

Removal of natural organic matter from aqueous solutions using electrocoagulation pulsed current: optimization using response surface methodology

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ABSTRACT

The use of the pulsed current can be an alternative to decrease the electrode polarization, as well as achieving lower energy consumption. This study investigated the electrocoagulation through pulsed current for the removal of natural organic matter from water. The experiments were carried out using Box–Behnken factorial design with the response surface methodology for the design of experiments, modeling and interpreting of the results. The electrocoagulation cell consisted of an acrylic reactor with 4 L capacity with four electrodes of aluminum, in parallel connection mode. The experimental independent variables studied were: current density (5.5 to 44.5 A m⁻²), electrodes spacing (2 to 7.6 mm), stirring rate (200 to 1,000 rpm), frequency (500 to 5,000 Hz), humic acid concentration (5 to 20 mg L⁻¹) and NaCl (100 to 300 mg L⁻¹) as supporting electrolyte, evaluating the residual apparent color (RAC) and electric energy consumption (EEC). The pH of the solution increased during the experiments, reaching basic values. The response surface regression procedure was employed to fit the second-order polynomial, and the model fitted well to the obtained values, reaching R² 0.9995 (RAC) and R² 0.9989 (EEC). The lowest RAC was 11.8 Hazen units (96.2% color removal), where the EEC was 0.393 kWh m⁻³.

Key words | Box–Behnken, electrocoagulation, NOM, pulsed current

HIGHLIGHTS

- Pulsed current was studied for natural organic matter (NOM) removal.
- The influencing factors on NOM removal were investigated: frequency, current density, humic acid concentration, NaCl concentration, stirring rate, and electrode spacing.
- The response surface regression procedure was employed and fitted the second-order polynomial to residual apparent color (RAC) and electric energy consumption (EEC) values obtained, achieving R² of 0.9995 and adjusted R² of 0.9982 (RAC), and R² of 0.9989 and adjusted R² of 0.9959 (EEC).
- The lowest RAC obtained was 11.8 HU, with the following settings: 500 Hz frequency, 25 A m⁻² current density, 200 mg L⁻¹ NaCl concentration, 20 mg L⁻¹ humic acid concentration, 1,000 rpm stirring rate, and 4.8 mm electrode spacing.

INTRODUCTION

The electrocoagulation process is currently a technological alternative used for the treatment of water/effluent. It is based on the process of destabilizing suspended, emulsified,

or dissolved contaminants in an aqueous environment by introducing an electric current to a pair of electrodes (anode and cathode), which are known as sacrificial

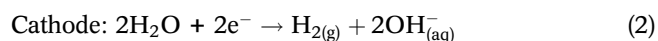
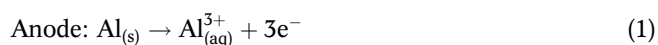
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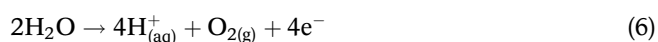
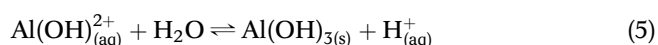
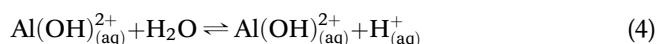
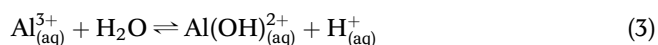
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electrodes. The anode is oxidized generating metallic ions into the solution, which will be hydrolyzed and form the coagulants (Emamjomeh & Sivakumar 2009; Hakizimana *et al.* 2017). Aluminum electrodes are widely used in electrocoagulation processes (Vepsäläinen *et al.* 2012; Attour *et al.* 2014; Hu *et al.* 2017). The main reactions that occur with the use of the aluminum electrode are (Equations (1) and (2)):



The aluminum generated by the anode oxidation reacts with the hydroxyls generated in the cathode to form monomeric and polymeric species, which are finally converted to $\text{Al}(\text{OH})_3$ (Equations (3)–(5)). This rapidly adsorbs the dissolved organic compounds in the solution, trapping the colloidal particles (Attour *et al.* 2014; Elazzouzi *et al.* 2017; Hu *et al.* 2017). In addition, there is the possibility of the evolution of oxygen gas in the anode (Equation (6)) and hydrogen gas in the cathode (Equation (2)) by the water electrolysis. The evolution of hydrogen and oxygen gases is important because they help in the removal of flocs by flotation.



Natural organic matter (NOM) is a heterogeneous mixture of humic substances (humic and fulvic acids, and humin), hydrophilic acids, proteins, lipids and carbohydrates with varying molecular characteristics, and is present in all surface waters. NOM is generated by the decomposition of plant and animal material into water systems and soils (Rosario-Ortiz *et al.* 2007). NOM in drinking water causes aesthetic concerns such as color, taste and odor. It can bind and transport harmful contaminant, and lead to the formation of undesirable disinfection by-products, as well as cause bacterial growth and biofilm formation in drinking water distribution systems (Rosario-Ortiz *et al.* 2007; Matilainen & Sillanpää 2010; Al-Omari *et al.* 2014; Hu *et al.* 2014; Metsämuuronen *et al.* 2014; Särkkä *et al.* 2015).

