

Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes

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Abstract

The removal of COD and oil–grease from dairy wastewater was experimentally investigated using direct current (DC) electrocoagulation (EC). In the EC of dairy wastewater, the effects of initial pH, electrolysis time, initial concentration of COD, conductivity and current density were examined. The COD and oil–grease in the aqueous phase were effectively removed when iron was used as sacrificial anode. The optimum operating range for each operating variable was experimentally determined. The batch experimental results revealed that COD and oil–grease in aqueous phase was effectively removed. The overall COD and oil–grease removal efficiencies reached 98 and 99%, respectively. The optimum current density, pH and electrolysis time for 18,300 mg COD/L and 4570 mg oil–grease/L were 0.6 mA/cm², 7 and 1 min, respectively. Mean energy consumption was 0.003 kWh/kg of COD.

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1. Introduction

The dairy industry, like most other agro-industries, generates strong wastewaters characterized by high biological oxygen demand (BOD) and chemical oxygen demand (COD) concentrations reflecting their high organic content [1]. Dairy waste effluents are concentrated in nature, and the main contributors of organic load to these effluents are carbohydrates, proteins and fats originating from the milk [2]. Dairy wastewater is invariably high in nutrients (i.e. nitrogen, phosphorus and potassium) and organic material (e.g. oils and fat, dissolved lactic acid, etc.) and consequently has a high biological oxygen demand (BOD). Furthermore, dairy-processing effluent also has high concentrations of dissolved salts (total dissolved solids, TDS). The use of acid and alkaline cleaners and sanitizers in the dairy industry additionally influences wastewater characteristics and typically results in a highly variable pH [3].

Conventional anaerobic treatment processes are often used for treating dairy wastewaters. Particularly anaerobic filters and

upflow anaerobic sludge blanket reactors (UASB) and anaerobic sequencing batch reactors (ASBR) are the most common reactor configurations employed [1,4,5]. Anaerobic treatment processes are favourable methods for treating dairy waste effluents, in comparison to aerobic processes, due to their well-known benefits for treating industrial wastewaters, particularly from agricultural industries with a high organic content [6–11]. However conventional aerobic treatment processes are also used for treating dairy wastewaters. Aerobic purification of dairy wastewater in batch reactors [12–14], aerobic purification of dairy wastewater in continuous regime [15–17] are used for treating dairy wastewaters. Aerobic treatment processes are commonly used together with anaerobic processes for dairy wastewater treatment, in order to achieve the effluent discharge limits for agro-industry wastewaters [1]. On the other hand, the physical/chemical methods that have been proven to be successful are coagulation/flocculation [18], nanofiltration (NF) and reverse osmosis (RO) membranes [19] membrane bioreactor (MBR) systems [20]. Membranes in bioreactor systems are the main solid–liquid separation devices.

Results for the yields achieved with the different techniques used to treat the dairy wastewaters are outlined in Table 1.

Electrocoagulation (EC)/flotation process can be other alternative process for treating dairy waste effluents. This technology

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Table 1
Treatment performance levels of various methods for dairy wastewaters

Initial COD (mg/L)	Method	COD removal efficiency (%)	Reference
9359	Anaerobic filter reactor (AF)	91.8	[7]
4000	Aerobic purification	96.8	[12]
3200	Buoyant filter bioreactor (BFBR)	90	[10]
10000	Nanofiltration and reverse osmosis membranes	95	[19]

has been very successfully employed in removing oil/grease and SS from a variety of industrial effluents (e.g. oil refinery waste) [21,22] and is a combined coagulation and flotation process induced by the passage of electric current. Electrocoagulation with aluminum and iron electrodes was patented in the US in 1909. The electrocoagulation of drinking water was first applied on a large scale in the US in 1946 [23–25]. In recent years, EC has been successfully tested to treat various industrial wastewater such as decolorization of dye solutions and textile wastewaters [26–35], treatment of electroplating and polishing wastewaters [36,37], removal of arsenic and fluoride ions from industrial wastewater [38–40], electrochemical degradation of organics [41–44], treatment of chromium(VI) from wastewater [45–47], removal of colloidal particles [48,49], removal of phenolic compounds [50], clarification of potable water [51], removal of phosphate [52], removal of boron [53] and petrochemical wastewater treatment [54].

2. A brief description of electrocoagulation mechanism

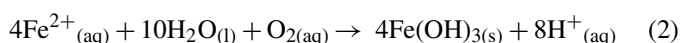
A simple electrocoagulating reactor is made up of one anode and one cathode. When a potential is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals [55].

If iron or aluminum electrodes are used, the generated $\text{Fe}^{3+}_{(\text{aq})}$ or $\text{Al}^{3+}_{(\text{aq})}$ ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides.

