Addition of hydrogen peroxide in electrocoagulation of dairy liquids

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ABSTRACT

Standing out on the national and world scene as an important economic and social activity, the dairy products industries are characterized by their high polluting potential, especially due to the liquid effluents generated. In this context, the present work aims to study the application of the electrocoagulation process applied associatively with hydrogen peroxide (H_2O_2) in the treatment of dairy effluents using iron electrodes. Effluent treatments were carried out with the electrocoagulation process in a continuous flow reactor. For the method using electrocoagulation, the removal efficiencies in relation to color, turbidity, total organic carbon, chemical oxygen demand and nitrogen removal were 97.2%, 97.0%, 77.5%, 63.3% and 92.2%, respectively. The addition of H_2O_2 to the beginning of electrocoagulation process in the treatment of dairy effluents did not contribute to an increase in the efficiency of removing organic matter. When applied after an electrocoagulation step, it demonstrated to be efficient, reaching COD removals of 97.7%. Therefore, the electrocoagulation demonstrated to be a technically viable alternative for the treatment of dairy effluent.

Keywords: *Electrocoagulation; dairy effluent; hydrogen peroxide; iron electrodes.*

1. INTRODUCTION

The Brazilian milk production is an agro-industrial system very significant, mainly for its social importance, since the dairy activity is practiced throughout the country, in thousands of rural properties. According to the Brazilian Institute of Geography and Statistics [1], Brazilian milk production in 2017 was 33.5 billion liters. Due to the large processing volume of this milk in the dairy industries, large quantities of effluents are also produced.

Milk processing requires a high amount of water, using approximately 2.5 L of effluent for 1 L of milk benefited, making dairy products remarkable generators of industrial effluents [2, 3]. For this reason, the reduction of the volume of these effluents, as well as the previous treatment of their liquid discharges [4] that have a high concentration of organic load such as lactose, proteins and fats [5, 6], are required.

In dairy industries, liquid effluents are most often treated using biological methods, such as the use of activated sludge treatment (aerobic or anaerobic), aerated or facultative ponds, and aerobic biological filters, among others. Electrochemical processes are a good alternative for primary wastewater treatment and are used to destabilize and remove dispersions of various effluents [7–10]. One of the benefits of this treatment is the absence of chemical agents, being a versatile, efficient and easy to handle technique, which is possible to automate and maintain safety, besides not using high temperatures [11, 12].

Electrocoagulation devices are composed of two electrodes with different polarities, anodes and cathodes [13]. When a voltage is applied, the anode oxidizes and the cathode reduces, electrochemically generating the coagulant. The positively charged material can react with the negative charges of the solution, occurring hydrolysis of water which releases hydroxide, responsible for the effluent treatment [14]. This technique combines three processes (electrochemical, coagulation and hydrodynamic) interdependently, operating synergistically to remove pollutants [15].

Techniques based on electrochemical technology are being studied and improved. Examples are electrocoagulation [13, 16], electrooxidation [17, 18], electro-Fenton [19–22], and photo-electro-fenton [23, 24]. The Electro-Fenton process consists of an Advanced Oxidative Process, where the generation of the oxidizing agent, the hydroxyl radical (•OH), manifests itself in an electrochemical environment using high voltage metallic electrodes [25, 26].

Regarding the oxidative process in the electro-Fenton system, it can manifest directly or indirectly. In direct electro-oxidation, the oxidative agent that promotes oxidation is the hydroxyl radical (•OH), which due to its high oxidizing power ($E0 = 2.8$ V) [27, 28] tends to provide, in a non-selective manner, the complete mineralization of organic pollutants. In indirect electro-oxidation, the oxidizing agent acts as chlorine (Cl_2) and hypochlorite (ClO^-) produced in the anode, when saline solutions are used, by oxidation of chloride ions (Cl^-). Even with lower oxidation potentials ($E0Cl2 = 1.4$V, $E0ClO- = 1.5$V) compared to the hydroxyl radical, both compounds contribute efficiently to the oxidative destruction of organic pollutants [11, 29]. The metallic iron plates used as electrodes in the electrolytic process can also contribute to the generation of hydroxyl radicals. In the latter case,

a heterogeneous system is generated since the precursor of catalytic decomposition of hydrogen peroxide (H_2O_2) is solid. Considering that the process of peroxide decomposition in hydroxyl radicals occurs by a redox reaction, more specifically through the consumption of electrons, electrocoagulation, which is an electrochemical process, should favor such a mechanism.

