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The efficiency of electrocoagulation using aluminum electrodes in treating wastewater from a dairy industry

Eficiência da eletrocoagulação no tratamento de efluente de uma indústria de laticínios usando eletrodos de alumínio

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ABSTRACT

This research deals with the investigation of electrocoagulation (EC) treatment of wastewater from a dairy plant using aluminum electrodes. Electrolysis time, pH, current density and distance between electrodes were considered to assess the removal efficiency of chemical oxygen demand (COD), total solids (TS) and their fractions and turbidity. Samples were collected from the effluent of a dairy plant using a sampling methodology proportional to the flow. The treatments were applied according to design factorial of half fraction with two levels of treatments and 3 repetitions at the central point. The optimization of parameters for treating dairy industry effluent by electrocoagulation using aluminum electrodes showed that electric current application for 21 minutes, an initial sample pH near 5.0 and a current density of 61.6A m^{-2} resulted in a significant reduction in COD by 57%; removal of turbidity by 99%, removal of total suspended solids by 92% and volatile suspended solids by 97%; and a final treated effluent pH of approximately 10. Optimum operating condition was used for cost calculations show that operating cost is approximately 3.48R$ m^{-3}.

Key words: *electrolysis, dairy industry, electrocoagulation.*

RESUMO

Eletrodos de alumínio foram usados para o tratamento de efluente de uma indústria de laticínios por eletrocoagulação. Tempo de eletrólise, pH, densidade de corrente elétrica e distância entre eletrodos foram os parâmetros operacionais usados para avaliar a eficiência de remoção da demanda química de oxigênio (DQO), sólidos totais (ST) e suas frações e turbidez. Amostras foram coletadas usando a metodologia de amostragem composta, proporcional à vazão. Os tratamentos foram aplicados segundo um delineamento fatorial de meia fração com dois níveis e 3 repetições no ponto central. As melhores condições operacionais foram tempo de eletrólise de 21 minutos, pH inicial de aproximadamente 5,0 e densidade de corrente elétrica de 61,6A m^{-2}, resultando em redução de 57% de DQO, remoção de turbidez de 99%, remoção de sólidos suspensos totais de 92% e sólidos suspensos voláteis de 97%. O pH do efluente tratado foi de aproximadamente 10. Para a condição otimizada, o custo operacional foi de aproximadamente 3, 48 R$ m^{-3}.

Palavras-chave: *eletrólise, indústria de laticínios, eletrocoagulação.*

INTRODUCTION

Water use in food processing generates large amounts of wastewater, which need to be treated before its release in receiving water bodies. Among the food industries, the contribution of dairy pollution of water bodies is very significant, since the processing of milk causes considerable pollution load, due to the presence of large amounts of organic matter in wastewater (MATOS et al., 2010).

Among chemical methods, electrochemical (EC) treatment is one of the advanced processes which offer high removal efficiencies in compact reactors with simple equipments for control and operation of the process (GUVEN et al., 2009). Electrocoagulation is the process of destabilizing suspended, emulsified, or dissolved contaminants in an aqueous medium by introducing an electric current into the medium (MOLLAH et al., 2004).

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This process involves applying an electric current to sacrificial electrodes inside a reactor tank where the current generates a coagulating agent and gas bubbles. In addition, electrocoagulation is a technique involving the electrolytic addition of coagulating metal ions directly from sacrificial electrodes. The metal ions form complexes with hydroxyl ions. The complexes formed depend on the pH of the medium. In the case of aluminum, there is a multitude of anionic and cationic complexes (EMAMJOMEH & SIVAKUMAR, 2009).These ions coagulate with pollutants in the water, similar to the addition of coagulating chemicals such as alum and ferric chloride, and allow easier removal of the pollutants by sedimentation and flotation (EMAMJOMEH & SIVAKUMAR, 2009).

Few studies have been carried out about the application of EC in wastewater treatment produced by real dairy wastewater. SENGIL & OZACAR (2006) used iron electrode and reported significant COD and oil-grease removal, while, TCHAMANGO et al. (2010) used aluminum electrodes for treatment of artificial wastewater and reported COD, nitrogen and turbidity removal efficiencies of 61, 81 and 100%, respectively. KUSHWAHA et al. (2010) also achieved using artificial effluent COD reduction of approximately 70% in optimal conditions, current density of 270 A m^{-2}, electrolysis time of 50min and pH 7.0 and iron the material used for construction of the electrodes. BAZRAFSHAN et al. (2013) using aluminum electrodes and potassium chloride as electrolytes shown that EC was efficient and able to achieve 98.84% COD removal, 97.95% BOD$_5$ removal and 97.75% TSS removal.

