



Removal of cyanobacteria from supply waters by electroflotation using DSA® electrodes

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ABSTRACT

The occurrence of cyanobacteria in freshwater is a global problem when considered as drinking water for human consumption. Cyanobacteria cells are difficult to remove in conventional treatment systems. The research objective was to study the removal of cyanobacteria from the water supply through the electroflotation process, using DSA®-type, dimensionally stable anodes composed of Ti/Ru_{0.3}Ti_{0.7}O₂. The effects of the operational variables of the electrochemical reactor were studied in the pilot system: water input rate and electric current density. The performance of the electroflotation process was determined by the removal of cyanobacteria cells in the treated water. According to the results, there was a cyanobacteria removal of approximately 73% after 30 min of electrolysis, and approximately 78% after 60 min, for the water input rate of 100.84 m³ m⁻² d⁻¹ and electric current density of 68.26 A m⁻². Under these conditions, the energy consumption was 1.28 kWh m⁻³. In addition, the electrochemical process showed a removal of 60% and 49% of the apparent color and turbidity of the water, respectively. These results encourage the applicability of the electroflotation process as a pre-treatment alternative for the cyanobacteria removal from the water supply.

Keywords: Cyanobacteria; DSA® electrodes; Electroflotation; Experimental planning; Water treatment

1. Introduction

The increasing demographic and industrial expansion observed in the last decades, as well as the inadequate disposal of effluents in water springs, have affected the water quality of rivers, lakes and reservoirs. This scenario led to the occurrence of algae blooms in reservoirs used for public supply, thus damaging their multiple uses.

Due to the algal blooms, the alteration of water quality in the springs compromises the operation of the treatment units, which directly influences the water supply system, reservoirs and distribution network. Among the main problems observed in water treatment plants (WTPs) that capture and

treat eutrophic waters for public supply, the most relevant is the presence of microalgae and cyanobacteria in the spring, which increase the consumption of chemical inputs during water purification, causing the presence of flavor/odor, a filtration run reduction as well as the risk of releasing cyanotoxins through cellular lysis.

Some genera and species of cyanobacteria that form blooms produce potent toxins, and there may be producing and non-producing toxin strains within a single species. Among the genera that present toxic species that form blooms, there are *Anabaena*, *Aphanizomenon*, *Cylindrospermopsis*, *Microcystis*, *Nodularina* and *Oscillatoria* [1].

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After treatment, the water from Peri Lagoon, located on the island of Florianópolis/SC – Brazil, is used to supply part of the population in the southern and eastern regions of the island by means of direct filtration. A peculiar characteristic of this lagoon water is the high concentration of cyanobacteria, predominantly *Cylindrospermopsis raciborskii* and *Pseudanabaena galeata*, both filamentous, producing hepatoxins and neurotoxins that cause acute and chronic intoxications, reaching the liver cells and the neuromuscular system, which can lead to the death of animals in minutes, hours or days [2].

Studies conducted in the Peri Lagoon have shown the presence of high density cyanobacteria, with a dominance of the *Cylindrospermopsis raciborskii* species with a density of 10^4 – 10^6 cells/mL [3,4].

As it is a filamentous cyanobacteria, its existence is unfavorable for filter operations, especially direct filtration, because transverse cells may occur, depending on the characteristics of the filter medium, significantly reducing the filtration run [5], which is not advantageous for the filtration process. Thus, it is necessary to apply a pretreatment that is capable of removing cyanobacteria without cell lysis and has low implantation and operational cost.

In this sense, studies performed by Garcia et al. [6] show that the electroflotation process is an efficient alternative for cyanobacteria removal from the Peri Lagoon water. In this study, aluminum electrodes were used and a cyanobacteria removal of 76.3% was obtained. However, it was reported that after the electroflotation process, there was an increased residual aluminum in the treated water. This increased aluminum most likely occurred due to the stability of the electrode material.

Nevertheless, this problem can be solved with the development of dimensionally stable anodes (DSA), which provides a wide application without the wear of the electrodes [7]. DSA has excellent electrochemical properties, which has encouraged studies on the application of these materials in water and effluent treatment in general [8–12].

