

**Palavras-Chave:** Lixiviado de Aterro Sanitário, Processos Oxidativos Avançados (POAs), Fenton, Alcalinidade, Delineamento Composto Central Rotacional.

**1 INTRODUCTION**

Mature landfill leachates are typically characterized by the presence of organic compounds resistant to biodegradation, mainly humic substances (HS) - around 70-85%. They are the main responsible for the dark brown color of the leachate. The molecular weight of humic substances varies widely according to the literature: 1,800 to 2,600 Da, 10,000 to 100,000 Da and 1,000 to 100,000 Da. Recalcitrant organic compounds, like HS, presents in surface water bodies may cause problems in the drinking water treatment facilities.

Biological processes are not effective in removing recalcitrant organic, so it is necessary used them combined with physicochemical processes. Advanced Oxidation Processes (AOPs) are alternatives for the removal of recalcitrant organic and color of
mature leachate. AOPs are based on the high oxidation power and low selectivity of the hydroxyl radical (•OH) released during the redox reactions of some oxidizing compounds such as hydrogen peroxide (H₂O₂), ozone (O₃), oxide zinc (ZnO), and titanium dioxide (TiO₂). The •OH radical has higher oxidation potential compared to conventional oxidants. The •OH radical is generated by the reaction between iron salts and H₂O₂, which is known as Fenton’s process. This redox reaction involves a chain of reactions, of which the main ones are represented in Equations 01 and 02.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{•OH} + \text{OH}^- \quad \text{Eq 01}
\]

\[
2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O}_2 \quad \text{Eq 02}
\]

The Fenton’s process has been widely applied to landfill leachate treatment. It uses low cost reagents, the byproducts generated are low toxicity and, moreover, there are no mass transfer limitations. The hydroxyl radicals (•OH) are powerful oxidizing agents able to carry out mineralization of organic pollutants or to reduce the sizes of organic molecules, which can enhance the biodegradability of these substances. Therefore, the combination of the application of Fenton’s process with other processes becomes appropriate.

Treatment with Fenton consists of the following steps: pH adjustment, reagents addition, hydroxyl radical liberation, time for oxidation and neutralization, followed by coagulation/flocculation and sedimentation. In spite of its simplicity, according to literature, treatment with Fenton's process involves a large number of factors such as: dosage of each reagent, molar ratio between the reagents, alkalinity, characteristics of the organic matter influent, reaction time, addition mode of reagents, pH, temperature, and dissolved oxygen in the medium.

The presence of H⁺ ions indicate that the reaction between Fe²⁺ and H₂O₂ (Eq. 02) must occur in an acid medium. Prior to the addition of the reagents, the pH of the medium should be adjusted to acidic values (2.0 - 4.5). After acidification of the medium, Fe²⁺ and H₂O₂ are added and mixed for the time required to generate •OH radicals and oxidation of the present compounds begins immediately.

In general, increasing the dosage of these reagents promotes greater removal of organic products; however, the saturation point of each reagent must be checked. The excess H₂O₂ can react with the •OH radical itself to form hydroperoxyl...
radical (HO•) which has less oxidation potential. In addition, iron has coagulant power, thus increasing its dosage promotes coagulation. On the other hand, there is an increase in sludge production and in the dissolved solids concentration in the effluent. After the oxidation time, the medium should be neutralized to interrupt oxidation reactions. In the reagents application there is a preference for single-stage dosing. However, this option can create an excess of reagent at the time of application, causing side effects of overdosing, whereas if the reagent is added in steps the reaction is carried out gradually over time. The average COD removal in mature leachate treatment by Fenton’s process has been above 60%. The main drawbacks this process is related to high reagents dosage once overdosing generates large volumes of sludge rich in iron. Another problem reported by researchers is the need to reduce the pH.

The aforementioned factors are those reported in the literature as the most important in the application of the Fenton’s process. Mostly, the results were obtained by factors analysis separately, one-factor-at-a-time, and hence do not consider the interaction between them. Only in the last decade was it possible to observe the application of factorial analysis.

In developing countries, Fenton’s process may be a feasible option for mature leachate post-treatment because of the lower cost of reagents and operating when compared with other systems. However, it still lacks information related to optimal reagent dosages and their interactions, as well as factors related to system operation. For this reason, the objectives this study were to: i) determine the main factors that influence in the application of Fenton's process for mature leachate treatment; and ii) optimize, by the response surface methodology (RSM), dosages of reagents for COD and color removal.

