Effects of Operating Parameters on Electrode Dissolution and Energy Consumption during Electrocoagulation Treatment of Petroleum Refinery Wastewater

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Abstract

In this work, the effects of the variations of current density, initial conductivity of wastewater, initial wastewater pH and electrolysis time on aluminum electrode dissolution and energy consumption ofthe electrocoagulation treatment of a petroleum refinery wastewater have been studied.A central composite design was used to generate the set of experiments that were used for the investigations. The results of the experiments showed that the electrode dose was linearly affected by the electrolysis time and interactively by the current density and the pH. Dissolution being affected by the pH revealed that chemical dissolution contributed to aluminum electrode dose during the experiments. The energy consumption, on the other hand, was found to be affected by all the factors investigated except the pH. The results of the analysis of variancesthat were carried out on the responsesof the process showed that the models developed for the electrode dose and the energy consumption were statistically significant because their p-values of 0.0178 and <0.0001 respectivelyfound were discovered to be less than the significance level of 0.05.

Keywords: Petroleum refinery wastewater, electrocoagulation, electrode dissolution, central composite design.

1. INTRODUCTION

Treatment of petroleum refinery wastewater is an important issue in environmental protection as the wastewater normally contains pollutants that, if not efficiently treated, can cause serious hazards to the environment including lives in the water body into which the wastewater is discharged.

Electrocoagulation is one of the widely used technologies in water purification and wastewater treatment. The process possesses advantages such as high efficiency, environmental friendliness, generation of reduced amount of sludge compared to chemical coagulation. Electrocoagulation has been successfully used to treat many industrial wastewaters on laboratory scale including biodiesel wastewater (Chavalparit and Ongwandee, 2009), petrochemical wastewater (Dimgolo et al., 2004; Giwa et al., 2012a; Giwa et al., 2013), and oily wastewater (Tir and Moulai-Mostefa, 2008). Electrocoagulation is an electrochemical process in which the coagulant generated by electrolytic oxidation or electrolytic and chemical oxidation of sacrifice electrodes is responsible for the destabilization of pollutants in water or wastewater.

In electrocoagulation, the first step is electro-dissolution of anode electrodes. At the cathode, water undergoes reduction to form hydroxyl ions and hydrogen gas. In the solution, metallic ion combines with hydroxyl ions to form coagulant. In case of aluminum electrode, these steps can be illustrated as shown in the following equations.

At the anode surface,

$$Al_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e^{-}{}_{(aq)} \quad (1)$$

At the cathode surface,

$$3H_2O_{(l)} + 3e^-_{(aq)} \rightarrow 3OH^-_{(aq)} + \frac{3}{2}H_{2(g)} \quad (2)$$

In the aqueous medium,

$$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_{3(s)} \quad (3)$$

In electrocoagulation, the quantity of soluble electrodes delivered to the solution is measured using the amount of current passed as explained by Faraday (Gu et al., 2009). Faradaic electrode dose can be expressed mathematically as given in Equation (4) below.

$$D_F = \frac{ItM}{zF} \quad (4)$$

Where, I, M, t, z and F are the current (in ampere), the molecular weight (for Al, this is equal to 27 g/gmol), the electrolysis time (in seconds), the number of electrons oxidized by one mole of metal (z_{Al}= 3) and the Faraday Constant (96485.3399 C/mol), respectively.

However, the amount electrode dose calculated from the Faraday law of electrolysis may be greater or less than the real electrode dosage delivered during electrocoagulation. Chemical dissolution of electrode is believed to contribute to electrode dose especially when the current efficiency is greater than 100%. The dissolution is thus known to be pH dependent.