The application of electrocoagulation to remove NOM such as humic acid and other humic substances has already been widely used. Several works were investigated involving

the effect of initial pH, current density, supporting electrolyte, electrolysis time, flow rate, interelectrode distance, and electrode area/volume ratio, analyzing the energy consumption and removal of color and/or dissolved organic carbon (DOC) (Feng *et al.* 2007; Koparal *et al.* 2008; Yıldız *et al.* 2008; Ghernaout *et al.* 2009; Mohora *et al.* 2012; Ulu *et al.* 2014). It is well known that some of the problems in electrochemical processes are the polarizations in the cathode and anode. Some research has used reverse polarity (alternating current) of the electrodes to avoid the passivation of electrodes (Eyvaz *et al.* 2009; Keshmirizadeh *et al.* 2011; Vasudevan & Lakshmi 2011; Secula *et al.* 2013; Mansoorian *et al.* 2014). The pulsed current mode can be used in order to reduce the polarization, where a given current is sent to the system in a pulsed (frequency) manner. Studies have already evaluated the use of pulsed current in electro-oxidation processes, but with few practical results (Wei *et al.* 2011; Lu *et al.* 2015; Rocha *et al.* 2018).

Several parameters and experimental conditions are directly related to the effectiveness of the electrochemical processes, and then the selection of the best experimental condition is ensured with statistical tools. In this sense the response surface methodology (RSM) is a multivariate technique used for optimization of experimental procedures, e.g. electrochemical processes. It results well in assessing the interactions of possible influencing parameters on treatment efficiency. The Box–Behnken design (BBD) is a kind of RSM that, using three-level factorial arrangement, gets a reducing number of tests and consequently reduces the costs associated with the experiments. The BBD has been used to better understand some electrochemical processes on removal of pollutants from water (Silveira *et al.* 2014; Thirugnanasambandham *et al.* 2015; Garg & Prasad 2016; Sandhwar & Prasad 2017).

The aim of this research is to study the removal of NOM from aqueous solutions using electrocoagulation by pulsed current, evaluating the residual apparent color (RAC) and electric energy consumption (EEC) under the effects of frequency, current density, NaCl concentration, humic acid concentration, electrode spacing and stirring rate.

MATERIALS AND METHODS

Chemicals and samples

A stock solution of humic acid (2,000 mg L⁻¹) was prepared in 0.02 mol L⁻¹ NaOH (VETEC) from a commercial humic acid formulation (Sigma-Aldrich, CAS: 1415-93-6). The

NaCl (Merck, CAS) was used as electrolyte to provide conductivity and the chosen concentrations (100, 200, and 300 mg L⁻¹) were in accordance with the chloride concentrations found in raw water in water reservoirs in Fortaleza, Brazil. So as to optimize the experimental variables a synthetic sample was prepared by diluting humic acid from the stock solution and NaCl. A sample of raw water from a water reservoir in Fortaleza, Brazil was collected to be treated with experimental variables optimized. The values of parameters of the raw water supply are shown in Table 1.

Electrolytic cell

The electrocoagulation experiments were performed in a batch cylinder reactor with a capacity of 4.5 L. The electrolytic cell, Figure 1, consisted of four aluminum electrodes (rectangular form) connected in parallel mode with a dimension 300 mm × 50 mm × 3 mm. Electricity was supplied by a direct current (DC) power supply (Minipa, MDL-3305). A homemade switch box (DC/PC (pulsed current) converter) was used to provide the specific frequencies (pulses) with a

50% rate of duty cycle. The pulsed waveforms and frequencies were monitored using an oscilloscope (Minipa, MVB-DSO). The average applied current was monitored using a digital multimeter (Minipa, MDM-8145A). The solution was mixed using a magnetic stirrer.

Experimental design and data analysis

The experiments were performed as follows. For each run a 4.0 L solution of synthetic sample was prepared using deionized water, humic acid, sodium chloride (for humic acid and sodium chloride, initial concentration varied with each experiment), pH 7.0, and initial temperature 25 °C. Once prepared, the synthetic sample was added to the reactor and the electrodes were immersed (spaced according to the experiment). Then, the stirring rate, frequency and electric current were adjusted. Each run was conducted for 10 minutes.

The RSM, through the BBD, was used to optimize the independent variables: frequency (f), current density (j), humic acid concentration (C_{HA}), NaCl concentration (C_{NaCl}), electrode spacing (ES), and stirring rate (SR). The dependent variables (responses) were: RAC and EEC. The experimental levels for each independent variable are shown in Table 2. The configuration of each run can be seen in Table S1 (Supplementary Material). The experimental data were analyzed by the response surface regression (RSREG) procedure to fit the following second-order polynomial model (Equation (7)):

$$y = \beta_0 + \sum_{i=1}^K \beta_i X_i + \sum_{i=1}^K \beta_{ii} X_i^2 + \sum_{i < j} \sum_j \beta_{ij} X_i X_j + e \quad (7)$$

where K is the number of independent variables, y is the response, β_0 is the model intercept coefficient, β_i , β_{ii} , and β_{ij}

