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Inovações e Soluções Sustentáveis em Engenharia Ambiental

Optimization of electrolytic process for the removal of the antibiotic ciprofloxacin from synthetic wastewater

Otimização de processo eletrolítico para remoção do antibiótico ciprofloxacina em água residuária sintética

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ABSTRACT

Ciprofloxacin (CIP), an antibiotic of the fluoroquinolone class, has low biodegradability and possible toxic environmental effects. Due to its extensive use, it is considered an emerging contaminant (EC) in environmental compartments such as water, sludge, and sewage that contribute to antimicrobial resistance. This work assessed the optimal conditions for removing CIP in synthetic wastewater using electrolytic treatment and a laboratory-scale reactor with aluminum electrodes. The experiments were carried out from reconstituted synthetic wastewater fortified with 10 mg L^{-1} of CIP. The operational parameters of the reactor, such as pH, voltage, and concentration of the supporting electrolyte (NaCl), were optimized based on the reduction of the CIP concentration through the complete factorial design 2^3 followed by optimization by the response surface methodology employing central composite rotational design (CCRD) from the regression analysis of the quadratic model. The best operational condition obtained was pH = 7.6, voltage = 5.6 V, and [NaCl] = 0.6 g L^{-1}. In the validation tests, the removal achieved over 120 min was 78%, with equilibrium established after 80 min. It is suggested that, in addition to removing CIP by electrocoagulation mechanisms, there is also degradation by the electro-oxidation mechanism, promoted by oxidizing species produced from components of the reaction medium. The applied electrolytic process proved favorable and promising for removing CIP in synthetic wastewater.

Keywords: Antibiotics; Emerging contaminants; Electrolytic treatment

RESUMO

A ciprofloxacina (CIP) é um antibiótico da classe das fluoroquinolonas, possui baixa biodegradabilidade e com possíveis efeitos tóxicos no meio ambiente. Pelo uso extensivo é considerado um contaminante emergente (CE) presente em compartimentos ambientais como águas, lodos e esgotos que contribui para o fenômeno da resistência a agentes antimicrobianos. Este trabalho buscou estudar as condições ótimas para a remoção da CIP em água residuária sintética, utilizando como proposta o tratamento eletrolítico, por meio de um reator em escala laboratorial com eletrodos de alumínio. Os experimentos foram realizados a partir de água residuária sintética reconstituída fortificada com 10 mg L^{-1} de CIP. Os parâmetros operacionais do reator: pH, tensão e concentração do eletrólito suporte (NaCl) foram avaliados com base na redução da concentração da CIP, por meio de planejamento fatorial completo 2^3. Posteriormente, foi empregando o delineamento composto central rotacional (DCCR) e otimizada as condições por meio da metodologia de superfície de resposta, a partir da análise de regressão do modelo quadrático. A melhor condição operacional obtida foi pH = 7,6, tensão = 5,6 V e [NaCl] = 0,6 g L^{-1}. A remoção alcançada em testes de validação ao longo de 120 min foi de 78 % , com estabelecimento de equilíbrio a partir de 80 min. Sugere-se que, além da remoção da CIP por mecanismos de eletrocoagulação, haja também a ocorrência da degradação pelo mecanismo de eletro-oxidação, promovido por espécies oxidantes produzidas a partir de componentes do meio reacional. Em linhas gerais o processo eletrolítico aplicado mostrou-se favorável e promissor para a remoção de CIP em água residuária sintética.

Palavras-chave: Antibióticos; Contaminantes emergentes; Tratamento eletrolítico

1 INTRODUCTION

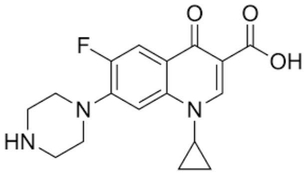
Considering the continuous growth of the global population, there is an increase in the consumption and subsequent disposal of medications. Thus, it becomes essential to monitor and conduct studies that assess the occurrence of pharmacological substances and explore technologies aiming to mitigate and remove residual pharmaceuticals from environmental compartments (Montagner, Vidal & Acayaba, 2017).

One of the main routes for pharmaceuticals to enter ecosystems is through domestic wastewater. This is attributed to the low or ineffectiveness of sewage treatment plants (STPs) in removing complex contaminants such as pharmaceuticals (Stumpf et al., 1999). This is mainly due to the characteristics of the bioactive molecules used in pharmaceuticals, including their ability to resist physical and chemical agents in the environments through which they pass. Another factor contributing to these compounds' occurrence in the environment is their low absorption by organisms, causing them to be excreted unchanged or partially metabolized (Melo et al., 2009, Lee et al., 2021).

Of the various classes of drugs currently being studied in environmental matrices, antibiotics contribute to bacterial resistance, an irreversible phenomenon potentially harmful to public health (Pinto, 2011). The primary antibiotics used in human medicine found in surface and wastewater are amoxicillin, ciprofloxacin (Gracia-Lor et al. (2011), tetracycline, and sulfamethoxazole (Branco et al., 2021).