Concomitantly with the generation of hydroxyl radicals resulting from the catalytic decomposition of H_2O_2, metallic iron (Feo) and ferrous ions (Fe^{2+}(aq)) are oxidized to iron III ions that hydrolyze water to generate iron hydroxide (III), which due to its low solubility tends to precipitate, generating clots, which when settling will form sludge, which requires an additional separation process for its removal from the medium [27, 30].

2. MATERIALS AND METHODS

The experiments were carried out at the Environmental Technology and Effluent Treatment Laboratory of the Universidade Regional Integrada do Alto Uruguai e das Missões (URI – Erechim-RS, Brazil).

The synthetic effluent with 2g of milk powder was prepared in one liter of water before the beginning of each treatment, adjusting the initial temperature at 20ºC and the initial pH at 7, being the closest to the characteristics of the dairy industry effluent.

Raw wastewater (real effluent) was obtained from a dairy company located in the North of Rio Grande do Sul State – Brazil. Samples were collected in four different days, transported to the laboratory, homogenized and stored in sanitized bottles at -18°C.

In this context, the electro-Fenton process is characterized as a combination of two mechanisms, one of coagulation and one of oxidation that occurs simultaneously in the electrochemical cell. This process stands out as an alternative for contaminant degradation in effluents, with numerous studies reported in the literature, in different areas of knowledge, with the most varied pollutants, such as textile dyes [25], cellulose effluents [31], organic acid removal [32, 33], wastewater treatment [34], cold cellulose incineration [35], and dairy effluents [3, 36].

In this sense, the objective of the present study was to investigate the application of the continuous flow electrocoagulation process, as well as associatively with H_2O_2 in the wastewater treatment from the dairy industry.

2.1. Continuous flow electrocoagulation tests.

Continuous flow electrocoagulation assays were performed and conducted in a glass electrocoagulation cell. The cell has a total volume capacity of 2 liters, with brackets for two iron electrode pairs (with electrode distance adjustment), which were coupled in parallel using copper wires to a direct current source with amperage adjustments (MIT DC Power Supply MS 3005). To adjust the effluent flows to be treated in the reactor, a peristaltic pump (Master Flex L/S, model 7518-10) was used. Figure 1(a) presents a schematic diagram of the electrocoagulation reactor used in this work.
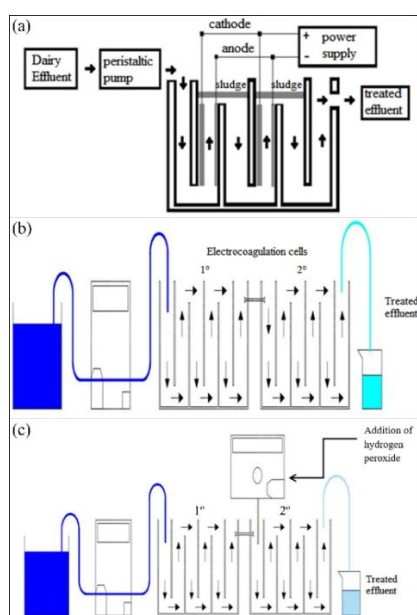

Figure 1. (a) Schematic diagram of the electrocoagulation reactor; (b) Continuous flow addition of H_2O_2 at the beginning of the process before the effluent was submitted to electrochemical treatment; (c) Continuous flow electrochemical treatment with the addition of H_2O_2 after an electrocoagulation step.

In this stage, the effects of electrode distance (DE) (1, 2 and 3 cm), amperage (1, 2 and 3 A) and hydraulic residence times (HRT) (15, 30 and 45min) were evaluated. To monitor process efficiency, aliquots of effluent samples were taken every 5min for 1h.

2.2. Treatment of H_2O_2 assisted electrocoagulation.

At this stage, the addition of H_2O_2 to the continuous flow electrocoagulation operating system was evaluated. H_2O_2 was added to two distinct samples, one corresponding to the raw effluent

and the other to the effluent submitted to a previous treatment step with electrocoagulation. The H_2O_2 concentration evaluated in this study, based on previous research for this manuscript, was up to 33 mg.L^{-1} to increase the rate of soluble organic matter removal from the analyzed effluent.