As an advantage, electroflotation presents the generation of small bubbles of hydrogen and chlorine gases generated from the reactions that occur in the cathodes and anodes, respectively. These small bubbles (mean diameter of approximately 20 μm) can cause a flotation of the flakes and coagulated materials [13].

The electroflotation process makes it possible to extend the treatment capacity of traditional physical–chemical treatment systems, since it uses the same basic coagulation–flocculation [14]. Due to this, some research was developed using the electroflotation process to remove algae [6,15] and microcystins [16,17] from the water supply. This research has shown a high efficiency (76%–98%) in the electroflotation process in removing cyanobacteria and microcystins.

In this context, the present research proposes the application of the electroflotation process, using DSA® electrodes, for removing cyanobacteria from the water supply.

2. Materials and methods

The present research was developed in the Laboratory of Water Potabilization (LAPOA), located in the Department

of Sanitary and Environmental Engineering of the Federal University of Santa Catarina (UFSC), Florianópolis/SC, Brazil.

2.1. Study water

The studied spring (Peri Lagoon) is located in the south-east region of the island of Florianópolis in Santa Catarina. It is a coastal lagoon that has a surface area of 5.2 km², and a contribution basin of 20.1 km², being fed mainly by two small rivers, the Cachoeira Grande River and the Ribeirão Grande River.

The Peri Lagoon connects to the sea through the Sangradouro channel, with a proportion difference of approximately 3 m, which means that the lagoon does not receive salt water. The lagoon has a volume of approximately $21.2 \pm 0.1 \times 10^6$ m³, average depth of 4.2 m and maximum of 11 m, a maximum length of 3.8 km (NE/SW axis) and maximum width of 1.8 km (E/W axis).

The raw water was collected at the influx channel of the Peri Lagoon Water Treatment Station and transported to LAPOA for the experiments. The procedures for collecting and preserving water followed the recommendations set forth by the American Public Health Association [18].

2.2. Pilot system

The experimental system used was an electrochemical reactor, a voltage stabilizer source (INSTRUTEMP – ITFA 5020), used to determine current density, a 1/2 HP centrifugal pump, used to recirculate water, a metering pump (Grabe – DDM 130-07-PP/TF-1), used to control the inflow of raw water, hydraulic and electric systems and two reservoirs with a capacity of 500 L (input/output) as presented in Fig. 1.

2.2.1. Electrochemical reactor

The utilized electrochemical reactor had an internal diameter of 115 mm and a volume of 2.08 L.

The electrodes used contained titanium cathodes and dimensionally stable anodes of the DSA® (“De Nora”) type, composed by $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$.

An arrangement of 10 electrodes was used in parallel, with 5 cathodes and 5 anodes that were intercalated, with a total effective area of 785 cm² and a distance of 8 mm between electrodes as shown in Fig. 2.

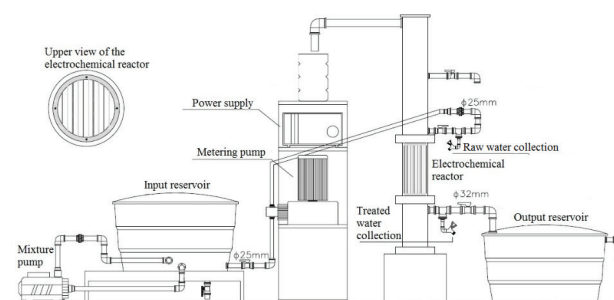


Fig. 1. Schematic of the pilot system used in the research.

2.2.2. Operation of the pilot system

After the introduction of the raw water into the inlet tank, the water was sucked into the electrochemical reactor by means of a metering pump, where the electroflotation process occurred due to the difference in potential applied to the electrodes through the electric power source. Water collection before and after treatment was performed on the raw and treated water collection taps, as shown in Fig. 1. After the treatment, the water was directed to the exit tank.