Ciprofloxacin (CIP) (Table 1) belongs to the quinolone class (fluoroquinolones). It is considered one of the most effective antimicrobials in treating gram-negative bacteria. It is, therefore, widely used to treat urinary, respiratory, gastrointestinal, skin, bone, and joint infections (Baptistucci, 2012).

Table 1 – Physicochemical Properties of Ciprofloxacin

Molecular structure	**Molecular mass (g mol^{-1})**	**Water solubility (g L^{-1})**	***log K_{ow}***	***pKa***
 $C_{17}H_{18}FN_3O_3$	331.4	>2,0	0.28	6.27 (-COOH) 8.87 (=NH_2^+)

Source: adapted from Schmitt-Kopplin et al. (1999)

It has been reported that global CIP consumption between 1995 and 2015 increased from 700 t year^{-1} to 2400 t year^{-1} (Odenkamp, Beusen & Huijbregts, 2019). Due to its large-scale use, it is frequently found in environmental matrices (Table 2), which raises concerns and stresses the importance of developing new techniques capable of removing antibiotics and other emerging contaminants (Lindberg et al., 2006; Rodrigues-Silva et al., 2014).

Preliminary studies indicate that removing most emerging contaminants in WWTPs is generally ineffective since the molecules are not biodegradable. In addition, there is a strong tendency for these molecules to transfer by sorption in sludge and sediments during passage through systems based on biological treatments (Costa Junior et al., 2017).

Table 2 – Presence of CIP in different environmental matrices

Concentration	**Matrix**	**Country**	**Reference**
2.5 ng L^{-1}	Surface water	Brazil	Locatelli et al. (2001)
259 mg d^{-1} 1000 hab^{-1}	Sewage	Itaty	Castiglioni et al. (2006)
45-120 ng L^{-1}	Primary effluent from WWTP	Switzerland	Golet et al. (2001)
45-108 ng L^{-1}	Tertiary effluent from WWTP	Switzerland	Golet et al. (2001)
0.020 µg L^{-1}	Surface water	USA	Kolpin et al. (2002)
1.4 µg L^{-1}	Aquaculture water	China	Zhang et al. (2013)
740 ng L^{-1}	Surface water	Espain	Gracia-Lor et al. (2011)
2.35-15.33 ng g^{-1}	Sediments	China	Li et al. (2021)
5.3 µg L^{-1}	Effluent from WWTP	Kenya	Kairigo et al. (2020)
2.5 µg L^{-1}	Surface water		
4125 µg kg^{-1}	Sediment		

Source: Organized by the authors (2024)

Thus, new techniques or improvements to existing ones are sought to complement conventional treatment systems in terms of removing contaminants such as pharmaceuticals before they reach environmental compartments. Consequently, some treatment approaches based on advanced oxidative processes (AOPs) and their combinations have been studied (Taoufik et al., 2021; Adeoye et al., 2024).

One alternative is using electrochemical processes to transform organic molecules into carbon dioxide and water or their separation by entrainment with microbubbles or sludge generated in the process (João et al., 2018). Thus, the use of electrolytic processes stands out in the field of advanced treatments. The techniques are based on non-particulate organic pollutants' flotation, coagulation, and oxidation. These processes are considered efficient and straightforward to operate, with short reaction time and low formation of residual sludge (Módenes et al., 2017).

The main mechanisms observed in the electrolytic process are the oxidation of the electrode to form coagulants – metal hydroxides – through the reaction with hydroxyl ions and the generation of gas bubbles due to the electrolysis of water and flotation.

The passage of electric current through an electrochemical cell causes an imbalance in the system, which results in various phenomena based on charge transfer involving pairs of redox reactions at the electrodes, ionic conduction that represents the movement of species in the solution, and electrode depolarization. Therefore, the main processes applied to the removal of contaminants in aqueous media are electrocoagulation, electroflotation, and electro-oxidation (Table 3) (Ticianelli, 2005; Espinoza-Quiñones et al., 2016).

Table 3 – Comparison of main Electrochemical methods

Process	Characteristics
Electrocoagulation	• The cell's constituent metal is dissolved, producing cations that are rapidly hydrolyzed to polymeric hydroxide. • Coagulation occurs when the cations combine with the negative particles generated at the anode. • The contaminants present in the solution are aggregated to the clots formed, generating sludge.
Electroflotation	• Hydrogen (cathode) and oxygen (anode) gases are released. • The microbubbles produced are responsible for flotation. They drag contaminants to the upper portion of the liquid phase.
Electro-oxidation	• Organic molecules are decomposed into carbon dioxide, water, or ammonia. • In direct oxidation, contaminants are adsorbed on the anode and degraded by anodic electrical transfer. • In indirect oxidation, strong oxidants such as oxonium, peroxide, hypochlorite, and chlorine are generated in situ and are capable of acting on the contaminants.