The aim of this study was to evaluate the efficiency of the use of aluminum electrodes for the treatment of real dairy effluent by electrocoagulation. The performance of this system was evaluated for its capacity to remove COD, turbidity, total solids and fractions; process parameters included current density, pH, electrolysis time and distance between the electrodes.

MATERIALS AND METHODS

Wastewater from a small milk-processing plant (15,000 liters of milk per day) with rinse waters from different sectors of the plant were pooled in a collection unit that was selected as site of sample collection.

Samples were collected using a sampling methodology proportional to flow. Beginning at 8:00h and ending at 17:00h, corresponding to the total processing time in the plant, samples were collected at 1h intervals. A total volume of 33L of wastewater was collected. The sub-samples were kept refrigerated until the required volume (33L) was collected and analysis began. The pH was measured in each sub-sample to assess changes over the period of operation of the plant. The parameters evaluated in this study were also used to characterize wastewaters. The experiment was performed in triplicate.

The analysis of chemical oxygen demand (COD) was carried out according to the American Public Health Association (APHA, 2005) colorimetric method 5200. Samples were digested in a MARCONI Dry Block MA 4004 heat block. Absorbance readings were performed using a GBC spectrophotometer model UV / VIS 911A at 600nm. The analysis of the levels of solids and their fractions were performed according to the APHA (APHA, 2005) gravimetric method 2540.

The pH measurements were performed following the potentiometric method, using a digital portable DIGIMED DMPH meter, model 2, according to the APHA (2005) method 4500 (H+). Turbidity was measured by the APHA (2005) method 2130; using a TECNOPON turbidimeter, model TB 1000.

The EC tests were performed in batches in a glass reactor (300 x 200 x135mm - l x w x h) with an aluminum electrode, as shown in VALENTE et al. (2012). The electrode was constructed from eight aluminum plates (130 x 200 x 1.5mm), maintaining a ratio between the area of the electrode and the volume of effluent of 27m^2 m^{-3} in each test. Teflon spacers allowed the distance between the plates of the electrodes to be adjusted as the test was conducted. The connection was a parallel-type monopole and applied constant direct current. The temperature of the effluent during the electrocoagulation tests was 20±2°C.

After each test, the polarity of the electrodes was performed and reversed to avoid wearing it out and to prevent the formation of passive films that reduce the efficiency of the system. The sample pH was adjusted to the conditions stipulated in the experimental design, using NaOH (1mol L^{-1}) or H_2SO_4 (0.05mol L^{-1}) as appropriate.

During the application of electric current, the liquid was agitated at 50rpm to ensure contact with the net mass of all of the electrodes. When the current application ceased, the agitation was stopped. After 20min, the time necessary for phase separation by flotation, a sample of the average depth of the reactor was collected for the analysis of the effluent properties (Figure 1).

A statistical design of the type fractional factorial 2IV4-1 with triplicate at the central point was used to evaluate the efficiency of wastewater treatment by electrocoagulation. The process parameters were electrolysis time (5 and 25min), current density (37.0 and 61.6A m^{-2}), pH (5.0 and 9.0) and distance between electrodes (0.6 and 1.4). Statistical analysis of the removal efficiency of the effluent characteristics under study was performed using the software MINITAB 17.0®.

Assay was realized to determinate operation cost in duplicate. The cost has been calculated for electrolysis time of 21 minutes, current density of 61.6A m^{-2}, pH 5.0 and distance of 0.6cm. The cost items included direct cost items such as electricity and material (electrodes and chemical reagents). The electrodes were washed thoroughly with water to remove any solid residues on the surfaces, washed with acetone to remove surface grease, and the impurities on the aluminum electrode surfaces which were removed by dipping for 5min in a HCl solution (35%), dried and weight. At the end of the run, the electrodes were washed again and reweighed to calculate sacrificial electrode consumptions (BAYRAMOGLU et al., 2006).

