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Optimization and kinetic modeling of electrocoagulation treatment of dairy wastewater

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ABSTRACT

The main objective of this work was the treatment of dairy wastewater by electrocoagulation using aluminum electrodes. Effects of operating parameters, such as, electrolysis time (0–60 min), initial pH (2–12), current density (2.5–35 mA/cm^2), and electrolyte concentration (NaCl), were evaluated for optimal conditions. The experimental results revealed that the greatest removal efficiencies of the overall turbidity, COD, and BOD5 attained, respectively, 98.91, 74.56, and 96.28% at the optimum conditions (operating time of 30 min, initial pH of 7, current density of 14 mA/cm^2, and electrolyte concentration of 1 g/L). For these optimal parameter values, the energy consumption was about 3.36 kWh/m^3. Adsorption kinetic showed that the adsorption followed a pseudo-first-order reaction.

Keywords: Dairy wastewater; Treatment; Electrocoagulation; Turbidity; COD; BOD5; Kinetics adsorption

1. Introduction

The dairy industry handles various types of milks and generates a large amount of wastewaters [1]. These effluents are characterized by high chemical oxygen demand (COD), biological oxygen demand (BOD5), fat nutriments, and high load of suspended solids [2]. Therefore, the treatment of dairy wastewater is very important not only for the environment but also for the purpose of recycling water for reuse in industrial processes [3].

Dairy wastewaters are generally treated using biological and physicochemical methods [4,5]. However, the biological treatment is limited because the high energy requirement [6] and in certain cases a further treatment is needed. Among physicochemical treatment, coagulation and flocculation are used for the treatment of effluents [7,8], but their disadvantages are the cost of added reagents and low removal of organic matter. As a consequence, they created a secondary pollution that can contaminate the treated water [9]. Therefore, other treatment technologies have been explored with the intention of finding suitable techniques. These technologies include membrane separation [10,11], adsorption [12], and reverse osmosis [13].

A review of literature indicated a certain number of studies that show the success of the electrochemical methods in the treatment of dairy effluents [14,15].

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Also, there are few studies in the literature utilizing electrocoagulation (EC) treatment successfully for dairy wastewaters. In the recent years, Sengil and Ozacar [16] studied the EC treatment with iron electrode whereas Tchamango et al. [17] used aluminum electrodes for the same process. Recently, Valente et al. [18] reported the results obtained in the treatment of wastewater from a dairy plant by EC using iron electrodes. They found that for optimal conditions the reduction in COD is not very important. However, their results showed that the removal of turbidity, suspended solids, and volatile suspended solids is very high.

EC is an electrochemical method based on the dissolution of sacrificial anodes and the production of coagulants. Many mechanisms are used in this process in order to separate organic pollutants from the aqueous effluent. Anodic oxidation leads to the production of hydrated aluminum hydroxides in the case of the use of aluminum electrodes. This reaction occurred simultaneously with cathodic one and the evolution of hydrogen gas responsible for flotation. The formed metal hydroxides with a large surface adsorb organic compounds. As a result, the removal of the formed flocs can be realized by the gas bubbles. This electrochemical method presents some advantages compared to conventional methods, such as simple equipment, less-retention time, reduction or absence of adding chemicals, and less sludge production [19].

In this study, the effects of operating parameters, such as electrolysis time, initial pH, current density, and electrolyte concentration using aluminum electrodes were investigated for the treatment of dairy wastewater. To evaluate the performance of the EC process, energy consumption was evaluated. In addition, kinetic models were applied to explain the phenomena of adsorption of organic matter on the metal hydroxide.

2. Materials and methods

2.1. Wastewater source

Wastewater was obtained from a unit of milk production situated in the region of Medea (Algeria). It was collected from the municipal sewer system which receives the global dairy effluent. The characteristics of the dairy wastewater are shown in Table 1.