Source: Organized by the authors (2024)

The electrolytic processes have been investigated in the removal of various pharmacological contaminants (Table 4). The results suggest potential for the application of these processes. However, there are still gaps to be explored regarding the behavior of the main compounds in the electrolytic processes.

Table 4 – Electrolytic processes applied to the removal of pharmacological contaminants

Drug	Matrix	Process type	Efficiency (%)	Reference
Sulfamethoxazole	Synthetic wastewater	Eletro-oxidation	28	Santos (2021)
Doxycycline	Wastewater	Electrocoagulation	96	Baran et al. (2018)
Ciprofloxacin	Wastewater	Electrocoagulation	99	Yoosefian et al. (2016)
Cefixime	Aqueous solution	Electrocoagulation	90	Mostafaloo, Yari & Mohammadi (2019)
Ibuprofen	Groundwater	Electrocoagulation	78	Negarestani et al. (2020)

Source: Organized by the authors (2024)

The factors that most affect the performance of electrolytic processes are the pH of the solution, the voltage, and the current density. The surface charges of the coagulant particles vary according to the pH of the solution, which interferes with removal (Santana, 2018; Mohammed et al., 2021). Thus, this study sought to optimize the variables pH, voltage, and concentration of the supporting electrolyte (NaCl) for the removal of the antibiotic ciprofloxacin (CIP) using an electrolytic system composed of aluminum electrodes, aiming at the prospect of a form of treatment for this compound in synthetic wastewater.

2 MATERIAL AND METHODS

2.1 Reagents, standards, solutions, and analytical determinations

The drug ciprofloxacin (CIP) was purchased as an analytical standard (Sigma-Aldrich) with purity ≥ 95.0%. Stock solutions were prepared at a concentration of 1000 mg L^{-1} added to ultrapure water containing 50 μL of 37 % HCl for solubilization. Afterward, they were stored at 4 °C under refrigeration and protected from light.

Anhydrous sodium chloride P. A. (NaCl, Didática) was used in the electrolytic test. In the pH adjustments, solutions of hydrochloric acid 0.01 mol L^{-1} (HCl, NEON) and sodium hydroxide solution 0.01 mol L^{-1} (NaOH, NEON) were used. To prepare the synthetic wastewater, sodium bicarbonate P. A. ($NaHCO_3$, Didática), calcium chloride dihydrate P. A. ($CaCl_2$ $2H_2O$, Dinâmica), magnesium chloride hexahydrate P. A. ($MgCl_2$ $6H_2O$, Merck), ammonium chloride P. A. (NH_4Cl, NEON) and monobasic potassium phosphate P. A (KH_2PO_4, Dinâmica) were used.

CIP concentration was determined in a single-beam scanning UV/VIS molecular absorption spectrophotometer (PerkinElmer™ LAMBDA XLS) in the range of 200 nm to 400 nm with a resolution of 2 nm. Quartz cuvettes with a 1 cm optical path were used. CIP calibration employed triplicates of solutions with concentrations of 2 mg L^{-1} to 22 mg L^{-1} at pH 4, 6, and 8 of the contaminant bulked in synthetic wastewater.

2.2 Reconstitution of synthetic wastewater and the electrolytic system

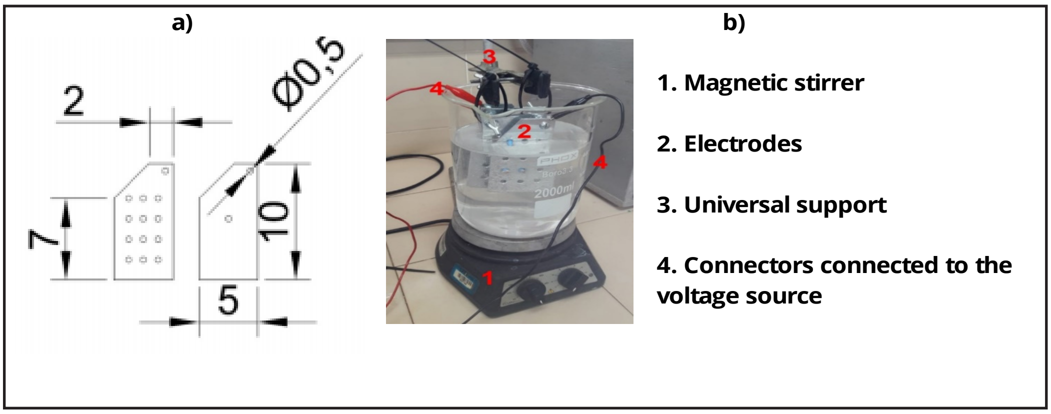
Synthetic wastewater was produced according to the methodology proposed by Marchesi (2020). Water from a local artesian well was used, adding organic matter in a proportion of 50% proteins, 40 % carbohydrates, and 10 % lipids. The organic compounds were incorporated from the addition of soybean extract, sucrose, cornstarch, and soybean oil, resulting in approximately 400 mg COD L^{-1}.