At acidic pH, around the anode, the following chemical reactions occur (Gu et al. 2009):

$$Al + H_2O \rightarrow Al(OH)^{2+} + H^+ \quad (5)$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \quad (6)$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+ \quad (7)$$

$$Al + 3H^+ \rightarrow Al^{3+} + \frac{3}{2}H_2 \quad (8)$$

At alkaline pH cathode, aluminum electrode can also undergo chemical dissolution according to Equation (9) (Gu et al., 2009).

$$Al + 2H_2O \rightarrow AlO_2^- + \frac{3}{2}H_2 + H^+ \quad (9)$$

It has been reported that electro-dissolution of aluminum electrode is dependent on current density and electrolysis time alone but neither dependent on pH (Gu et al., 2009) nor on supporting electrolyte concentration (Canizares et al 2005), using traditional experimental plan in which one factor is varied at a time while other factors are kept constant. Also, according to Giwa et al.(2012b),the results of the experiment carried out according to a statistical design with unaltered initial pH showed that aluminum dose was singly and interactively affected by only the current density and the electrolysis time. In their work, the effect of initial pH on the dissolution could not be evaluated because the experiments were carried out at the natural pH of the wastewater that was used.

Therefore, in this work, the effects of variations of the current density, the initial conductivity, the initial pH and the electrolysis time on aluminum dissolution during the treatment of a petroleum refinery wastewater as well as the energy consumption of the treatmenthave been investigated.

2. MATERIALS AND METHODS

2.1 Experimental Design

With the aid of Design Expert 7.0.0, a central composite design was used to design a set of 30 experimental runs according to which the petroleum refinery electrocoagulation treatment was carried out. The investigated factors of this study were the current density, the initial conductivity, the initial pH and the electrolysis time while the responses considered were the electrode dose and the energy consumption. The details of the design matrix used for the experimental design are given in Table 1. The experiments were carried out according to the central composite design consisting of a full 2^4 factorial experiments, 8 axial experiments and 6 center points. The design matrix and the factors together with the responses obtained from the experiments carried out are given in Table 2 (in the results and discussions section).

Table 1. The levels of the factors in the design matrix

Actual variable, unit	Factor	Levels				
		-2	-1	0	1	+ 2
Current density, mA/cm^2	X_1	4.17	7.29	10.42	13.54	16.67
Conductivity, mS/cm	X_2	2	3	4	5	6
pH	X_3	6	7	8	9	10
Electrolysis time, min	X_4	10	15	20	25	30

The combination of the factors and the experimental responses were analyzed with the aid of the same Design Expert 7.0.0 by choosing a model that was quadratic. The quadratic model type was chosen for the models in order to incorporate the interactions among the factors into the process models.

2.2Electrocoagulation Experiments

Each electrocoagulation experiment was carried out using 4 aluminum electrodes in a plexi glass made reactor with a capacity of 1.5L. The 45mm x 60mm x 3mm plates having a total effective area of 96 cm^2 were placed vertically in the reactor at a distance of 1.5 cm apart and connected in a monopolar mode to a DC power source. Before and after each experimental run, the electrodes were thoroughly rinsed with distilled water to remove the impurities found on their surfaces. A laboratory stirrer (MTOPS, MS-3020) was used to gently and continuously stir the solution during the experiment to achieve uniform concentration. The initial conductivity and the pH of the wastewater were adjusted by the addition of H_2SO_4/NaOH (0.5 M) and NaCl, and measured using conductivity and pH meters (Mettler Toledo M200 easy), respectively. During the experiments, the control of the wastewater temperature was achieved through the use of a water bath (Hoefer, RCB20-PLUS). The electrode dose (D) at specific experimental conditions was determined using the gravimetric method in which case that the weights of the electrodes were measured before and after each experiment using an analytical balance (Scaltec, SBC 31).

The schematic diagram of the experimental set up is as given in Figure 1 below. The mathematical expressions given in Equation (4) together with Equation (10) was used to calculate the current efficiency. Also, the energy consumption for each experimental run was calculated using Equation (11).