Table 1
Characterization of dairy wastewater

Parameters	Value
pH	7.11
Conductivity (mS/cm)	1.63
BOD5 (mg O_2/L)	1,400
COD (mg O_2/L)	2,850
COD/BOD5	2.03
Turbidity (NTU)	703

2.2. Experimental apparatus and procedure

The electrochemical apparatus, consisting of a cylindrical vessel provided with two parallel plate aluminum electrodes, was used in a batchwise. Aluminum electrodes (150 × 34 × 1 mm) were immersed in 500 mL of dairy wastewater to a depth of 60 mm and a distance of 10 mm. The electrodes were connected to a power supply (HPS3025). All solutions were magnetically stirred at 500 rpm and carried out at 20–22°C. The electrodes were cleaned with detergent and acetone, and then rinsed with distilled water. After treatment, the collected samples were separated by decantation and then filtered through a filtration system using Whatman filter paper (pore size 11 μm) and then analyzed.

2.3. Analytical procedures

The pH of the treated solution was measured using a pH meter (Metrohm). The temperature and electrical conductivity were measured using a conductivity meter (type Mettler Toledo EL 30). Turbidity was determined using a turbidity meter (model HF Instruments DRT 100B). BOD5 was evaluated by a respirator Oxi Top (WTW, Germany). COD was determined by oxidation in acid medium by an excess of potassium dichromate at a temperature of 150°C of oxidizable under the test conditions in the presence of silver sulfate as catalyst and mercury sulfate.

3. Results and discussion

3.1. Effects of operating parameters on the efficiency of treatment

3.1.1. Effect of current density

The current density is considered as a critical parameter in EC [20]. This is attributed to the fact that a high current density will produce a significant amount of aluminum oxide, resulting in a greater amount of precipitate of colloidal particles to remove. Furthermore, the increase in current density leads to an increase in the density of microbubbles and a decrease in their sizes [21]. As a result, a greater ascending flow and better removal of pollutants and sludge by flotation are obtained.

The influence of current density on treatment of dairy wastewater was studied at natural pH of wastewater, operating time of 15 min, electrolyte concentration of 1 g/L, and current density ranges from 2.5 to 60 mA/cm^2. The effect of this parameter on the removal efficiencies is shown in Fig. 1. It was noticed that for high values of current density, percentage reductions of turbidity, COD, and BOD5 remain constant; this is probably due to the large amount of Al^{3+} ions released by the dissolution of electrodes. As a consequence, the formed molecules ($Al(OH)_3$) are entrained to the surface without the presence of contaminants due to the saturation of the adsorption sites formed by the aluminum hydroxide. According to our experiments, a current density of 14 mA/cm^2 appears to be sufficient for an improved electrolytic treatment.

3.1.2. Effect of initial pH

To examine the effect of initial pH, its value was adjusted to the desired level for each experiment by adding sodium hydroxide or hydrochloric acid aliquots. It was varied between 2 and 12 while the other factors were maintained constant (current density of 14 mA/cm^2, electrolyte concentration of 1 g/L, and electrolysis time of 15 min). The variations of the percentage of removal as a function of pH are shown in Fig. 2. The maximum removal efficiencies were observed at neutral pH (around 7). These results are in agreement with many previous studies related to EC using aluminum electrodes [15]. The removal efficiencies were estimated as follows: 99.23% for turbidity, 71.57% for COD, and 97.14% for BOD5.

When the initial pH tends toward acid or basic values, the removal efficiency decreases; this is ascribed to the amphoteric character of aluminum hydroxide $Al(OH)_3$ that precipitates at pH 6–7 and whose solubility increases when the solution becomes either more acidic or alkaline [22]. Consequently, the flocs of aluminium hydroxide are less reactive and the flocculation is less effective, because the formation of flocs of small size.

3.1.3. Effect of electrolyte concentration

The use of sodium chloride (NaCl) is often favored by the presence of chloride ion which can considerably reduce the adverse effects of other anions and avoid the precipitation of calcium ions contained in the wastewater, and train an insulating layer on the surface of the electrode and then decreases the dissolution of electrode metal or increases the resistance of the electrochemical cell [15]. The effect of supporting electrolyte concentration on the percentage removal of turbidity, COD, and BOD5, by EC was investigated for a current density of 14 mA/cm^2, pH of 7.11, and operating time of 15 min (Fig. 3).

