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Modeling of Adsorption Isotherms of Oil Content through the Electrocoagulation Treatment of Real Oily Wastewater

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Abstract. The adsorption equilibrium isotherms of oil content via the electrocoagulation treatment of real oily wastewater were studied and modeled. Ten isotherm models (Langmuir, Freundlish, Temkin, Dubinin–Radushkevich, Kiselev, Fowler–Guggenheim, Elovich, Hurkins-Jura, Jovanovic and Hill–de Boer models) were selected to predict the adsorption equilibrium isotherms and their characteristics parameters. A triple aluminum tubes was manufactured in a monopolar-concentric arrangement to investigate the purpose of treating real oily wastewater (523.11 ppm of oil content) produced from crude oil wells location (West Qurna 1 /Basra-Iraq) under the impacts of the operational variables; the electrolysis time (2-20 min.), the current density (4.4 mA/cm^2), the initial pH equaling 6.5, and the agitation speed fixed as 200 rpm. The results showed that the studied models fitted the data in the order as: Freundlish (R^2=0.9991) > Langmuir (R^2=0.9960) > Hurkins-Jura (R^2=0.9926) > Temkin (R^2=0.9922) > Elovich (R^2=0.9906) > Jovanovic (R^2=0.9573) > Fowler–Guggenheim (R^2=0.8676) > Hill–de Boer (R^2=0.8294) > Dubinin–Radushkevich (R^2=0.7928) > Kiselev (R^2=0.7366) isotherms. The modeling of adsorption isotherm revealed that the interaction of oil content with the electro-coagulant is characterized as physical adsorption process. There is no formation of complex between the adsorbed molecules due to the repulsion among them. Additionally, the heat of adsorption will decrease with loading via the electrocoagulation treatment of real oily wastewater.

INTRODUCTION

Millions of cubic meters of oily wastewater are discharged to the aquatic system and soil every year around the world due to the continuous demand for crude oil and its derivatives [1,2]. In order to overcome this crisis of pollution, several types of treatment methods are employed to remove contaminants from the oily wastewaters, such as the chemical precipitation, membrane filtration, adsorption and electrochemical methods [3].

The latter technique i.e. the electrochemical methods, are using the electrical current as the main parameter in their operation [4-6]. The electrocoagulation method is one of the electrochemical methods, which depends extremely on adsorption process occurring via the electrolysis treatment of different contaminants, such as the removal of pigment [5], heavy metals [6-10], detergent [11] and oil content [4,12] depending on the autocatalytic behavior of the electrocoagulation reactor [13,14] to produce electro-coagulants as adsorbent without adding any external materials [10].

The followings are the reactions taking place in the electrocoagulation reactor when the electrodes are made of aluminum [15]:

At the anode electrodes, the aluminium ions required to generate coagulants are released as a result of the dissolution of electrodes. Moreover, the oxygen gas bubbles released will contribute in soft agitation as well as they are carrying the light pollutants toward the surface of wastewater along the duration of electrochemical treatment:

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

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$2H_2O \Rightarrow O_2 + 4H^+ + 4e^-$ (2)

At the cathode electrode, the Hydrogen gas bubbles are evolved and contributed in the soft mixing and the floatation of the light contaminants toward the surface of the contaminant water, while hydroxyl ions will be reacted with the aluminium ions to form coagulants:

$2H_2O + 2e^- \Rightarrow H_{2(g)} + 2OH^-_{(aq)}$ (3)

$Al^{3+} + 3OH^- \Rightarrow Al(OH)_3$ (4)

The amount of these electro-coagulants is assumed to be equal to the value of the the theoretical value of the electrodes consumption (mtheo.) that could be calculated from Eq. (5) as follows:

$m_{theo}\ (g) = CD \cdot t \cdot M / Z \cdot F$ (5)

Where, CD is the electric current density in (mA/cm^2), t is the contact time in (second), M is the molecular weight of electrodes metal in (g/mol.), Z is the number of electrons presented in the reaction (for Al is 3 and Fe is 2), and F is Faraday's constant which equals (96485.34 Columb/mol.).