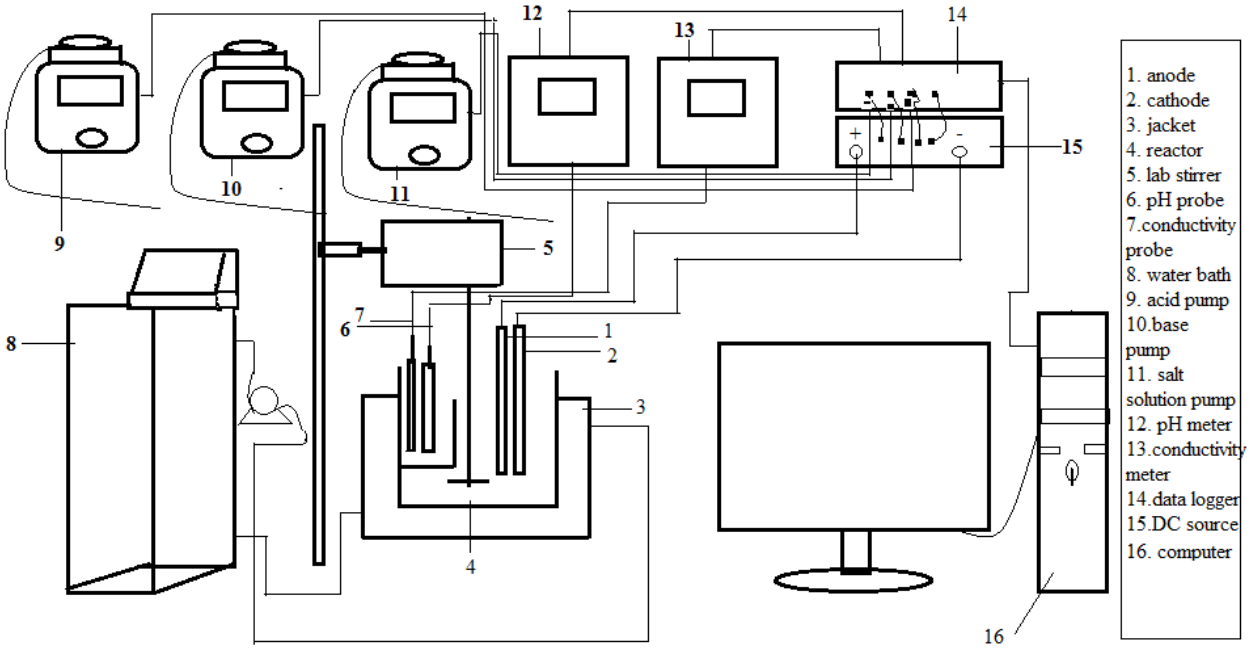

Figure 1. The schematic diagram of the experimental set up

$$CE = \frac{D}{D_F} \times 100 \quad (10)$$

$$E\ (kWh/m^3) = \frac{VIt}{v} \quad (11)$$

3. RESULTS AND DISCUSSIONS

The results obtained from the experiments carried out using the designedexperimental plan matrix generated according to the central composite design are as given in Table 2.

Table 2. The design matrix and the experimental results

	Factors				Responses			
Run/no	X_1	X_2	X_3	X_4	E, kWh/m^3	D, g	D_F, g	CE, %
1	10.41	4	8	20	3.6667	0.0405	0.1119	36.182
2	13.54	3	9	25	9.4792	0.1396	0.1819	76.74845
3	7.29	5	9	25	2.0417	0.427	0.0979	435.9708
4	7.29	5	9	15	1.2250	0.1181	0.0588	200.9686
5	10.41	4	10	20	3.6667	0.1455	0.1119	129.9872
6	13.54	3	9	15	6.6625	0.0404	0.1091	37.01812
7	10.41	6	8	20	3.0000	0.1583	0.1119	141.4225
8	7.29	3	9	15	2.0125	0.1937	0.0588	329.6157
9	7.29	3	7	25	3.3542	0.1291	0.0979	131.8122
10	10.41	4	6	20	4.3333	0.1869	0.1119	166.9732
11	16.66	4	8	20	11.2000	0.0571	0.1791	31.8826
12	10.41	4	8	20	3.6667	0.1987	0.1119	177.5152
13	10.41	4	8	10	2.1667	0.0693	0.0560	123.8229
14	13.54	3	7	25	11.3750	0.321	0.1819	176.4775
15	13.54	5	7	25	7.5833	0.2822	0.1819	155.1462