Table 1 | The characterization of drinking water supply from the reservoir

Parameter	Unit	Value (mean ± S.D.)
Apparent color	HU	74.3 ± 3.2
True color	HU	63.4 ± 1.3
Turbidity	NTU	12.6 ± 2.4
Dissolved organic carbon	mg L ⁻¹	12.3 ± 0.4
Conductivity	μS cm ⁻¹	476 ± 1.4
Chloride	mg L ⁻¹	116.3 ± 5.3
pH		7.3 ± 0.2

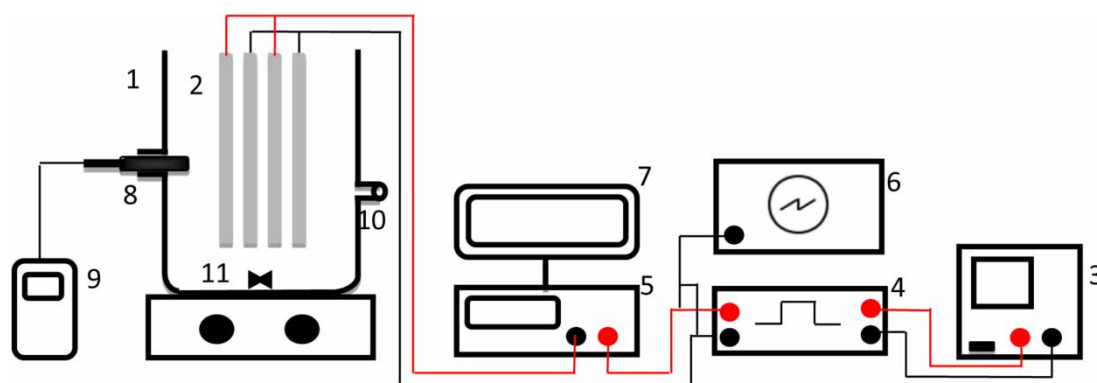


Figure 1 | Representation of the used electrolytic cell (adapted from Rocha et al. 2018); 1. reactor; 2. Al electrodes; 3. power supply; 4. switch box; 5. amperemeter; 6. oscilloscope; 7. computer; 8. multiparameter probe; 9. meter; 10. sampling port; 11. magnetic bar.

Table 2 | Independents variable and actual values used in the experimental design

Independent variables	Variable levels		
	- 1	0	1
f (Hz)	500	2,750	5,000
j ($A\ m^{-2}$)	5.5	25.0	44.5
C_{HA} ($mg\ L^{-1}$)	5.0	12.5	20.0
C_{NaCl} ($mg\ L^{-1}$)	100	200	300
ES (mm)	2.0	4.8	7.6
SR (rpm)	200	600	1,000

are parameters for linear, quadratic, and interaction factor effects, respectively, X_i and X_j are independent variables, and e is the residual term. Analysis of variance (ANOVA) was used to evaluate the quality of the model fit, with confidence limits to 95% (0.05). After defining the best model, a desirability function was performed, which is a simultaneous optimization technique that consists of finding the factor values that optimize one or more responses, or at least maintain them in desirable ranges, using programmable non-linear methods. The experimental data were processed using the software Statistica 6.0 (StatSoft, Tulsa, OK, USA).

Instrumental analysis

The pH, oxidation-reduction potential, temperature, total dissolved solids, and electrolytic conductivity of solution were monitored *in situ* through an HI 7629829 probe and an HI 98290 meter (Hanna), turbidity was measured using a turbidimeter (Hanna, HI 98703). The DOC was measured using an organic carbon analyzer (Shimadzu, TOC-L) equipped with auto-sampler (OCT-L), and the sample was first filtered ($0.45\ \mu m$). The apparent and true color of the solution was determined using a colorimeter (Digimed, DM-Cor). The EEC was calculated using Equation (8):

$$EEC \left(\frac{kWh}{m^3} \right) = \frac{i \cdot T \cdot t}{1,000 \cdot V} \quad (8)$$

where V is the volume of solution (m^3), t is the time of experiment (h), i is the current (A), and T is the applied tension (V).

RESULTS AND DISCUSSION

The current density controls the amount of coagulant that will be released into the solution, the hydrogen and oxygen gases production, and energy consumption of the

process (Vepsäläinen *et al.* 2012; Hakizimana *et al.* 2017; Moussa *et al.* 2017). Thus, increasing the current density, more coagulant and gases are released, then leading to a better transport of coagulated material, which may result in a better removal efficiency of pollutants. However, high current density may not get the best removal efficiency of the pollutants, due to the possibilities of electrode polarization: activation and resistance (ohmic drop). In addition, the control of the ionic concentration is required because it diminishes the ohmic drop, demanding a lower tension applied to get the desired current. This problem can be bypassed by using a chloride-like electrolyte that can dissolve the diffuse passive layer formed on the electrode surface of the aluminum, facilitating the dissolution of the aluminum from the electrode. (Mouedhen *et al.* 2008; Drouiche *et al.* 2009). Fajardo *et al.* (2014) considered that the pitting corrosion occurred due to the presence of chloride ions. Also, the humic acid molecule has negative surface charges, and can be attracted to the anode by the electric field, depositing itself on the electrode surface, forming an inert layer, and passivating the electrode (Kretzschmar *et al.* 1997).