For both tests, the flow rate employed was 230 mL.min^{-1}, with a H_2O_2 concentration of 33 mL.L^{-1}. The operating conditions used for both electrocoagulation treatments were 2A, DE = 2cm, and HRT = 30min, pH 7 and conductivity of 2000µs.

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H_2O_2 was added at two different times. The first one was in the synthetic raw effluent. After a homogenization step, it was subjected to an electrocoagulation/electrooxidation step. Figure 1(b) presents the process scheme. For the other condition, the peroxide was added during the test, after an electrocoagulation step, the H_2O_2 was added to the previously treated effluent. After a homogenization step, it was submitted to a new electrocoagulation/electrooxidation step. It was a series process, with a physicochemical treatment in the first stage (Electrocoagulation) and an oxidative in the second stage (Electrooxidation), as shown in Figure 1(c).

2.3. Analytical Determinations.

The analyses described below were performed according to the methodologies described in the Standard Methods for Examination of Water & Wastewater [37].

2.3.1. Apparent Color.

The apparent color is a consequence of dissolved substances present in the sample. For the determination of apparent color, a HACH colorimeter (model DR870 program 19) was used where the result is given in Pt mg.L^{-1}.

2.3.2. Turbidity.

A HACH colorimeter (model DR870 program 95) was used, where the result was expressed in UNT - Nephelometric Turbidity Unit. The method is based on comparing the reading of the light scattered by the sample under defined conditions and the light scattered by a standard solution under the same conditions.

2.3.3. Total Organic Carbon.

Total Organic Carbon (TOC) analysis determines organically bound carbon. The sample was prepared from an aliquot of the 1 mL effluent, previously filtered with a membrane (0.45 μm) and diluted to 25 mL with distilled water. Subsequently, it was analyzed by TOC analyzer equipment (Shimadzu, TOC-TOC-VCSH). Determinations were performed by catalytic oxidation at high temperature (680 °C). The TOC content was determined by the difference between total carbon and inorganic carbon concentrations. Results were expressed in mg.L^{-1}.

2.3.4. Chemical Oxygen Demand.

Chemical oxygen demand (COD) is a measure of the amount of oxygen used in the chemical oxidation of inorganic and organic matter present in wastewater. The method used is the microscale colorimetric (5220D, APHA, 1992), which uses as reagents standard solutions of potassium acid phthalate, acidic solution (Ag_2SO_4 in concentrated H_2SO_4) and digesting solution (composed of diluted $K_2Cr_2O_7$, $HgSO_4$, and H_2SO_4 in water). The method consists in the reduction of chromium (Cr^{6+} to Cr^{3+}) and subsequent analysis by color modification in a spectrophotometer. The digestion of the samples was conducted in a thermoreactor (Dry Block MA 4004, Marconi) at 150 °C for 2h After cooling the samples, the readings were taken in a digital colorimeter (HACH, DR870) previously calibrated with standard potassium acid phthalate solutions. Results were expressed in mg.L^{-1}.

2.3.5. Total Nitrogen.

For Total Nitrogen (N_{total}) analysis, the samples were prepared from an aliquot of 1 mL effluent, previously filtered with a membrane (0.45 μm) and diluted to 25 mL with distilled water. Subsequently, the samples were analyzed by analyzer equipment (Shimadzu, TOC-TOC-VCSH). Determinations were performed by catalytic oxidation at high temperature (720 °C). Results were expressed in mg.L^{-1}.

2.3.6. pH.

The pH was measured directly in the sample in a bench digital pHmeter (pH LAB 827, Metrohm), previously calibrated with appropriate standards, at room temperature (25±2 °C).

2.3.7. Conductivity.

Conductivity measurements were performed directly on the samples at room temperature (25±2 °C) using a digital conductivity meter (WTW, model LF 191). Results were expressed in μS.cm^{-1}.

2.3.8. Carbonyl Determination Test.

In a test tube, 4 drops of the sample with 1 mL of 2,4 - dinitrophenylhydrazine reagent were added and it was stirred vigorously. The presence of carbonyl groups was indicated by the appearance of a precipitate, 2,4-dinitrophenylhydrazone.

2.3.9. Aldehyde Determination Test (Schiff-based Reaction).

In a test tube, 5 drops of sample were placed and 3 drops of Schiff reagent were added. The presence of aldehyde groups was indicated by the appearance of a color that varies from purple to violet. A pink color indicates a negative test.