The removal efficiencies of turbidity, COD, and BOD5 increase with the increase in electrolyte concentration in the range of 0–1 g/L. By exceeding the concentration of 1 g/L of NaCl, the removal efficiency of turbidity varies slightly; however, the removals of COD and BOD5 decrease with increasing electrolyte concentration. The minimum values of COD and BOD5 were observed at 2 g/L of NaCl. The effect of NaCl could be explained by the higher rate of dissolution of aluminum electrodes [23]. The experimental results show that the maximal removal efficiencies were observed for NaCl concentration of 1 g/L.

The addition of the electrolyte contributes to the improvement of the removal efficiency by increasing the conductivity of the solution. The presence of NaCl in solution can also generate strong oxidizing agents capable of oxidizing organic molecules present in the

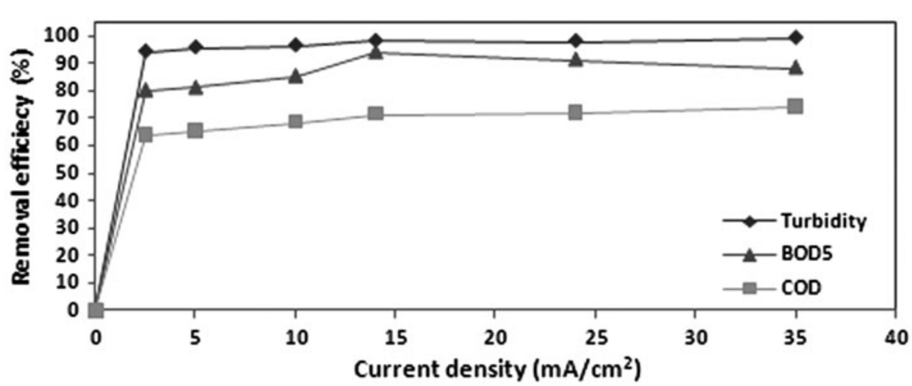

Fig. 1. Effect of current density on the turbidity, COD and BOD5 removal efficiency (operating time = 15 min, C_e = 1 g/l, pH 7.11, T = 20–22˚C).

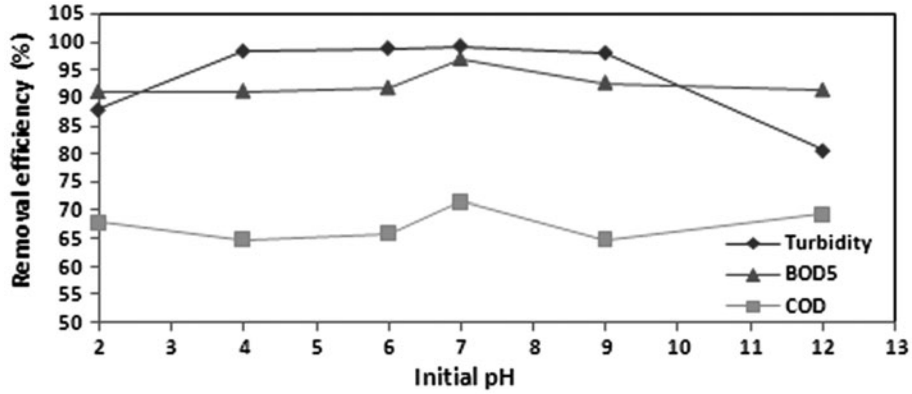

Fig. 2. Effect of initial pH on the turbidity, COD and BOD5 removal efficiency (operating time = 15 min, i = 14 mA/cm^2, C_e = 1 g/l, T = 20–22°C).