The Fe(II) ions are the common ions generated the dissolution of iron. In contrast, OH^- ions are produced at the cathode. By mixing the solution, hydroxide species are produced which cause the removal of matrices (dyes and cations) by adsorption and coprecipitation. In the study of iron anodes, two mechanisms for the production of the metal hydroxides have been proposed [56–58]:

Mechanism 1

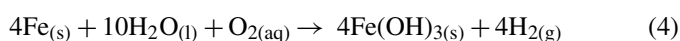
Anode:



Cathode:

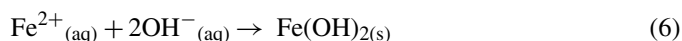


Overall:



Mechanism 2:

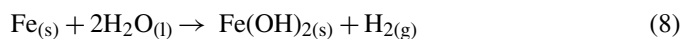
Anode:



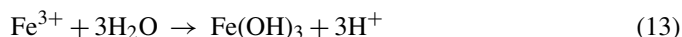
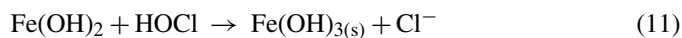
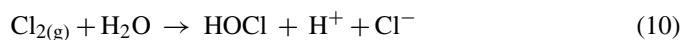
Cathode:



Overall:



Oxidation



The $\text{Fe}(\text{OH})_{n(\text{s})}$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the waste matter from wastewater either by complexation or by electrostatic attraction followed by coagulation.

Ferric ions electrogenerated may form monomeric ions, ferric hydroxo complexes with hydroxide ions and polymeric species, namely, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^+$, $\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$, $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{2+}$ and $\text{Fe}(\text{OH})_4^-$ depending on the pH range [31]. The complexes (i.e. hydrolysis products) have a pronounced tendency to polymerize at pH 3.5–7.0 [55–59].

2.1. Electrocoagulation mechanism of an oil–water emulsion

Oil–water emulsion is a colloidal dispersion in which oil constitutes the dispersed phase and water forms the continuous phase. A common example of an emulsion is milk, which contains fat dispersed in water. Emulsions are normally stabilized by the presence of an emulsifying agent, such a surfactant. In milk, the (natural) emulsifying agent casein, a protein that contains phosphate groups. The anionic head groups on the surfactant molecules prevent aggregation and coagulation of the oil droplets via electrostatic repulsion. During electrolysis in an electrocoagulation procedure, the sacrificial iron anode is oxidized to polymeric ionic species. With progressive electrolysis,

the ionic strength of the medium increases. Ionic polymeric iron species can neutralize the surface charge of surfactant molecules. They can either generate bridges between surfactant molecules. Simultaneously, hydrogen as well as hydroxides is generated at the cathode (Eq. (7)). The pH of the medium rises as a result of this electrochemical process. The net result of the reactions is that the emulsion is destabilized, and the colloidal oil particles begin to coalesce [60].

3. Materials and methods

3.1. Electrochemical reactor

The batch experimental setup is schematically shown in Fig. 1. The EC unit with bipolar electrodes in parallel connection consists of an EC cell, a DC power supply and electrodes. The iron cathode and iron anode consist of pieces of iron electrodes separated by a space of 2.5 cm and dipped in the wastewater. The EC of dairy wastewater was carried out in the reactor (650 mL) using magnetic stirrers to agitate the solutions. There were four electrodes connected in a bipolar mode in the electrochemical reactor, each one with dimensions of 10 cm × 5 cm × 0.2 cm. The total area submerged into the solution of the electrode plates was 0.0333 m². A stirring intensity of 100 rpm was used in order to get a correct homogenization of the wastewater–flocs mixture. EC experiments were carried out at 298 K. The DC source was used to power supply the system with 0–15 and 0–3 A.

3.2. Wastewater samples and experimental procedure

Wastewater was obtained from a tank containing a mixture of exhaust solutions at a dairy factory in Turkey (Sakarya) producing approximately 50 m³ of wastewater per day. The composition of the wastewater is shown in Table 2. The pH were adjusted to a desirable value using HCl and NaOH solutions. The conductivity of the wastewater was adjusted to the desired levels by adding an appropriate amount of NaCl. This adjustment has shown negligible effect on the initial pH of the wastewater.