2.3. Experimental procedure

In order to identify the best conditions of the reactor operating parameters (ROPs), preliminary tests were performed in which the water was treated at room temperature ($25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$) under different conditions, varying the water input rate and the electric current density.

After 30 min of each test, aliquots of treated water were collected and cyanobacteria counts were performed.

In order to determine the optimal conditions of the ROP and to identify the maximum efficiency of the electroflotation process, experimental planning was carried out using Statística® software.

2.4. Experimental planning and statistical analysis

A central composite rotational design (CCRD) 2^2 was performed in triplicate at the central point and four axial points, totaling 11 tests. The levels of the variables analyzed in the optimization of the electroflotation process can be observed in Table 1.

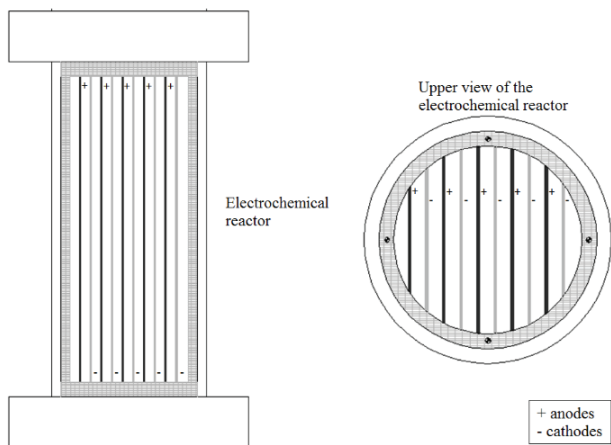


Fig. 2. Schematic of the electrochemical reactor used in the research.

Table 1
Levels of independent variables investigated in the electroflotation process

Independent variable	Variables	Levels				
		-1.68	-1	0	+1	+1.68
Input rate ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)	q_1	49.6	70.0	100.0	130.0	150.4
Current density (A m^{-2})	q_2	16.56	38.21	70.06	101.91	125.56

The independent variables studied in the electroflotation process were water input rate (q_1) and electric current density (q_2). The response variable was the cyanobacteria removal rate.

The water input rate values were defined according to the maximum capacity of the metering pump used (130 L h^{-1}).

The values referring to the electric current density were defined according to the current intensity and the effective area of the electrodes, and the values for the electric current intensity were defined as a function of the maximum current intensity tolerable by the anode used, which was 13.0 A.

The CCRD 2^2 matrix in triplicate at the center point and four axial points, with the encoded values of the independent variables are shown in Table 2.

The results obtained in the experimental design were statistically analyzed, which included the analysis of variance (ANOVA), statistical model prediction and contour plot. Statística® software was used to obtain these outcomes.

In this way, higher performance operating conditions of the evaluated treatment system were obtained.

2.5. Optimization of the electrolysis time as a result of the cyanobacteria removal from water

Experiments were carried out using the optimal ROP conditions obtained in the experimental planning, taking water samples of 100 mL, at 0, 15, 30, 45 and 60 min intervals, to analyze the cyanobacteria removal. At this stage, complementary analyses of pH, temperature, apparent color and turbidity were performed.

Table 2
CCRD 2^2 experimental planning matrix in triplicate at the central point and four axial points

Test	Experimental conditions	
	q_1	q_2
1	-1	-1
2	+1	-1
3	-1	+1
4	+1	+1
5	-1.68	0
6	+1.68	0
7	0	-1.68
8	0	+1.68
9	0	0
10	0	0
11	0	0

Cyanobacteria count analyses were performed according to the procedures described in Method 10900 C of the Standard Methods for the Examination of Water and Wastewater [18]. The other evaluations were carried out according to the procedures described in the Standard Methods for the Examination of Water and Wastewater [18].

3. Results and discussion

3.1. Statistical analysis of electroflotation process results

The experimental design used for the interaction between all variables and levels, and the results obtained in the cyanobacteria removal from the water through the electroflotation process are presented in Table 3.

According to the data presented in Table 3, the cyanobacteria removal ranged from 23.65% to 72.16%, considering all the effects of the independent variables and their interactions, within the experimental range examined in this study.