The typical mineral salts present were included from the dissolution of salts so that there were 60 mg L^{-1} of bicarbonate, 20 mg L^{-1} of sodium, 13 mg L^{-1} of calcium, 8.5 mg L^{-1} of chloride, 8.5 mg L^{-1} of magnesium, 50 mg L^{-1} of ammoniacal nitrogen, 5.6 mg L^{-1} of phosphorus, and 16 mg L-1 of potassium. After homogenization, the aliquot of the CIP stock solution was added, totaling 10 mg L^{-1}.

A laboratory-scale reactor operating in batch mode and consisting of a 2000 mL beaker was placed on a magnetic stirrer (Fisatom). A tripod was used to fix the electrodes inside the beaker (Figure 1). The electrodes were made of aluminum with a width of 5 cm at the base and 2 cm at the top, a length of 10 cm on the right side and 7 cm on the left side, a thickness of 0.3 mm, and containing 12 holes with a diameter of 0.5 mm for better circulation of the liquid phase (Figure 1a).

An AFR-DC Regulated Power Supply, model FA3005T, was used and connected to the electrodes inserted in the beaker.

Figure 1 – System used in electrolytic tests. a) electrode. b) reactor



Source: Authors (2024)

2.3 Optimization of experimental conditions and removal test

In order to verify the best combination for the independent variables pH, electrical voltage, and NaCl concentration as a supporting electrolyte in the treatment process of synthetic wastewater containing CIP, an experimental design (DoE) was used.

Initially, a 2^3 factorial design (+1 and -1) with three repetitions at the central point (0) was defined, totaling 11 tests (Table 5). The CIP concentration was set at 10 mg L^{-1}, and the treatment time was 30 min.

Table 5 – Coded and real levels of independent variables used in experimental designs

Independent Variables	**Coded and actual levels of independent variables**							
	Full factorial 2^3			**CCRD**				
	-1	**0**	**+1**	**-1.68**	**-1**	**0**	**+1**	**+1.68**
pH	7	8.5	10	5.3	6	7	8	8.7
voltage (V)	4	6	8	2.98	4	4.5	6	7.02
NaCl (g L^{-1})	0.2	0.4	0.6	0.23	0.3	0.4	0.5	0.57

Source: Organized by the authors (2024)

To optimize the conditions based on the information obtained in the initial factorial design, a central composite rotational design (DCCR), consisting of a 2^3 factorial with two levels (-1 and +1), 3 repetitions at the central point (0) and 6 axial points (-1.68 and +1.68) was applied, totaling 17 tests (Table 5).

The Statistica software, version 8.0 (StatSoft™, USA), was used to determine the effects of the independent variables (pH, voltage, and concentration of supporting electrolyte (NaCl)) and for optimization by the response surface methodology. This method consists of modeling and displacement steps, which are repeated until the optimal region of the studied surface is obtained (Barros Neto, Scarminio & Bruns, 2001). In the statistical analysis, the percentage of CIP removal was used as the response of each test and its adjustment to the quadratic model using ANOVA regression with a 95 % confidence level.

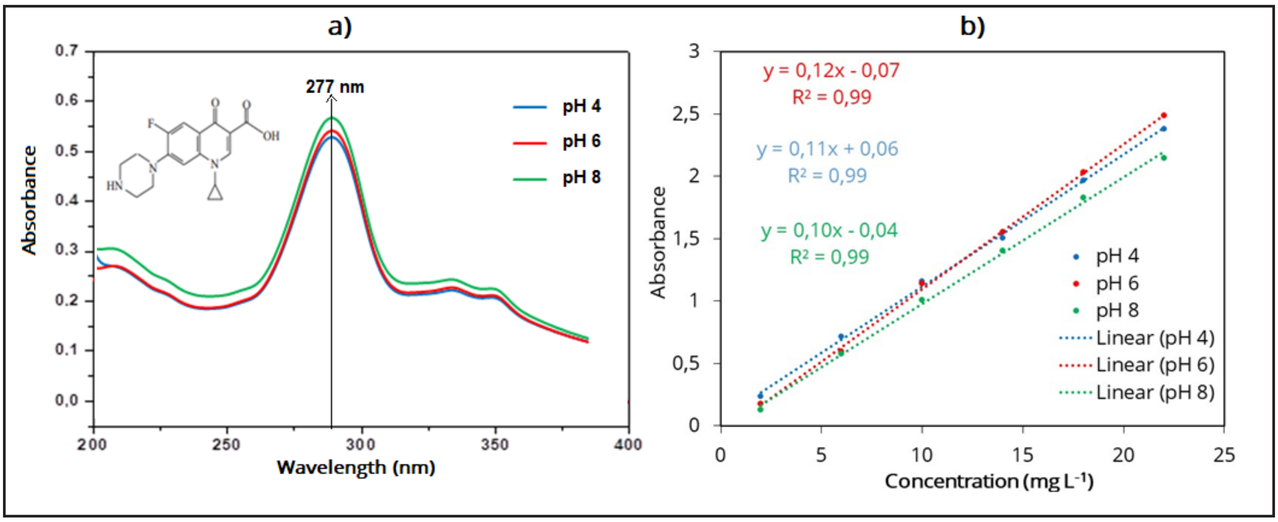
From the optimized condition, the CIP removal test in synthetic wastewater was conducted by the electrolytic process by measuring the analyte concentration at regular intervals (0 min, 2.5 min, 5 min, 10 min, 20 min, 30 min, 50 min, 80 min and 120 min) for 2 h.

