



Adsorption of lead from simulated wastewater via electrocoagulation process: kinetics and Isotherm Studies

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Abstract:

The present research was carried out to study the adsorption phenomenon via a batch electrocoagulation cell. Simulated wastewater contain heavy metal such as lead is used as an experimental solution. This simulated solution was natural and the effecting other parameters were a constant stirring speed (150 rpm), (5-60) minutes of contact time, (10-300) ppm of lead concentration, and (0.2-2.6) Ampere of applied direct current. The results show that equilibrium isotherm curves gave a good fitting with Langmuir and Freundlich models with square regression values (0.975 and 0.767) respectively. Moreover, this research study the kinetics of adsorption using Lagergren's first-order equation and Ho's second-order expression. The intra-particle diffusion model is studied to explore the intra-particle diffusion graphically. The thermodynamic parameters ΔG , ΔH , and ΔS were studied, the result shows that the adsorption process of lead was spontaneous and endothermic in nature.

Keywords: Heavy metals, Wastewater treatment, Batch electrocoagulation, Adsorption, Isotherm models

Introduction

Heavy metals pollution has become the most effective ecological problem in the last years as a result of releasing hazard materials into the environment [1; 2]. The continuous development of industries cause heavy metals wastewaters to be directly or indirectly discharged into the environment increasingly [3; 4]. Various techniques were used to treat these toxic materials such as electrocoagulation process. It's an attractive method for the treatment of wastewater which regarded as rapid and well-controlled that require fewer chemicals and produce less sludge [5; 6].

Electrocoagulation is a clean electrochemical process, which uses an applied voltage (i.e. electrical current) to remove metals from solution [7]. The contaminants present in wastewater such as lead ions are maintained in solution by electrical charges [8]. When these ions and other charged particles are neutralized with ions of opposite electrical charges provided by electrocoagulation system, they tend to be destabilized and then precipitate in a stable form [9].

Several parameters affect the efficiency of electrocoagulation process such as initial concentration of the metal, contact time, pH, current density or current, cell voltage, anode–cathode materials, batch or continuous, flow rate, inter-electrodes distance, conductivity of solutions, energy consumption, and the electrodes configuration [10 ; 11].

In the present study, aluminum electrodes were used to investigate the adsorption phenomenon via electrocoagulation process depending on the production of adsorbent materials (i.e. aluminum hydroxyl flocs) as a result of applied current to the cell. Equilibrium isotherm models under specified parameters will be studied and to conclude which type of isotherm is efficient. Moreover, thermodynamic parameters should be studied to investigate which the reaction is endothermic or exothermic and to know which the reaction is spontaneous or not.

Material and Methods

Apparatus

The schematics of electrocoagulation cell are shown in Fig.1 and Fig.2, which consist of three concentric aluminum tubes with different diameters and thicknesses as given in Table(1) with an active area of approximately 285 cm². Other tools as follow:

- 1- Digital DC- power supply (SYADGONG company-305D); 0-30 volt and 0-5 Ampere.
- 2- Digital balance (500g x 0.01g) (PROF company).
- 3- Magnetic Stirrer (ALFA company: HS-860) ; 0-1000 rpm.
- 4- pH meter (ATC company).
- 5- Digital timer (SEWAN company).
- 6- Aluminum tubes with different diameters and thicknesses.

Tables 1 and 2 explain the description and configuration of the concentric electrodes that made of aluminum tubes which consist of the height of electrodes, wet height, outer and inner diameters, distance in between, and electrodes thicknesses individually.