On the other hand, the energy consumption is affected by the spacing between the electrodes; for example, when the spacing decreases, the applied voltage is smaller to obtain the expected result. Electrode spacing also affects the diffusion and migration of ions, which may cause electrode polarization. The stirring rate also affects the process: an increase implies the formation of clustered flocs which precipitate more easily (Modirshahla *et al.* 2008; Khandegar & Saroha 2013). Mass transport is also affected by the stirring rate (Hakizimana *et al.* 2015).

On average, the initial apparent colors for each humic acid concentration were 71.3, 177.1, and 294.6 HU (Hazen units) for 5.0, 12.5, and 20.0 $mg\ L^{-1}$, respectively. Figure 2 and Table S1 (Supplementary Material) show the values of the RAC and EEC for the experiments. The results for RAC were in the range of 11.8 to 300.0 HU, and EEC 0.036 to 1.649 $kWh\ m^{-3}$. The lowest RAC obtained were achieved for experiments: 3 (14.2 HU), 4 (13.2 HU), 8 (13.1 HU), 29 (13.3 HU), 30 (14.2 HU) and 31 (11.8 HU). These results were obtained with the following levels for each variable: frequency 500 and 5,000 Hz, current density 25.0 and 44.5 $A\ m^{-2}$, NaCl concentration 200 $mg\ L^{-1}$, humic acid concentration 5.0 and 20.0 $mg\ L^{-1}$, stirring rate 600 and 1,000 rpm, and electrode spacing 4.8 mm. Higher current densities promote better removal of contaminants due to the higher amount of coagulant generated; consequently, the double layer of pollutant is compressed,

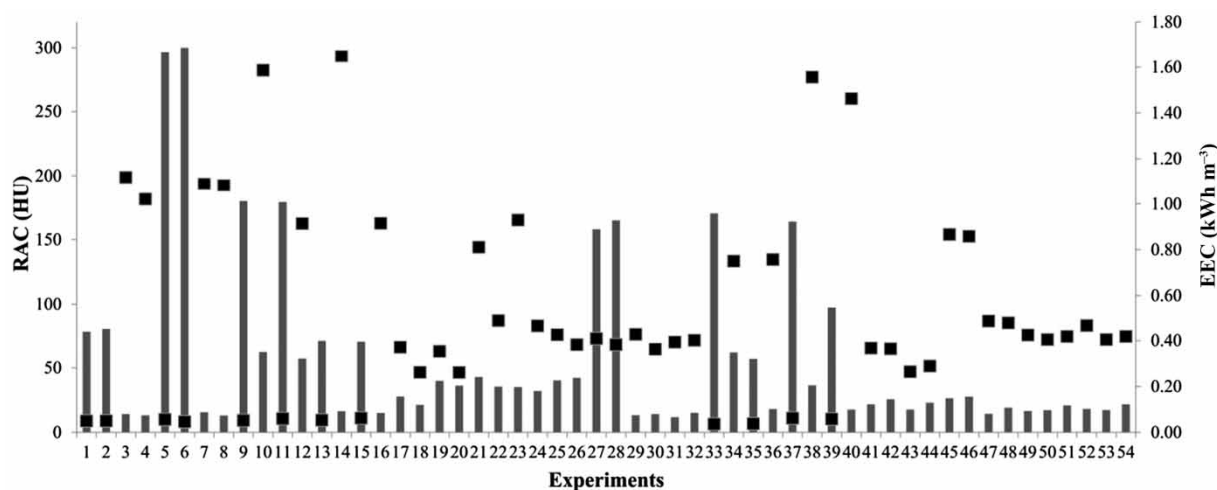


Figure 2 | RAC and EEC values for the experiments 1–54. Gray bar: RAC; black square: EEC.

favoring the formation of flocs for subsequent precipitation (Garcia-Segura et al. 2017; Hu et al. 2017). The process of flocs formation is also influenced by the stirring rate. High stirring rates can promote better transport of the coagulant species, providing a better homogenization of the solution and, consequently, a greater contact between the coagulant and pollutant species (Bayar et al. 2011). As previously mentioned, 4.8 mm of electrode spacing provided the lowest RAC values. Optimal spacing must be found, because large or small spacing decreases the efficiency in the formation of flocs (Ghosh et al. 2008a, 2008b; Modirshahla et al. 2008).