3 RESULTS AND DISCUSSION

3.1 Spectroscopic characteristics of CIP

CIP has a maximum absorption band at 277 nm in the mid-ultraviolet region (Figure 2a). Considering that the spectroscopic behavior may vary according to the pH of the medium, the analytical calibration in the CIP determinations in synthetic wastewater was performed at pH 4, 6, and 8 (Figure 2b). Thus, in the concentration range of 2 mg L^{-1} to 22 mg L^{-1}, straight-line equations with a coefficient of determination (R^2) close to 1 were obtained. This demonstrates that the calibration was adequate to quantify the CIP in the study.

Figure 2 – a) UV-Vis absorption spectra at 5 mg L^{-1} and b) Calibration curves in the range of 2 mg L^{-1} to 22 mg L^{-1} for CIP at pHs 4, 6, and 8



Source: Authors (2024)

3.2 Optimization of removal conditions

The independent variables of electrical voltage, pH, and concentration of the supporting electrolyte (NaCl) were investigated in the electrolytic process of CIP removal using the experimental designs and the response surface methodology. In the initial stage, the 2^3 complete factorial design with central points was explored (Table 6).

Inspection of Table 6 allows us to observe that the highest CIP removal occurred in test 5 (95 %). This test corresponds to the lowest level (-1) of pH (7) and voltage (4 V) and the highest level (+1) for the concentration of the supporting electrolyte (0.6 g L^{-1}). The central points (pH = 8.5, voltage = 6 V and NaCl concentration = 0.4 g L^{-1}) exhibited percentage values in the 82 % to 90 % range and were equally important for delimiting the most favorable conditions of the electrolytic process.

Table 6 – Matrix of the 2^3 full factorial design with central points for the electrolytic process of CIP removal in synthetic wastewater

Test		Factors			Response variable
		coded (real)			
		pH	Voltage (V)	Supporting electrolyte (NaCl) (g L^{-1})	Removal (%)
Factorial part	1	-1 (7)	-1 (4)	-1 (0.2)	58
	2	+1 (10)	-1 (4)	-1 (0.2)	1
	3	-1 (7)	+1 (8)	-1 (0.2)	72
	4	+1 (10)	+1 (8)	-1 (0.2)	0
	5	-1 (7)	-1 (4)	+1 (0.6)	95
	6	+1 (10)	-1 (4)	+1 (0.6)	30
	7	-1 (7)	+1 (8)	+1 (0.6)	89
	8	+1 (10)	+1 (8)	+1 (0.6)	6
Central Points	9	0 (8.,5)	0 (6)	0 (0.4)	90
	10	0 (8.5)	0 (6)	0 (0.4)	85
	11	0 (8.5)	0 (6)	0 (0.4)	82

Source: Organized by the authors (2024)

Analyzing the removal pattern obtained by the initial planning allowed the displacement of the variables under study. It resulted in new ranges of values for pH (6 to 8), voltage (4 V to 6 V), and support electrolyte (0.3 g L^{-1} to 0.5 g L^{-1}) (Table 5). These data were applied to the central composite rotational design (DCCR), generating the axial points necessary to reach an optimized condition for CIP removal in synthetic wastewater. Table 7 presents the data obtained through the implementation of the CCRD, in which the highest CIP removals occurred in the tests whose pH was 6 to 8, voltage from 4.5 V to 6 V, and NaCl concentration from 0.3 g L^{-1} to 0.5 g L^{-1}. The best removal percentage was obtained in test 7 (86 %), corresponding to pH 6, voltage of 6 V, and support electrolyte concentration of 0.5 g L^{-1}. However, greater homogeneity and maintenance of the percentages were obtained at the central points (tests 9 to 11) with average removals of 74 %. It suggests the existence of an optimal region around these points.