The results obtained were statistically analyzed by combining the actions among the variables, using the proposed model presented in Eq. (1) as follows:

$$R(\%) = 70.87 - 0.53 * X_1 - 1.50 * X_2 - 16.01 * X_1^2 - 14.97 * X_2^2 - 6.59 * X_1 * X_2 \tag{1}$$

where R (%) is the percentage of cyanobacteria removal; 70.87 is a constant; X_1 is the water input rate ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$), X_2 is the electric current density (A m^{-2}), X_1^2 is the water input rate ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$), X_2^2 is the electric current density (A m^{-2}) in quadratic terms of the equation and $X_1 * X_2$ is the interaction between the factors.

The results obtained produced a suitable adjustment of the model between the predicted and observed values for the cyanobacteria removal ($r^2 = 0.98$) as shown in Fig. 3.

The values acquired through the mathematical model and those observed in the experiments showed little dispersion, with r^2 of 0.98 (Fig. 3), which confirms the suitability of the model for the experimental data, since the dispersion is directly related to an appropriate correlation between the predicted and experimental data achieved.

To validate the suitability of the proposed model, ANOVA was performed. The ANOVA results are shown in Table 4.

The ANOVA result showed that the predicted model (Eq. (1)) is valid in the 95% confidence interval as shown in Table 4. Since $F_{\text{calculated}} (48.77) > F_{\text{tabulated}} (5.05)$, the values of the experimental responses ($R\%$) resulted in an advantageous reproduction of the data. The value of the residual (75.87) was low when compared with the regression (3,699.57), and

Table 3
Experimental conditions and results of the CCRD 2² in triplicate at the central point and four axial points for the cyanobacteria removal (%) from the water using the electroflotation process for 30 min of electrolysis

Test	Input rate ($\text{m}^3 \text{m}^{-2} \text{d}^{-1}$)	Current density (A m^{-2})	Cyanobacteria removal (%)
1	70	38.21	34.63
2	130	38.21	53.41
3	70	101.91	40.12
4	130	101.91	32.55
5	49.6	70.06	27.30
6	150.4	70.06	23.65
7	100	16.56	28.13
8	100	125.56	25.25
9	100	70.06	69.79
10	100	70.06	72.16
11	100	70.06	70.50

Table 4
ANOVA of the predicted model for the values of cyanobacteria removal from water through the electroflotation process, at a 95% confidence level ($p < 0.05$)

Parameter	Source of variance	Sum of squares	Degrees of freedom	Mean squares	F		Significance level (%)
					Calculated	Tabulated	
Cyanobacteria count	Regression	3,699.57	5	739.91	48.77	5.05	<0.01
	Residual	75.87	5	15.17			
	Lack of fit	72.91	3	24.30			
	Pure error	2.96	2	1.48			
	Total	3,775.44	10				

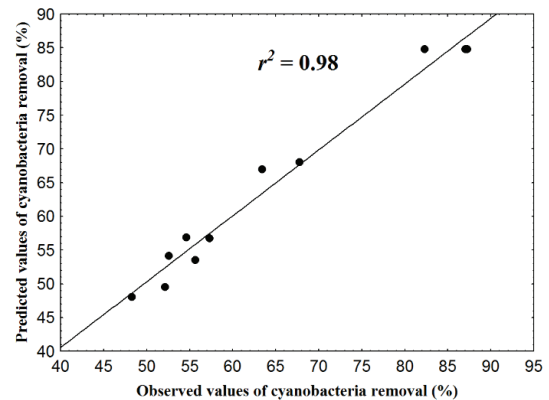


Fig. 3. Correlation between the values observed in the cyanobacteria removal and their corresponding values predicted by the statistical model proposed for the water treatment through the electroflotation process.

the value of the pure error (2.96) indicates a valuable reproducibility of the analysis.

According to the statistical analysis and the interpretation of the obtained results, the higher efficiency of the electroflotation process in the cyanobacteria removal is achieved in the following operating conditions of the electrochemical reactor: $100.84 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ water input rate and 68.26 A m^{-2} of electric current density.