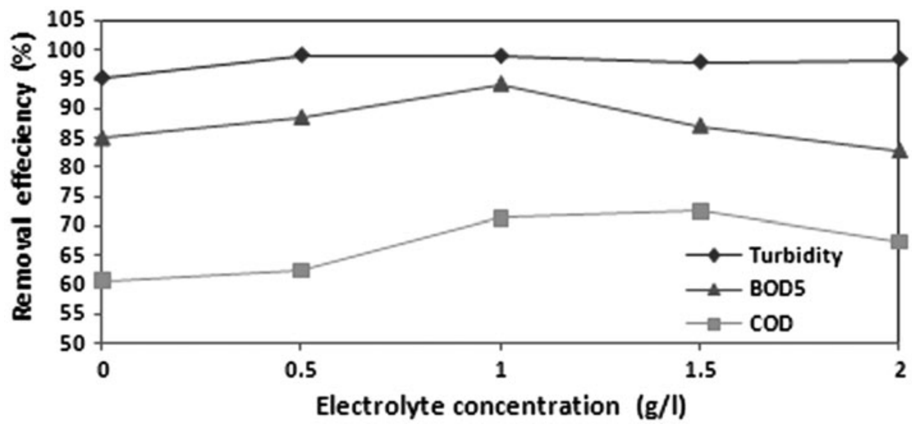

Fig. 3. Effect of electrolyte concentration on the turbidity, COD and BOD5 removal efficiency (i = 14 mA/cm^2, pH 7.11, T = 20–22°C, t_{ec} = 15 min).

wastewater and subsequently contributes to the elimination of pollutants.

3.1.4. Effect of electrolysis time

The operating (electrolysis) time is an important factor in the electrochemical process, according to Faraday's law. The amount of aluminum released is influenced by the processing time and subsequently leads to the increase of Al^{3+} ions released into the treated solution [16]. Effect of operating time on the treatment of dairy wastewater using EC process was studied at an initial pH of 7.11, current density of 14 mA/cm^2, and electrolyte concentration of 1 g/L. Fig. 4 shows the different removal efficiencies of turbidity, COD, and BOD5 as a function of time. It was noted that after 10 min of treatment there was a significant removal efficiency of turbidity, COD, and BOD5. The optimum time of electrolysis was obtained at 30 min leading to maximum removals (98.91% of turbidity, 74.56% of COD, and 96.28% of BOD5). Exceeding the optimal value, the removal efficiencies remain almost constant; this may be due to the saturation of ions released from the electrodes and the formation of new flocs.

3.2. Energy consumption

In addition to aluminum electrodes consumed, major operating cost of EC is associated with the electrical energy consumption during the electrochemical process [24]. The consumed energy E (kWh/m^3) was calculated by the following equation:

$$E = \frac{U \cdot i \cdot t_{ec}}{V} \tag{1}$$

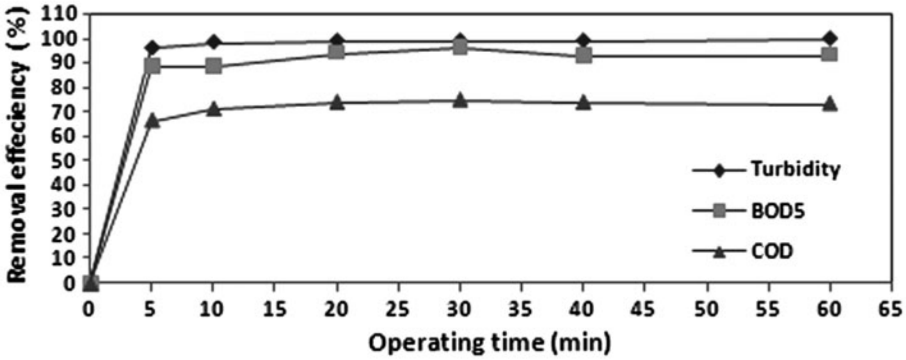

Fig. 4. Effect of operating time on the turbidity, COD and BOD5 removal efficiency ($i = 14\,mA/cm^2$, $C_e = 1\,g/L$, pH 7.11, $T = 20–22$°C).

where U is the cell potential in the reactor, i is the current intensity, t_{ec} is the electrolysis time, and V is the volume of the dairy wastewater.