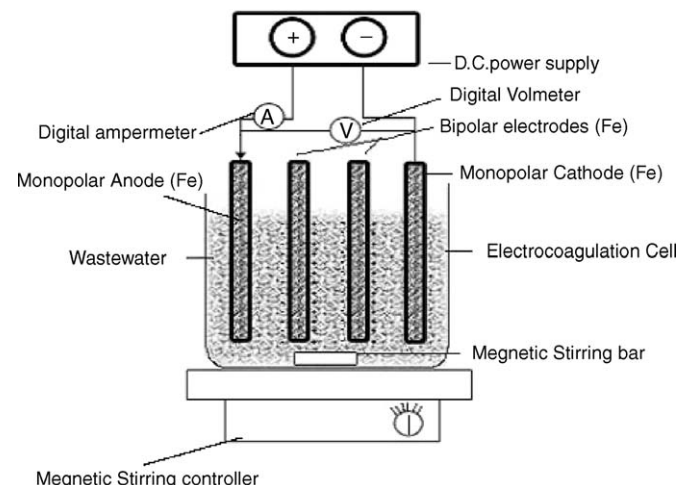


Fig. 1. Bench-scale EC reactor with bipolar electrodes in parallel connection.

Table 2
Characteristics of wastewater used

Characteristics	Value
Chemical oxygen demand (COD) (mg/L)	18300
Oil and grease (mg/L)	4570
TSS (mg/L)	10200
Conductivity (μ S/cm)	1200
pH	6.0–7.5

The salt concentrations for conductivity were 0.77, 1.54, 2.30, 3.07, 4.61 mg/L. pH and current density values were 3.5–10 and 0.3–1.8 mA/cm², respectively.

At the beginning of a run, the wastewater was fed into the reactor and the pH and conductivity were adjusted to a desired value. The electrodes were placed into the reactor. The reaction was timed starting when the dc power supply was switched on.

Iron salts produce electrode passivation and it causes a 50% increase in treatment time and power requirements. Eliminating the salt formation at the anode could reduce this effect. The cell was cleaned after each experiment to obtain same experimental conditions. For this reason, the electrodes were rinsed in the diluted HCl (1 + 1) solution after the each experiment. Samples were periodically taken from the reactor. The particulates of colloidal ferric oxyhydroxides gave yellow-brown colour into the solution after EC. All the suspended solids were removed by electrocoagulation and electrolytic flotation. Thus, during electrolysis, the clear solution was obtained. All the suspended solids were removed by electrocoagulation and electrolytic flotation. Therefore, filtration was not markedly effect COD and oil–grease removal. Sludge generating during treatment was separated from the solution by filtration using Whatman filter paper (pore size 11 μ m) and then the solution was analyzed. COD and oil–grease analysis were carried out according to the standard methods for examination of water and wastewater [61].

4. Results and discussion

4.1. Effect of initial pH

4.1.1. Effect of initial pH on the removal efficiency of COD and oil–grease

It has been established that pH is an important parameter influencing the performance of the EC process [55]. To examine its effect, the sample was adjusted to a desired pH for each experiment by using sodium hydroxide or hydrochloric acid. Figs. 2 and 3 show the removal efficiency of COD and oil–grease as a function of the initial pH. pH of the medium increased during the process. The maximum removals of COD and oil–grease were observed at pH around 6–7. Best removal results for 6 min electrolysis duration were observed at a pH of 6–7 and 0.6 mA/cm². However, as shown in Fig. 3, at 1.2 mA/cm², the process is clearly more efficient from pH 6 to 7 for only 2 min of electrolysis. For both current density, it is clear that COD and turbidity removals show the same trend. The removal (%) of the COD and oil–grease in this pH region was 98–99%.

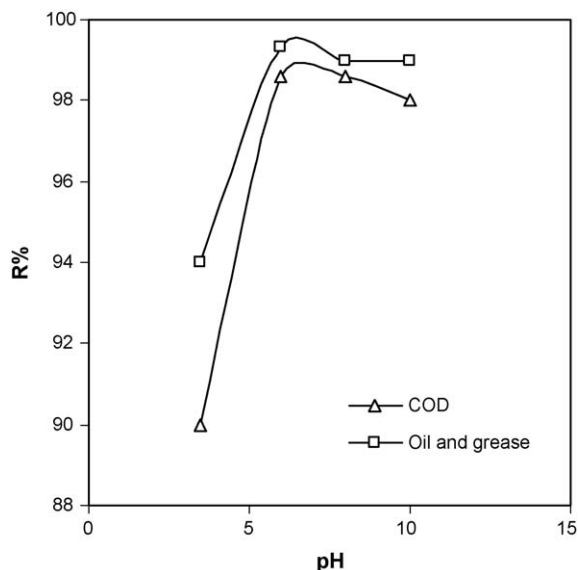


Fig. 2. Effect of initial pH on the removal efficiency of COD and oil-grease, $R\%$ ($C_{o,COD}$: 18,300 mg/L; $i=0.6$ mA/cm²; duration of electrolysis:6 min; m_{NaCl} : 3 g/L).