2 EXPERIMENTAL MATERIALS AND CHEMICALS

2.1 LANDFILL LEACHATE

The Leachate was collected from the municipal solid waste landfill in Londrina (PR, Brazil), which was in operation between 1974 and 2010. The collected leachate was stored at room temperature in the laboratory to supply the experimental system. The physicochemical composition of the raw leachate was: pH: 8.2 - 8.5; Alkalinity: 4831 - 7205 mgCaCO₃ L⁻¹; BOD: 145-211 mg O₂ L⁻¹; CODFiltered: 1985-3096 mgO₂ L⁻¹;
COD\textsubscript{Total}: 2015-3576 mg O\textsubscript{2} L\textsuperscript{-1}; and ammonia: 819-1370mg N-NH\textsubscript{3} L\textsuperscript{-1}. The range of variation in some parameters reflects rainfall throughout the year in Londrina, a humid subtropical climate region, with an average rainfall of 1626 mm year\textsuperscript{-1} and average temperature of 21.1°C\textsuperscript{60}.

The leachate was submitted to biological treatment for removing biodegradable organic matter and ammonia before physicochemical process with Fenton's process. This consisted of an aerobic reactor (90 L) followed by an anoxic reactor (27 L) and clarifier. Table 01 shows the characteristics of the leachate (after biological treatment) used in the three stages of Fenton's process treatment.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>I and II</td>
</tr>
<tr>
<td>Alkalinity (mgCaCO\textsubscript{3} L\textsuperscript{-1})</td>
<td>1095±41.5</td>
</tr>
<tr>
<td>Color\textsubscript{True} (uC)</td>
<td>7416±176.4</td>
</tr>
<tr>
<td>COD\textsubscript{Filtered} (mgO\textsubscript{2} L\textsuperscript{-1})</td>
<td>2248±49.4</td>
</tr>
<tr>
<td>Ammonia-(mgN-NH\textsubscript{3} L\textsuperscript{-1})</td>
<td>208±88.9</td>
</tr>
<tr>
<td>Nitrite (mgN-NO\textsubscript{2} L\textsuperscript{-1})</td>
<td>4.0±1.67</td>
</tr>
<tr>
<td>Nitrate (mgN-NO\textsubscript{3} L\textsuperscript{-1})</td>
<td>199.1±99.6</td>
</tr>
</tbody>
</table>

2.2 TREATMENT WITH FENTON’S PROCESS

Assays with Fenton’s process were performed using a jar test equipment, the volume used in each vessel was 1.0 L. The first stage consisted of adjusting the pH, which was tested for an interval from 2.0 to 5.0, afterward, the reagents were added, firstly the H\textsubscript{2}O\textsubscript{2} and after a short interval, ferrous sulfate. The stirring speed was maintained around 120 rpm for 2.0 h for step I and III and 2.5 h for step II. At the end of the mixing period the pH was adjusted to values near neutral to stop the oxidation reaction. After the neutralization, the effluent was settled by 1.0 h. Samples were collected for analysis (COD filtered and true color) after the sedimentation time. The H\textsubscript{2}O\textsubscript{2} solution was used in 30% (v/v), analytical grade (MW=34.01g and γ=1.11g cm\textsuperscript{-3}) and The Fe\textsuperscript{2+} ions were obtained using granular ferrous sulfate heptahydrate (Fe(SO\textsubscript{4})\textsubscript{2}H\textsubscript{2}O) (MW=278.01 g). The pH was adjusted with NaOH (6N) or H\textsubscript{2}SO\textsubscript{4} (6N).

2.3 PHYSICOCHEMICAL ANALYSIS

The physicochemical analyses were carried out according to Standard Methods APHA\textsuperscript{61} except for the nitrate, which followed the method of salicylic acid\textsuperscript{62}. The samples to color and COD determination were filtered through fiberglass membrane.
(mesh 1.20 μm). The excess of H₂O₂ may interfere in the COD values, overestimating them, thus, the residual H₂O₂ in this study was disregarded, since the efficiency achieved in the tests would be underestimated.

2.4 EXPERIMENTAL PLANNING

In the experimental design two variable responses were used: (y1) organic matter, measured as COD, and (y2) colour removal efficiency. Statistical analysis was performed using R Statistical Software and Statistica, versão 7.0 (Statsoft., 2004), to a significance level (α) of 5%.

The experimental design was divided into three steps. In Step I assays were run to select the values range for the factors x1 ([H₂O₂]), x2 ([H₂O₂]/[Fe²⁺]), x3 (pH) and x4 (number of reagent dosages) in relation to variable y1 (COD). The addition of reagents was carried out in five fractions during the reaction time of the assays.