The lowest EEC values were achieved with the experiments: 1 (0.050 kWh m^{-3}), 2 (0.050 kWh m^{-3}), 5 (0.056 kWh m^{-3}), 6 (0.047 kWh m^{-3}), 9 (0.052 kWh m^{-3}), 33 (0.036 kWh m^{-3}), and 35 (0.038 kWh m^{-3}), Figure 2 and Table S1. However, these experiments obtained high RAC values. In these experiments, current density may have been the main cause of low EEC values and high RAC values. It is observed that in these experiments the current density used was its lowest value, 5.5 A m^{-2} . It is known that the lower the current density values are, the lower the coagulant generation and applied voltage will be, Equations (9) and (10):

$$m = \frac{M \cdot i \cdot t}{F \cdot z} \quad (9)$$

$$T = R \cdot i \quad (10)$$

where m (g) is the coagulant mass generated, M (g mol^{-1}) is the molecular weight of aluminum, i is the applied current (A), t is the electrocoagulation operating times, F is the

Faraday constant ($96,487 \text{ C mol}^{-1}$), z is the number of electrons involved in the oxidation/decrease reaction ($z \text{ Al} = 3$), and R (Ω) is resistance. Certainly, the amount of coagulant species generated were not sufficient to neutralize the pollutant charges and the double layer of the pollutant was not compressed, which did not favor the formation of aggregations, and did not promote their precipitation or flotation (Garcia-Segura et al. 2017). In addition, the stirring rate used was 200 rpm (lowest value) in experiments 9, 11, and 33.

The pH is one of the most important factors in the process, since it influences the balance of coagulant species, as well as the chemical structure of the pollutant. To understand the removal mechanism, Figure 3(a) shows the pH profile for experiments 3, 4, 8, 29, 30 and 31. Those experiments were chosen because they reached the lowest apparent colors (see Figure 2 and Table S1). Throughout the experiments, the pH increased, becoming basic as experiment time increased, reaching the highest value of 8.9 in experiment 29. The increase in pH can be explained by the generation of cathode hydroxyls, Equation (2). For experiment 31, there was a variation of 0.2 in the pH value from baseline to 8 minutes of experiment time. Evaluating the configuration of experiments 29 and 31 there is a difference only in the concentration of humic acid used, which may be the cause of that difference. Humic acid concentrations were 5.0 and 20 mg L^{-1} for experiments 9 and 31, respectively.

Figure 3(b) shows species distribution for Al-H₂O considering only mononuclear species. In general, soluble Al^{3+} solution prevails when pH is below 4, while $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_3$ species in the pH range 4–7, and at higher pH than 7 the $\text{Al}(\text{OH})_4^-$ species prevail. The insoluble $\text{Al}(\text{OH})_3$ species forms an amorphous precipitate and

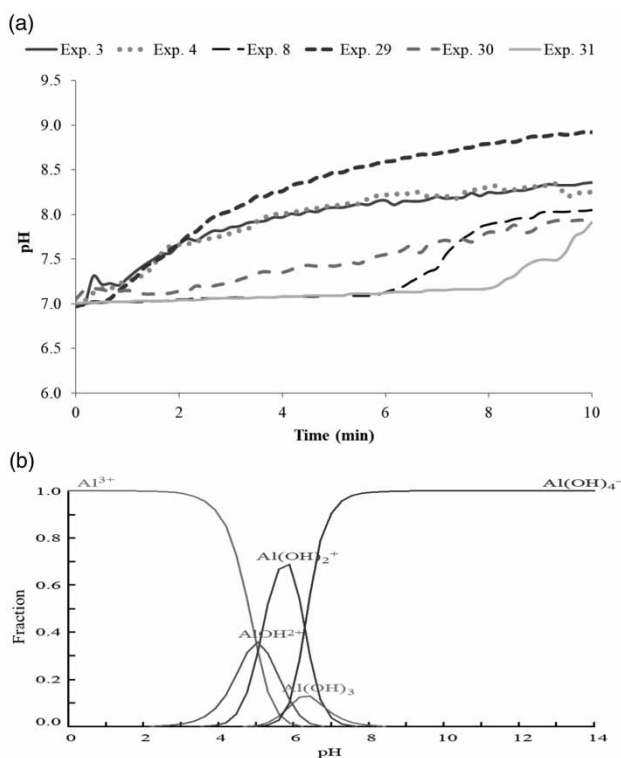


Figure 3 | (a) Profile of pH for the experiments. (b) Distribution diagram of Al-H₂O in equilibrium with amorphous hydroxide, 25 °C.

initiates the formation of other polymeric species, the main ones reported being $Al(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$ and $Al_{13}O_4(OH)_{24}^{7+}$ (Duan & Gregory 2003). Finally, aluminum monomeric and polymeric species induce $Al(OH)_3$ flake formation (sweeping process) with considerable surface areas and porosity, aiming at rapid adsorption of soluble organic compounds and entrapment of colloidal particles (Can *et al.* 2003; Kobya *et al.* 2006; Hu *et al.* 2017).

The pH values observed in the experiments indicate a probable removal of HA by neutralizing the electrostatic charge of cells between hydrolysis products and HA molecules at the beginning of the process. However, at the beginning of the process (pH 7), the predominant species is $Al(OH)_4^-$, and this species is not desired because it is not efficient. At pH > 9, the zeta potentials of humic substances gradually increase due to the deprotonation of some functional groups, such as $COOH^-$, and the zeta potentials of $Al(OH)_3$ crystals decrease as the pH of the solutions increases. (Lu *et al.* 1999; Duan *et al.* 2002). A research study has indicated that pH with values of 4–9.5 leads to the $Al(OH)_3(s)$ species as predominant; however, the speciation of this amorphous hydroxide promotes the formation of polyhydroxides that further will assist in the electrocoagulation process (Mouedhen *et al.* 2008).