This study aims to study the adsorption equilibrium isotherms through the electrocoagulation treatment of real oily wastewater discharged from drilling wells located in (West Qurna 1 /Basra-Iraq) under specific values of current density (4.4 mA/cm^2), pH (6.5) and agitation speed (200 rpm) along the period of the electrolysis time (2-20 min). The present reactor, which has been invented by the author (Forat Y. AlJaberi, 2018) [16], consists of triple aluminum tubes, which was designed in a concentric-monopolar mode. According to the literature and our experience, there is no previous study that is concerned about studying these responses for this kind of electrodes configuration.

Experimental Work

Chemicals and Analytical Analysis

The real oily wastewater was attained from the discharging of the Wet Oil's Unit, a petroleum station located in West Qurna 1/Basra-Iraq as explained its characterization in Table 1. It was collected and treated by an electrocoagulation technique using the experimental batch apparatus depicted in Fig. 1.

TABLE 1. Characterization of oily wastewater.

Parameters	Oil content (OCT) (mg/L)	pH	Turbidity (TUR) (NTU)	TDS (mg/L)	Conductivity (ms/cm)
Value	523.11	6.5	168	112140	126

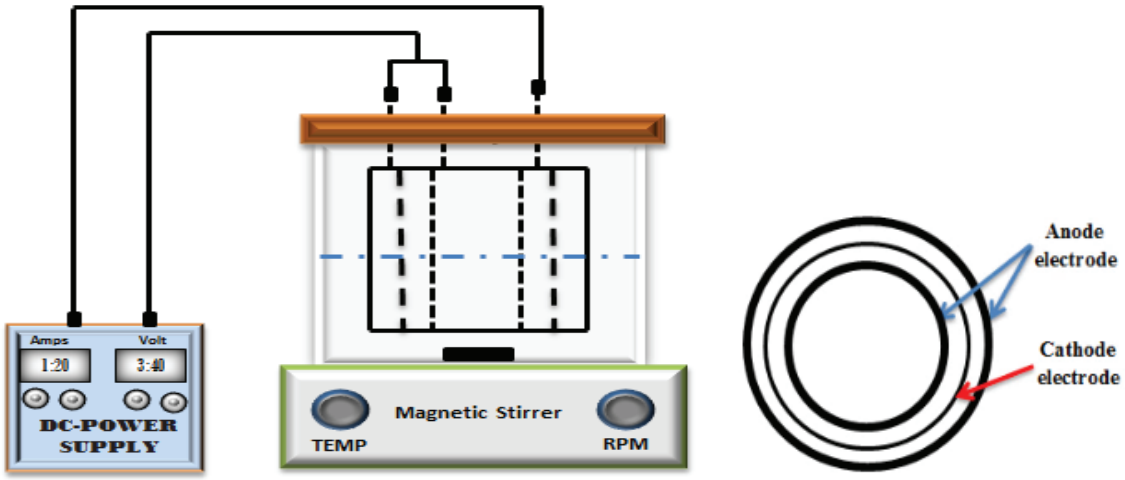

FIGURE 1. The electrocoagulation reactor and its electrodes configuration.

At the end of each run, the analytical determination of oil content in the treated samples after the filtration process was carried out using a UV-1800 spectrophotometer (Shimadzu Inc., Japan). The removal efficiency was estimated according to the following equation:

$$\%\boldsymbol{RE} = [(\frac{\boldsymbol{C0-C}}{\boldsymbol{C0}})* 100] \quad (6)$$

Where, C_0 and C are the initial and final values of pollutant (mg/l), respectively

Adsorption Equilibrium Isotherms

Langmuir adsorption isotherm

It is a two-parameter model and assumes that the sorption sites are completely having equal affinity to the pollutants. The Langmuir model could be written in a linear form as follows:

$$\frac{\boldsymbol{C_e}}{\boldsymbol{q_e}} = \frac{\boldsymbol{C_e}}{\boldsymbol{q_{max}}} + \frac{\boldsymbol{1}}{\boldsymbol{bq_{max}}} \quad (7)$$

Where, C_e is the equilibrium concentration of oil content (mg/l), q_e is the quantity adsorbed at equilibrium (mg/g), b is the Langmuir isotherm constant (the energy of adsorption; l/mg) and q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface (mg/g).