In the Step II the interaction of factors was studied by application of fractional factorial design (2⁴⁻¹) to levels (-1, 0, 1). Level "0" (zero) refers to center points, which together with the replicas are used for the calculation of the error analyzes. After determination of significant factors and their interactions (Step II), a Central Composite Design (CCD) was applied to determine the optimum process factors for the response variables, COD and color removal (Step III). The analysis of results was performed by RSM (response surface methodology) procedure to fitted model, a generic model can be seen in Equation 03.

\[ y = \beta_0 + \sum_i \beta_i x_i + \sum_i \sum_j \beta_{ij} x_i x_j + \sum_i \sum_j \sum_k \beta_{ijk} x_i x_j x_k + \ldots \] Eq. 03

Where y is the response variable, xᵢ and xⱼ are the independent variables, and β₀, βᵢ, βᵢᵢ, and βᵢⱼ are the regression coefficients of the model.

The CCD (Table 02) was formed by the full factorial design levels (-1, 0, +1), plus the axial points (-α, 0, +α). The levels of axial points were obtained from Equation 04, being k=4 and resulting in α=2. The center points were the same for the fractional and CCD factorial.

\[ \alpha = \left(2^k\right)^{1/4} \] Eq. 04
Table 02. Full Factorial design (2^4) and CCD.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Ranges and levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>x1 [H2O2]</td>
<td>-2 30, -1 143, 0 255, 1 368, 2 480</td>
</tr>
<tr>
<td>x2 [H2O2]/[Fe]</td>
<td>-2 2, -1 4, 0 6, 1 8, 2 10</td>
</tr>
<tr>
<td>x3 pH</td>
<td>-2 2.0, -1 2.8, 0 3.5, 1 4.3, 2 5.0</td>
</tr>
<tr>
<td>x4 dosage*</td>
<td>-2 1, -1 2, 0 3, 1 4, 2 5</td>
</tr>
</tbody>
</table>

*number of fractions

3 RESULTS AND DISCUSSION

The proposed experimental design was carried out to analyze the factors (x1, x2, x3, x4) for the response variables y1 (COD) and y2 (color). After defining the range of values in Step I, in Step II fractional factorial design (2^4-1) was performed to evaluate the interactions between factors and then to determine the most significant factors. In Step III the fractional factorial design was expanded to a CCD, with the axial points inclusion. Then the CCD coupled with RSM were used to optimize conditions for the application of Fenton’s process.

3.1 STEP I - DEFINITION OF THE RANGE OF VALUES FOR THE FACTORS

The assays realized in Step I indicated divergent results when compared to the literature consulted, mainly for molar ratio [H_2O_2]/[Fe^{2+}] and for the initial pH. It was expected that for higher H_2O_2 concentration the production of •OH radicals would be greater and therefore, the removal of organic matter would be greater until saturation concentration. In this step, this tendency was not observed. Furthermore, 86% COD removal was achieved without initial adjustment of pH, different from that reported in the classic literature. In recent years it is possible to observe in some papers the application of Fenton’s reagent at neutral pH, Koc-Jurczyk and Jurczyk obtained 58% COD removal of landfill leachate and Jurczyk and Koc-Jurczyk applied the Fenton’s reagent to improve the leachate biodegradability. Thus, these results show the possibility of influencing of other factors, including the presence of some ions in the leachate and the characteristics of HS. Therefore, it was necessary to expand the range of values to study.

3.2 STEP II - ANALYSIS OF VARIANCE TO DEFINE THE SIGNIFICANT FACTORS (FRACTIONAL FACTORIAL)

Based on the results of the fractional factorial (2^4-1) the main effects of the factors and their interactions were estimated, but the higher-order interactions were neglected.
The average effects (Standardized Effects, t-values) were plotted against half-normal probability (Fig.1a and 1b). The main effects and interactions (x1, x2, x4 and x1x2, x1x3), were significant for COD (y1) and also for color (y2), except the effect of factor x4 for color. This result confirms the importance of [H₂O₂] (x1) and its relation to the [Fe²⁺] (x2) in the production of •OH radicals. The dosage range applied was of 0.45 to 7.26 mg H₂O₂ mg COD⁻¹ and 0.075 to 5.96 mgFe²⁺ mg COD⁻¹. It is evident that effect of x1 factor has greater significance than x2, which show possibility of using other catalyst, such as ion Fe³⁺ 66,67, zero valent iron, FeCl₂ 46,53, the synthesis of NiFe₂O₅ 50, clay and oxide minerals 52,71,72.