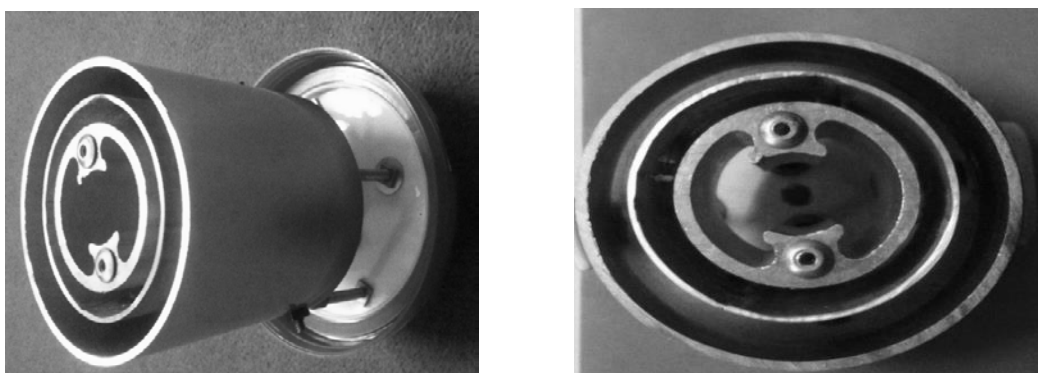


Fig. 1. Concentric electrodes

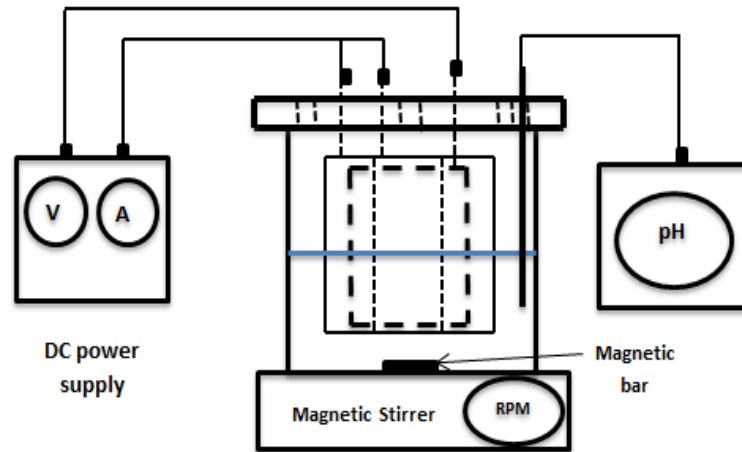


Fig. 2. The schematic of electrocoagulation reactor

Table 1. Description of aluminum electrodes

Electrode Location	Height (cm)	Wet Height (cm)	Electrode thick (cm)	Outer diameter (cm)	Inner diameter (cm)	Distance in between (cm)
Outer electrode	9.70	4.00	0.20	7.50	7.30	1.60
Mid. electrode	8.50	4.00	0.15	5.70	5.55	1.55
Inner electrode	7.10	4.00	0.30	4.00	3.70	-----

Table 2. Electrodes configuration

Configuration type	Electrodes	
	Anode electrode(s)	Cathode electrode(s)
one cathode – two anodes	Outer and inner	Mid only

The batch electrocoagulator is made of plexiglass with the volume of 1000 mL. The parameters selected in the present experiments were described as follows in (Table 3).

Table 3. Experimental parameters

Parameters	Range or Constant value
Initial lead concentration (ppm)	10-300
pH	7
Current or current density (A or mA/cm ²)	0.2-2.6 or (0.702-9.123)
Stirring speed (RPM)	150
Contact time (min)	5 - 60

Materials

Simulated wastewater samples with an initial concentration of lead were prepared by dissolving lead nitrate $Pb(NO_3)_2$ in distillate water. Where the required mass of this salt could be measured according to the following equation:

$$\text{Weight of salt (grams)} = \text{Volume of solution (liter)} \times \text{Initial concentration of lead ions in solution (ppm)} \times (\text{M.wt of the lead nitrate} / \text{Atomic weight of lead}) \quad (1)$$

In order to prevent the formation of an oxide layer on the anode electrode and to increase the conductivity of the simulated solution, an amount of sodium chloride was added. Hydrochloric acid (0.1 N) and sodium hydroxide (0.1 N) was used to adjust the value of pH to be the solution neutral.

The simulated wastewaters of the experiments were prepared by dissolving $Pb(NO_3)_2$ having 99.99 of purity (*B.D.H-England*) in 500mL of distilled water. The value of pH was adjusted by using 0.1 N HCl and 0.1 N NaOH. Electrical conductivity and decreasing passivation enhance removal efficiency by using 0.5 g/L of NaCl.

When the electrodes of the concentric tubes immersed in the synthesis wastewater, DC- current switched on to supply current to the cell. Samples are collected from the treated simulated wastewater each 15 minutes and filtered by the cellulose Glass-Microfibre discs (Grade: MGC; pore diameter is 0.47 micrometer- MUNKTELL) before the analysis by the Atomic Absorption Spectroscopy (AAS- Type-SHIMADZUAA-7000F) for measuring quantities of lead ions present in the samples. At the end of each experiment, electrodes were washed one time with 0.1N HCl and more than one time with water to ensure it was cleaned well. The same procedure was repeated for the next experiment.

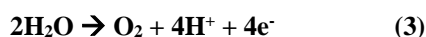
Results and discussion:

Adsorption mechanisms are complicated as no simple theory adequately explains the adsorption of metal ions on the adsorbent surface [12]. But the mechanism of adsorption via electrocoagulation process consists of the following stages [13]:

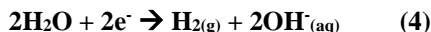
- (i) Electrolytic oxidation of the electrode to form coagulants.

