Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22640

124 (2018) 146–152
August

Application of electro-oxidation by direct and pulsed current associated to ozonation on raw water treatment

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Received 31 October 2017; Accepted 9 July 2018

ABSTRACT

Raw water was submitted to a treatment process using electro-oxidation and ozonation, evaluating the parameters color, dissolved organic carbon (DOC), turbidity, UV-Vis adsorption spectrum, SUVA, and energy consumption. In the electro-oxidation process were used two current densities (22 and 44 A m^{-2}) ruthenium electrodes and two types of current, (direct and pulsed). The percentages of removal of apparent and true color varied from 40.84 to 70.17% and from 47.09 to 80.06%, respectively. The electro-oxidation by direct current in the presence of ozone had the best removal efficiencies. DOC removal reached levels of 1.55–15.69%. The use of the electro-oxidation by pulsed current has obtained lower values of energy consumption.

Keywords: Pulsed current; Electro-oxidation; Ozonation; Raw water; Natural organic matter

1. Introduction

According to the chemical, physical, biological and radiological characteristics of a water source to be made available for human consumption, it must undergo specific treatments in order to meet drinking standards. Among the undesirable constituents in raw water for drinking water, we can highlight the dissolved organic matter, suspended solids, pathogenic microorganisms, nutrients and metals, which confer color, turbidity, taste and odor to the water.

From dissolved organic matter, we can mention the natural organic matter (NOM), which is defined as all the organic matter existing in reservoirs or natural ecosystems, differing from living organic matter and compounds of anthropic origin. Among the compounds that are part of NOM there are the humic substances (HS), which are the main constituents of NOM [1]. HS are substances of high molecular weight and heterogeneous structure, presenting aliphatic and aromatic hydrocarbons with various functional groups, including carboxylic and phenolic groups [2,3]. In addition, HS is not desirable in waters for human consumption, because confer color, odor and unpleasant taste to the water. Another problem related to the presence of HS in water is that they are precursors of chlorine disinfection byproducts, such as trihalomethanes and haloacetic acids [4,5].

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Electrolytic processes such as electro-oxidation have been applied as water treatment techniques [6,7]. The electrochemical oxidation has potential to completely oxidize organic pollutant to CO_2 and H_2O, or to transform refractory compounds into biodegradable compounds [8,9]. This ability is due to the production of hydroxyl radicals on the surface of the electrode, with electro-oxidation being considered an advanced oxidative process [10,11].

The combustion/conversion electrochemical of organic compounds to oxide anodes can be described as [12]:

$$MO_x + H_2O \rightarrow MO_x(HO^\bullet) + H^+ + e^- \quad (1)$$

The water is discharged at the anode producing adsorbed hydroxyl radicals, called physical-adsorbed active oxygen, Eq. (1). Subsequently, the hydroxyl radicals can interact with the oxygen present in the anode and form the MO_{x+1}, called chemo-adsorbed active oxygen:

$$MO_x(HO^\bullet) \rightarrow MO_{x+1} + H^+ + e^- \quad (2)$$

However, for both forms of active oxygen, there is production of oxygen:

$$MO_x(HO^\bullet) \rightarrow ½\,O_2 + H^+ + e^- + MO_x \quad (3)$$

$$MO_x + 1 \rightarrow MO_x + ½\,O_2 \quad (4)$$

The degradation of the organic material is achieved with $HO^\cdot$ and the conversion with MO_{x+1}.

However, the biggest challenge for electrolytic processes is to achieve good efficiency with low power consumption. Thus, the pulsed current (PC) appears as an alternative that fits this need. The use of pulsed current in electrolytic processes is not a new technique, but has not yet been studied enough to treat water or effluent. In the past, it was studied for the production of hydrogen [13–15]. Some researchers have attributed a better production of hydrogen and oxygen to a better mass transfer [16,17].

The use of pulsed current allowed a greater removal of sewage sulphide than direct current, due to non-passivation at the anode and scaling at the cathode [18]. Wei and co-workers [19] studied the degradation of phenol using pulsed current and obtained a significant reduction in energy consumption compared to direct current. Martins and co-workers [20] reached 84.74% of COD from textile wastewater using electro coagulation (steel stainless electrodes) by pulsed current.