It was also observed that significant factors (x1, x2, x4 and x1x2, x1x3) were the same for COD removal (y1) and true color (y2), except for the effect of factor x4, which indicates a strong relationship between the removal of organic matter and color of leachate, as will be discussed at 3.3.

The factor pH (x3) was not significant in the analysis of variance (Fig.1), but the first order interactions between factors x1 and x3, on both response variables (y1 and y2), was significance. In addition, the classical literature cites the pH factor as important 5,10,25,33,34,36,37,38, due to the presence of ion H⁺ in the reaction between Fe²⁺ and H₂O₂ 11, thus this factor was maintained for the next step. Lastly, the number of dosage fractions (factor x4) was significant for COD but was not significant for color, however, it was also maintained, since it brought operational benefits to the Fenton’s process application: that is distribution of reagents over time 25,34,46 and lower foaming 25,31,34,41,45,46,49,73,74.

**Figure 1** - Standardized Effects (t-values) against expected normal value (a) COD, (b) color

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3.3 STEP III - DEFINITION OF THE SIGNIFICANT FACTORS AND DEFINITION OF THE FINAL MODEL

From the evaluation of the fractional factorial results (Step II), we proceeded to the assays of Step III. In this a CCD and RSM were used to optimize the factors (x1, x2, x3, x4). The experimental design matrix and the results of the response variables are shown in Table 3.

A full model was tested to evaluate the main factors (first and second order) and their interactions (first order). Analysis of variance (ANOVA) for this full model is showed in Table 4, the significant factors for α=5% (p-value<0.05 or F-value>F_{0.05, 1, 39}=4.09) are shown in bold underline. ANOVA indicated only a few factors as significant in the evaluation of the complete model. The lack of fit of the full model for the two variable responses was significant (F-value>F_{0.05, 10, 29}=2.18), such that a new analysis was made considering models with different combinations of factors, to evaluate whether the removal or entry of factors would represent a significant improved fit.

The ANOVA indicated few factors as significant when evaluating the complete model, such that a new analysis was made considering models with different combinations of factors, that is analyzing whether the removal or entry of factors really represents a significant improvement in the adjustment.

Models with more parameters generally fit better (smaller QMRes, larger F and R^2 near the unit), but in building a model for application is important to consider which factors should be included, since not all predictors are important. In addition, simpler models make it easier statistical analysis and its interpretation, so one should select the most important predictors without losing accuracy. Then, the Akaike information criterion (AIC) was used to compare models with the different combinations of factors. The AIC rewards models that reach a high goodness-of-fit score and penalizes them if they become overly complex.

Table 3. Experimental design matrix and responses results (COD and color removal efficiency)

<table>
<thead>
<tr>
<th>[H2O2]</th>
<th>[H2O2]/[Fe]</th>
<th>pH</th>
<th>number dosage</th>
<th>COD</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x1</td>
<td>143</td>
<td>4</td>
<td>2.8</td>
<td>2</td>
<td>76</td>
</tr>
<tr>
<td>x2</td>
<td>143</td>
<td>4</td>
<td>2.8</td>
<td>4</td>
<td>77</td>
</tr>
<tr>
<td>x3</td>
<td>143</td>
<td>4</td>
<td>4.3</td>
<td>2</td>
<td>76</td>
</tr>
<tr>
<td>x4</td>
<td>143</td>
<td>4</td>
<td>4.3</td>
<td>4</td>
<td>73</td>
</tr>
<tr>
<td>R1</td>
<td>143</td>
<td>8</td>
<td>2.8</td>
<td>2</td>
<td>72</td>
</tr>
<tr>
<td>R2</td>
<td>143</td>
<td>8</td>
<td>2.8</td>
<td>4</td>
<td>70</td>
</tr>
</tbody>
</table>
AIC presents a relative measure of information lost when a model is used to represent experimental data. The magnitude of AIC is not really important, because for the model selection the relative values of the AIC are considered, the objective is to select the model with the lowest AIC. With the aid of software R (function stepAIC of MASS package), the best set of parameters for the model was selected using the AIC (smallest AIC) for the response variables COD and color.

The models selected using AIC for response variables are shown by the Equations 05 (COD) and 06 (color). The analysis of variance to the chosen models is shown in Table 5. It may be observed that for response variable COD (Eq.05) the factor x3(L) is not significant, but its removal does not improve model fit.