Oxidation and reduction operations occur on anode and cathode electrodes respectively as explained below:

- At the anode electrode with metal M:



- At the cathode electrode:



The formation of hydroxide ions at the cathode electrode will affect the pH value of the simulated wastewater to be increased.

(ii) Destabilization of the pollutants, particulate suspension, and breaking of emulsions.

- At the cathode surface:



(iii) Aggregation of the destabilized phases to form flocs which to be much larger and more stable than chemical flocs; that can be separated faster by filtration.

The Langmuir and Freundlich models are commonly used to describe the sorption isotherms of the adsorption processes [14-16]. Where the sorption isotherm is used to describe the mechanism of how adsorbate ions interact on the surface of adsorbent[12]. There are several isotherm equations available to analyze the experimental sorption equilibrium parameters, but the well-known adsorption isotherm models used for single solute systems are Langmuir and Freundlich isotherms[10]. Both adsorption isotherm models are found to be more suitable to describe the relationship between q_e (quantity adsorbed at equilibrium, mg/g) and C_e (concentration of adsorbate remained in the bulky solution at the equilibrium, mg/L).

$$q_e = (C_i - C_e)m/V \quad (6)$$

where C_i and C_e are the initial and equilibrium concentration of adsorbate respectively (mg/L), m is the mass of the adsorbent (g) and V is the volume of the solution (liter).

So, The Langmuir and Freundlich isotherms were tested for the results concerned with the adsorption of lead on aluminum hydroxides flocs at steady state condition.

Langmuir isotherm: It assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface. Once a site is filled, no further sorption can take place at that site. This indicates that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved. The isotherm is represented by:

$$C_e/q_e = (1/b q_{\text{max}}) + C_e/q_{\text{max}} \quad (7)$$

The constants b (L/mg) and q_{max} (mg/g) relate to the energy of adsorption and maximum adsorption capacity corresponding to complete monolayer coverage on the surface [16-19], and their values are obtained from the slope and interception of the plot and are presented in following tables.

Freundlich isotherm: It is introduced as an empirical model, where q_e represents the amount adsorbed per amount of adsorbent at the equilibrium (mg/g), C_e represents the equilibrium concentration (mg/L), and K_f and n parameters that depend on the adsorbate and adsorbent.

$$q_e = K_f C_e^{1/n} \quad (8)$$

Where K_f [(mg/g)(l/mg)^{1/n}] and n are Freundlich constants which correspond to adsorption capacity of the adsorbent [16 ; 20] and adsorption intensity, respectively. Freundlich equilibrium constants were determined from the plot of $\ln q_e$ versus $\ln C_e$ on the basis of the linear form of Freundlich equation. Moreover, The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.

The n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if $n=1$ then adsorption is linear, if $n<1$ then adsorption is a chemical process; if $n>1$, then adsorption is a physical process. The n value in Freundlich equation within the range of 1–10 represent good adsorption [13]. Langmuir and Freundlich adsorption

constants and correlation coefficients (R^2) are presented in the following tables. To find the most appropriate model for the metal ions adsorption; data were fitted to Langmuir and Freundlich isotherm models.

The higher values of R^2 indicate that Langmuir adsorption isotherm was the best model for the metal ions adsorption onto Aluminum hydroxide flocs for different applied currents under conditions of effective surface area of electrodes equals 283cm^2 . The effective weight of flocs (i.e. the weight of adsorbent) was varying along the period of runs with respect to the consumption of each of anode and cathode electrodes which estimated from the modeling of actual anode and cathode consumption responses. To predict the affinity between the adsorbate and adsorbent, Langmuir adsorption isotherm parameter can be used as a dimensionless constant [17] called *separation factor* or *equilibrium parameter* R_L which presented as follows:

$$R_L = 1 / (1 + b C_i) \tag{9}$$

Where b is the Langmuir constant and C_i is the initial concentration. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), linear ($R_L = 1$), unfavorable ($R_L > 1$), or favorable ($0 < R_L < 1$) [3,5,8].

Removal efficiency

High value of removal efficiency predicted under this technique of treatment as shown in (Table 4) and Fig. 3.