3. RESULTS

3.1. Treatment of synthetic dairy effluent by continuous electrocoagulation.

Based on previous research for this manuscript [4], this study was developed by setting the electric current at 2A and the electrode distance at 2 cm, varying the hydraulic residence time at 15, 30 and 45min. Color removal, COD, TOC, and N_{total} were evaluated in relation to reaction time (Table 1). For all parameters, under all conditions evaluated, the same trend is observed: an increase in efficiency as a function of reaction time.

For the TOC, N_{total} and especially COD responses, a positive effect of HRT is observed, with an increase, even if small, in the removal efficiency with increasing HRT.

For the color (Table 1), there was an oscillation in the removal with the reaction time. Amongst the three conditions evaluated, the highest hydraulic residence time (45min) was the one that presented the lowest efficiency, with the lowest removals. The negative behavior observed for responses is due to the leaching of iron ions to the medium. It interferes negatively in both responses by presenting tonality. With the increase in HRT, the effluent remained in contact with the electrodes for a longer period and, consequently, there was a higher leaching of coagulant (iron ions) to the reaction medium, providing a positive effect for coagulation.

Similar values for color removal and COD were reported by Tchamango et al. [38] in the treatment of electrocoagulation with aluminum electrodes in batch mode using a synthetic milk effluent at a concentration of 1g.L^{-1}. Approximately 100% color and turbidity removals were achieved within 20 reaction min. Lower COD removal efficiency (61%) was also described by the authors. Low COD removal efficiency was also reported by Chen et al. [39] in the batch electrocoagulation treatment of restaurant effluents.

Table 1. Color, COD, TOC and Ntotal removal with reaction time.

Addition of hydrogen peroxide in electrocoagulation of dairy liquids				
HRT (min)	Removal (%)			
	Color	COD	TOC	N_{total}
15	86.7	52.3	71.5	84.2
30	87.1	63.3	77.1	91.6
45	78.8	64.3	78.3	94.7

HRT: hydraulic residence time

The authors associate this behavior of COD with the presence of dissolved organic compounds, which are difficult to remove by coagulation processes as a treatment. According to Tchamango et al. [38], the low COD removal in milk effluent is linked to the presence of lactose, a carbohydrate with high water solubility.

Panizza and Cerisola [26] investigated the efficiency of electrode coagulation with iron electrodes applied for wastewater treatment of a car wash effluent. The best results for electrocoagulation were achieved in 6min, a result similar to that one presented in this work.

Electrocoagulation is efficient for the removal of flocculable organic compounds. The remaining organic charge in the effluent after electrochemical treatment is due to compounds with high solubilities, such as sugars present in milk, which are difficult to aggregate. Removal of these compounds is only possible through the use of auxiliary systems based on the employment of membranes or oxidative processes. In this context, aiming for better efficiency of the process a new study was conducted to employ an associated system between electrocoagulation and H_2O_2.

3.2. Electrocoagulation associated with H_2O_2 in the treatment of dairy effluents.

In this stage, the effect of the combined use of electrocoagulation and H_2O_2 on process efficiency was investigated. Two distinct tests were conducted to evaluate the effect of H_2O_2: (i) one with the addition of H_2O_2 at the beginning of the process, before the effluent was submitted to electrochemical treatment (electrocoagulation); and another (ii) with the addition of H_2O_2 during the process. The effluent was treated by electrocoagulation, treated with H_2O_2 and subjected to a new electrocoagulation process.

3.2.1. H_2O_2 added to synthetic crude effluent.

The results of the evolution of the removal efficiency of color, COD and N_{total} (%) of the synthetic effluent as a function of the operating time for the electrochemical process applied to the H_2O_2 are shown in Figure 2. For comparative purposes, the results of the electrochemical treatment of the effluent without peroxide addition are also presented.

Regardless of the response, both systems (in the absence and presence of peroxide) showed the same trend. An increased removal over time up to approximately 10min was observed, remaining stable over this time. Among the responses, the largest differences in terms of removal between the two systems (approximately 15%) were observed for COD and N_{total}, especially at the beginning of the process (up to 15 reaction min).