This affinity between the adsorbent and the adsorbate could be predicted by using the separation factor R_L:

$$R_L = \frac{1}{1+bC_o} \quad (8)$$

Where, the value of this factor indicates the status of Langmuir isotherm, which is irreversible (R_L=0), linear (R_L=1), favorable (0< R_L<1) or unfavorable (R_L>1).

Freundlish Adsorption Isotherm

It is a two-parameter model and used to describe the relation between the quantity adsorbed at equilibrium (q_e) and the equilibrium concentration of oil content (C_e) in an exponential relation based on the equilibrium adsorption on heterogeneous surfaces. The linear expression of this model is shown in the following equation:

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \quad (9)$$

Where, K_f and n are known as the Freundlish isotherm constants. They refer to the relative adsorption capacity ($mg^{1-(1/n)}\ L^{1/n}\ g^{-1}$) and the adsorption intensity, respectively. The value of (n) indicates the degree of nonlinearity between the quantity adsorbed and the solution concentration as follows: if n equals one, the adsorption is linear; if n<1, the adsorption is chemical and if n>1, the adsorption is physical. In general, the adsorption is in a good manner when the value of (n) is ranging between 1 and 10.

Temkin Adsorption Isotherm

This model assumes that the heat of adsorption decreases along the electrolysis time as the surface coverage increases due to the indirect electro-coagulants -pollutants interactions and uniform distribution of the binding energies. This model could be represented in a linear form (Eq. 10) as follows:

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (10)$$

Where, K_T is the Temkin isotherm constant (l/mg), b is the heat of adsorption (J/mol), R is the universal gas constant (kJ mol^{-1} K^{-1}) and T is the absolute temperature (K).

Dubinin–Radushkevich adsorption isotherm

The adsorption process depends on the porosity of the electro-coagulants, i.e. a pore filling mechanism, under this model for the heterogeneous surfaces. D-R model is applicable for the physical adsorption under the effect of Van Der Waal's forces in case of multilayer character. This model is classified as a temperature dependent and it could be presented in the following linear form:

$$\ln q_e = \ln q_s + K_{DR}\, \varepsilon^2 \quad (11)$$

Where:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (12)$$

$$E = \frac{1}{(2K_{DR})^{1/2}} \quad (13)$$

Where, (q_s) is the theoretical isotherm saturation capacity (mg/g) and (E) is the mean free energy required for removing a molecule from its location in the sorption space to the infinity (kJ/mol).

Kiselev Adsorption Isotherm

This model is applicable in localized monomolecular layer when the surface coverage ($\theta = q_e/q_{max}$) is more than (0.68). The linear expression of Kiselev isotherm is demonstrated in Eq. 14 as follows:

$$\frac{1}{C_e(1+\theta)} = \frac{K_K}{\theta} + K_K K_n \quad (14)$$

Where K_K, and K_n are the Kiselev equilibrium constant (l/mg) and the constant of complex formation between the adsorbed molecules, respectively.

Fowler–Guggenheim Adsorption Isotherm

This model is taking the lateral interaction of the adsorbed molecules into account, where the heat of adsorption process varies positively or negatively with loading. Meanwhile, when the interaction energy is positive, i.e. attractive interaction force, the heat of adsorption is directly increasing with loading. While it decreases with loading in the case of repulsive interaction energy of the adsorbed molecules. The form of this model in a linear manner is elucidated in Eq. 15:

$$\mathbf{\ln\left[\frac{C_e(1-\theta)}{\theta}\right] = -\ln K_{FG} + \frac{2W\theta}{RT}} \quad \mathbf{(15)}$$

Where, K_{FG} is the Fowler–Guggenheim equilibrium constant (l/mg), and W is the interaction energy between the adsorbed molecules (kJ/mol).

Elovich Adsorption Isotherm

The Elovich model assumes that the adsorption sites raise exponentially with a multilayer adsorption process basing on the kinetic principle. Equation 16 represents the linear form of this adsorption isotherm as follows:

$$ln\frac{q_e}{C_e} = \ln(K_E\ q_{max}) - \frac{q_e}{q_{max}} \quad (16)$$

Where, K_E is the Elovich equilibrium constant (l/mg).