Table 7 – CCRD matrix for the electrolytic process of CIP removal in synthetic wastewater

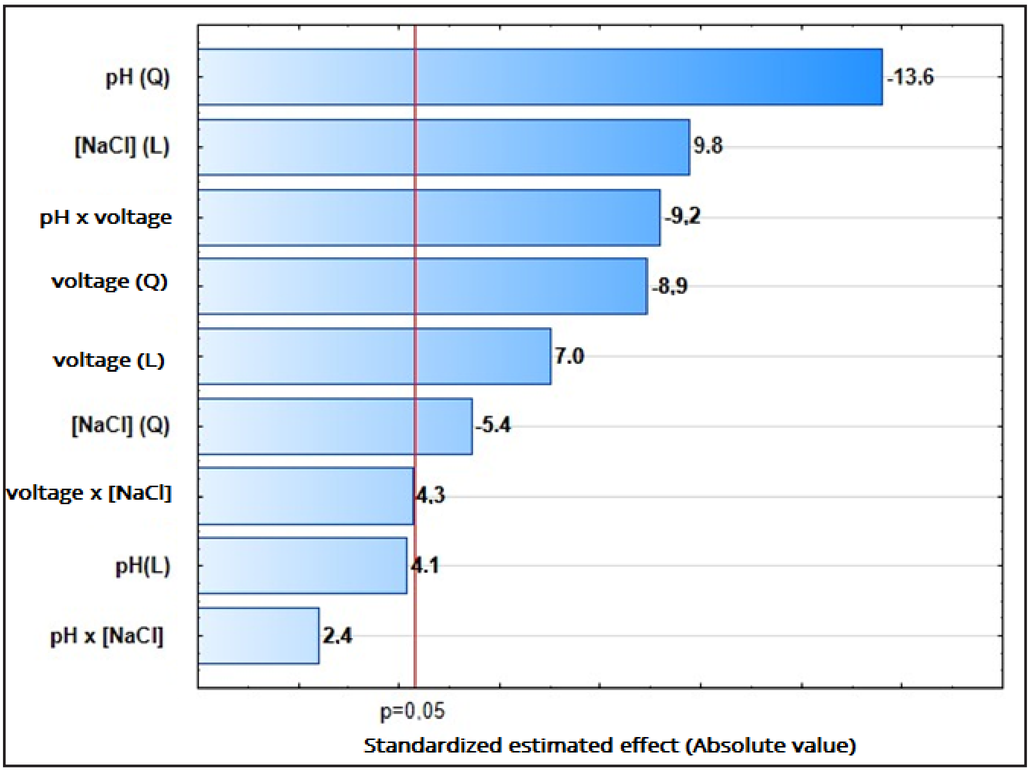
Test		Factors			Response variable
		coded (real)			
		pH	Voltage (V)	Supporting electrolyte (NaCl) (g L^{-1})	Removal (%)
Factorial part	1	-1 (6)	-1 (4)	-1 (0.3)	36
	2	+1(8)	-1 (4)	-1 (0.3)	34
	3	-1 (6)	+1 (6)	-1 (0.3)	12
	4	+1(8)	+1 (6)	-1 (0.3)	70
	5	-1 (6)	-1 (3)	+1 (0.5)	42
	6	+1(8)	-1 (3)	+1 (0.5)	53
	7	-1 (6)	+1 (6)	+1 (0,5)	86
	8	+1(8)	+1 (6)	+1 (0.5)	55
Central Points	9	0 (7)	0 (4.5)	0 (0.4)	77
	10	0 (7)	0 (4.5)	0 (0.4)	72
	11	0 (7)	0 (4.5)	0 (0.4)	72

Source: Organized by the authors (2024)

The analysis was conducted using the experimental data presented in Table 7, and the ANOVA regression table for the quadratic model was generated to derive the response surfaces. Additionally, the estimated effects on each independent variable were evaluated using the Pareto chart (Figure 3). Values with a p-value greater than 0.05 were considered significant at the 95% confidence interval.

Figure 3 shows that all individual variables and interactions significantly influenced the removal of the CIP drug in the 95 % confidence interval, based on the quadratic model. The negative values of the coefficients for pH (Q) (-13.6) and voltage (Q) (-8.9) indicate that the CIP removal efficiency in the system under study tends to increase with decreasing levels applied to these variables.

Figure 3 – Pareto diagram for CIP removal in synthetic wastewater by electrolytic process



Source: Authors (2024)

In turn, the positive coefficients for the concentration of the supporting electrolyte (NaCl) (L) (9.8) and voltage (L) (7) indicate that the removal of CIP increases with the increase in its levels. Among the binary interaction effects, only the combination of pH and voltage demonstrated a significant effect (-9.2), which was antagonistic to the efficiency of CIP removal.

From the adjustment of the quadratic model to the experimental data, the mathematical equation and its respective coefficient of determination (R^2) were obtained based on the regression ANOVA (Table 8).