Fig. 5 shows the variation of the electric energy consumed by meter cube of wastewater as a function of electrolysis time and current density. It was noticed that when the time increases from 5 to 30 min for a current density of $14\,mA/cm^2$, the energy increases from 0.56 to $3.36\,kWh/m^3$, COD increases from 66 to 74.56%, BOD5 from 88 to 96.28%, and turbidity changes slightly. After 30 min of treatment, all the dependent parameters are constant, but the energy consumption increases significantly. We can, therefore, consider that the electrolysis time of 30 min provides the optimum conditions for maximum removals of COD and BOD5.

Thus, the energy consumption increases with the current density and operating time. For example, for an electrolysis time of 10 min, the system can consume 0.06, 0.2, 0.55, 1.12, 2.97, and $6.3\,kWh/m^3$ when the current density is 2.5, 5, 10, 14, 24, and $35\,mA/cm^2$, respectively. We can conclude that the optimum current density of $14\,mA/cm^2$ leads to an optimal value of the energy consumed by the system with the best removal efficiencies of COD (74.56%) and BOD5 (96%). The value of the energy consumption for the optimal conditions (electrolysis time of 30 min and current density of $14\,mA/cm^2$) is about $3.36\,kWh/m^3$.

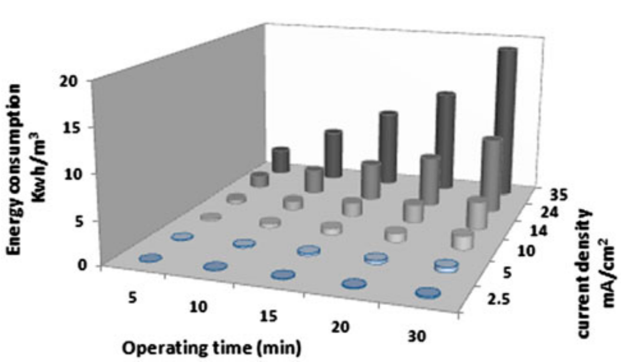

Fig. 5. Variation of the energy consumption with electrolysis time and current density.

3.3. Kinetics studies

EC is the result of adsorption of the pollutant on the solid formed after prior electrochemical dissolution of the aluminum electrodes. The phenomenon which leads to the EC separation is extremely complex. Generally, two steps occur in this process: capture of the microparticles by the hydrogen bubbles, then an agglomeration on the free surface to create easily separable flocs. The removal of pollutant is similar to conventional adsorption except the generation of flocs [25]. The electrode consumption and amount of generated flocs can be estimated according to Faraday's Law [25]. Since the amount of coagulant can be estimated for a given time and, the pollutant removal can be modeled using the adsorption kinetics. In order to investigate the kinetic mechanisms which control the EC process in the treatment of dairy wastewater, the pseudo-first-order [26] and pseudo-second-order [27] models were tested and their validities were verified by linear equation analysis.

The pseudo-first-order equation is expressed as follows:

$$\frac{dq}{dt} = K_1(q_e - q_t) \quad (2)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t and k_1 is the rate constant of pseudo-first-order adsorption.

After integration and applying boundary conditions ($t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$), the integrated form of Eq. (2) becomes:

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - K_1 \frac{t}{2.303} \quad (3)$$

The pseudo-second-order adsorption kinetic rate equation as expressed by Ho et al. [27] is given by:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = K_2 (q_e - q_t)^2 \quad (4)$$

where K_2 is the rate constant of pseudo-second-order adsorption.

From the boundary conditions ($t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$), the integrated form of Eq. (4) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K \cdot t \quad (5)$$

This is the integrated rate law for a pseudo-second-order reaction. Eq. (5) can be rearranged to obtain Eq. (6), which has a linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e} t \quad (6)$$

The kinetic data were fitted to the pseudo-first-order model (Eq. (3)). The plot of log ($q_e - q_t$) versus t for the COD on aluminum hydroxide is shown in Fig. 6, where K_1 and q_e are determined from the slope and intercept respectively.