The lack of fit of the reduced models was significant (Tab.5) for both the response variables, COD (F-value=4.91 > F0.05, 18, 29=1.97) and color (F-value=24.35 > F0.05, 22, 29=1.92). However, the models (Eq. 05 and 04) were able to explain 86.7 and 80.3% of the variance around the average in the COD and color removal.

\[
y_1 = 51.67 + 1.77E^{-01}x_1 - 3.41x_2 + 7.19x_3 - 2.40E^{-04}x_1^2 - 1.55x_3^2 + 7.82E^{-01}x_2x_3 \quad \text{(Eq.05)} \\
y_2 = 62.78 + 2.32E^{-01}x_1 - 3.60E^{-04}x_1^2 \quad \text{(Eq.06)}
\]
The difference in the saturation point (470 mM; CODo=2834 mg L⁻¹) and lower than those found by Lopez et al. 37 (97 mM; CODo=10540 mgL⁻¹) and Santin-Gusman et al. 57 (9.17 mM; CODo=2296 mg L⁻¹) and lower than Moravia et al. 48 (470 mM; CODo=2834 mg L⁻¹) and Badawy et al. 39 (653mM; CODo=13650 mg L⁻¹). The difference in the saturation point of the dosage of H₂O₂ can be explained by

Some predictors of the new fitted models (Eq. 5 and Eq. 6), were chosen for the axes of the response surface plots to account for curvature of the surfaces (Fig.2). The relationship between the efficiency of removing (measured values) COD and color and the respective values predicted by the models are shown in Fig. 3. The COD results (Fig.3a) show linear trend indicating that the model represents the experimental range studied, but in the case of color results (Fig. 3b) this is not verified. The normal probability plot against the residues (Fig. 4) shows a behavior that follows the normal distribution with deviations, which are greater for the residues of the color removal efficiency.

From the response surfaces (Fig. 2) it is observed that the saturation point for the dosage of H₂O₂ is equal to approximately 300 mM, such that from this point increasing the dosage does not result in gain efficiency. It is possible to verify for the variable y₂ (Fig. 2c and 2d) that after this point removal efficiency decreases, which may be caused by reaction between the H₂O₂ excess and •OH radicals. Besides consuming •OH radical and generating HO₂ radicals with lower oxidation potential 10, 25, 34, 38.
variability in the leachate, not only the difference in COD, but also in the concentration of the present ions such as chlorides and alkalinity.

<table>
<thead>
<tr>
<th>Table 5 – ANOVA for selected model</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
</tr>
<tr>
<td>SS</td>
</tr>
<tr>
<td>X1(L)</td>
</tr>
<tr>
<td>X1(Q)</td>
</tr>
<tr>
<td>X2(L)</td>
</tr>
<tr>
<td>X3(L)</td>
</tr>
<tr>
<td>X3(Q)</td>
</tr>
<tr>
<td>X2X3</td>
</tr>
<tr>
<td>Lack of Fit</td>
</tr>
<tr>
<td>Pure Error</td>
</tr>
<tr>
<td>Total SS</td>
</tr>
</tbody>
</table>

In this study, the [Fe^{2+}] was not evaluate alone, only of the [H_2O_2]/[Fe^{2+}] ratio was. The [H_2O_2]/[Fe] ratio was significant to the conditions evaluated, as the presence of iron ions is essential for the oxidation to occur, since these are catalysts of H_2O_2 to form the hydroxyl radical \(^{17,19,20,23}\).

There is dosage saturation point, after which the concentration of iron ions increases the color of the effluent, due to the presence of iron in excess, as well as the sludge production, salinity and conductivity \(^{17,20,25,28,32,45,66}\). In according to Wu et al. \(^{40}\), for the landfill leachate tested, the Fe^{2+} ions dosages limit was 160 mM, Amiri and Sabour \(^{45}\) determined 207 mM and 150 mM. Singh and Tang \(^{38}\) in your review paper identified an optimum Fe^{2+} dose in the range of 0.01 to 14.9 mg Fe^{2+} mg COD\(^{-1}\) with a median of 0.8 mg Fe^{2+} mg COD\(^{-1}\), whereas in this study the range of 0.10 to 2.62 mg Fe^{2+} mg COD\(^{-1}\) resulting in maximum dosage of 127.5 mM. Further studies should investigate the required [H_2O_2] dosage for Fe^{2+} activation, which is likely to be smaller than the one that has been used, as a result, the reagent consumption and sludge production will be lower. Sludge production decreases as the oxidation should predominate over coagulation/flocculation.
Figure 2. Response surface to removal efficiency of response variables $y_1$ (a and b) and $y_2$ (c and d) to the factors $[\text{H}_2\text{O}_2]$ versus $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ and $[\text{H}_2\text{O}_2]$ versus pH