These results may be better visualized in Fig. 4, where the contour plot was constructed using the proposed statistical model, which relied on the responses ($R\%$) obtained in the experimental design.

In Fig. 4 it can be observed that the best responses were the tests at the central point (0), that is, the highest percentages of cyanobacteria removal occurred when the values of the water input rate and the current density were close to the central values of the experimental planning.

It can also be observed that the increased cyanobacteria removal rate, with the electric current density at values close to the central point, occurs due to the increased gas bubbles that are generated in the electroflotation process, allowing a greater efficiency in cyanobacteria removal. In a similar study, Lucero et al. [17] also observed that the electric current density is a fundamental parameter in the electroflotation process, since it has a direct effect on cyanobacteria removal.

As observed, the values of electric current density above the central point of the experimental design will not have a significant effect with regard to the efficiency of cyanobacteria removal. Increasing the electric current density from that point will only increase the power consumption, but not the removal efficiency, so it is not a viable option. The deceleration of cyanobacteria removal in excess of 68.26 m^{-2} , which likely occurs due to the large amount of chlorine bubbles that is produced, since excess chlorine bubbles reduce the efficiency of the removal rate due to their coalescence [19].

3.2. Results of the optimized electrolysis time due to cyanobacteria removal from water

For the electroflotation process, using DSA®-type electrodes, operating under optimal conditions: water input rate

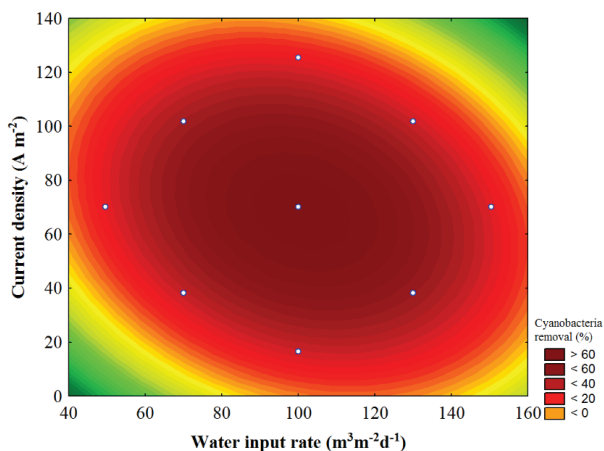


Fig. 4. Contour plot for the evaluation of the cyanobacteria removal as a function of the water input rate and electric current density.

of $100.84 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ and electric current density of 68.26 A m^{-2} obtained satisfactory results of cyanobacteria removal from water.

The cyanobacteria count values of the water for up to 60 min of treatment through the electroflotation process can be observed in Fig. 5.

As observed in Fig. 5, the first 30 min of electrolysis had a removal of approximately 73% (406,500 cells/mL) from the total number (1,504,500 cells/mL) of cyanobacteria cells. From 30 min of electrolysis, a linear tendency of the experimental points of removal is observed. At 60 min of electrolysis, cyanobacterial cell numbers were removed by approximately 78% (331,500 cells/mL), with an energy consumption of 1.28 kWh m^{-3} . This value of energy consumption was similar to the value obtained by Tumsri and Chavalparit [15]. In spite of presenting a relatively high-energy consumption, it was decided to use the electroflotation process as a pre-treatment in the cyanobacteria removal. Some other pre-treatment strategies were studied, however pre-treatments such as riverbank filtration and microfiltration present some limitations in water contaminated with cyanobacteria. Riverbank filtration is not usually appropriate in lakes due to the limitation of the type of soil that is not favorable (rocky/clayey). Microfiltration due to the presence of large amounts of cyanobacteria is also not appropriate in this case, as there is a rapid clogging of the filter medium. Therefore, it was decided to use electroflotation technology, once it present good results in presence of large amounts of cyanobacteria.