Hurkins-Jura Adsorption Isotherm

This model of adsorption isotherm is performed for a multilayer adsorption process depending on the heterogeneous pore distribution and it could be expressed in a linear form, as in Eq. 17:

$$\frac{1}{q_e^2} = \frac{B_H}{A_H} - \frac{1}{A_H}\ logC_e \quad (17)$$

Where, A_H (g^2/l) and B_H (mg^2/l) are the H-J model's parameters characterizing the adsorption equilibrium.

Jovanovic Adsorption Isotherm:

The possibility of mechanical contacts between the pollutants and the electro-coagulants and the retention capacity is taken into consideration in this model in addition to the same assumptions considered in the Langmuir adsorption model. The linear form of this model is evinced as follows in Eq. 18:

$$\ln q_e = \ln q_{max} - K_J\ C_e \quad (18)$$

Where, K_J (l/g) is the parameter of Jovanovic model.

Hill-de Boer Adsorption Isotherm

This model considers the mobile adsorption as well as the lateral interaction among the adsorption molecules where the affinity is increased or decreased depending on the kind of force among the adsorption molecules whether is attractive or repulsion according to the value of model's parameter. The H-B model could be described in a linear expression as revealed in Eq. 19:

$$\mathbf{\ln\left[\frac{C_e(1-\theta)}{\theta}\right] - \frac{\theta}{1-\theta} = -\ln K_1 - \frac{K_2\theta}{RT}} \quad (19)$$

Where K1 (l/mg) and K2 (kJ/mol) are the H-B model's parameter and the energetic constant of the interaction between the adsorbed molecules along the electrocoagulation treatment of oily wastewater.

RESULTS AND DISCUSSION

Removal Efficiency and Calculations

According to the restricted values and range of the operational variables, Table 2 shows the obtained results and the required calculations for estimating the studied adsorption isotherms.

TABLE 2. The obtained results and the required calculations.

Time (min)	Oil content removal %	C_e (mg/l)	q_e (mg/g)	Temp. (K)	Theoretical adsorbent (g)	ε^2 (kJ/mol)^2	θ
2	12.88	455.75	684.382	300	0.049	29.861	0.89
4	24.79	393.44	658.723	301	0.098	40.248	0.86
6	35.73	336.18	633.064	301	0.148	55.360	0.82
8	45.72	283.97	607.404	302	0.197	77.901	0.79
10	54.73	236.81	581.745	303	0.246	112.438	0.76
12	62.78	194.71	556.086	303	0.295	166.900	0.72
14	69.86	157.65	530.426	304	0.344	255.354	0.69
16	75.98	125.65	504.767	305	0.394	403.022	0.66
18	81.13	98.69	479.108	305	0.443	654.426	0.62
20	85.32	76.79	453.449	306	0.492	1082.089	0.59

Modeling of Adsorption Isotherms

The aim of this work is to find the adsorption models that can describe clearly the obtained results of several adsorption isotherms. The experimental adsorption isotherms of oil content from real oily wastewater onto electro-coagulants via the electrocoagulation reactor are revealed in Figs. 2 and 3. The obtained results showed that the studied models fitted the data in the order as: Freundlish (R^2=0.9991) > Langmuir (R^2=0.9960) > Hurkins-Jura (R^2=0.9926) > Temkin (R^2=0.9922) > Elovich (R^2=0.9906) > Jovanovic (R^2=0.9573) > Fowler–Guggenheim (R^2=0.8676) > Hill–de Boer (R^2=0.8294) > Dubinin–Radushkevich (R^2=0.7928) > Kiselev (R^2=0.7366) isotherms. The modeling of adsorption isotherm manifested that the interaction of oil content with electro-coagulant is characterized as physical adsorption process. There is no formation of complex between the adsorbed molecules due to the repulsion among them. Additionally, the heat of adsorption will decrease with loading via the electrocoagulation treatment of real oily wastewater. The values of models, parameters are explained in Tables 3 and 4 as follows:

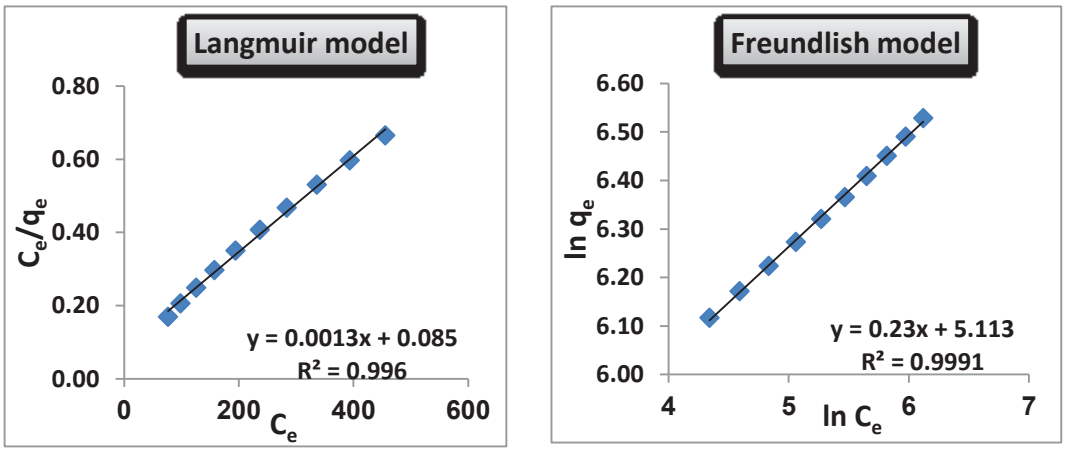

FIGURE 2. Modeling of adsorption isotherms (Part 1)

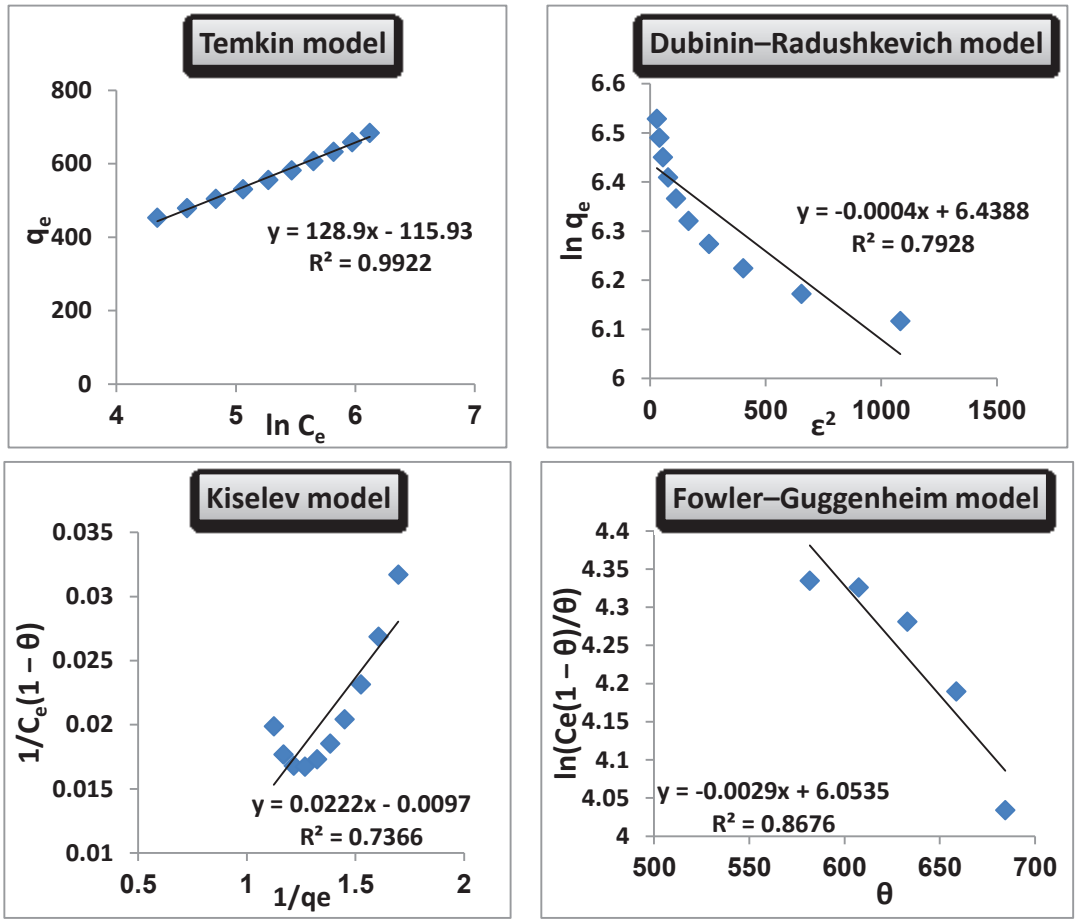

FIGURE. 2 continued Modeling of adsorption isotherms (Part 1)