In according to Equation 02, the equilibrium of the reaction occurs in the presence of $\text{H}^+$ ions, in acid medium, the appropriate pH range for the reaction is between 3.0 and 5.0. However, this range could be obtained during the Fenton's process reactions, without need for prior adjustment of the pH. This could justify factor $x_3(L)$ not have been significant in the variance analysis, although the factor $x_3(Q)$ and the interaction $x_2 ([\text{H}_2\text{O}_2]/[\text{Fe}^{2+}])$ and $x_3(\text{pH})$ were, for that reason, other conditions should be evaluated. In the literature, there is no separation in the analysis of the reaction medium for the formation of hydroxyl radicals and for oxidation of organic matter. Equation 02 indicates that the formation of radicals should take place in an acid medium, however, this condition is also treated and discussed as ideal for the organic matter oxidation. Acidification prior to Fenton's process does not only have the function of reducing the pH, but it should also remove alkalinity. The carbonate and bicarbonate ions may react with the $\text{•OH}$ radical, thereby reducing the available radicals for the oxidation of the desired compounds.
In mature landfill leachates, in addition to carbonate and bicarbonate ions, the influence of chlorides and sulfates in the treatment with Fenton´s reagent should also be evaluated \(^{10, 20, 29, 39, 44, 76}\). Finally, the model adopted in the present study indicates that the factor pH (linear) is not significant, that may be related to the fact the medium can become acid by addition of reagents (H\(_2\)O\(_2\) and Fe\(^{2+}\)), which are inherent to the treatment, or the alkalinity reduction promoted by the nitrification in biological process previous, but according to the results obtained there is no basis for this statements. Therefore, further studies investigating the relationship between initial alkalinity and the need to correct the initial pH should be performed.

The factor x4, relating to fractionation of the reagent dosages (divided dosages) was not significant for the ranges of values studied, but assists in the operation of the process, favoring lower foaming. The analysis used in the present study enabled to assess the factors x1, x2, x3 and x4 concurrently, wherein all possible interactions were studied. Although some of these factors had not been significant, it was possible to get the values of these combinations that resulted in improved removal efficiency of COD (y1) 89% and
color (y2) 99%. The parameters that provided the best results were \([H_2O_2] = 480\ \text{mM}, \ [H_2O_2]/[Fe^{2+}] = 6\), an initial pH of 3.5, and dosage divided into three fractions. In this study, COD removal efficiency got (89%) was high when compared to other treatment processes reported in the literature for leachate with similar characteristics.

### 4 CONCLUSIONS

This study was performed to optimizing operational parameters for maximum COD and color removal from biologically pretreated landfill leachate using Fenton’s process. The treatment of mature landfill leachate by Fenton resulted in 89% organic matter, as COD, and 99% color removal. The reagent/COD$_{\text{removed}}$ ratios obtained were in the order of \(6.02 \ \text{mg}\ H_2O_2 \ \text{mg}\ \text{COD}^{-1}\) and \(1.65 \ \text{mg}\ Fe^{2+} \ \text{mg}\ \text{COD}^{-1}\) to reagents applied in three doses, with correction of the initial pH to 3.5.

Based on the statistical design, it was observed that for the conditions studied and for the tested value ranges for factors: \([H_2O_2], \ [H_2O_2]/[Fe^{2+}], \ \text{pH}\) and numbers dosage fractions of reagents, the factor \([H_2O_2]\) had the biggest influence for COD and color removal. The models established by response surface methodology were able to explain 86.7 and 80.3% of the variance around the average in the COD and color removal.

It was observed that the alkalinity and characteristics of the leachate used may interfere in the Fenton’s process efficiency. Here Fenton was applied in leachate previously submitted to the process of nitrification. This process is characterized by a reduction in the values of alklinity, because, as soon as the reagents of own Fenton have been added they already reduce the pH. For reason, it is possible the initial pH factor have not being significant for the range studied (2.0 – 5.0).

The addition of the reagents divided in some fractions was not significant in the treatment by Fenton’s process, however, the fractionation of reagents dosagem is recommended for optimal system operation, avoiding foam formation in the reactor.

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