Analyses of variance, and building of model

The RSREG procedure was employed to fit the second-order polynomial to RAC and EEC, and the results are shown in Table S2 (Supplementary Material), where can be observed the effect values from each variable and interactions effects between the variables. The significance of each variable and the interactions were assessed by effect value, in module, and p -value < 0.05. The most significance variables for RAC were current density, humic acid concentration, and stirring rate, as well as the interactions between them. The EEC had as significant variables: current density, NaCl concentration, and electrodes spacing. The ANOVA for the observed results confirms the effects values of each variable, Tables S3–S4 (Supplementary Material). The larger F-statistic and smaller p -value show the more significant of the corresponding variables. The ANOVA of the RAC and EEC values of the pulsed current show that the lack of fit of the model was not significant, where the respective p -values were higher than 0.05, thus, a good fit of the model to the data. The determination (R^2) and adjusted determination (R_a^2) coefficients were calculated and checked regarding their fitness to the model observed responses, where the values were R^2 0.9995 and R_a^2 0.9982 (RAC), and R^2 0.9989 and R_a^2 0.9959 (EEC), Figures S1 and S2.

Effects of the variables

As stated previously, the significant variables for the RAC response were current density, humic acid concentration and stirring rate. The frequency was also significant, but less than the other variables according to p -value, Tables S2–S3. Figure 4 shows the response surface relating two variables to the RAC. It is possible to note that the increase in stirring rate and current density caused lower RAC values, Figure 4(a). Although, agitation rate and current density promoted an improvement in the process, the lowest RAC was not obtained using the highest values (44.5 A m^{-2} , and 1,000 rpm), possibly due to high agitation rates that can destroy the flocs, generating small flocs that are not removed, and the excess coagulant generated (Bayar *et al.* 2011). Figure 4(b) shows the interaction of frequency and current density, and it can be observed that low current densities and frequency, near the center, presented a lowest RAC. However, by increasing the current density, the frequency does not seem to influence the RAC, and at the maximum current density, a lower RAC is achieved by aiming to the extremes of the frequency. The fact that there were differences in the RAC influenced by the frequency might be due to a

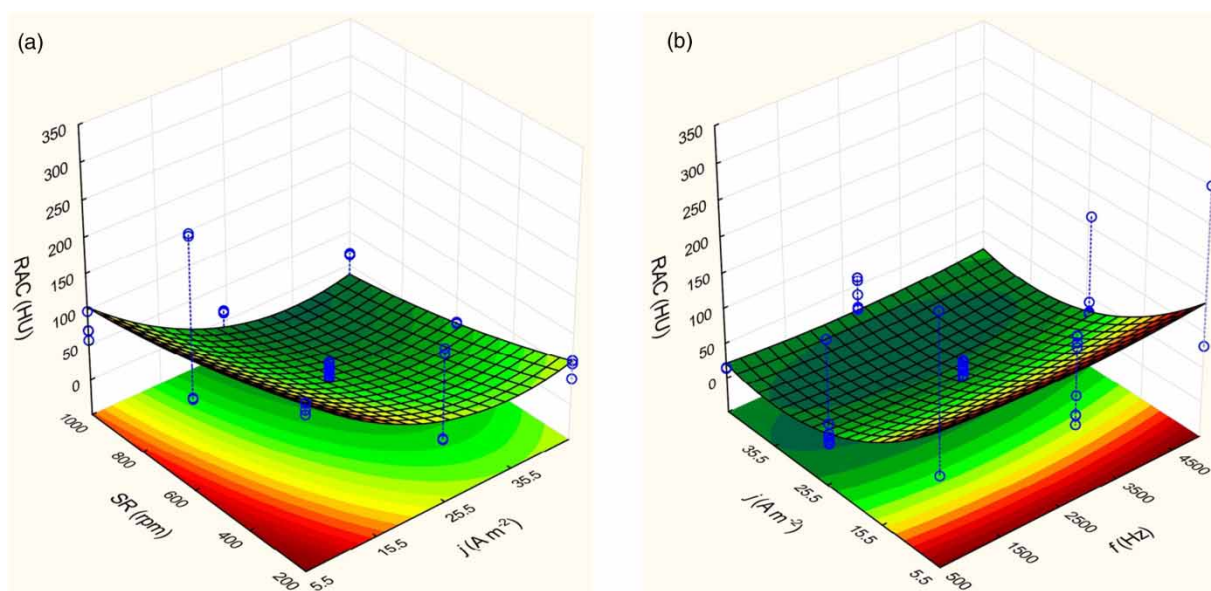


Figure 4 | Response surface plots showing (a) the effect of the current density and stirring rate, and (b) the effect of the current density and frequency for RAC.

better mass transport in certain frequencies. Some authors in their studies using pulsed current in the electrolytic process have reported that increasing the frequency harms the process by the fact that the compounds are not able to follow the potential (Amatore *et al.* 1998; Lu *et al.* 2015).

