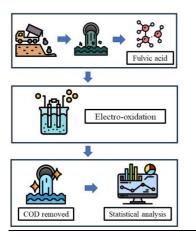
Statistical evaluation of operating parameters in the treatment of landfill effluent containing fulvic acid using electro-oxidation

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Landfills face major problems with the treatment of leachate because it contains recalcitrant compounds. Aiming to collaborate solve this challenge, the objective of this study was to apply electro-oxidation technology to the treatment of a synthetic effluent containing fulvic acid. To this, a set of electrodes was used, in which a potential difference was applied to generate an electric current, in a batch system, for 2 hours. A statistical evaluation was carried out of the influence of two operating parameters, electric current density and reactor volume, on the degradation of Chemical Oxygen Demand (COD). The technology showed efficient, achieving the highest COD removal of 94.33%. In addition, the two parameters analyzed and their interaction were statistically significant for removal, with higher electric current densities and smaller volumes showing better results.

Introduction

With the accentuated growth in population, there has been a significant increase in the generation of solid waste, with landfill being the most common method of disposing of this waste [1], [2]. One of the problems with landfills is the generation of leachate, which has high toxicity and recalcitrant compounds such as fulvic acid [1], [3]. This compound has different functional groups and a long carbon chain. making it difficult to degrade. As a result, the electrooxidation process has become an alternative for the treatment of leachate, as it offers high efficiency in the removal of impurities, using compact and simple equipment for the operation and control of the process. This technology consists of electrodes, usually a cathode and an anode, and takes place through a non-spontaneous chemical reaction generated by the application of a continuous electric current [4]. In order to achieve greater efficiency, it is different necessarv to evaluate operating parameters. Aiming to optimise experiments, time and the overall cost of the research, factorial planning helps to evaluate the ideal experimental conditions for better process efficiency [5]. In this context, this research aims to evaluate the degradation of fulvic acid using electro-oxidation technology, analysing the responses statistically with a view to better applicability.

Material and Methods

This study used a synthetic fulvic acid effluent, with an initial concentration of 2 g·L⁻¹, and electrodes composed of noble metal alloys and iron-chromium alloys. The tests were carried out for 2 hours in a batch system. Electrical current densities of 0.15 e 0.20 A·cm⁻² and volumes of 2 and 5 L were used for the 2² factorial design, considering a 95% confidence level. Chemical oxygen demand (COD) is one of the most important parameters when it comes to legislation on the correct disposal of effluents. Therefore, the results were analysed by evaluating the percentage of COD removal (%), obtained using Equation 1.

$$Y(\%) = \frac{c_0 - c_f}{c_0} x \ 100\% \tag{1}$$

Where Y is the COD removal in percentage (%), C_0 is the initial COD concentration in the solution in $mg \cdot L^{-1}$ and C_f is the final COD concentration in the solution in $mg \cdot L^{-1}$. The results were analysed using Statistica 7 software (StatSoft Inc., USA).

Results and Discussion

The results obtained in terms of COD removal are shown in Table 1.

 Table 1. COD removal results according to different electric current densities and volume.^a

j (A·cm⁻²)	Volume (L)	COD removed (%)
0.15	2	67.61 ± 2.39
0.15	5	45.02 ± 3.36
0.20	2	94.71 ± 0.53
0.20	5	47.15 ± 4.63

 a j: current density; COD removed: average \pm standard deviation COD removed .

Table 1 shows that using the highest current density $(0.20 \text{ A} \cdot \text{cm}^2)$ and the smallest volume (2 L) resulted in a higher percentage of COD removal. With the results obtained from the statistical analysis, it was possible to verify and specify the better experimental operating conditions, as well as evaluating the influence of the individual parameters and their

interaction according to response evaluated.

Table 2 shows the data obtained from the analysis of variance (ANOVA), which describes the significance of the terms that influence the electro-oxidation process. Analysing Table 2, is evident that all the p-values are less than $5 \cdot 10^{-2}$, within the established range of significance. This means that both the electric current density and volume factors and their interaction are statistically significant. Thus, all the parameters compose the statistical model described by Equation (2).

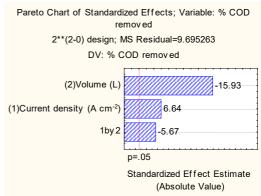
$$y(x_1, x_2) = 63.62 + 14.61x_1 - 35.08x_2 - 12.49x_1, x_2$$
(2)

In relation to Equation (2), the value of 63.62 ± 1.10 represents the effect of the interception factor. It can also be noted that the volume terms (x_2) and the interaction of the terms (x_1, x_2) are negative, while the electric current density term (x_1) is positive.

Negative terms imply parameters that are inversely proportional to COD removal, i.e. to achieve greater COD removal it is necessary to use smaller volumes. Positive terms are also directly proportional, i.e. higher current densities are required for greater COD removal. Furthermore, in order to assess the quality of the fit of the statistical model, the F values obtained in Table 2 can be compared with the theoretical F value using the Fisher-Snedecor test. As the value of F(3.4) 0.95 is equal to 6.59, the

theoretical value, it can be verify that the F values of the factors analysed as well as their interaction are greater than the tabulated F at the 5% significance level. This means that the model fits the results well. Finally, Figure 1 shows the Pareto chart, which illustrates the magnitude and positive or negative influence of the effects, also observed in the statistical model. Note that the vertical line on the Pareto chart corresponds to a p-value of $5 \cdot 10^{-2}$. Values that exceed this vertical line are considered statistically significant. In other words, this confirms that the current density and volume factors, as well as their interaction, are significant.

The magnitude of the p-values can be verify in Table 2. In addition, as it has a larger horizontal bar, volume is the factor that most influences COD removal, followed by current density and then their interaction. Finally, for greater efficiency in terms of COD removal using electro-oxidation in effluents containing fulvic acid, it is necessary to use higher current densities and smaller volumes.





Factor	df	SS	MS	Effect	F	р
(1) Current density (A cm ⁻²); x ₁	1	427.05	427.05	14.61	44.05	2.67 10 ⁻³
(2) Volume (L); x ₂	1	2460.86	2460.86	-35.08	253.82	9.10 10 ⁻⁵
Interaction (1) by (2); x_1x_2	1	311.87	311.87	-12.49	32.17	4.77 10 ⁻³
Error	4	38.78	9.70	2.20		
Total SS	7	3238.57				

Table 2. ANOVA of the regression model representing % COD removed after electro-oxidation.^a

^a df: degrees of freedom; SS: sum of squares; MS: medium square.

Conclusions

This work showed that electro-oxidation is a promising technology for reducing COD in effluents containing fulvic acid. Statistical analysis indicated that the parameters of current density and volume, as well as their interaction, are significant in COD removal. Thus, higher current densities and lower volumes tend to promote greater COD removals from fulvic acid solutions using electro-oxidation.

Acknowledgments

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