In connection, ozone is a powerful oxidizing agent and one of most used in the removal of organic matter and as a disinfectant agent in water/wastewater [21–24]. The ozone molecule may react with water molecule, in basic pH, to generate hydroxyl radical [25].

$$H_2O + O_3 \rightarrow O_2 + 2HO \quad (5)$$

Thus, the aim of this study was to apply the electro-oxidation associated to ozonation in the treatment of raw water, evaluating the parameters apparent and true color, turbidity, dissolved organic carbon (DOC), specific ultraviolet absorption (SUVA) and energy consumption (EC).

2. Materials and methods

2.1. Raw water sample

The water sample was taken from a reservoir located in the metropolitan area of Fortaleza - Ceara- Brazil. The samples were collected in May/2017. The results obtained to chemical and physical parameters of the raw water are shown in Table 1.

2.2. Electrolytic cell

The electrolytic cell consisted of 4 ruthenium electrodes (Ru, Metal Mixed Oxide, Magneto @ Special Anodes-HOL) connected in parallel mode with dimensions 300 mm × 50 mm × 1 mm. The electric power was supplied by a voltage source (DC) (Minipa, MDL-3305). An electronic circuit (DC/PC converter) was used to supply the frequency 1000 Hz (PC). The shape and frequency of the pulsed current were monitored using an oscilloscope (Minipa, MVB-DSO). The applied current was monitored using a digital multimeter (Minipa, MDM-8145A), and can be visualized in Fig. 2. Ozone generator 3.5 g h^{-1}, 70 W (Ozone Line, GO5000AA-INX) was used to provide ozone. The sample was kept under stirring with the aid of a magnetic stirrer and a magnetic bar.

From T_{on} and T_{off} we can find the duty cycle [Eq. (6)] another electric attribute, as well as the pulsed current, which deserves attention. The pulsed current worked with a duty cycle 50%.

$$Duty\,cycle(\%) = \frac{T_{on}}{T_{on} + T_{off}} \quad (6)$$

2.3. Analyzes

The pH and electrolytic conductivity of the solution were monitored by the probe (HANNA, HI 7629829), the sample turbidity was evaluated using a turbidimeter (HANNA, HI 98703). The dissolved organic carbon (DOC) was determined using an organic carbon analyzer (SHIMADZU, TOC-L) equipped with self-sampler (OCT-L), and the samples were previously centrifuged. The apparent and true color of the samples were determined using a colorimeter (DIGIMED, DM-Cor), the true color was obtained of the centrifuged samples. The UV-Vis absorption spectrum (190–800 nm) was obtained using a spectrophotometer

Table 1
The physical and chemical parameters of raw water

Parameter	Mean value ± SD
Apparent color (HU)	41.43 ± 1.80
True color (HU)	29.36 ± 3.10
Turbidity (NTU)	8.16 ± 0.91
Conductivity (µS cm^{-1})	445.43 ± 10.49
pH	7.40 ± 0.46
DOC (mg L^{-1})	12.86 ± 0.76
Chloride (mg L^{-1})	116.5 ± 2.30

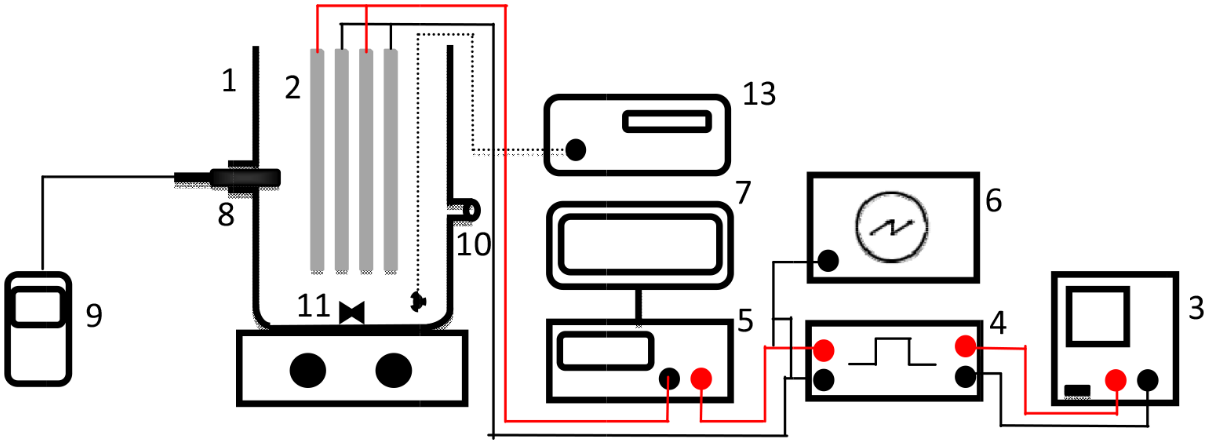

Fig. 1. Configuration of the equipment and the electrolytic cell; 1. Reactor; 2. Electrodes; 3. Voltage source; 4. Electronic circuit; 5. Ammeter; 6. Oscilloscope; 7. Computer; 8. Multi parameter probe; 9. Meter; 10. Sampling port; 11. Magnetic bar; 12. Magnetic stirrer; 13. Ozone generator.