Table 4. Removal efficiency

Removal efficiency (%)	
after 15 minutes	after 30 minutes
99.62	99.91

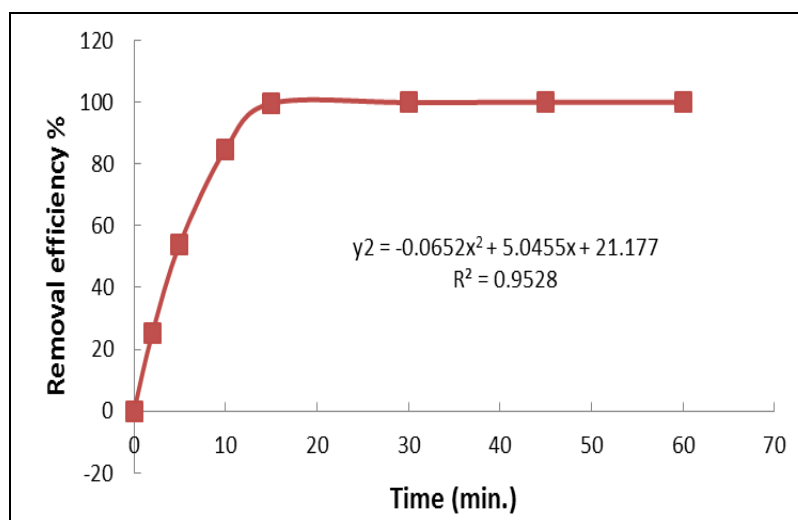
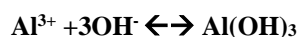


Fig. 3. Removal efficiency of lead from simulated wastewater

The rising of removal efficiency value along the period of experiment are proportional with the increasing of the applied current because of the excess amount of aluminum and hydroxides ions release within the electrocoagulation reactor where flocs are formed due to the polymerization of aluminum oxy-hydroxides.



Moreover, the highest removal efficiency values can be achieved in the medium and minimum solubility of the aluminum hydrolysis products in the specified pH range.

Equilibrium isotherm

In general, adsorption process is a phenomenon intrinsically very fast and essentially limited by the mass transfer of adsorbate towards adsorbent. As mentioned before that Langmuir and Freundlich models are commonly used to describe the sorption isotherms where Freundlich isotherm is used to describe the reversible adsorption and not restricted to monolayer formation as valid by using Langmuir isotherm which assumes uniform energies of sorption on the adsorbent surface and no transmigration of sorbate in the plane of the surface.

At mean values of parameters for different period of time, the isotherm models of Langmuir and Freundlich as follows:

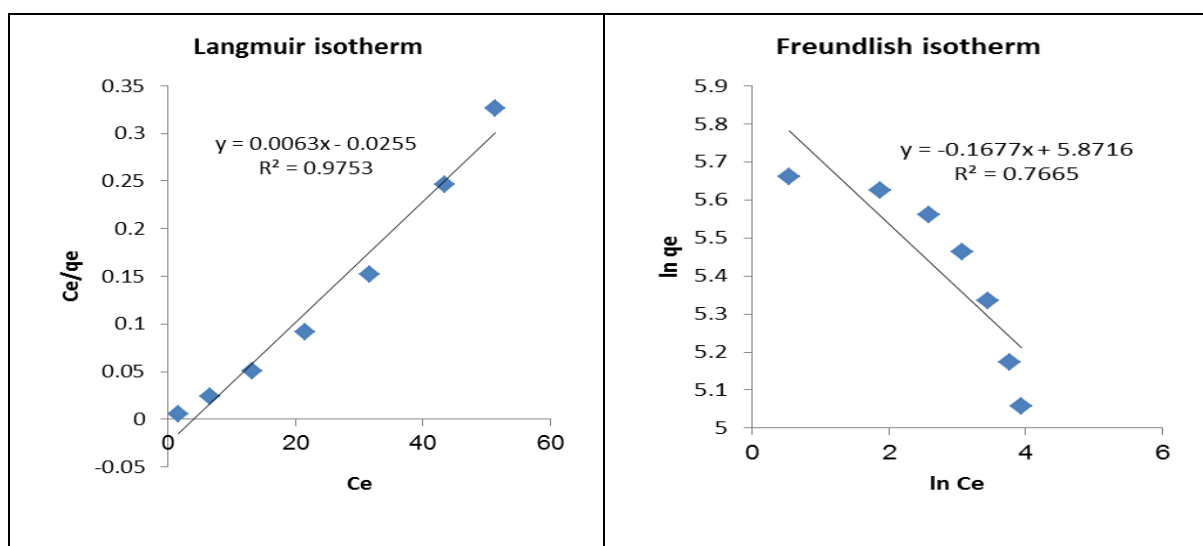


Fig. 4. Langmuir and Freundlich models at mean values of parameters for different values of contact time

Table 5. Langmuir and Freundlich models and their constant at mean parameters values for different values of contact time

Model	Correlation	n	q _{max}	K _f	b	R ²	R _L	Case
Langmuir	y = 0.0063x - 0.0255	----	158.73	----	0.247	0.975	0.025	favorable
Freundlich	y = -0.1667x + 5.872	5.963	-----	354.816	-----	0.766	-----	Physical adsorption

As seen that Langmuir isotherm equation gives a better fit than the Freundlich isotherm model equation. The following equations represent the suggested Langmuir and Freundlich isotherm models for lead removal from simulated wastewater by electrocoagulation process.