4.1.2. Effect of initial pH on electrode consumption

The electrode consumption values were calculated according to Faraday's law in following manner:

$$m_T = \frac{MIt}{zF} \times 3600 \quad (14)$$

where m_T is the theoretic amount of consumed iron (g/h), M is the atomic mass of iron (=56 g/mol), z is the valence ($z_{Fe} = 2$), I is the current (A) and F is Faraday's constant (9.65×10^4 C equiv⁻¹). According to Eq. (14), amount of the consumed iron depends on conductivity of the solution. The mass of substance dissolved at an electrode during electrolysis is proportional to the number

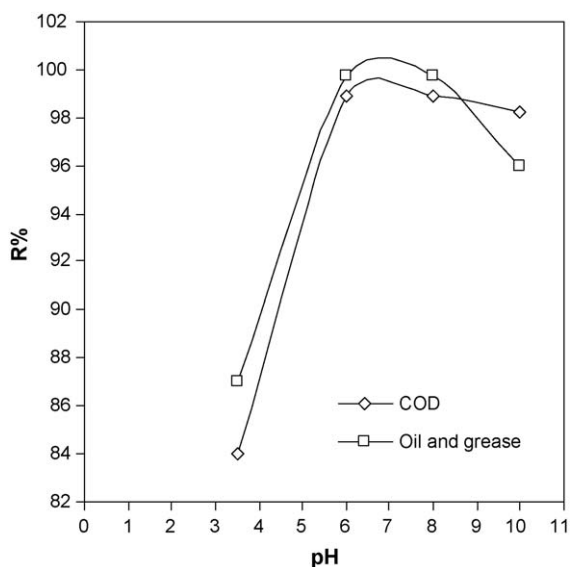


Fig. 3. Effect of initial pH on the removal efficiency of COD and oil-grease, $R\%$ ($C_{o,oil-grease}$: 4698 mg/L; $i: 1.2$ mA/cm²; duration of electrolysis: 2 min; m_{NaCl} : 3 g/L).

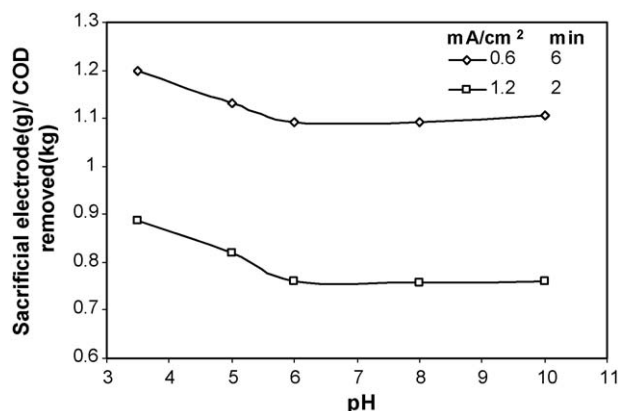


Fig. 4. Effect of initial pH on electrode consumption ($C_{o,COD}$: 18,300 mg/L; m_{NaCl} : 3 g/L).

of moles of electrons (the quantity of electricity) transferred at that electrode. When conductivity is high, the effects of pH of wastewater on electrocoagulation are reflected by the solubility of metal hydroxides [62].

Faraday's laws give theoretical prediction of electrodisso-lution in an ideal situation. In a real application, many factors influence the electrodisso-lution quantity and quality. In the potential region in which the metal dissolution rate is not limited by mass transport, the kinetics of active dissolution is generally expressed by Tafel behavior. High rate electrodisso-lution kinetics of iron has been studied in chloride solutions. The influence of chloride ions and pH levels on the anodic dissolution of iron has been investigated over a wide range of pH and Cl⁻ concentrations. Depending on the polarization conditions, pH level, and chloride ion concentration, the Tafel slope was found to vary between 0.04 and 0.11 mV, suggesting the formation of several chloro-iron complexes as adsorbed reaction intermediates [63].

Fig. 4 shows the electrode consumption in g per kg of COD removed in relation to initial pH in EC. As can be seen in Fig. 4, the lower electrode consumption values were obtained for $6 < \text{pH} < 10$ for 2 min electrolysis time at 1.2 mA/cm² current density and for $6 < \text{pH} < 10$ for 6 min electrolysis time at 0.6 mA/cm² current density. The minimum electrode consumption was 0.758 g electrode per kg COD at 1.2 mA/cm² current density and $6 < \text{pH} < 10$ for 2 min electrolysis times.