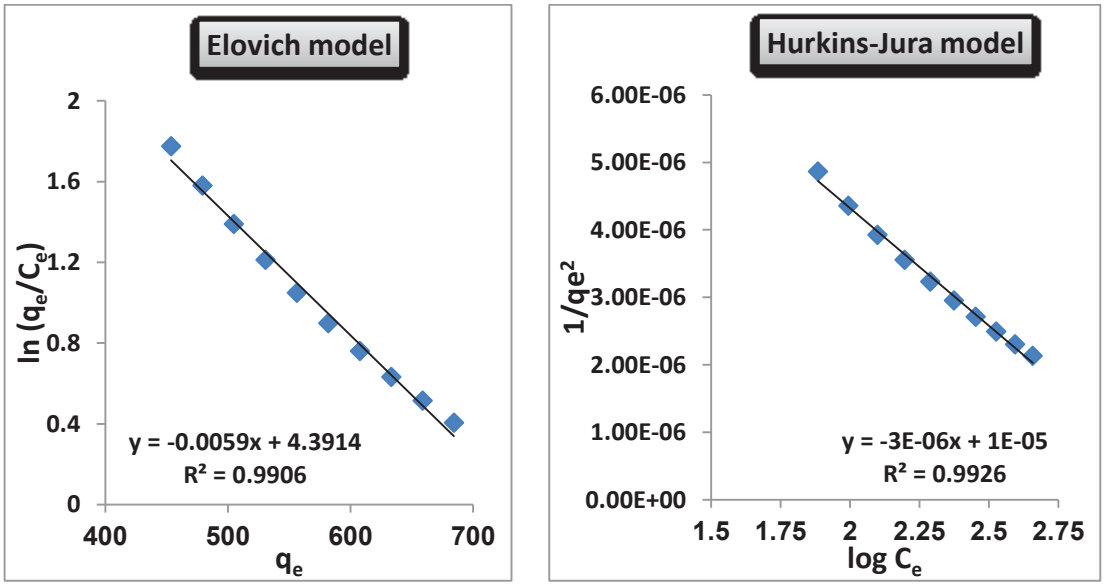

FIGURE 3. Modeling of adsorption isotherms (Part 2)