Langmuir:
$$q_e = \frac{39.206 C_e}{1 + 0.247 C_e} \quad (10)$$

Freundlich:
$$q_e = 354.82 C_e^{0.168} \quad (11)$$

Figure 5 explains the concentration-time decay curve for Pb (II) adsorption onto flocs at mean other parameters.

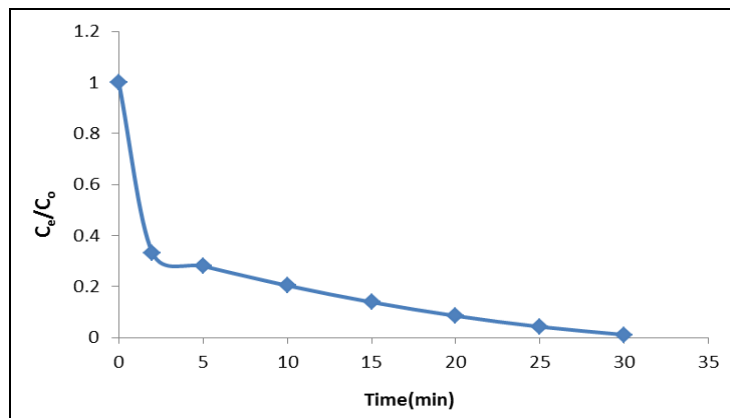


Fig. 5. Concentration-time decay curve for Pb (II) adsorption onto flocs at mean other parameters

The following results explain the calculations and figures of adsorption isotherms for both Langmuir and Freundlich models in case of different values of lead concentrations and applied current for different contact time at mean values of pH and stirring speed.

Table 6. Constants values and determination coefficients of Langmuir and Freundlich models at different values of applied current and contact time, 10 ppm initial metal concentration and mean values of pH and stirring speed

Applied current (Amps)	Langmuir model: $C_e/q_e = (1/b q_{max}) + (C_e/q_{max})$					
	correlation	q_{max}	b	R^2	R_L	Case
0.2	$y = 0.3720x + 0.9884$	2.688	0.377	0.850	0.210	favorable
0.6	$y = 0.1544x + 0.2134$	6.494	0.723	0.874	0.122	favorable
1	$y = 0.0550x + 0.0780$	18.182	0.705	0.948	0.124	favorable
1.4	$y = 0.0189x + 0.1294$	52.632	0.147	0.922	0.405	favorable
1.8	$y = 0.0144x + 0.0849$	71.429	0.165	0.695	0.378	favorable
2.2	$y = 0.0315x + 0.0155$	31.250	2.000	0.834	0.048	favorable
2.6	$y = 0.0383x + 0.0082$	26.316	4.750	0.891	0.021	favorable

Applied current (Amps)	Freundlich model: $\ln q_e = \ln K_f + (1/n) \ln C_e$				
	correlation	n	K_f	R^2	Case
0.2	$y = -0.9294x + 3.4887$	1.075	32.786	0.750	Physical adsorption
0.6	$y = -0.2524x + 4.2437$	3.968	69.686	0.285	Physical adsorption
1	$y = -0.3444x + 4.7976$	2.907	121.268	0.836	Physical adsorption
1.4	$y = -0.6982x + 4.9149$	1.433	136.319	0.996	Physical adsorption
1.8	$y = -0.728x + 4.5718$	1.374	96.737	0.977	Physical adsorption

2.2	$y = -0.1267x + 4.0254$	7.874	55.980	0.607	Physical adsorption
2.6	$y = -0.1497x + 4.0478$	6.667	57.283	0.754	Physical adsorption