RESULTS AND DISCUSSION

Wastewater characterization

The decision to use composite sampling proportional to the flow of wastewater was made because of the wide variation in the composition of effluent from the dairy industry. The variation in the average values of physical and chemical characteristics of the dairy effluent studied soon after all of the samples were collected was: pH (1.0-5.4), turbity (267-1000NTU), COD (2060-5249mg L-1), total solids (TS) (1965-3723mg L-1), total volatile solids (TVS) (1560-3434mg L-1), total fixed solids (TFS) (405-592mg L-1), total dissolved solids (TDS) (1521-3083mg L-1), volatile dissolved solids (VDS) (1198-2843mg L-1), fixed dissolved solids (FDS) (240-492mg L-1), total suspended solids (TSS) (444-758mg L-1), volatile suspended solids (VSS) (397-658mg L-1), fixed suspended solids (FSS) (47-100mg L-1) and settleable solids (SS) (0.4-0.5mL L-1). These results are corroborated by previously published data (MATOS et al., 2010).

Figure 1 - Phase separation after treatment by electrocoagulation. The example shown was performed under the conditions of the test at optimized condition.

High concentration of organic matter in the dairy effluent, predominantly in dissolved form was found as expected. This concentration may be higher in plants that have cheese production lines and do not use whey. The unit evaluated did use cheese whey, so this was not discarded with the effluent. It was observed predominantly floating material and some sedimented material after the effluent has been treated by electrocoagulation; immediately after flotation of material, the treated effluent was colorless; figure 2 shows an example. The estimates of the effects represented in the normal probability plot of zero mean and variance to assess which effects were significant (α=0.05) for all treatments are shown in figure 2.

The application time of the electric current and pH adjusted was significant for some fractions of solids, TSS (Figure 2A) and VSS (Figure 2B) and turbidity removal (Figure 2C). The current density applied was significant in the removal of COD (Figure 2D). For the other parameters evaluated, none of the variables were significant. The distance between electrodes is important for cost, but is also important because of hydrogen bubble distribuition in the electroflotation process.

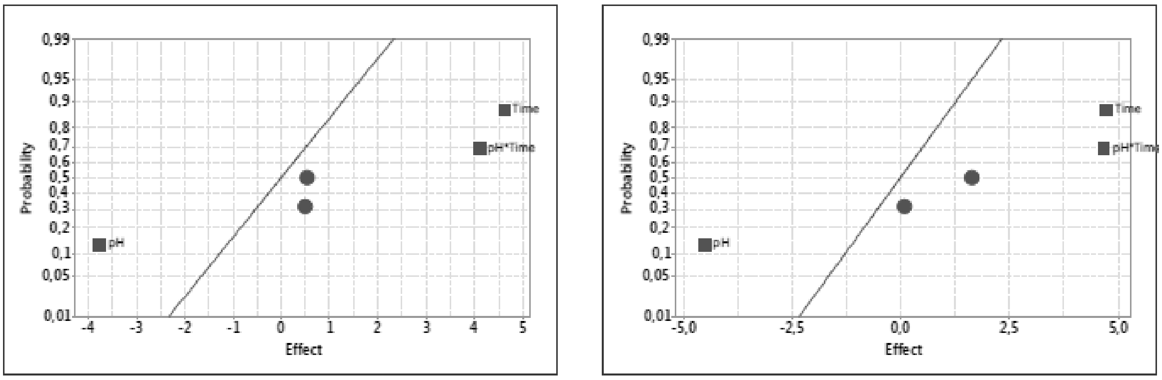
Based on these results, it can express the removal of COD as a function of electrolysis time, pH adjusted and current density. The model adjusted for the removal efficiency of COD is presented in equation 1:

$$Z = 76.8 - 10.6\,pH - 2.17\,t + 0.533\,j + 0.447\,pH\,t \quad (1)$$

Where, Z is the percentage of COD removed, t is time of electric current application, pH is pH adjusted and j is current density. For current density of 61.6A m^{-2} occurred higher removal of COD. It is well-known that current not only determines the coagulant dosage rate but also the bubble production