Table 8 – Regression ANOVA and quadratic model for CIP removal efficiency in synthetic wastewater

Source of Variation	**Sum of squares**	**Degrees of Freedom**	**Mean squares**	F_{cal}	$F_{tab\ (95\%)}$	F_{cal}/F_{tab}
Regression (model)	4991.2	9	554.6	6.5	4.8	1.4
Residual	599.1	7	85.6	-		
Lack of fit	582.5	5	116.5	14.0	39.3	0.4
Pure error	16.6	2	8.3	-	-	-
Total	5590.3	16	-	-	-	-
Model	Removal (%) = -1065±(75)+217±(14)*pH-11±(0.8)*pH^2+10±(6)*voltage-3±(0.4)*voltage^2+1068±(111)*[NaCl]-468±(86)*[NaCl]^2-93±(10)*pH*[NaCl] +29±(7)*voltage *[NaCl]					

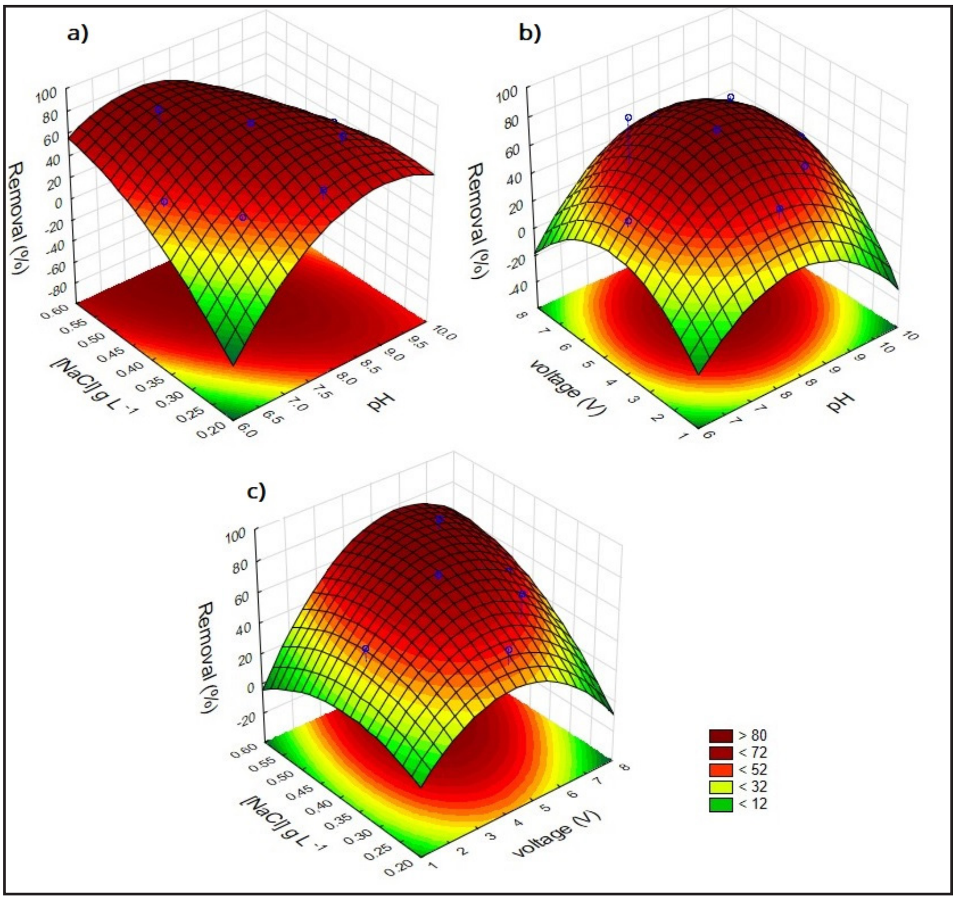
Source: Organized by the authors (2024)

Table 8 shows that the ratio of F_{cal} = 6.5 to F_{tab} = 4.8 for the regression showed a value greater than 1, indicating that the regression to the quadratic model was significant at the 95 % level. Thus, the equation obtained can be used to statistically predict the removal of the analyte. Figure 4 shows the behavior of the removal efficiency of CIP in synthetic wastewater in the electrolytic process, considering the response surface obtained from the regression model.

The CIP removal efficiency (%) reached average values between 60% and 80% predicted by the model. These regions are highlighted as maximum points in red and indicate that the ranges of values explored in the CCRD include optimal removal values.