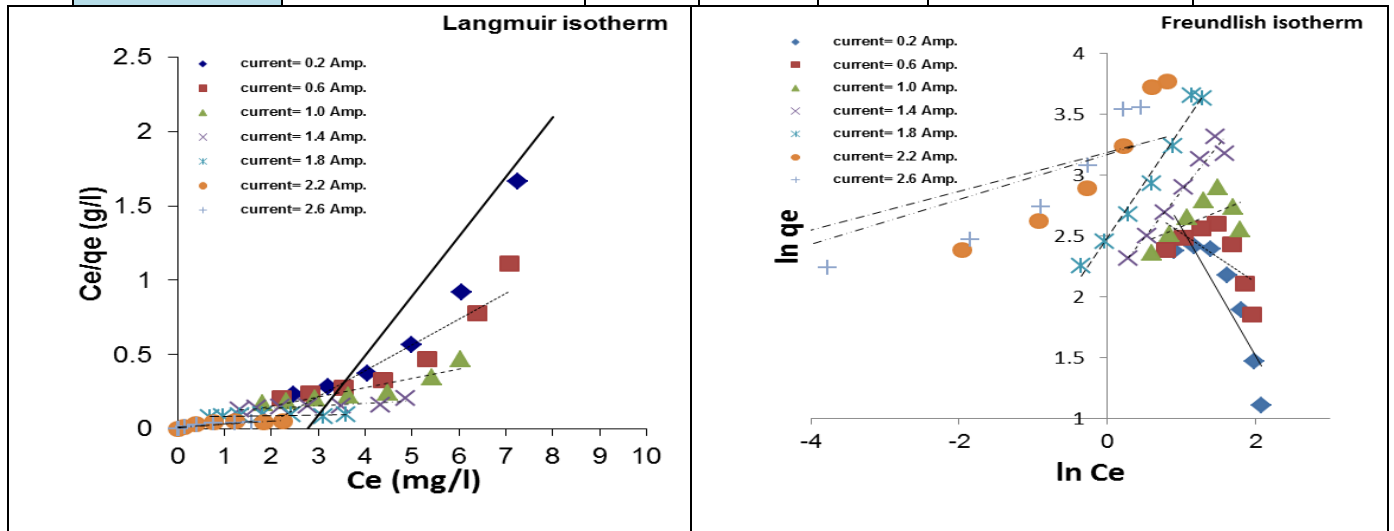


Fig. 6. Langmuir and Freundlich models at different values of applied current and contact time, 10 ppm initial metal concentration and mean values of pH and stirring speed

Table 7. Constants values and determination coefficients of Langmuir and Freundlich models at different values of applied current and contact time, 50 ppm initial metal concentration and mean values of pH and stirring speed

Applied current (Amps)	Langmuir model: $C_e/q_e = (1/b q_{max}) + (C_e/q_{max})$					
	correlation	q_{max}	b	R^2	R_L	Case
0.2	$y = 0.043x + 0.3903$	23.256	0.110	0.889	0.154	favorable
0.6	$y = 0.0194x + 0.0693$	52.632	0.275	0.906	0.068	favorable
1	$y = 0.0075x + 0.0677$	125.000	0.118	0.997	0.145	favorable
1.4	$y = 0.004x + 0.0804$	250.000	0.050	0.908	0.286	favorable
1.8	$y = 0.004x + 0.0485$	250.000	0.082	0.796	0.197	favorable
2.2	$y = 0.0062x + 0.0142$	166.667	0.429	0.852	0.045	favorable
2.6	$y = 0.0078x + 0.0074$	125.000	1.143	0.910	0.017	favorable

Applied current (Amps)	Freundlich model: $\ln q_e = \ln K_f + (1/n) \ln C_e$				
	correlation	n	K_f	R^2	Case
0.2	$y = -0.6014x + 5.6836$	1.664	294.124	0.702	Physical adsorption
0.6	$y = -0.0696x + 4.3874$	14.286	80.399	0.056	Physical adsorption
1	$y = -0.402x + 3.3049$	2.488	27.249	0.988	Physical adsorption
1.4	$y = -0.6142x + 2.9782$	1.629	19.648	0.989	Physical adsorption

