Degradation of Phenacetin in Wastewater by Electro-Oxidation: Effect of Variables and Evaluation of Acute Toxicity

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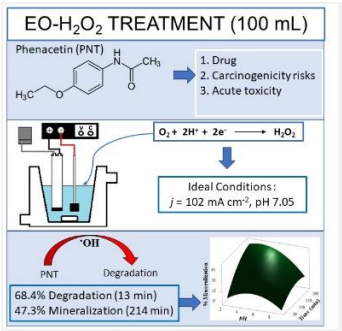

This study aims to optimize the electro-oxidation (EO) process, to efficiently degrade phenacetin, through a central composite design based on response surface methodology. The process was carried out in a reactor containing 100 mL of solution, with boron-doped diamond (BDD) anode and carbon-PTFE air-diffusion cathode. According to the results, from the analysis of variance, the model presents a good correlation between the observed and predicted values. Thus, under optimal operation conditions (pH = 7.05, j = 102 mA cm^{-2} and 13 min for degradation and 214 min for mineralization), 65.6% degradation and 51.9% mineralization were achieved. The use of EO-H_2O_2 process reduced the toxicity, as shown by acute ecotoxicity tests using *Artemia salina*.

Introduction

In recent years, concern about the impact of pollution from emerging contaminants has focused on conventional pollutants. However, there is a growing interest in investigating another group of substances: pharmaceuticals [1,2]. Phenacetin (PNT, N-(4-ethoxyphenyl)-acetamide) is an analgesic, being the first drug successfully synthesized as an antipyretic [3]. Due to its potential carcinogenicity, it was banned in many countries in the 70s [4]. However, it is still permitted in medications in combination with other drugs [5]. Considering that prolonged exposure to phenacetin can pose serious health risks and its removal through conventional treatments has not been effective [6], advanced oxidation process (AOPs), including electro-oxidation (EO), emerges as a promising technology to remove PNT from the environment [7] efficiently. Considering the above premises, the elimination of the PNT in a real effluent was evaluated by the EO-H_2O_2 process following a central composite design (CCD) 2^3 factorial planning. Additionally, the acute toxicity of the treated solutions was tested using *Artemia salina*.

Material and Methods

The electrolytic system was an undivided electrochemical cell jacketed for water recirculation at 25 ºC. An air-diffusion electrode made of a carbon-PTFE supplied by E-TEK (Somerset, NJ, USA) and a boron-doped diamond (BDD) thin film electrode supplied by NeoCoat (La-Chaux-de-Fonds, Switzerland) were used as cathode and anode, respectively, both with an area of 3 cm^2 and separated by 1 cm. A 100-mL solution of PNT containing 0.05 mol L^{-1} Na_2SO_4 as the electrolyte was employed for the electrolyses. These solutions were prepared in actual wastewater samples from the up-flow anaerobic sludge blanket (UASB) post-reactor effluent (i.e., secondary effluent) from a treatment plant in the municipality of Campo Grande, Brazil. The mineralization was assessed with a Shimadzu TOC-V CPN analyzer. PNT decay was monitored by high-performance liquid chromatography using a Shimadzu SPD-M20A chromatograph with a C18 column and diode array detector. The acute toxicity tests were first conducted with *Artemia salina* nauplii. A CCD 2^3 was applied to investigate and optimize the system variables applied current, j (60 mA cm^{-2} as a central point), pH (5.5 as a central point) and time (8 and 130 min to degradation and mineralization times, respectively, as a central point). A total of 17 experiments were conducted, being distributed as: 8 cube points (levels -1 and +1), 6 axial points (levels -1.63 and +1.63) and 3 replicates at the central point (0). All experimental designs in this work were analyzed using the Minitab 19 statistical software program.

Results and Discussion

Analysis of variance (ANOVA) was evaluated to determine model fit. This model is highly significant (Table 1), with a p-value = 0.000 for both degradation and mineralization. The high values of the regression coefficients for degradation and mineralization (R^2 of 98.2% and 98.7, respectively) confirm the adequacy of the model. All linear factors were significant for degradation and mineralization. The quadratic terms Time*Time for degradation and mineralization and the pH*pH for mineralization were significant,

suggesting that these terms tend to be more effective at intermediate values. The significant interactions for the model were *j**pH and *j**Time for PNT degradation and pH*Time for mineralization. Using the Minitab Statistical program, the ideal conditions to treat PNT were obtained: j = 102 mA cm^{-2}, pH = 7.05, and reaction time of 13 and 214 min for degradation and mineralization, respectively. Under these conditions, 68.4% of degradation and 47.3% of mineralization are predicted. Triplicate tests were carried out to confirm these conditions, achieving 65.6% and 51.9% for degradation and mineralization, respectively.

The toxicity of PNT and its byproducts was evaluated in *Artemia salina* larvae. The toxic effect of the raw effluent and the raw effluent enriched with 25 mg L^{-1} of PNT presented a high mortality rate of the organism with a LC50 of 80.5 and 70.8 mg L^{-1}, respectively, indicating high toxicity for the test organism. Regarding the treated solutions, no significant acute toxicity was observed.

Table 1. ANOVA results for PNT removal by EO-H_2O_2 process.

Source	Degradation			Mineralization		
	(%)	F-value	p-value	(%)	F-value	p-value
Model	98.2	41.7	0.000	98.7	57.1	0.000
Linear	86.5	110.3	0.000	82.2	142.7	0.000
j	21.9	83.5	0.000	20.5	107.0	0.000
pH	4.8	18.5	0.004	18.5	96.2	0.000
Time	59.8	228.7	0.000	43.2	225.0	0.000
Interaction	5.6	7.1	0.016	3.1	5.4	0.031
*j**pH	3.5	13.2	0.008	0.8	4.0	0.084
*j**Time	2.0	7.5	0.029	0.2	0.9	0.386
pH*Time	0.1	0.5	0.510	2.1	11.2	0.012
Quadratic	6.1	7.8	0.012	13.4	23.3	0.001
*j***j*	2.1	2.2	0.179	0.2	3.8	0.091
pH*pH	0	0.9	0.371	8.3	60.3	0.000
Time*Time	4.0	15.4	0.006	4.9	25.6	0.001
Lack of fit	1.3	1.1	0.545	1.2	3.0	0.271
Error	1.8			1.3		
Summary	R^2 = 98.2%; R^2_{Adj} = 95.8%			R^2 = 98.7%; R^2_{Adj} = 96.9%		

Conclusions

The effectiveness of the EO-H_2O_2 process for eliminating PNT in real wastewater was confirmed by the 100% removal of 25 mg L^{-1} of the drug after 90 min under optimized conditions, along with a high mineralization percentage after 300 min. The treated solutions reduced the toxicity and showed promising results for the remediation of PNT residues in wastewater.

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