4.1.3. Effect of initial pH on energy consumption

Fig. 5 shows the specific energy consumption versus pH for iron electrodes during the electrocoagulation, expressed in kWh consumed per kg COD. As Fig. 5 shows, the minimum energy consumption appears for $6 < \text{pH} < 10$ at 6 min electrolysis time and 0.6 mA/cm² current density.

4.2. Effect of electrolysis time and current density

As shown in Figs. 6 and 7, as the time of electrolysis increases comparable changes in the removed efficiency of COD and oil-grease are observed. To explore the effect of operating

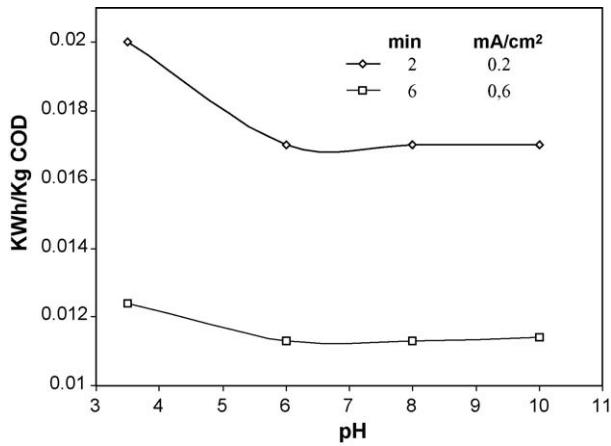


Fig. 5. Effect of initial pH on energy consumption ($C_{o,COD}$: 18,300 mg/L; m_{NaCl} : 3 g/L).

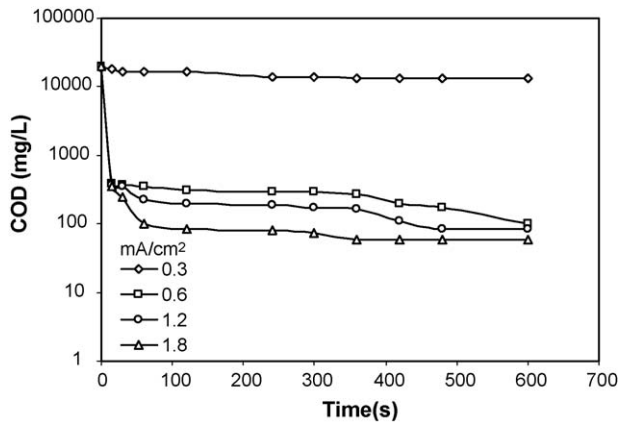


Fig. 6. Effect of electrolysis time on the removal of COD ($C_{o,COD}$: 18,300 mg/L; pH 7; m_{NaCl} : 3 g/L).

time, the current density and pH were held constant. COD and oil–grease was decreased as a function of elapsed time. After 60 s of electrolysis COD and oil–grease efficiency reached a maximum at all current density values except for 0.3 mA/cm² current density; a 98–99% COD and oil–grease removal was achieved under this condition.

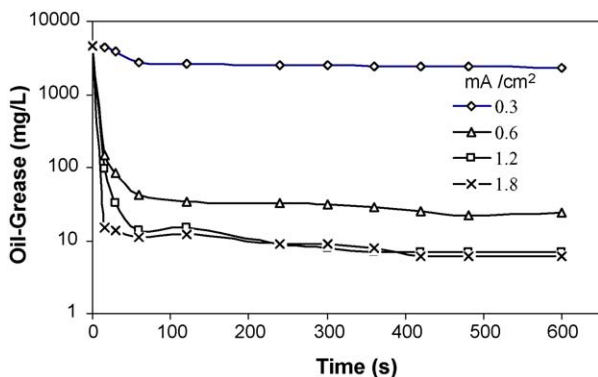


Fig. 7. Effect of electrolysis time on the removal of oil–grease ($C_{o,oil-grease}$: 4698 mg/L; pH 7; m_{NaCl} : 3 g/L).