Tumsri and Chavalparit [15] studied the optimization of the electroflotation process for algae removal using aluminum anodes and graphite cathodes. It was observed that at a current density of 20 A m^{-2} and 60 min electrolysis, a removal efficiency of 96.0%–98.1% was obtained. Under these conditions, the energy consumption was 1.84 kWh m^{-3} .

Lobón et al. [16] studied microcystin removal in tap water through the electrochemical process using titanium electrodes. In this study, the electric current (1.5 and 5 V) and the electrolysis time (10–60 min) were varied. The authors noted that the largest removal of microcystins (values >90%) occurred with an electric current of 1.5 V and 60 min of electrolysis. Under these conditions, the energy consumption was $0.000025 \text{ kWh m}^{-3}$.

The results obtained in this research differ somewhat from those achieved in previous studies, most likely as a result of the electrode material and the experimental conditions.

In addition to the cyanobacteria removal analyses, the behavior of pH, temperature, apparent color removal and

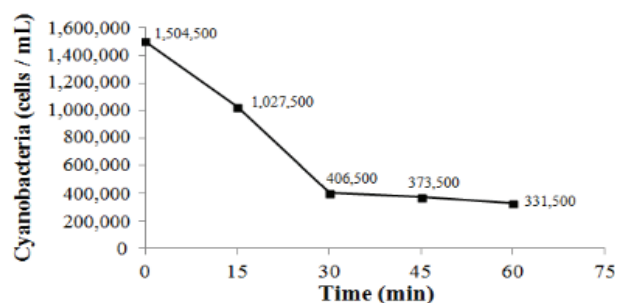


Fig. 5. Cyanobacteria removal from water as a function of electrolysis time.

water turbidity was also monitored. The results of these analyses can be observed in Figs. 6 and 7.

As displayed in Fig. 6(a), the pH values of the water increased after the application of the electroflotation process.

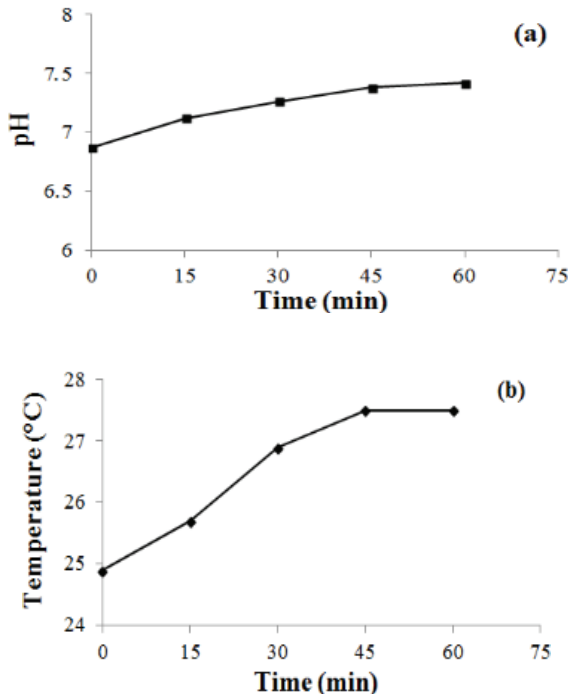


Fig. 6. Values of pH (a) and temperature (b) of water as a function of the electrolysis time.

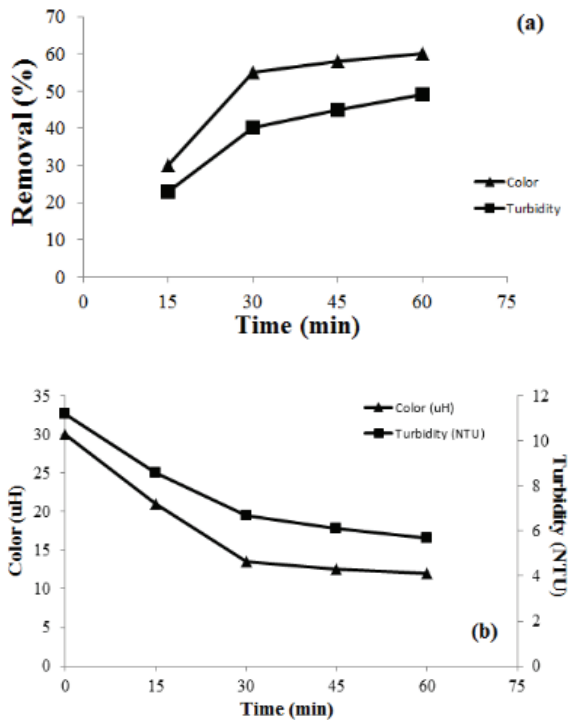


Fig. 7. Percentage (a) and values (b) of apparent color removal and water turbidity as a function of the electrolysis time.