A. Removal of TSS

B. Removal of VSS



C. Removal of turbity

D. Removal of COD

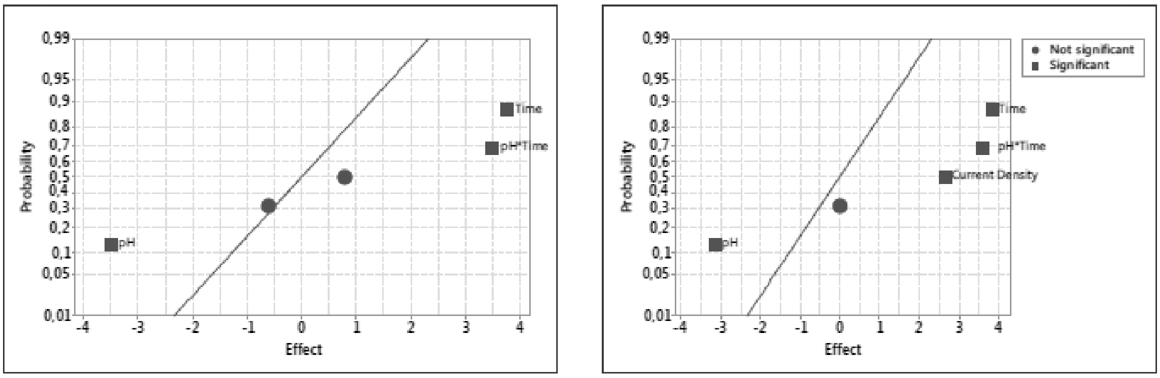


Figure 2 - Estimations of the effects on the removal of TSS, VSS, turbidity and COD, represented in the normal probability plot (α=0.05) of zero mean and variance.

rate and size and the flocs growth. The removal of COD, turbidity, TSS and VSS as a function of time and pH adjusted (Figure 3). All controlled parameters showed the same trend (Figures 3A, 3B, 3C and 3D), the treatment efficiency was higher for pH~5.0 and electrolysis time of 25 minutes. EC can be considered as an accelerated corrosion process. The rate of reaction will depend on the removal of [H+] via H2 evolution. This reaction will occur fast for low pH values (MORENO-CASILLAS et al., 2007). In addition it was demonstrated that too high pH will increase Al(OH)3 solubility and lead to the formation of soluble AlO2 (ADHOUM & MONSER, 2004). Figure 4 shows contours of removal (%) of TSS, VSS, turbidity, and COD as a function of time (min) and adjusted pH.

An analysis of this response on figure 3E and experiments data made possible to determinate the location of the region optimized. For pH near 5.0 and electrolysis time upper 21 minutes made possible to remove approximately 57% of COD, 99% of turbity, 97% of VSS and 92.5% of TSS.

The models adjusted for the removal efficiency of turbidity, TSS and SSV as a function of time and pH adjusted are presented below in equations 2, 3 and 4:

$$W = 18.6.1 - 19.61\ pH - 3.85\ t + 0.811\ pH\ t \quad (2)$$

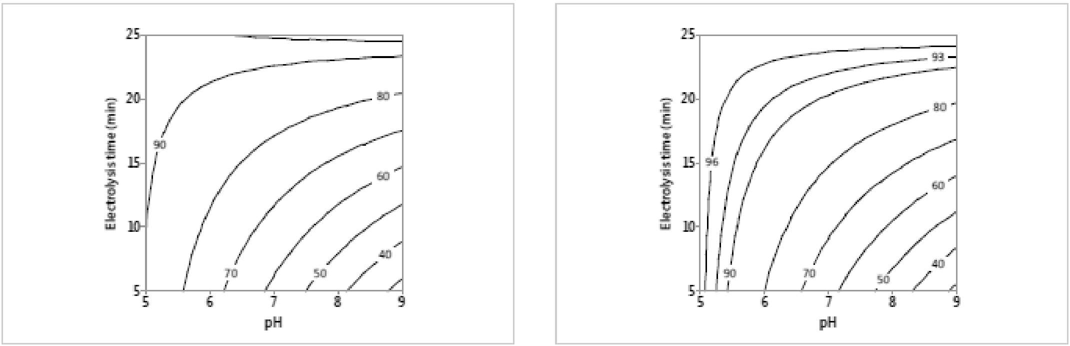
$$Y = 205.6 - 21.68\ pH - 4.38\ t + 0.881\ pH\ t \quad (3)$$