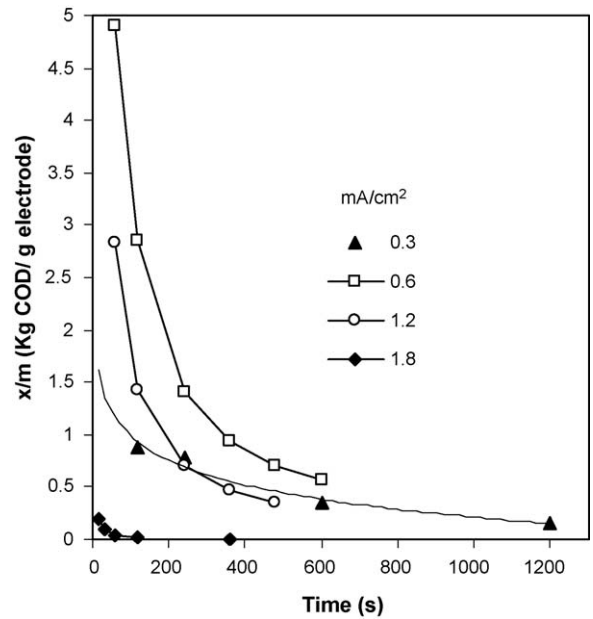


Fig. 8. The effect of electrolysis time on COD removed per unit of electrode consumption ($C_{o,COD}$: 18,300 mg/L; m_{NaCl} : 3 g/L).

4.2.1. Effect of current density and electrolysis time on electrode consumption

The effect of electrolysis time on COD removed per unit of electrode consumption (g Fe) is shown in Fig. 8. According to Fig. 8, maximum COD removed per unit of electrode consumed was obtained for 0.6 mA/cm² at 60 s electrolysis time. Under these conditions, the electrode consumption is 4.90 kg COD removed/g electrode or 0.0204 g electrode/kg COD removed. Differential analysis of the data was used to evaluate all the terms in the rate equation including the derivative, $-dc/dt$. The best fit values for the order ‘ n ’ and constant ‘ k ’ for the rate equation $-dc/dt = kc^n$ were found out from Fig. 9. The values of n and k are 10.4 and 6.6×10^{10} , respectively.

4.2.2. Effect of current density on energy consumption

The Effect of current density on energy consumption (kWh/Kg COD removed) is shown in Fig. 10. Increase of the current density up to 0.6 mA/cm² caused a decrease in power

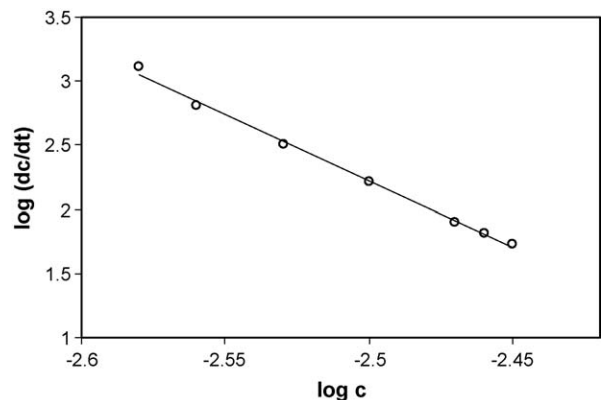


Fig. 9. $\log(dc/dt)$ vs. $\log(c)$ ($C_{o,COD}$: 18,300 mg/L; m_{NaCl} : 3 g/L; i : 0.6 mA/cm²; pH 7) ($r^2 = 0.9964$).

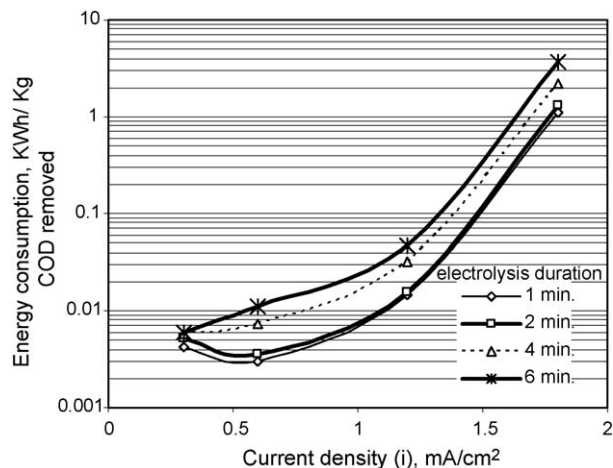


Fig. 10. Effect of current density on energy consumption ($C_{0,COD}$: 18,300 mg/L; pH 7; m_{NaCl} : 3 g/L).

requirement for 1 and 2 min electrolysis time. The minimum energy consumption was 0.003 kWh/kg COD at 0.6 mA/cm² current density for 60 s electrolysis time. The energy consumption in the high current density was increased by Joules.

5. Effect of the initial concentration on the removal efficiency of COD and oil–grease

As can be seen from Fig. 11, when the initial concentration of COD was increased from 1550 to 19,800 mg/L, the removal (%) of the COD was increased from 88 to 98%. The reason for this is the existence of excess colloids for the adsorption in high COD concentrations.