Figure 5(a) shows the EEC affected by the current density and electrode spacing, where, when presenting in a direction of the highest values of each variable, the energy consumed increases. It is known that a higher current density requires a higher voltage applied, and increasing the spacing electrodes increases the resistance of the medium to the current passing, requiring a higher voltage to achieve a certain current value. At lower values of NaCl concentration, higher values of energy consumed at a given current density were observed, Figure 5(b). Again, it is caused by the fact that the medium has a greater resistance to the current passing in a lower concentration of electrolytes present. In general, increasing the current density and electrodes spacing and decreasing the NaCl concentration enables the experiment to obtain higher values of energy consumed (Mouedhen *et al.* 2008; Bayar *et al.* 2011; Attour *et al.* 2014).

Desirability

The desirability function was proposed by Derringer & Suich (1980) and aims to find operational conditions that

satisfy two or more responses, with values between 0 and 1, where 0 represents an undesirable value and 1 a desirable value. The desirability function was used to find the lowest RAC and EEC. The desirable RAC is 15 HU (according to the Brazilian legislation that establishes the maximum color limit in a drinking water), and the desirable EEC is $0.036 kWh m^{-3}$. The desirable EEC value was the lowest observed value taken from Figure 2 and Table S1. Figure S3 (Supplementary Material) presents the optimal conditions (level of variables) predicted by the model in the form of graphs. The two graphs in the last column show the profiles of the desirability of the two responses. Vertical red lines indicate conditions of maximum overall desirability (d). As can be observed, the optimal conditions were at central levels of each variable, indicating the optimal condition predicts RAC 18.18 HU and EEC $0.428 kWh m^{-3}$, with d 0.860.

Raw water treatment

From the optimal conditions found by the desirability function, a sample of raw water was submitted to the electrocoagulation treatment by PC and DC using current density $25 A m^{-2}$, frequency 2,750 Hz, stirring rate 600 rpm, and electrodes spacing 4.8 mm. The process efficiency was evaluated through the parameters apparent (AC) and true color (TC), DOC, pH, electrical conductivity,

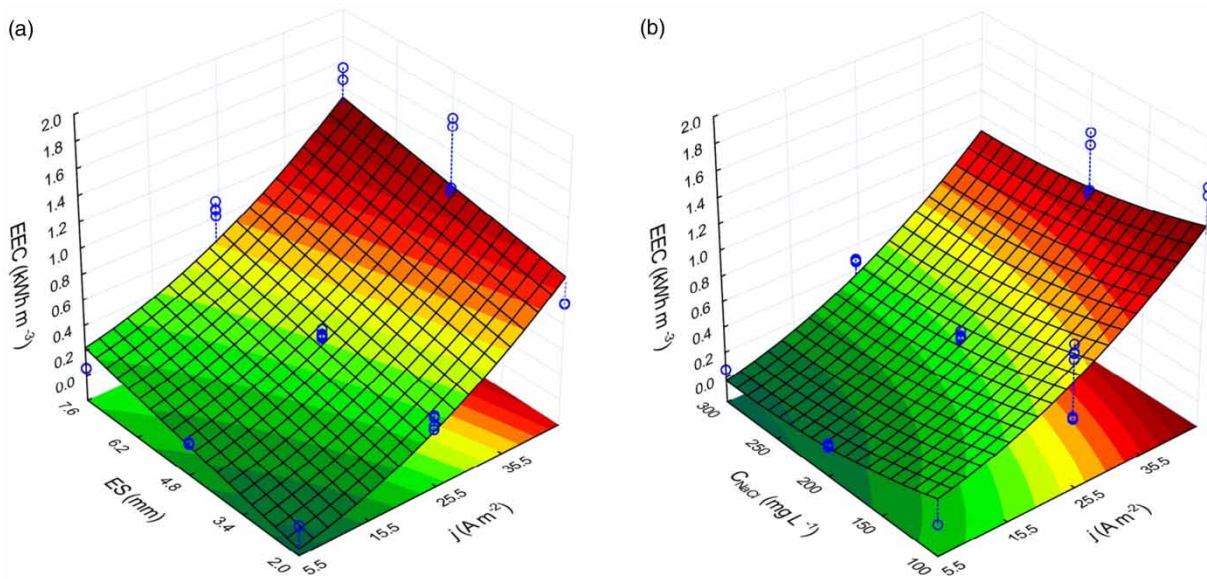


Figure 5 | Response surface plots showing (a) the effect of the current density and electrode spacing, and (b) the effect of the NaCl concentration and current density for EEC.

and electrical energy consumed. The final AC was 18.6 HU (75.7% removal) and 14.1 HU (78.4% removal) for PC and DC, respectively, [Figure 6\(a\)](#). The final TC was 13.4 HU (32.5% removal) and 6.8 mg L⁻¹ (42.6% removal) for PC and DC, respectively, [Figure 6\(a\)](#). The final DOC was 8.5