$$U = 187.9 - 17.56\ pH - 3.41\ t + 0.703\ pH\ t \quad (4)$$

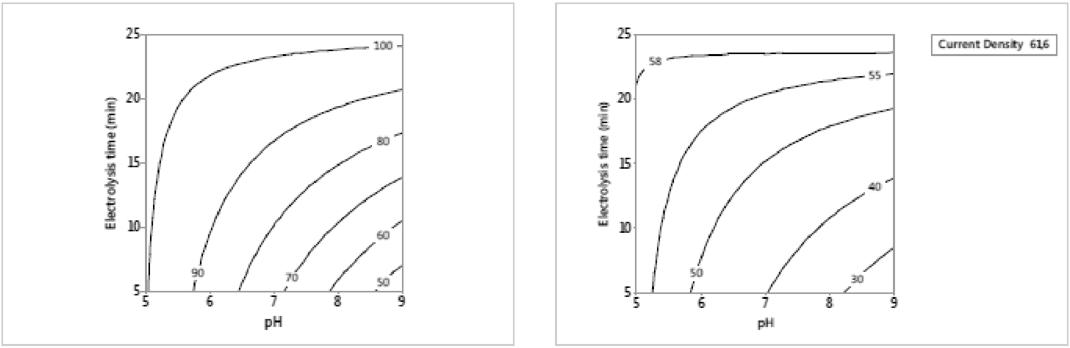
Where, W is the percentage of TSS removed, Y is the percentage of VSS removed, U is the percentage of turbity removed, t is time of electric current application and pH is pH adjusted.

In figure 4, shows a comparison between the experimental and calculated values using the equations 1, 2, 3 and 4. The data show

A. Removal of TSS B. B. Removal of VSS



C. Removal of turbity D. Removal of COD



E.

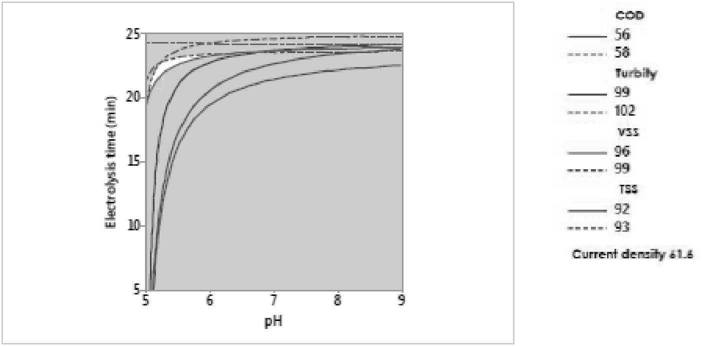


Figure 3 - Percentage removal of TSS, VSS, turbidity, and COD as a function of time (min) and pH adjusted.

that, compared to the experimental results, the equations accurately predicted the treatment efficiency.

The effect on the final pH of the treated effluent as a function of time of electric current application and the adjusted pH of the sample. A final pH of approximately 10 results from an electrolysis time upper 21min and a sample with an initial pH near 5.0 (Equation 5). Model adjusted for final pH of effluent as a function of time and initial pH is shown below.

$$V = -2.02 + 1.42\ pH + 0.473\ t - 0.051\ pH\ t \qquad (5)$$

Where V is the final pH, pH is the adjusted pH and t is the electrolysis time.

The rise in the pH of the effluent was also observed by MORENO-CASILLAS et al. (2007). The distance between electrodes was not a significant