16	13.54	5	7	15	4.5500	0.3531	0.1091	323.542
17	10.41	4	8	20	3.6667	0.201	0.1119	179.5699
18	4.17	4	8	20	0.8000	0.1028	0.0448	229.5994
19	7.29	3	9	25	3.6458	0.1395	0.0979	142.4307
20	10.41	4	8	30	7.0000	0.2665	0.1679	158.7243
21	13.54	5	9	25	7.5833	0.2783	0.1819	153.0021
22	10.41	4	8	20	3.6667	0.1521	0.1119	135.8835
23	7.29	5	7	25	2.6250	0.2024	0.0979	206.6522
24	7.29	5	7	15	1.2250	0.1111	0.0588	189.0568
25	10.41	4	8	20	3.6667	0.1551	0.1119	138.5637
26	10.41	2	8	20	6.8333	0.1817	0.1119	162.3277
27	13.54	5	9	15	4.8750	0.1266	0.1091	116.0023
28	10.41	4	8	20	3.6667	0.1901	0.1119	169.8321
29	7.29	3	7	15	2.2750	0.1833	0.0588	311.9182
30	13.54	3	7	15	6.5000	0.1874	0.1091	171.7128

Looking at Table 2, it was noticed from the results of the axial experiments (run numbers 5, 10, 7, 26, 11, 18, 13 and 20) that the only factor that significantly affected the dissolution was electrolysis time, especially considering run 13 and 20. Also, from the results of the factorial experiments, it was discovered that only simultaneous of variations of current density and pH affected the aluminum dissolution positively. As can be seen from the table, increasing the current density and pH led to increase in electrode dose. For instance, at 5 mS/cm and 25 min, increasing the current density and the pH from 7.29 mA/cm^2 and 7 to 13.54 mA/cm^2 and 9, respectively led to 0.0759 increase in aluminum dissolution (runs 21 and 23). Also, varying the current density and the pH in similar manner at 5 mS/cm and 15 min made the dissolution to increase from 0.1111 g to 0.1266 g (runs 24 and 27). The dissolution being affected interactively by the variationsin the current density and the pH has revealed that during the experiment, aluminum electrode corroded both by chemical and electrolytic methods. The values of the electrode dose calculated according to the Faraday's law of electrolysis were found to be less than the ones obtained experimentally, except for few runs. As a result, the current density were mostly greater than 1 (100 %). The Faradic dose were less than actual electrode dose in four of the experimental runs only (runs 1, 2, 6 and 11).

The results of the ANOVA that was carried out on the responsesof the aluminum dissolution given in Table 2 as well confirmed that the electrolysis time, the current densityand the pH were the factors that significantly affected the aluminum dissolution during the experiments. The p-value for the electrolysis time and current density-pH combination were both less than 0.05 (see Table 3). This confirmed the two terms as being significant for the reduced quadratic model developed for the aluminum dissolution. The model itself (given in Equation 12) was found to be significant with a p-value of 0.0178. In addition, according to the results shown in Table 3, the lack of fit value for the model was found to be insignificant. As seen in Figure 2,there were just fairly good agreements between the dissolution predicted by the model and the ones obtained experimentally. The square of the correlation coefficient (R^2) of the model was obtained to be 0.5021.

$$D = -0.6465 + 0.16107X_1 + 0.021583X_2 0.051306X_3 - 0.032248X_4 - 0.016224X_1X_3 + 5.0725E-03X_3X_4 - 1.41625E-03X_1^2 \quad (12)$$

Table 3. Results of ANOVA for electrode dose model

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	0.12	7	0.017	3.17	0.0178
X_1-current density	7.37E-04	1	7.37E-04	0.14	0.7119

X_2-conductivity	0.011	1	0.011	2.12	0.1592
X_3-pH	6.31E-03	1	6.31E-03	1.2	0.2854
X_4-electrolysis time	0.042	1	0.042	7.91	0.0101
X_1X_3	0.041	1	0.041	7.81	0.0106
X_3X_4	0.01	1	0.01	1.95	0.176
X_1^2	5.51E-03	1	5.51E-03	1.05	0.3175
Residual	0.12	22	5.27E-03		
Lack of Fit	0.097	17	5.73E-03	1.56	0.3281
Pure Error	0.018	5	3.67E-03		
Cor Total	0.23	29			