5.1. Adsorption isotherms

The $Fe(OH)_n(s)$ complexes formed remains in the aqueous stream as a gelatinous suspension. These gelatinous charged hydroxo cationic complexes can effectively remove pollutants by adsorption to produce charge neutralization, by complexation, by electrostatic attraction and by enmeshment in a pre-

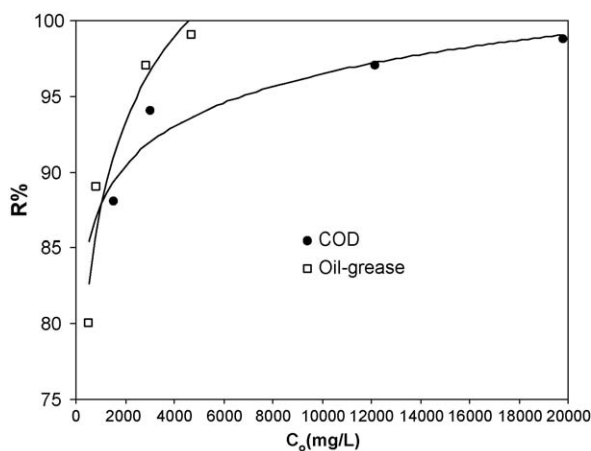


Fig. 11. Effect of initial concentration on the removal efficiency of COD and oil–grease (pH 7; i : 0.6 mA/cm²; duration of electrolysis: 3 min; m_{NaCl} : 3 g/L).

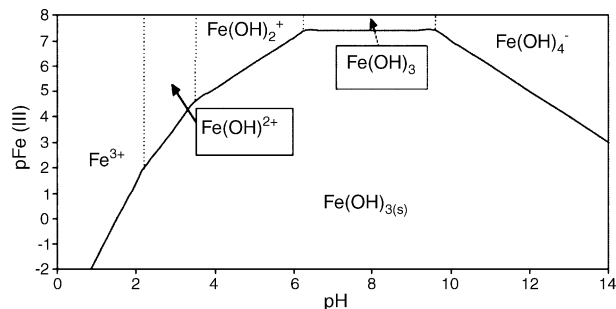


Fig. 12. Predominance-zone diagrams for Fe(III) chemical species in aqueous solution. Note that, in this case, the solid line represents the solubility equilibrium of $Fe(OH)_3$ and the dotted line represents the predominance limits among soluble chemical species [32].

cipitate [56]. $Fe(OH)_3$ is dominant species at pH 7 according to predominance-zone diagrams for Fe(III) chemical species in aqueous solution. A solubility diagram for Fe(III) in water is presented in Fig. 12 [26]. The objective of this study is to systematically examine adsorption isotherms of $Fe(OH)_3$ for removal of COD from dairy wastewater. The electrode consumption according to Faraday's Law is 0.0105 g Fe at 3 min and 0.6 mA/cm². 0.02 g $Fe(OH)_3$ is formed by Fe dissolved stoichiometrically.

Fig. 13 show adsorption isotherm, the relationship between the amount of COD adsorbed per unit mass of gelatinous charged hydroxo cationic complexes (Q_e) and final COD in the aqueous phase (C_e). The plots of COD uptake against equilibrium concentration indicate that adsorption increases initially with concentration but then reaches saturation.

The linearized Freundlich isotherm equation is shown in Eq. (15) agents:

$$\ln Q_e = \log K_F + \frac{1}{n} \ln C_e \quad (15)$$

where K_F and n are Freundlich constant. The linear plot of $\ln Q_e$ versus $\ln C_e$ indicates the applicability of the Freundlich isotherm and for the present system exhibits monolayer coverage of the adsorbate on the outer surface of the adsorbent. The K_F and n values were calculated from the intercept and slope of the plot.

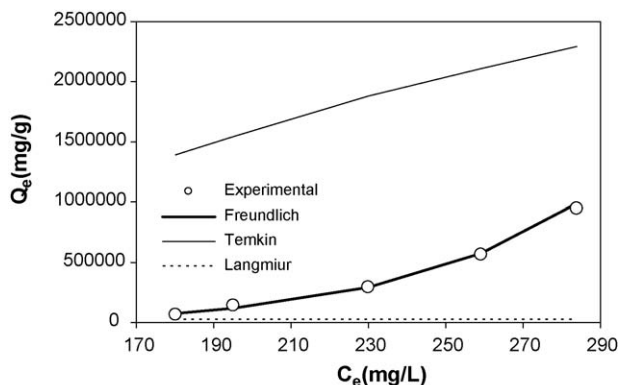


Fig. 13. Adsorption isotherms of COD by charged hydroxo cationic complexes (pH 7; i : 0.6 mA/cm²; duration of electrolysis: 3 min; m_{NaCl} : 3 g/L).