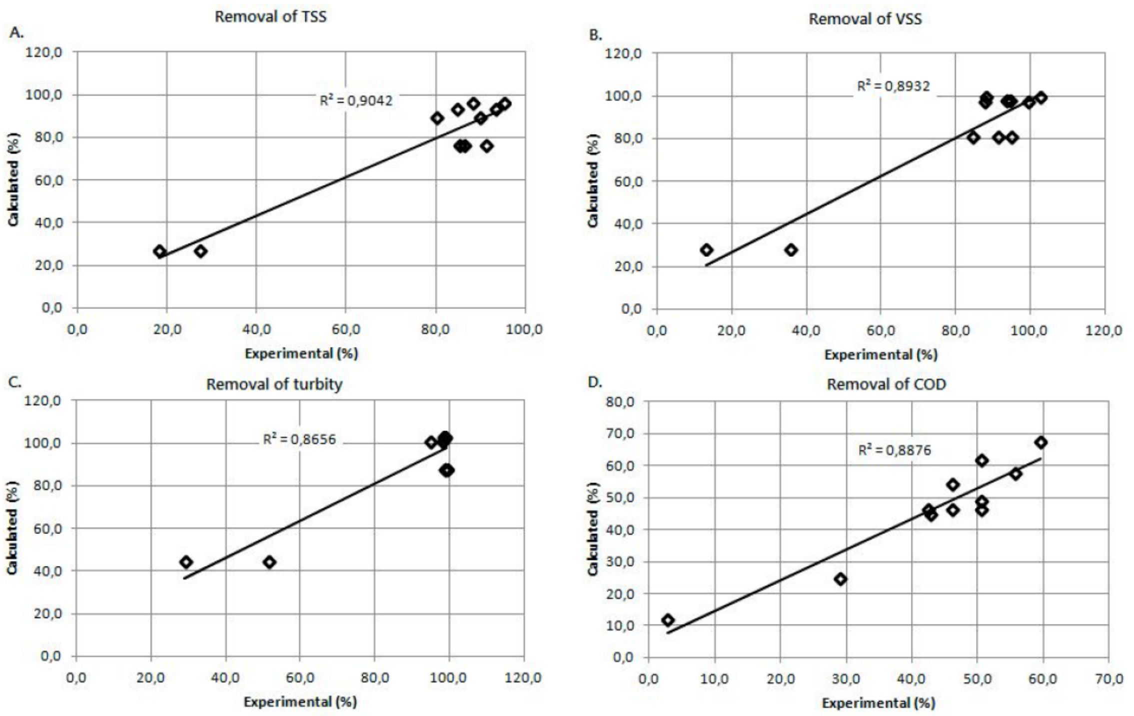


Figure 4 - Comparison between experimental and calculated values.

factor for organic matter removal under the tested conditions. Electrode distance is an important parameter in the operational cost of the treatment plant because reducing the distance between the electrodes reduces the energy required to run the EC reactor and therefore lowers the cost of operation.

The dissolved solids fraction was the most negatively affected fraction using the electrocoagulation process. It is observed reduction of 23.6% in the concentration of TDS, 27.10% and 7.71% in the concentration of SDV and FDS, respectively. The EC showed low removal efficiency of TS, VTS, FTS and FSS, on average 35.1; 39.3; 14.5 and 47.6% respectively.

COD reduction was found to be significantly lower than previously reported by Tchamango et al. (2010) and KUSHWAHA et al. (2010) that used artificial wastewater l. It was obtained a removal efficiency of 57% of COD in this study, in contrast to the high value, 98%, obtained by SENGIL & OZACAR (2006) where the suspended solid content in effluent was high. In the study presented here, the effluent had a high concentration of dissolved solids, representing 80% of total solids. The removal efficiency is related to the predominant type of solid fraction as cited by MORENO-CASILLAS et al. (2007) and VALENTE et al. (2014). In the case presented here, the predominant fraction of dissolved solids in the effluent of the dairy plant (approximately 80% of total solids) was not efficiently removed, while the TSS removal was favored.

Values of the operating cost are calculated based on economic data, electricity (0.33R\$ kW^{-1} h^{-1}), aluminum electrode (5.40R\$ kg^{-1}), H_2SO_4 (23.00R\$ kg^{-1}) and NaOH (R\$ kg^{-1} 30.00). Optimum operating conditions were used for cost calculations show that operating cost is approximately 3.48R\$ m^{-3}. The electricity cost and electrode consumptions corresponding to 69 and 30% of operating cost, respectively.

CONCLUSIONS

According to the obtained results, the following can be concluded: The optimization of parameters for the treatment of dairy industry effluents, using aluminum electrodes in the process of electrocoagulation, showed that an electric current applied for 21 minutes, with a sample with an initial pH close to 5.0 and a current density of 61.6A m-2 showed a significant reduction in COD by 57%; removal of turbidity, total suspended solids and volatile suspended solids by 99, 92.5, 97%, respectively. The final pH of treated effluent was approximately 10. Optimum operating conditions were used for cost calculations that show operating cost of approximately 3.48R$ m-3. Dairy wastewaters are generally treated usually using biological methods such as activated sludge process, aerated lagoons, aerobic bioreactor. Aerobic biological processes are high energy intensive, whereas anaerobic treatment of dairy wastewater reflects very poor nutrient removal, and effluents treated by anaerobic biological processes need additional treatment. This study shows that electrocoagulation treatment would be used with biological process. Electrocoagulation treatment for removal of TSS and biological treatment for removal TDS.

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