The mean pH value of the water before treatment was 6.87 and after the electrochemical process, it was 7.42 (an increase of approximately 8%). According to Motheo and Pinheiro [20], this increase in pH can be explained by the products that are formed on the electrode surfaces. In the cathode, there was an occurrence of water reduction with the consequent formation of hydrogen gas and an increase in the pH value due to the formation of hydroxyl anions (OH⁻). In the anode, three reactions occurred simultaneously: formation of oxygen gas, chlorine gas and organic oxidation. As opposed to the formation of hydroxyl in the cathode, the formation of H⁺ species occurred in the anode, which consequently decreased the pH value. Nonetheless, this variation of the pH value for lower values does not have the same magnitude of the increased pH value in the cathode, because the charge balance involves chlorine gas formation and organic oxidation as well.

In relation to the water temperature, there was a small variation throughout the treatment process as observed in Fig. 6(b). The initial water temperature was approximately 25°C and the final temperature was 27.5°C, showing an increase of 1.5°C after the electroflotation process. According to Larue et al. [21], the increase in water temperature after electrolysis is caused by the conversion of electric energy into heat, known as the Joule effect, which can be considered low in this case.

Fig. 7 shows the graphs with percentages (a) and values (b) of apparent color removal and water turbidity during 60 min of electrolysis.

It is observed in Fig. 7 that with 30 min of electrolysis, there was 55% removal of the apparent color (13.5 uH) and approximately 40% of the water turbidity (6.7 NTU). After 60 min of treatment, there was a 60% removal of the apparent color (12 uH) and 49% of the water turbidity (5.7 NTU). Garcia et al. [6] observed a similar result. The cyanobacteria removal from the water supply through the electroflotation process was studied and color removal of 37.9% was obtained.

Finally, it was noted that all the results suggest that the application of the electroflotation process, from the use of DSA® type electrodes, proves to be an attractive option. Besides providing a wide application without the wear of the electrodes [7], it promotes a good removal of the cyanobacteria present in the water supply. Electroflotation still stands out among other cyanobacterial removal methods for its economic and environmental benefits [17].

It is emphasized that after the electroflotation process, the treated water will still be subjected to the filtration and disinfection process before being distributed to the final consumer.

4. Conclusions

With the use of experimental planning as a tool to evaluate the effects of the independent variables and their interactions on the rate of cyanobacteria removal for the water from Peri Lagoon, it was possible to establish “optimized” operating conditions to have a higher index of cyanobacteria removal.

From the evaluation of the “optimized” operating conditions, a study of the cyanobacteria removal from the Peri Lagoon water can be conducted as a function of the electrolysis time, thus optimizing the reaction time, which makes the treatment of larger volumes of water per day possible when applied to the reality of a WTP.

According to the statistical analysis, it was verified that the higher efficiency of the electroflotation process in cyanobacteria removal was achieved in the following operating conditions of the electrochemical reactor: water input rate of $100.84 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ and electric current density of 68.26 A m^{-2} . Under these conditions, 60 min of electrolysis achieved a cyanobacteria removal of approximately 78%, with an energy consumption of 1.28 kWh m^{-3} . With 60 min of treatment, the electroflotation process also showed a removal of 60% of apparent color and 49% of water turbidity.

It can be concluded that the water treatment of Peri Lagoon through the electroflotation process, using DSA®-type electrodes, was efficient and can be applied as a pre-treatment method for cyanobacteria removal from the water supply.

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