The color response showed no difference in terms of removal between the two systems. Two factors may have contributed to these results. The first one is the rapidity of its manifestation, with 5min presenting 100% removal, which makes it difficult to observe any trend in this process whose points were collected every 5min. On the other hand, the second factor is that color is a property linked to molecular structure, and it is sufficient

to break a bond for its removal. Indeed, the molecular resonance is easily obtained by both electrochemical and oxidative processes.
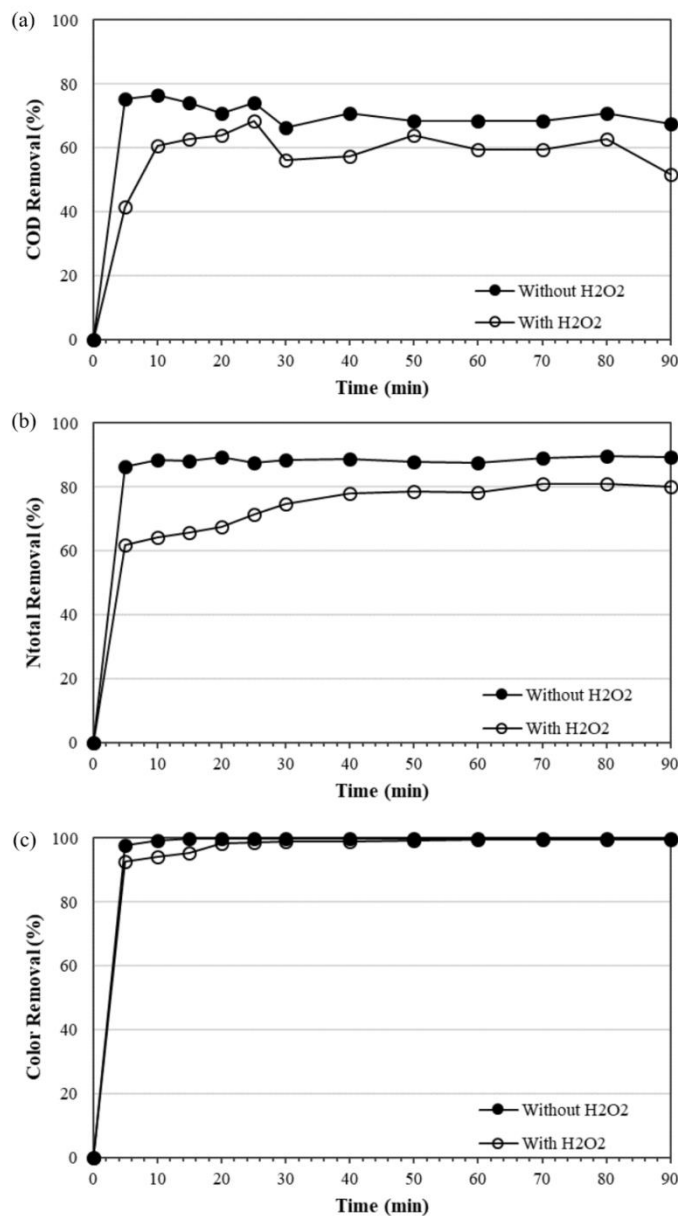

Figure 2. Evolution of COD, Ntotal and Color removal from raw synthetic effluent, in the absence and presence of H_2O_2 (33 mL.L^{-1}), submitted to electrochemical treatment. Conditions: 10V, DE = 2cm, HRT = 30min, pH 7 and conductivity of 2000µs.

In general, unlike expected, the system employing H_2O_2 had a lower removal performance than the system conducted in the absence of peroxide, indicating a negative effect of peroxide on the efficiency of the electrochemical process when added to the effluent at the beginning of the process. This trend was linked to structural changes in the organic compounds present in the effluent, induced by the oxidative process of peroxide, thus generating carbonyl groups and aldehydes. Oxidation is a process of destructive characteristics, provided by the incorporation of oxygen in the molecules, with the ultimate purpose of mineralizing them.

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However, the amount of oxidizing agent/peroxide was restricted or the organic load to be mineralized was high, as observed in the synthetic effluent. The oxidative process, instead of leading to mineralization, tends to generate highly oxygenated byproducts, such as alcohols, ketones, aldehydes, and carboxylic acids, usually of smaller organic chains, with high polarity.