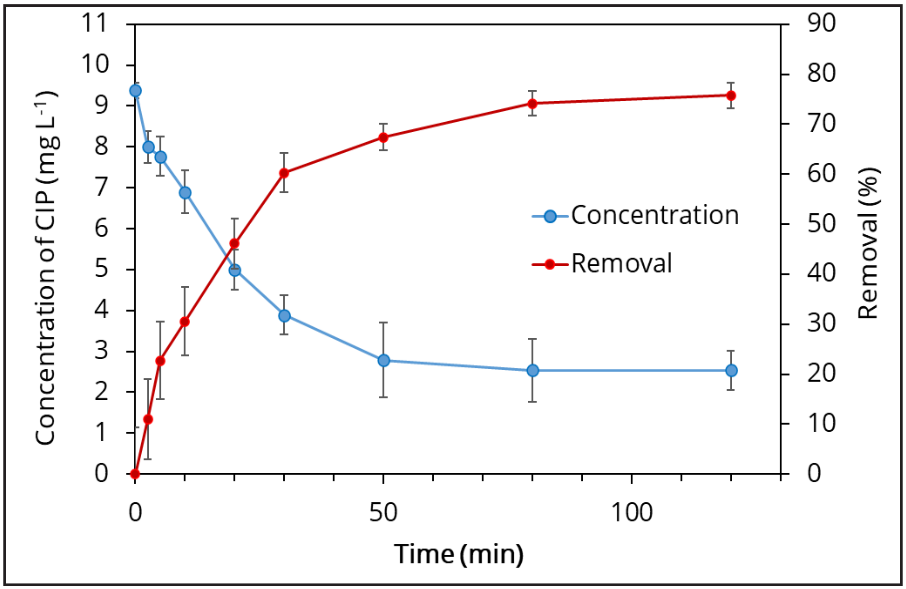
According to the analysis of the response surfaces, the best conditions observed are pH = 7.6, Voltage = 5.6 V, and support electrolyte concentration (NaCl) = 0.6 g L^{-1}. Based on this information, the validation test was performed, in which approximately 68.5 % was removed during the first 30 min of the process. A removal study was conducted, monitoring the CIP concentration over 120 min to explore the condition obtained (Figure 5).

Figure 4 – Response surfaces for CIP removal by the electrolytic process according to the quadratic model



Source: Authors (2024)

Figure 5 – CIP removal efficiency in synthetic wastewater using the electrolytic process. [CIP] = 10 mg L^{-1}, t = 120 min, [NaCl] = 0.6 g L^{-1}, voltage = 5.6 V and pH = 7.6



Source: Authors (2024)

The CIP removal reaches approximately 45 % after 20 min of electrolytic treatment (Figure 5), reducing the initial concentration from 9.5 to 4.8 mg L^{-1}. Between 20 min and 50 min, it varies from 45 % to 70 %, continuing more slowly until 120 min, stabilizing at approximately 78 %. The removal profile monitored over time suggests that equilibrium is established in the process around 80 min.

In a study of the electrocoagulation process using aluminum electrodes for the removal of CIP in hospital effluent, a percentage of 76.54 % was reported after 23 min of treatment (Ahmadzadeh et al., 2017). The value is higher than that observed in this study and is possibly related to the effluent's complexity.

An optimization of the electrocoagulation process using a Box-Behnken design obtained 86.6% removal of CIP (pH = 4, Ci = 5 mg L^{-1}, current density of 4.325 mA cm^{-2} and t = 10 min) (Barışçı & Turkay, 2016). Another investigation of CIP removal in an aqueous solution using a continuous flow electrolytic process obtained an efficiency of 88 % (pH = 5.6, t = 100 min, current density of 5.6 mA cm^{-2} and flux of 25.9 mL min^{-1}) (Parsa et al., 2016).

Research involving the application of electrolytic processes for CIP removal is scarce. Furthermore, the few available studies vary substantially regarding the parameters of the process, such as mechanisms, analyte concentration ranges and reaction time, aqueous matrix, pH, current density, and electrode sizing, which impairs efficiency comparisons.

In terms of mechanism, it is considered that CIP removal in the electrolytic process performed may involve the adsorption of the drug on colloids and flakes and oxidation, with possible formation of degradation products promoted by ClO^- species and •OH radical resulting from reactions involving water and the supporting electrolyte. Therefore, it is suggested that the final percentage of removal attested is the combination of these two processes.

4 CONCLUSION

This study aimed to optimize the removal of CIP in synthetic wastewater by employing an electrolytic system composed of aluminum electrodes.

Using the 2^3 complete factorial design and DCCR allowed for identifying the optimal operating conditions for the electrolytic system within the specified ranges for the variables pH, voltage, and concentration of the supporting electrolyte. The ideal conditions for the process were determined to be a pH of 7.6, a voltage of 5.6 V, and a NaCl concentration as the electrolyte of 0.6 g L^{-1}, as defined using the response surface methodology based on the quadratic regression statistical model.

When these conditions were applied in removal tests to validate the model, a removal percentage of 78 % was achieved at equilibrium after 80 min. The electrolysis-based process proved to be a promising technology for treating water and effluents contaminated with CIP. However, additional factors should be evaluated on a larger scale.

For future studies, it is recommended to utilize liquid chromatography coupled with mass spectrometry could to identify potential by-products generated during the process and elucidate the predominant mechanism involved in removing CIP in this electrolytic system.

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