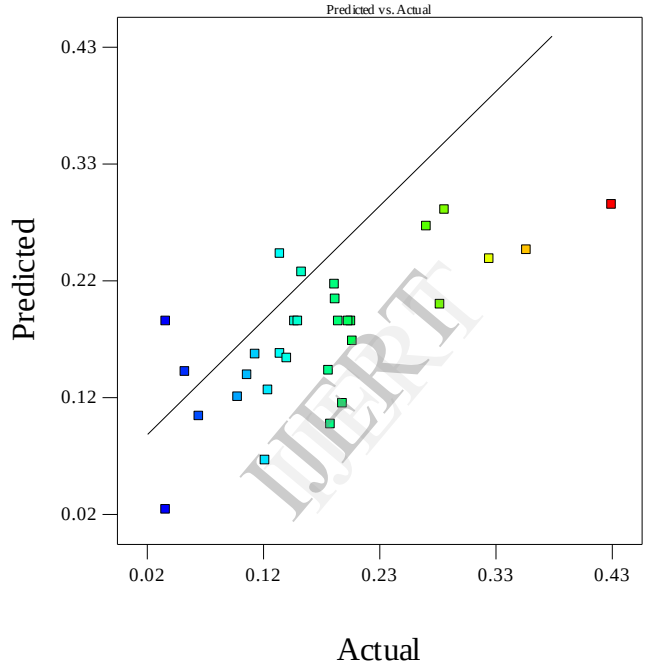

Figure 2. Plot of experimental and predicted electrode dose (the solid line represents the model data)

As shown in Table 2, it was found that the energy consumption was significantly affected by all the factors except the pH. In the axial experiments, increasing the current density and the electrolysis time led to increase in the energy consumption. For instance, when the current density was increased from 4.17 mA/cm^2 to 16.67 mA/cm^2, the energy consumption increased from 0.8 kWh/m^3 to 11.2 kWh/m^3 (Runs 18 and 11). Similarly, increasing the electrolysis time from 10 min to 30 min madethe energy consumption to increase from 2.1667 kWh/m^3 to 7 kWh/m^3 (Runs 13 and 20). On the other hand, increasing the initial conductivity of the wastewater under treatment made the energy consumption of the treatment to decrease. At 10.14 mA/cm^{2}of the current density, the pH of 8 and 20 min electrolysis time, when the conductivity was 2 mS/cm, the energy consumption was 6.833 kWh/m^3 (Run 26), and under the same conditionsbut with conductivity increased to 6 mS/cm, the energy consumption dropped to 3 kWh/m^3 (Run 7). Considering the center experimental set,the change of the current density, the electrolysis time and the conductivity also affected the energy consumption.

Furthermore, the results of the factorial experiments showed that, apart from the single variation of the current density, the electrolysis time and the conductivity, the simultaneous variations

of the current density-conductivity and current density-electrolysis time also affected the energy consumption. For instance, increasing the current density and the electrolysis time led to increase in the energy consumption (compare runs 2 and 8). Similarly, simultaneous variations of the current density and the conductivity increased the energy consumption (runs 9 and 15), even though the decreasing effect ofthe conductivity on the response was still noted. Direct proportionality of the energy consumption to the current, and the electrolysis time justified the increase of the energy consumption with increase in the current density and the electrolysis time. Also, the decrease in the energy consumption with increase in the solution conductivity wasfound to be attributed to the inverse proportionality of voltage to conductivity because according to Ohm's Law, voltage varies with resistance at a constant current valueand conductivity is reciprocal of resistivity.

Table 4. Results of ANOVA for energy consumption model

Source	Sum of squares	df	Mean square	f-value	p-value
Model	225.02	14	16.07	149.24	< 0.0001
X_1-current density	155.06	1	155.06	1439.82	< 0.0001
X_2-conductivity	18.84	1	18.84	174.91	< 0.0001
X_3-pH	0.45	1	0.45	4.2	0.0583
X_4-electrolysis time	32.73	1	32.73	303.96	< 0.0001
X_1X_2	1.73	1	1.73	16.02	0.0012
X_1X_3	0.046	1	0.046	0.42	0.5251
X_1X_4	4.52	1	4.52	41.97	< 0.0001
X_2X_3	0.13	1	0.13	1.21	0.2881
X_2X_4	0.37	1	0.37	3.47	0.0821
X_3X_4	0.36	1	0.36	3.38	0.086
X_1^2	9.01	1	9.01	83.63	< 0.0001
X_2^2	2.51	1	2.51	23.26	0.0002
X_3^2	0.15	1	0.15	1.36	0.2619
X_4^2	1.31	1	1.31	12.2	0.0033
Residual	1.62	15	0.11		
Lack of Fit	1.62	10	0.16		
Pure Error	0	5	0		
Cor Total	226.64	29			