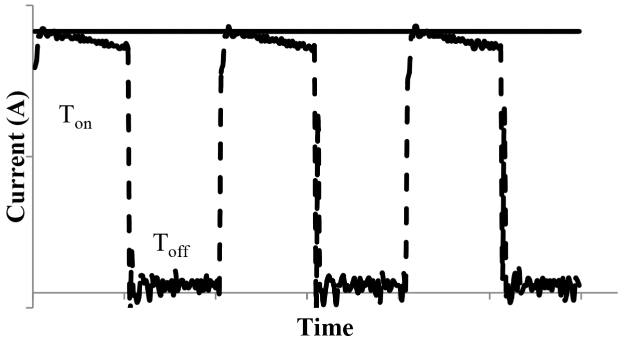

Fig. 2. The shape from pulsed current (---) and direct current (—).

(SHIMADZU, UV-1800). The specific ultraviolet light absorbance (SUVA) was calculated using the absorbance ratio at 254 nm and DOC (mg L^{-1}), Eq. (7). The energy consumption (EC) was calculated using Eq. (8).

$$SUVA\left(\frac{L}{mg\cdot m}\right)=\frac{abs_{254}\times 100}{DOC} \tag{7}$$

$$\mathrm{EC}\left(\frac{kWh}{m^3}\right)=\frac{1}{1000\mathrm{V}}\left[\int_{\mathrm{t=0}}^{\mathrm{t=x}}\mathrm{i(t)T(t)dt}+Poz\right] \tag{8}$$

where V is the solution volume (m^3), t is the experiment time (h), i is the electric current (Ampere), T is the applied voltage (Volts), and Poz is the power (Watts) of the ozone generator. The Poz was measured by wattmeter during whole the experiment, and taken the average value of watts and used it on the equation of energy consumption [Eq. (8)].

2.4. Experiments

The treatment of the raw water was carried out for a total time of 60 min, and the samples were collected at the times of 10, 20, 30, 45 and 60 min. The variables studied were: stirring rate 600 rpm, current mode: pulsed and direct, current densities 22 and 44 A m^{-2}, and ozone (3.5 g h^{-1}). The conditions of each experiment (in duplicate) are shown in Table 2.

3. Results and discussions

Figs. 3 and 4 show the behavior of the apparent and true color during the application of the experiments. For all experiments there was a higher rate of apparent color removal in the first ten minutes. The experiment 1 showed the lowest apparent color removal efficiency, which can be explained by the lower electrical current density and absence of ozone using pulsed current. For the experiment 8 was obtained a better efficiency, when highest density current, presence of ozone and direct current were applied. The experiments 2 (pulsed current, 22 A m^{-2}, and ozone presence) and 7 (direct current, 44 A m^{-2}, and ozone absence) had similar results. In Brazil, the maximum value permitted of the apparent color is 15 HU for drinking water, thus, only the experiments 2, 6, 7 and 8 reached this value. The percentage values to apparent color removal were in the range of 40.85–70.18%, and can be observed in Table 3. The true color removal showed behavior similar to the apparent color, where again experiment 8 obtained the best efficiency. The true color removal varied to 47.09–80.07%.

Table 2
Setup of the experiments

Experiment	Current mode	Current density (A m^{-2})	Ozone
1	Pulsed	22	Absence
2	Pulsed	22	Presence
3	Pulsed	44	Absence
4	Pulsed	44	Presence
5	Direct	22	Absence
6	Direct	22	Presence
7	Direct	44	Absence
8	Direct	44	Presence

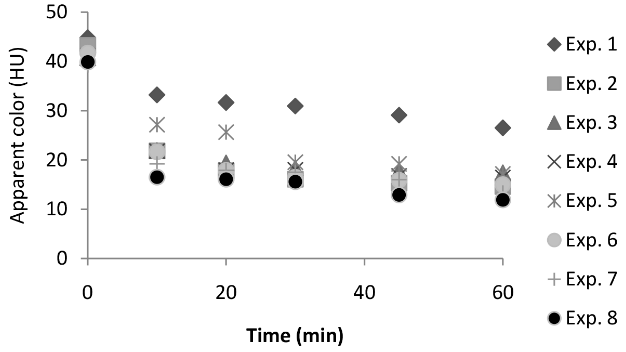

Fig. 3. Apparent color removal behavior due to the experiments.