We observed that the effluent electrochemically treated in the presence of H_2O_2 presented a positive response for aldehyde groups. The result suggests the incorporation of oxygenated functional groups in its structure, indicating that they are increasing their polarity. This increase in polarity favors the increase of solubility of the components in the aqueous effluent and, consequently, the increase in the efficiency of the electrochemical process, whose principle of action is based on coagulation. The other conditions tested showed a negative result for carbonyl groups and aldehydes.

3.2.2. H_2O_2 added to effluent previously treated by electrocoagulation.

An effluent previously treated by electrocoagulation was used, with the flocculable organic charge removed. H_2O_2 was added to the effluent at a concentration of 33 ml.L^{-1}. After a homogenization step, the effluent was subjected to a new electrochemical treatment, which aimed at the oxidative degradation of the soluble organic fraction. At the same time, for comparative purposes, an electrochemical test was conducted with the effluent without the presence of H_2O_2. This study aimed to evaluate a possible contribution of electrocoagulation in the electrooxidative assay.

The results of color removal, turbidity, COD, TOC and N_{total} for both samples, with and without H_2O_2 after these new electrochemical treatments, are presented in Table 2.

Table 2. Color, turbidity, COD, TOC and Ntotal removal for the synthetic effluent: (a) treated by electrocoagulation (2 times); and (b) treated by the electrocoagulation/electrooxidation system with the addition of H_2O_2 (33 mL.L^{-1}). Conditions: 10V, DE = 2cm, HRT = 30min, pH 7 and conductivity of 2000µs.

Time (min)	Without hydrogen peroxide (H_2O_2)									
	Color removal		Turbidity removal		COD removal		TOC removal		N_{total} removal	
	Ptmg.L^{-1*}	%	NTU**	%	mg.L^{-1}	%	mg.L^{-1}	%	mg.L^{-1}	%
ES	6,875	-	900	-	5,563	-	910.3	-	79.0	-
0	617	91.0	62	93.1	3,298	40.7	346.3	62.0	9.9	87.4
5	33	99.5	12	98.7	2,320	58.3	252.3	72.3	7.4	90.6
10	33	99.5	12	98.7	2,205	60.4	265.0	70.9	6.8	91.4
15	30	99.6	11	98.8	2,084	62.5	269.5	70.4	7.2	90.9
20	31	99.5	11	98.8	2,010	63.9	299.8	67.1	6.4	91.9
25	29	99.6	11	98.8	2,305	58.6	293.5	67.8	6.1	92.3
30	25	99.6	9	99.0	2,568	53.8	274.5	69.8	5.6	93.0
40	25	99.6	8	99.1	2,475	55.5	275.3	69.8	5.7	92.8
50	24	99.6	7	99.2	2,005	64.0	277.8	69.5	6.2	92.2
60	24	99.6	7	99.2	2,359	57.6	297.3	67.3	6.7	91.6
70	24	99.6	7	99.2	2,362	57.5	298.3	67.2	4.9	93.9
80	23	99.7	3	99.7	2,095	62.3	296.8	67.4	6.4	91.9
90	23	99.7	3	99.7	2,078	62.6	290.8	68.1	5.9	92.5
With hydrogen peroxide (H_2O_2)										
ES	6,875	-	900	-	5,563	-	910.3	-	79.0	-
0	505	92.6	200	77.8	3,250	41.6	301.0	66.9	29.9	61.7
5	27	99.6	5	99.4	188	96.6	178	80.4	3.7	95.3
10	27	99.6	5	99.4	188	96.6	190.8	79.0	3.6	95.5
15	25	99.6	4	99.6	375	93.3	176.3	80.6	3.7	95.3
20	22	99.7	4	99.6	438	92.1	192.0	78.9	3.5	95.5
25	20	99.7	3	99.7	563	89.9	197.8	78.3	3.5	95.6
30	17	99.8	3	99.7	438	92.1	176.8	80.6	3.7	95.3
40	16	99.8	2	99.8	313	94.4	182.5	80.0	3.8	95.2
50	14	99.8	2	99.8	438	92.1	160.5	82.4	3.8	95.2
60	12	99.8	2	99.8	313	94.4	166.3	81.7	3.9	95.0
70	12	99.8	3	99.7	313	94.4	151.8	83.3	3.8	95.3
80	10	99.9	1	99.9	375	93.3	136.3	85.0	3.5	95.5
90	8	99.9	1	99.9	313	94.4	123.0	86.5	3.2	96.0

* milligram of platinum per liter. ** Nephelometric Turbidity Units.