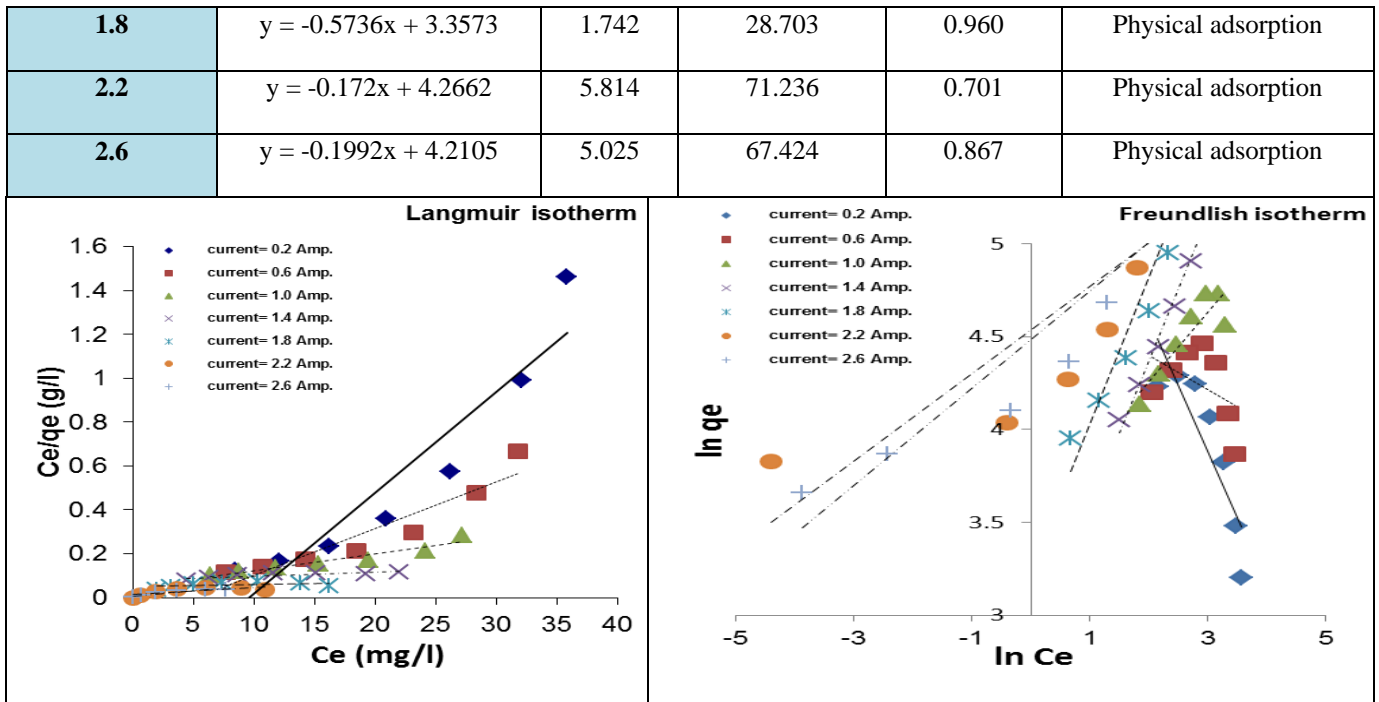


Fig. 7. Langmuir and Freundlich models at different values of applied current and contact time, **50 ppm** initial metal concentration and mean values of pH and stirring speed

Table 8. Constants values and determination coefficients for Langmuir and Freundlich models at different values of applied current and contact time, **100 ppm** initial metal concentration and mean values of pH and stirring speed

Applied current (Amps)	Langmuir model: $C_e/q_e = (1/b q_{max}) + (C_e/q_{max})$					
	correlation	q_{max}	b	R^2	R_L	Case
0.2	$y = 0.0128x + 0.1333$	76.923	0.098	0.925	0.093	favorable
0.6	$y = 0.0060x + 0.0091$	166.667	0.659	0.961	0.015	favorable
1	$y = 0.0035x + 0.0340$	285.714	0.103	0.996	0.089	favorable
1.4	$y = 0.0025x + 0.0410$	400.000	0.061	0.939	0.141	favorable
1.8	$y = 0.0028x + 0.0229$	357.143	0.122	0.885	0.076	favorable
2.2	$y = 0.0034x + 0.0122$	294.118	0.279	0.899	0.035	favorable
2.6	$y = 0.0044x + 0.0057$	227.273	0.772	0.940	0.013	favorable

Applied current (Amps)	Freundlich model: $\ln q_e = \ln K_f + (1/n) \ln C_e$				
	correlation	n	K_f	R^2	Case
0.2	$y = -0.3363x + 6.0339$	2.976	417.339	0.630	Physical adsorption
0.6	$y = -0.0630x + 4.9607$	15.873	142.694	0.162	Physical adsorption
1	$y = -0.3212x + 4.2565$	3.115	70.563	0.992	Physical adsorption