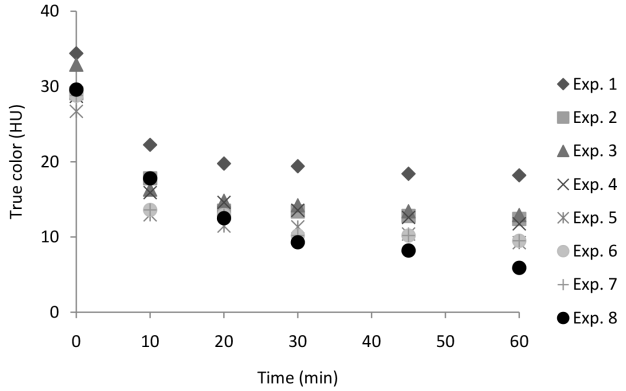

Fig. 4. True color removal behavior due to the experiments.

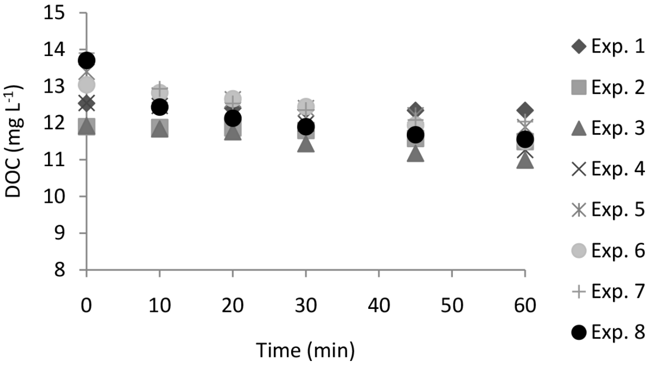

Fig. 5. DOC removal behavior due to the experiments.

Unlike the removal of apparent and true color, the process did not obtain the DOC removal good, being the greatest efficiency, 15.69%, reached with the experiment 8, Fig. 5. By increasing the electric current density there was an increase in DOC removal in the two modes of current. The use of ozone also promoted a better DOC removal when compared to the experiments of same current density. The DC obtained better DOC removal than the PC, which can be explained by the greater amount of current applied to the process, since the PC has the same current density than DC only at certain moments. Thus, DC can generate more oxidant species in the medium. The achieved values of true color removal and DOC indicate that the compounds, which conferred color to the solution, had their bonds broken to the point of color reduction, but there were not completely mineralized. This behavior can be explained by the fact that Ru electrodes are known as active anodes, and the reaction mechanism occurs by the formation of an oxide (MO_{x+1}), [Eq. (2)], which does not promote the complete combustion of organic matter [26].

Looking for the contribution of ozone in the clarification of raw water, it can be observed that the use of the ozone improved, but slightly, the clarification of the raw water

Table 3
Values of initial and final from parameters, and percentage of removal (R)

Apparent color (HU)								
	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8
Initial	44.80	43.25	40.75	40.60	41.20	41.7	39.30	39.90
Final	26.50	14.60	17.40	16.45	17.15	15.00	13.30	11.90
% R	40.85	66.24	57.30	59.48	58.37	64.02	66.16	70.18
True color (HU)								
Initial	34.40	29.10	32.90	28.70	26.70	24.70	28.80	29.60
Final	18.20	12.40	12.90	11.75	9.25	7.85	9.50	5.90
% R	47.09	57.39	60.79	59.06	65.36	68.22	67.01	80.07
DOC (mg L^{-1})								
Initial	12.54	11.90	11.92	12.55	13.40	13.04	13.90	13.71
Final	12.34	11.49	10.99	11.27	11.89	11.50	12.04	11.56
% R	1.55	3.41	7.83	10.20	11.24	11.81	13.42	15.69
Turbidity (NTU)								
Initial	9.55	8.57	8.82	7.18	7.26	8.05	7.11	8.78
Final	6.18	4.54	3.79	2.79	3.17	1.69	1.97	1.85
% R	35.25	47.08	57.01	61.18	56.37	79.06	72.29	78.93

when comparing two experiments that only differentiate in the presence of ozone. A possible explanation for the low influence of ozone on true color removal and DOC was the quick contact time between ozone and organic matter, because the ozone bubbles quickly went up to the surface of the sample. However, ozone bubbles aided the flotation of suspended material, which helped to remove turbidity from the sample, Fig. 6 and Table 3, where the percentages of turbidity removal were higher in the presence of ozone compared to experiments in absence of ozone using the same current density.