The removal results for all responses indicate that the electrocoagulation itself (parallel run test) with very low removals contributes little to the efficiency of the oxidative process (electro-Fenton) in previously chemically treated effluents (coagulation). This trend was expected by the characteristics of the effluent. Once having already been subjected to chemical coagulation, theoretically, it did not present in its composition flocculable organic matter, a necessary condition for the electrocoagulation to manifest itself effectively. Concerning the sample submitted to the electro-Fenton (oxidative) process, provided by the incorporation of H_2O_2, there was an improvement in the removal efficiency for all evaluated responses, especially the removal of COD and TOC. This is because electrocoagulation is efficient in the removal of suspended and colloidal organic substances whereas electrooxidation is mostly for the breakdown of dissolved organic substances [9].

The best performance observed for the COD and TOC responses was linked to two factors: (i) a lower efficiency presented

by the electrocoagulation for these responses, with removals of approximately 60% for the COD and 70% for the TOC, if compared to the other responses (Color, Turbidity and N_{total}) that had removals $\geq$ 90%; and (ii) higher starting values observed for COD (approximately 2500 mg.L^{-1}) and TOC (approximately 250 mg.L^{-1}) if compared to the other parameters (color of approximately 30 mgPt.L^{-1}; turbidity of approximately 10 NTU; and N_{Total} of approximately 7.0 mg.L^{-1}). Both properties enabled greater removals, making it easier to see the improvement in process efficiency, as seen for COD in Figure 3a. This may be due oxidation of the organic pollutants which occurs on the anodes by active oxygen, like hydroxyl radicals (•OH), with the direct oxidation route [40]. The favorable effect of H_2O_2 addition on reaction kinetics is generally associated with the generation of a higher % OH quantity [41].

The oxidative process provided a significant reduction in COD from approximately 3000 mg.L^{-1} to less than 500 mg.L^{-1} in 10 reaction min remaining stable between 300 and 500 mg.L^{-1} throughout the essay.

The observed decrease in TOC and COD values were linked to oxidation/mineralization of soluble charge. The manifestation of the oxidative process can be evidenced by the positive results for the carbonyl (C = O) and aldehyde (CHO) group identification tests observed for the H_2O_2 treated. These results were negative for the sample submitted only to electrocoagulation.

This tendency to partial oxidation of organic compounds present in the effluent with the generation of new more oxygenated compounds, provided by the electrooxidation step, has also been reported elsewhere. Davarnejad and Nikseresht [36] observed a 93.93% COD removal and 97.32% color removal through the electro-Fenton process in dairy wastewater treatment.

Sandhwar and Prasad [32] evaluated the removal of terephthalic acid present in a synthetic aqueous solution using electrocoagulation and electro-Fenton, achieving a COD removal of 79.56%, and 89.68%, respectively.

3.3. Application of electrooxidative process in the treatment of real effluent.

Based on the results obtained above, the electrooxidative treatment with the addition of H_2O_2 to the real effluent was applied using a continuous flow. The tests were conducted at a flow rate of 230 mL.min^{-1} with a H_2O_2 concentration of 33 mL.L^{-1}. The conditions used for this treatment were 10V, DE = 2cm and TRH = 30min, pH 7 and conductivity of 2000µs. The cell had a total usable volume capacity of 2 L. The color, turbidity and COD results obtained for these tests as a result of reaction time are presented in Table 3.
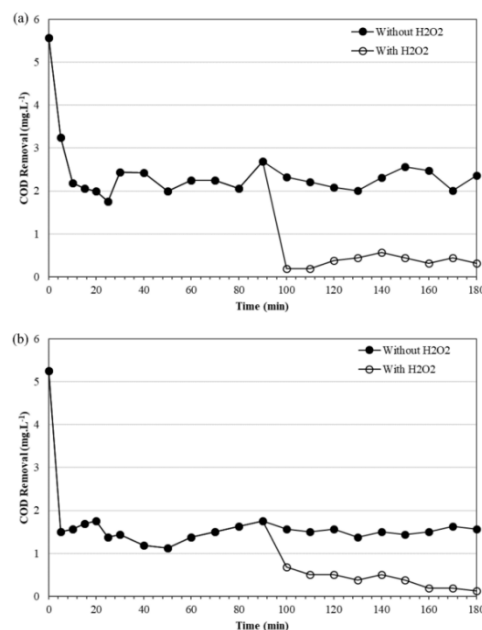

Figure 3. Evolution of COD removal from the (a) synthetic effluent and (b) real effluent treated by electrocoagulation (2 times) and by the electrocoagulation/electrooxidation system with the addition of H_2O_2 (33 mL.L^{-1}). Conditions: 10V, DE = 2cm, HRT = 30min, pH 7 and conductivity of 2000µs.