The plot was found to be linear with a good correlation coefficient ($R^2 = 0.97$). The theoretical q_e (cal) value agree well to the experimental q_e (exp) value that imply that the pseudo-first-order kinetic model can describe the adsorption of COD onto aluminum hydroxide with good agreement between experimental and theoretical data. Different educational parameters were collected in Table 2.

The pseudo-second-order model is represented by Eq. (6). The plot of log t/q_t vs. t for the COD on aluminum hydroxide is shown in Fig. 7, where K_2 and q_e can be determined by slope and intercept, respectively.

The predictive linear regression equations and R^2 values for the pseudo-second-order equation are given also in Table 2. The results show that the theoretical q_e (cal) value does not agree to the experimental q_e (exp) value with a diminution of correlation coefficient comparing with the pseudo-first-order model ($R^2 = 0.95$). Thus, it can be concluded that the pseudo-first-order kinetic model describes better the adsorption of COD on aluminum hydroxide with better fit of experimental data than the pseudo-second order.

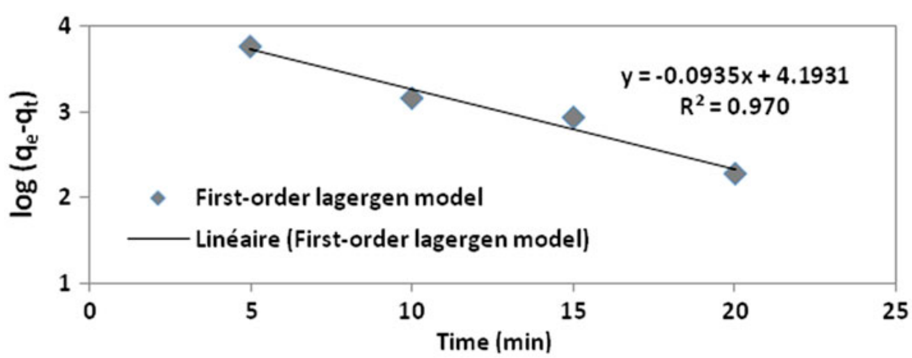

Fig. 6. First-order kinetic model plot for adsorption of COD on aluminum hydroxide.

Table 2
Calculated kinetic parameters and correlation coefficient for pseudo-first order and pseudo-second order for adsorption of COD on aluminum hydroxide

Pseudo-first order				Pseudo-second order			
K (min^{-1})	q_e (cal) (mg g^{-1})	q_e (exp) (mg g^{-1})	R^2	K (min^{-1})	q_e (cal) (mg g^{-1})	q_e (exp) (mg g^{-1})	R^2
0.215	15,599	15,820	0.97	-1.42×10^{-4}	1,000	15,820	0.95

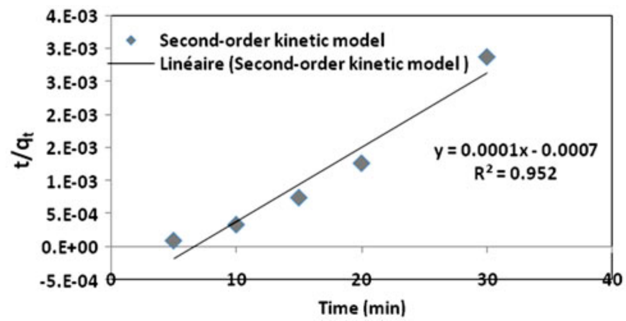

Fig. 7. Second-order kinetic model plot for adsorption of COD on aluminum hydroxide.

4. Conclusion

The treatment of dairy wastewater by EC in presence of soluble aluminum electrodes was studied. The optimum operating conditions were determined and the obtained values are pH 7, current density = 14 mA/cm^2, operating time = 30 min, and electrolyte concentration = 1 g/L, respectively. The corresponding removal efficiencies of turbidity, COD, and BOD5 in dairy wastewater were 98.91, 74.56, and 96.28%, respectively. The energy consumption for these conditions was found to be equal to 3.36 kWh/m^3. Kinetics adsorption studies showed that the pseudo-first-order equation gives a better fit to the adsorption process of COD on aluminium hydroxide with a good correlation between experimental and theoretical data.

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