The results showed that there was a decrease in SUVA values in all the experiments, Fig. 7. SUVA provides a quantitative measure of aromaticity and humic fraction content of natural organic matter [27].

The sample conductivity for each experiment during the treatment is shown in Fig. 8. It can be observed a decrease in the conductivity throughout the treatment, being more pronounced using direct current (exp. 5–8). This reduction may have been due to the fact that the chloride, present in the sample, undergoes oxidation at the anode, generating the chlorine gas which formed hypochlorous acid/hypochlorite (HClO/ClO⁻):

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^- \tag{9}$$

$$Cl_{2(g)} + H_2O \rightarrow HClO_{(aq)} + Cl^-_{(aq)} + H^+_{(aq)} \tag{10}$$

$$HClO_{(aq)} \leftrightarrow H^+_{(aq)} + ClO^-_{(aq)} \tag{11}$$

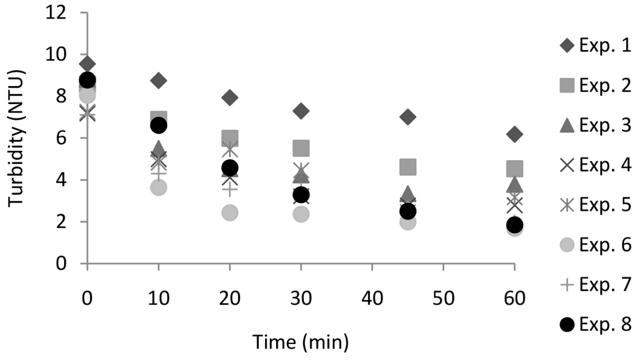

Fig. 6. Turbidity removal behavior due to the experiments.

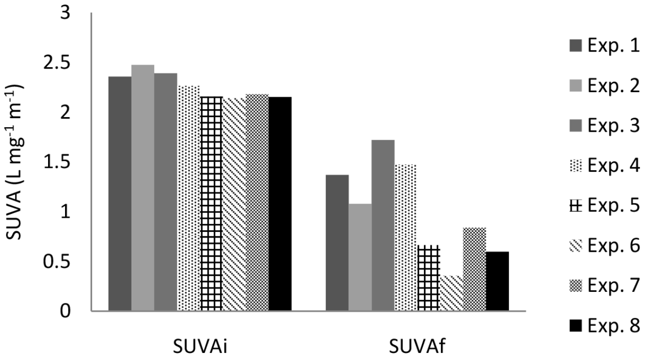

Fig. 7. SUVA values before and after experiments.

The formation of hypochlorous acid was observed by absorption band with the maximum absorption at 290 nm, Fig. 9. In experiments 7 and 8, the highest absorption bands occurred due to the highest current density applied. Santos et al. [28] also observed the same formation of an absorption band with the maximum at 290 nm in their experiments using electrodes Ti/RuO$_2$ and NaCl as electrolyte. The absorption band becomes more evident from experiment 3, the experiments being absent of ozone which presented larger bands, with the possibility that the present ozone may have reacted with ClO⁻ generating chloride, [Eq. (12)] [29]. The formation of the HClO/ClO⁻ oxidizing species may have aided in the color and DOC removal .

$$ClO^-_{(aq)} + O_{3(g)} \rightarrow 2O_{2(g)} + Cl^-_{(aq)} \tag{12}$$

Water treatment techniques always seek the best contaminant removal without forgetting the energetic costs involved. The energy consumption for the experiments was monitored, and the results are shown in Figs. 10 and 11. The experiments with pulsed current had lower values of energy consumption compared to the values of the experiments of direct current in the same densities of electric current. Fig. 11 shows the voltage applied to each experiment, and it is observed that the higher voltages were for experiments 7 and 8 due to a higher current density used. The use of ozone caused an increase in the energy consumption.