Table 3. Color, turbidity and COD removal for the real effluent treated by electrocoagulation (2 times) and by the electrocoagulation/electrooxidation system with the addition of H_2O_2 (33 mL.L^{-1}). Conditions: 10V, DE = 2cm, HRT = 30min, pH 7 and conductivity of 2000µs.

Time (min)	Electrocoagulation without hydrogen peroxide (H_2O_2)						Electrooxidation with hydrogen peroxide (H_2O_2)					
	Color removal		Turbidity removal		COD removal		Color removal		Turbidity removal		COD removal	
	Ptmg.L^{-1}*	%	NTU**	%	mg.L^{-1}	%	Ptmg.L^{-1}*	%	NTU**	%	mg.L^{-1}	%
EB	925	-	200	-	5,250	-	925	-	200	-	5,250	-
0	296	70.9	48	76.0	2,354	55.2	226	75.6	84	58.0	2,144	59.2
5	33	96.4	10	95.0	1,563	70.2	24	97.4	1	99.5	688	86.9
10	27	97.1	10	95.0	1,500	71.4	20	97.8	0	100	500	90.5
15	40	95.7	8	96.0	1,563	70.2	26	97.2	0	100	500	90.5
20	52	94.4	5	97.5	1,375	73.8	15	98.4	0	100	375	92.9
25	45	95.1	3	98.5	1,500	71.4	13	98.6	0	100	500	90.5
30	51	94.5	2	99.0	1,438	72.6	17	98.2	0	100	375	92.9
40	39	95.8	2	99.0	1,500	71.4	15	98.4	0	100	188	96.4
50	38	95.9	2	99.0	1,625	69.0	14	98.5	0	100	188	96.4
60	36	96.1	1	99.5	1,563	70.2	15	98.4	0	100	125	97.6
70	33	96.4	1	99.5	1,500	71.4	13	98.6	0	100	122	97.7
80	37	96.0	1	99.5	1,525	71.0	12	98.7	0	100	123	97.7
90	32	96.5	1	99.5	1,650	68.6	14	98.5	0	100	124	97.6

* milligram of platinum per liter. ** Nephelometric Turbidity Units.

The real effluent presented similar behavior to the synthetic effluent. For electrocoagulation, a high efficiency (> 95%) for the removal of color and turbidity and a reasonable removal for

the COD (approximately 70%) was obtained. With the consortium application of the electrooxidative system, COD removal increased

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from 70% to 97% after 50 reaction min (Figure 3b), indicating a significant improvement in process efficiency.

The use of H_2O_2 (electrooxidation) for synthetic effluent treatment was more effective in removing COD when compared to the effluent treated using the only electrocoagulation. Electrooxidation provides removal of soluble and non-flocculable organic charge, which is not removed by electrocoagulation. The

load is linked to the presence of sugars such as lactose. With the consortium use of electrocoagulation/electrooxidation, the results obtained, mainly for COD, comply with the current environmental legislation in Rio Grande do Sul state (FEPAM - *Fundação Estadual de Proteção Ambiental Henrique Luiz Roessler*), which stipulates a COD of 300 mg L^{-1} for effluent disposal.

4. CONCLUSIONS

Electrocoagulation in continuous mode increased the efficiency of color, TOC, N_{total}, and COD removal as a function of reaction time under all conditions evaluated in this work. The addition of H_2O_2, for the best performance of H_2O_2, should be done after a flocculable organic matter removal step. If added to the raw effluent, the oxidative process makes the flocculable organic matter aggregation difficult and causes less efficiency than the

electrocoagulation itself due to the partial oxidation of the pollutants, making them more polar and more soluble in water. In summary, the current work demonstrated the technical versatility of the treatment of dairy effluents (real and synthetic). The results represent a solution to water treatment within the sustainability concept, besides complying with current environmental legislation.

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