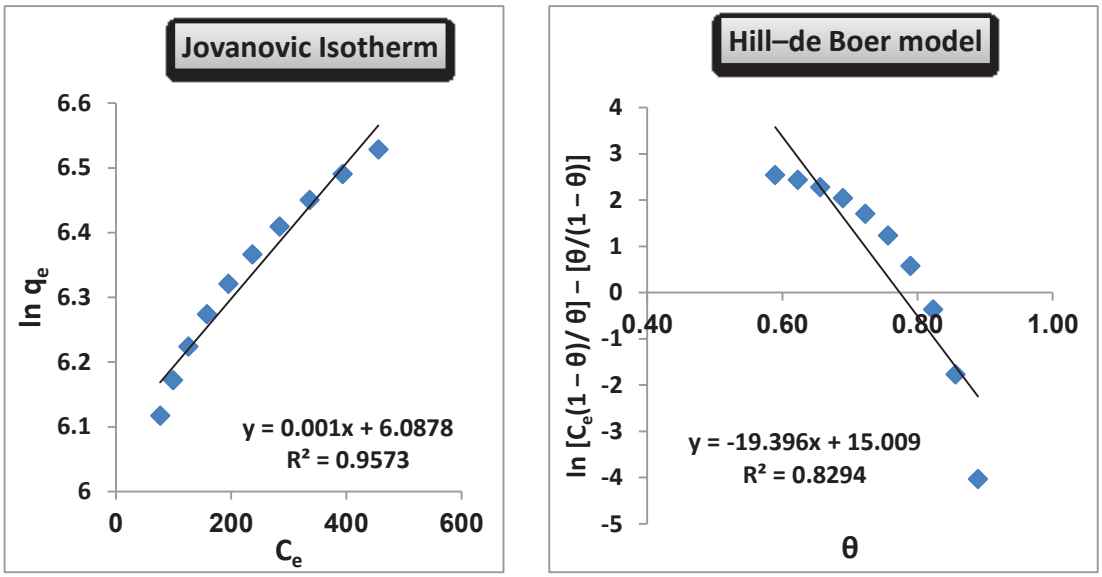

FIGURE. 3 continued Modeling of adsorption isotherms (Part 2)

TABLE.3 Isotherms constants for oil content adsorption on electro-coagulants (Part 1)

Models	Parameters	Interpretations
Langmuir	q_{max}= 769.23 mg/g b= 0.0153 l/mg R_L= 0.179 R^2 = 0.9960	• Maximum monolayer coverage capacity. • Energy of adsorption. • Favorable status.
Freundlish	K_F= 166.168 mg/g n= 4.348 R^2 = 0.9991	• Freundlish isotherm constant. • Physical process and good adsorption.

TABLE.4 Isotherms constants for oil content adsorption on electro-coagulants (Part 2)

Models	Parameters	Interpretations
Temkin	B=128.9 kJ/mol K_T=0.407 l/gm R^2 = 0.9922	• Heat of adsorption. • Equilibrium binding Temkin constant.
Dubinin–Radushkevich	K_{DR}=0.0004 $(mol/kJ)^2$ E=0.0354 kJ/mol q_s= 625.655 mg/g R^2= 0.7928	• D-R model's constant. • Mean free energy. • Theoretical isotherm saturation capacity.
Kiselev	K_K=0.0222 l/mg K_n= - 0.437 R^2=0.7366	• Kiselev equilibrium constant. • There is no formation of complex between the adsorbed molecules.
Fowler–Guggenheim	K_{FG}=0.00235 l/mg W= - 3.593 kJ/mol R^2=0.8676	• F-G model's constant. • Heat of adsorption will decrease with loading.
Elovich	K_E=0.5024 l/mg R^2=0.9906	• Elovich model's constant.
Hurkins-Jura	A_H=333333.3 g^2/l B_H=3.333 mg^2/l R^2=0.9926	• H-J model's parameter • H-J model's parameter • The existence of a heterogeneous pore distribution.
Jovanovic	K_J= - 0.001 l/g R^2=0.9573	• Jovanovic model's parameter.
Hill–de Boer	K_1=3.032E-07 l/mg K_2= - 48054.99 kJ/mol R^2=0.8294	• H-B model's parameter. • Repulsion interaction between adsorbed molecules.

The present treatment of the real oily wastewater by using an electrocoagulation reactor is extremely depending on the adsorption technique which is characterized as multilayer physical adsorption.

CONCLUSIONS

Several mathematical models can be performed to explain the details of adsorption isotherms via the electrocoagulation treatment of (523.11 ppm of oil content) produced from crude oil wells location (West Qurna 1 /Basra-Iraq) under the impacts of the operational variables; the electrolysis time (2-20 min.), the current density (4.4 mA/cm^2), the initial pH equaling 6.5 and the agitation speed fixed as 200 rpm. The equilibrium data were modeled with ten models, which were the Langmuir, Freundlish, Temkin, Dubinin–Radushkevich, Kiselev, Fowler–Guggenheim, Elovich, Hurkins-Jura, Jovanovic and Hill–de Boer models. The results elucidated that:

1. The Freundlish model possesses the highest regression factor (R^2=0.9991) and could correlate the obtained data, whereas the Kiselev model possesses the lowest value of the regression factor (R^2=0.7366).
2. The modeling of adsorption isotherm showed that the interaction of oil content with electro-coagulant is characterized as physical adsorption process. There is no formation of a complex between the adsorbed molecules due to the repulsion among them. Additionally, the heat of adsorption will decrease with the loading via the electrocoagulation treatment of real oily wastewater.

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