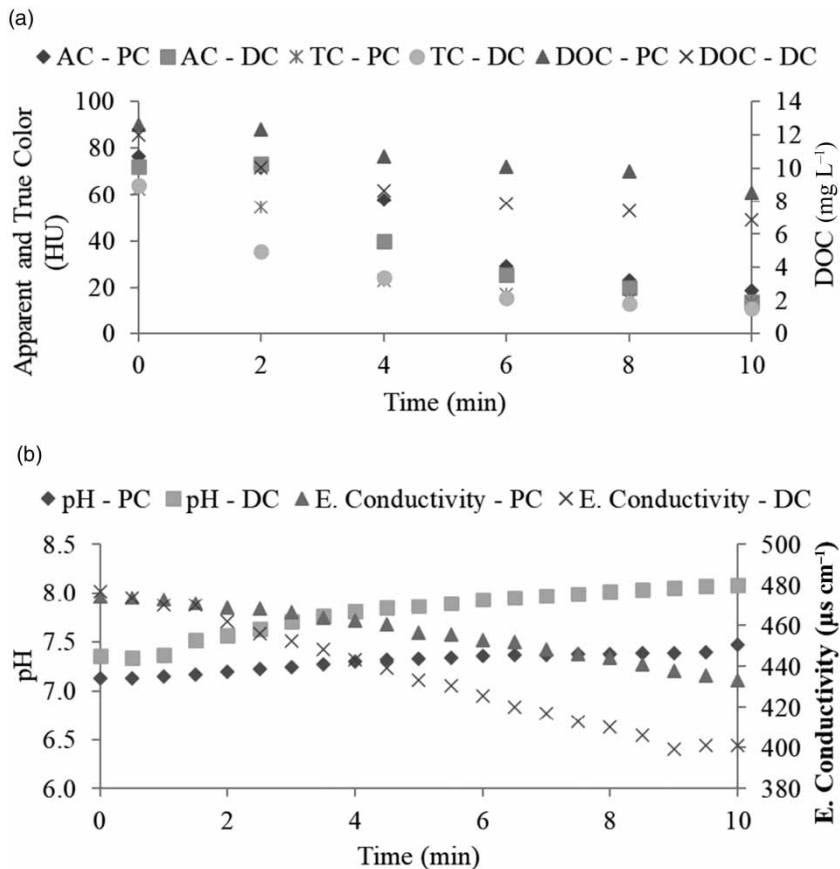


Figure 6 | (a) Profile of AC, TC and DOC removal for PC and DC from the raw water sample. (b) Profile of pH and electrical conductivity for PC and DC from the raw water sample.

and DC, respectively, Figure 6(a). The DC has shown a slightly better color and DOC removal than PC. The decrease in the process efficiency due to the electrode polarization can be avoided with the use of the PC. The PC works by sending an electric current in interruptible mode (time-on, time-off) to the electrolytic cell. But, the average current sent to the electrolytic cell by the PC was less than by the DC. Thus, the DC generated more electrolytic reactions; for example, at the anode, metal is oxidized into cations (Equation (1)) and the cathode water is reduced into hydrogen gas and hydroxyl anions (Equation (2)). This can be evidenced by the increase of the pH in the experiments using DC, Figure 6(b). The DC also provided a greater reduction in electrical conductivity, Figure 6(b), probably because a greater amount of flocs generated there are able to aggregate other ions such as chloride, sulfate, and phosphate, which are possibly present in raw water. Although the DC achieved better color and COD removals, the electrical energy consumed by the DC was greater than the PC. The values obtained for electrical energy consumed by PC and DC were 0.280 and 0.880 kWh m⁻³, respectively, showing an energy saving of almost 70% in the use of PC

CONCLUSION

The electrocoagulation process by pulsed current regarding the NOM removal has been studied under the effects of frequency, current density, NaCl concentration, humic acid concentration, stirring rate and electrode spacing, evaluating the apparent color removal and electrical energy consumption. It can be concluded that the system is capable of removing NOM.

1. The RSREG procedure was employed and fitted the second-order polynomial to RAC and EEC values obtained, achieving R² 0.9995 and R_a² 0.9982 (RAC), and R² 0.9989 and R_a² 0.9959 (EEC).
2. For the RAC, the most influencing variables were current density, humic acid concentration and stirring rate. Frequency has some influence on RAC, which needs further investigation.
3. The lowest RAC obtained was 11.8 HU, with the following setting 500 Hz (*f*), 25 A m⁻² (*j*), 200 mg L⁻¹ (C_{NaCl}), 20 mg L⁻¹ (C_{HA}), 1,000 rpm (SR), and 4.8 mm (EE). This configuration had an EEC 0.393 kWh m⁻³. Lower EEC values were obtained, but with higher RAC.
4. The pH of the solution increased over the course of the experiment, producing a basic solution, predominated by Al(OH)₄⁻ species.

5. From the desirability function, the best condition to be recommended is to use a current density of 25 A m⁻², stirring rate of 600 rpm, and electrodes spacing at 4.8 mm.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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