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OPTIMIZATION OF *IN SITU* H₂O₂ GENERATION FOR ELECTROCHEMICAL TREATMENT OF EFFLUENTS SYNTHETICS AND REAL WITH CAFFEINE, PARACETAMOL AND NORFLOXACIN RESIDUES (Poster)

R.J.A. Felisardo^{a,*}, F.E. Durán^a, C.H.M. Fernandes^a, G.O. Santiago^a, M.A. R. Rodrigo^b, M.R.V. Lanza^{a,*}

^aSão Carlos Institute of Chemistry, University of São Paulo, 400 São Carlos, SP 13566-590, Brazil.

^bUniversidad de Castilla La Mancha, Ciudad Real, 13071, Spain.

The search for effective solutions for the treatment of complex effluents has been considered essential to the growing challenge of water scarcity in the world (Singh *et al.*, 2023). Advanced oxidation processes, especially those based on the electrochemical production of oxidants, such as hydrogen peroxide (H₂O₂), are gaining importance in this context. This is largely due to the fact that *in situ* generation of H₂O₂ allows the development of safer and more economical systems, since it eliminates the need to transport large volumes of this reagent (Dan *et al.*, 2022). However, the efficiency of this technology depends on the catalytic material used and the operating conditions used, which, if optimized by statistical tools, can provide significant advances in their viability. This study aimed to evaluate and optimize the *in situ* generation of H₂O₂ using Printex L6 carbon-based gas diffusion electrodes (GDE/PL6C), through an experimental design in the central composite rotational design (CCRD) model, for simultaneous degradation of synthetic and real effluents containing caffeine, paracetamol and norfloxacin residues.

The GDE/PL6C was prepared following the standard method established by the research group in previous works (Silva *et al.*, 2023; Marques Cordeiro-Junior *et al.* 2022). The operating system consisted of a single-compartment cylindrical glass electrochemical cell, which in addition to the GDE/PL6C ($A_{\text{geo}} = 20 \text{ cm}^2$) as cathode, was equipped with an Ag/AgCl reference electrode and a dimensionally stable counter electrode (Ti/RuO₂-TiO₂). The O₂ flow injected directly into the GDE/PL6C was fixed at 0.1 L min^{-1} , while the temperature of the electrochemical cell was kept constant at 20°C. The working volume was 250 mL. The CCRD design was a 2³ factorial, with 1 genuine replicate and 4 replicates at the center point, designed at the following levels: $-\alpha$ (-1.68), -1, 0, +1, $+\alpha$ (+1.68), in order to expand the experimental design and verify more complex quadratic and/or nonlinear effects. Key parameters such as support electrolyte concentration ($[\text{K}_2\text{SO}_4] = 0.025, 0.050 \text{ and } 0.075 \text{ mol L}^{-1}$), current density ($j = 15, 30 \text{ and } 45 \text{ mA cm}^{-2}$) and solution pH (3.0, 6.0 and 9.0) were chosen to reflect the conditions of electrogeneration of H₂O₂ accumulated in 90 min of electrolysis.

The experimental results indicated that in the mathematical regression model, all isolated variables had a positive effect on the electrogeneration of H₂O₂, with j being the most intense effect. On the other hand, despite the nonlinear relationship observed between the studied variables, only $[\text{K}_2\text{SO}_4]$ showed a pronounced quadratic effect. The greatest impact of j can be attributed to the higher rate of O₂ reduction in the GDE/PL6C, while the positive effect of increasing $[\text{K}_2\text{SO}_4]$ may be due to the improvement in the electrical conductivity of the solution, which facilitates the O₂ reduction reaction. The benefit of increasing pH may be related to the stability of the generated H₂O₂. However, when analyzing the results of the CCRD matrix, it was observed that the maximum accumulated production of H₂O₂ occurred under the condition of $[\text{K}_2\text{SO}_4] = 0.075 \text{ mol L}^{-1}$, $j = 45 \text{ mA cm}^{-2}$ and pH = 9.0, reaching approximately 1220 mg L^{-1} in 90 min of electrolysis. In the maximum axial point condition for $[\text{K}_2\text{SO}_4]$, with other variables at central values, the second highest production rate was obtained, equivalent to approximately 998 mg L^{-1} of H₂O₂, suggesting that the concentration of the supporting electrolyte plays a crucial role

in the process efficiency. Nonetheless, the response surface graphs, which describe the interaction between the studied variables, revealed that $[K_2SO_4]$ exerts a more pronounced influence at $j > 30 \text{ mA cm}^{-2}$, i.e., above central values. The response surface model was statistically validated using analysis of variance (ANOVA) and Fisher distribution (F_{test}). The results showed that the regression is statistically significant and effectively represents the experimental results, since the ratio between the mean square of the regression and the residual exceeds the theoretical value tabulated. However, the ratio between the mean square of the lack of fit and the pure error is above the theoretical value tabulated, suggesting that the lack of fit is low, but the pure error tends to zero. Pareto chart analysis demonstrated excellent correlation between variables and standardized effects, while the predicted versus experimental values plot indicated that the regression model adjusted to the experimental data. Under the optimized H_2O_2 electrogeneration condition, the simultaneous degradation of effluents containing caffeine, paracetamol and norfloxacin residues showed that the inherent complexity impacts the rate and kinetics of compound degradation, but that the electrochemical process with H_2O_2 is efficient in synthetic and real aquatic matrices, whether in complete or partial degradation of the compounds. In summary, by addressing the problem of complex effluent treatment and the use of statistical tools for process optimization, this study has a significant impact and contributes to the advancement of complex effluent treatment technology with potential for application in different water pollution scenarios.

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References

- Dan, M., Zhong, R., Hu, S., Wu, H., Zhou, Y., Liu, Z.-Q., Chem Catalysis, 2 (2022) 1919.
 Marques Cordeiro-Junior, P.J., Sáez Jiménez, C., Vasconcelos Lanza, M.R. de, Rodrigo Rodrigo, M.A., Separation and Purification Technology, 300 (2022) 121847.
 O. Silva, T., A. Goulart, L., Sánchez-Montes, I., O. S. Santos, G., B. Santos, R., Colombo, R., R. V. Lanza, M., Chemical Engineering Journal, 455 (2023) 140697.
 Singh, B.J., Chakraborty, A., Sehgal, R., Journal of Environmental Management, 348 (2023) 119230.