Table 3

Langmuir, Freundlich and Temkin isotherm constants for adsorption of COD on Fe(OH)₃

Langmuir			Freundlich			Temkin		
K_L (L/g)	a_L (L/mg)	r^2	K_F (L/g)	n	r^2	B	A (L/g)	r^2
172.4	-0.0034	0.81	1.94×10^{-8}	0.179	0.99	2×10^6	0.011	0.95

The widely used Langmuir isotherm has been successful applied to many real sorption processes and is expressed as:

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} \cdot C_e \quad (16)$$

where the constant K_L is the Langmuir equilibrium constant. Therefore, a plot of C_e/Q_e versus C_e gives a straight line of slope a_L/K_L and intercept $1/K_L$.

A basic assumption of Temkin isotherm is that the heat of sorption of all the molecules or ions in the layer decreases linearly with coverage owing to sorbate-sorbate interactions. The Temkin isotherm has been used in the following form:

$$Q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad (17)$$

$$\frac{RT}{b} = B \quad (18)$$

where A and B are Temkin constant. A plot of Q_e versus $\ln C_e$ enables to determine the constants A and B .

Based on the correlation coefficient (r^2) shown in Table 3, the adsorption isotherm with hydroxo cationic complexes can be better described by the Freundlich equation. Also, in all cases the Freundlich equation represents a better fit of experimental data than the Temkin and Langmuir.

6. Effect of the amount of NaCl salt on the removal efficiency of COD and oil-grease

In general, NaCl is used to obtain the conductivity in EC process. The conductivity of the wastewater is adjusted to the desired levels by adding an appropriate amount of NaCl [35]. The effect of NaCl concentration on the removal efficiency is shown in Fig. 14. When the concentration of NaCl salt in solution increases, conductivity of the solution and the current density increase. The higher ionic strength will generally cause an increase in current density at the same cell voltage or, equivalently, the cell voltage decreases with increasing wastewater conductivity at constant current density. Consequently, the necessary voltage for attainability to a certain current density will be diminished and the consumed electrical energy will decrease. According to Vlyssides et al., when chlorides are presents in the solutions the products from anodic discharge of chlorides are Cl_2 and OCl^- . The OCl^- itself is a strong oxidant, which capable of oxidizing organics molecules present in wastewater. So, added NaCl not only increases the conductivity but also contributes strong oxidizing agents [64]. It can be seen that there is an increase in the removal efficiency of COD and oil-grease up to 100% when the concentration of NaCl salt in the solution is 0.3 g/L.

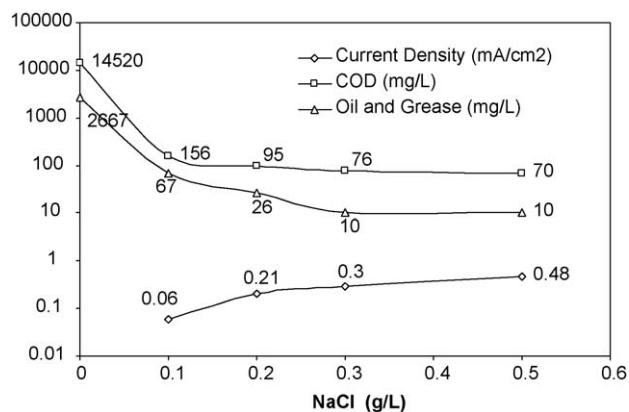


Fig. 14. Effect of the amount of NaCl on the removal efficiency of COD; duration of electrolysis: 6 min; pH 7.

7. Conclusions

Electrocoagulation is a feasible process for treating the dairy wastewater, characterized by high oil and grease content, fluctuated COD, BOD₅ and SS concentrations. The treating of the dairy wastewater using of iron sacrificial anode was affected by the initial pH, the current density, the amount of NaCl and the initial COD and oil-grease concentration. The results showed that COD and oil-grease was effectively removed at initial pH 6–7 when the initial concentration of COD and oil-grease was 18,300 and 4570 mg/L, respectively. The results also indicated that the removal efficiency of the COD and oil-grease was raised to 98 and 99%, respectively. The optimal current density was 0.6 mA/cm² for an operating times of 1 min. Under these conditions, the electrode consumption is 0.0204 g electrode/kg COD removed. At these optimal conditions the power requirement were 0.003 kWh/kg COD. The experimental results showed that optimal NaCl amount was 0.3 g/L. The gelatinous charged hydroxo cationic complexes generated in EC can effectively remove pollutants by adsorption. The equilibrium data fit well in the Freundlich adsorption isotherm model. The predictions of Freundlich adsorption isotherm model are in very good agreement to the experimental data.

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