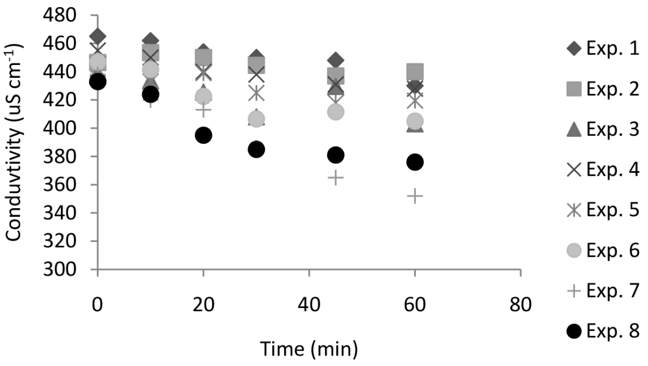

Fig. 8. Conductivity behavior to the experiments.

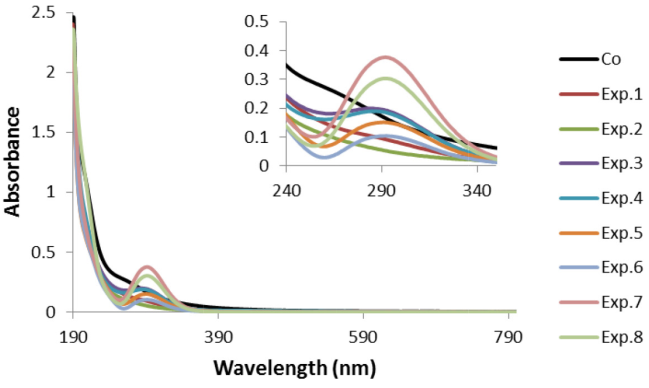

Fig. 9. UV-Vis absorbance of raw water after 60 min of the experiments.

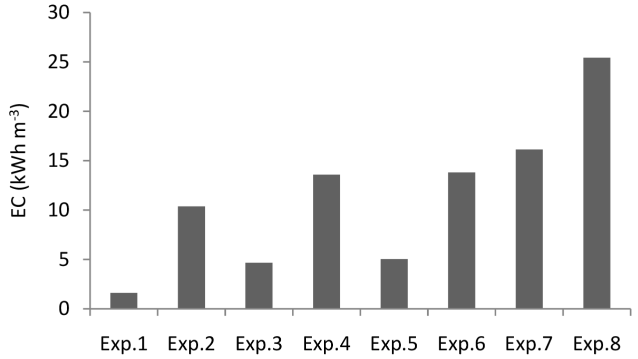

Fig. 10. Energy consumption for all the experiments.

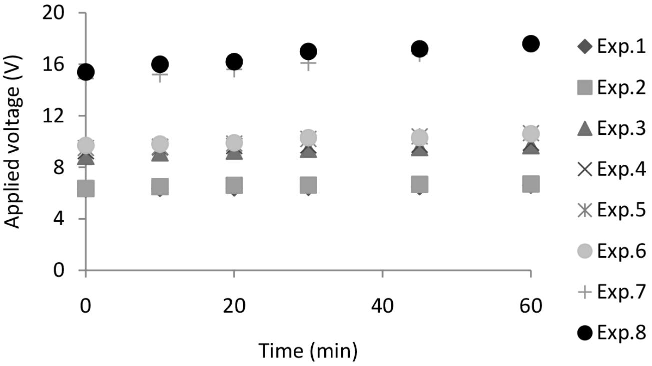

Fig. 11. Applied voltage throughout experiments.

4. Conclusion

The use of electro-oxidation by direct current with or without ozone provided a better removal of true color, apparent color, and turbidity than pulsed current obtaining values of apparent color below the maximum value allowed by Brazilian legislation (15 HU). The percentages of apparent color, true color, DOC and turbidity removals were varied of 40.85 to 70.18%; 47.09 to 80.07%; 1.55 to 15.69% and 35.25 to 78.93%, respectively. The advantage of using the pulsed current was to obtain lower energy consumption. Organic matter (DOC) was not mineralized by complete, only converting, as shown by SUVA results and UV-Vis absorption spectra.

Acknowledgments

The authors thank CAPES, FUNCAP (proc.: BMD-0124-00241.01.00/17; P13-0086-00057.01.00/13) and CNPQ (proc. 402835/2013) for financial support.

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