From the results obtained from the ANOVA of the responses of the energy consumption of the treatment, it was shown that the quadratic model obtained for the energy consumption (given in Equation 13) was statistically important with p-value less than 0.0001 (see Table 4). Also, X_1, X_2, X_4, X_1X_2, X_1X_3, X_1^2, X_2^2, X_3^2 and X_4^2 were found to be significant model terms because each of had p-values that were less than 0.05. The importance of these model terms on the model confirmed the effects of the current density, the electrolysis time and the conductivity on the energy consumption of the treatment, as earlier observed using the design matrix and the experimental results (shown in Table 2). The developed quadratic model of the energy consumption was thus found to be significant with p-value less than 0.0001 and with a high square of correlation coefficient (R^2) of 0.9929.

$$E = 11.44905 - 0.53225X_1 - 2.32066X_2 - 0.88649X_3 - 0.10737X_4 - 0.10508X_1X_2 - 0.017083X_1X_3 + 0.034017X_1X_4 + 0.090365X_2X_3 - 0.030573X_2X_4 - 0.030156X_3X_4 + 0.05868X_1^2 + 0.30221X_2^2 + 0.073047X_3^2 + 8.75521E-03\,X_4^2 \quad (13)$$

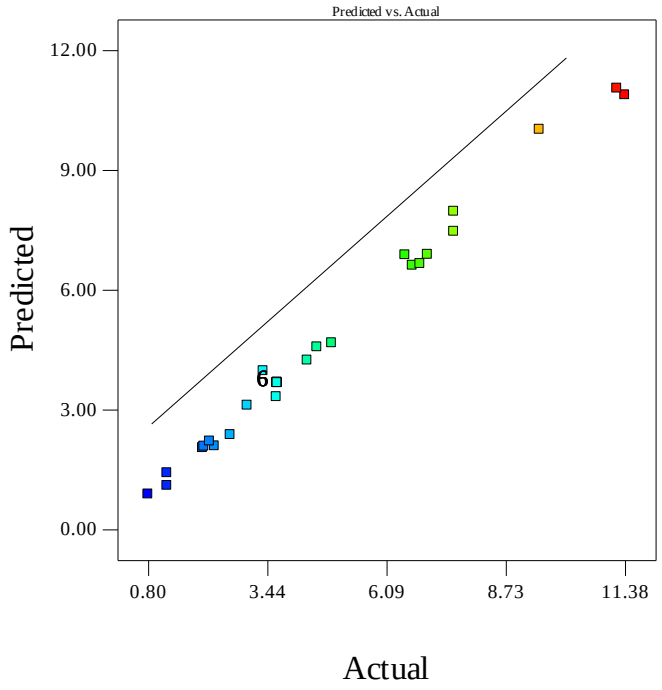

Figure 3. Experimental and predicted energy consumptions. The solid line represents the model values.

The very high R^2 value of the developed model for the energy consumption indicated that the simulated results obtained from the developed model correlated very well with the experimental results. This was also seen evidentlyin the plot of the energy consumption predicted by the model and those obtained from the experiments that were carried out, as shown in Figure 3.

4. CONCLUSIONS

The results of the studies carried out in this work have revealed that the aluminum electrode dose during the experiments was found to be affected singly by the electrolysis time and interactively by the current density and the pH. In addition, the effect of pH on the dissolution showed that chemical dissolution contributed to the aluminum electrode dose during the experiments. On the other hand, the energy consumption was found to be affected by the variationsin the current density, the wastewater initial conductivity and the electrolysis time. However, the effect ofthe current density on this response (the energy consumption) was discovered to be the most significant because, while the simultaneous variations of the conductivity and the electrolysis had no effect on it, the current density-conductivity and the current density- electrolysis time interaction significantly affected it (the energy consumption).

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