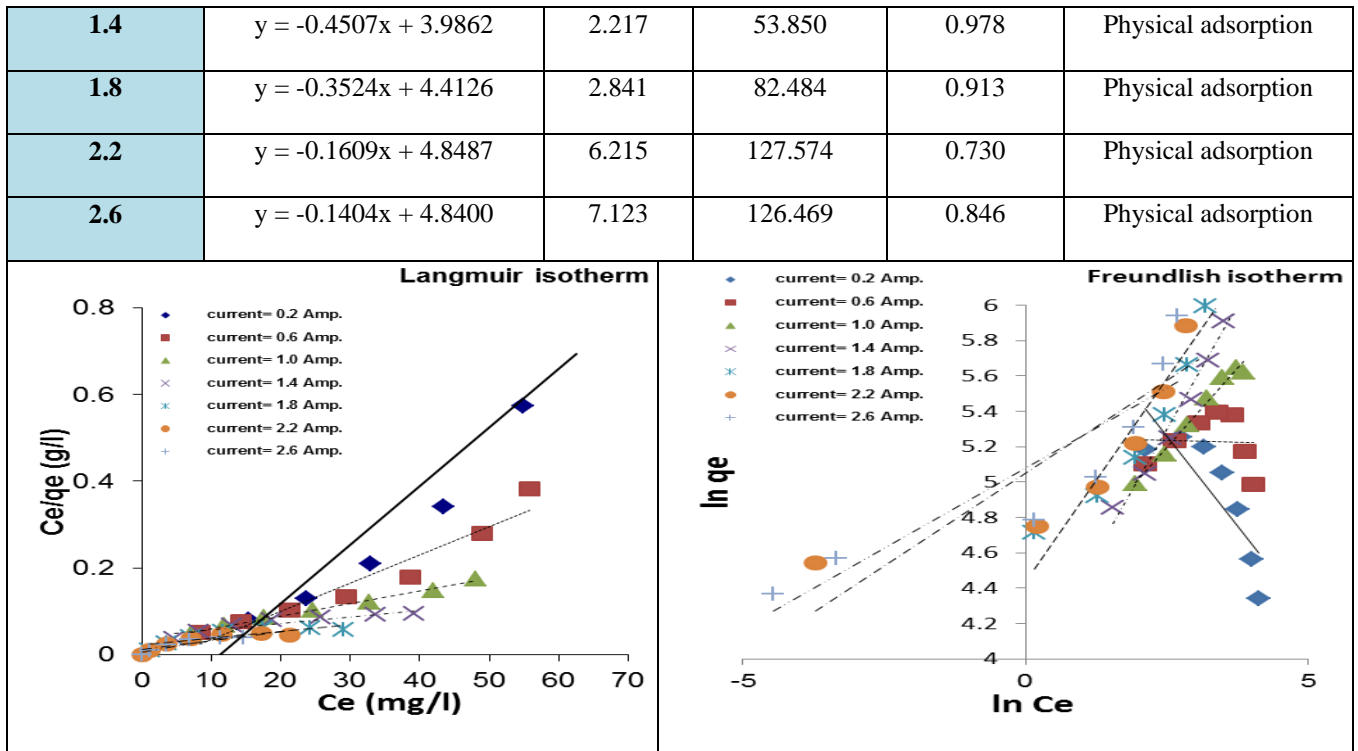


Fig. 8. Langmuir and Freundlich models at different values of applied current and contact time, 100 ppm initial metal concentration and mean values of pH and stirring speed

Table 9. Constants values and determination coefficients for Langmuir and Freundlich models at different values of applied current and contact time, 150 ppm initial metal concentration and mean values of pH and stirring speed

Applied current (Amps)	Langmuir model: $C_e/q_e = (1/b q_{max}) + (C_e/q_{max})$					
	correlation	q_{max}	b	R^2	R_L	Case
0.2	$y = 0.0058x + 0.0453$	172.414	0.128	0.950	0.049	favorable
0.6	$y = 0.0034x + 0.0065$	294.118	0.523	0.983	0.013	favorable
1	$y = 0.0026x + 0.0127$	384.615	0.205	0.996	0.032	favorable
1.4	$y = 0.0022x + 0.0192$	454.545	0.115	0.972	0.055	favorable
1.8	$y = 0.0024x + 0.0129$	416.667	0.186	0.943	0.035	favorable
2.2	$y = 0.0027x + 0.0101$	370.370	0.267	0.946	0.024	favorable
2.6	$y = 0.0034x + 0.0051$	294.118	0.667	0.966	0.010	favorable

Applied current (Amps)	Freundlich model: $\ln q_e = \ln K_f + (1/n) \ln C_e$				
	correlation	n	K_f	R^2	Case
0.2	$y = -0.115x + 5.9188$	8.696	371.965	0.411	Physical adsorption
0.6	$y = -0.0465x + 5.5683$	21.505	261.988	0.262	Physical adsorption

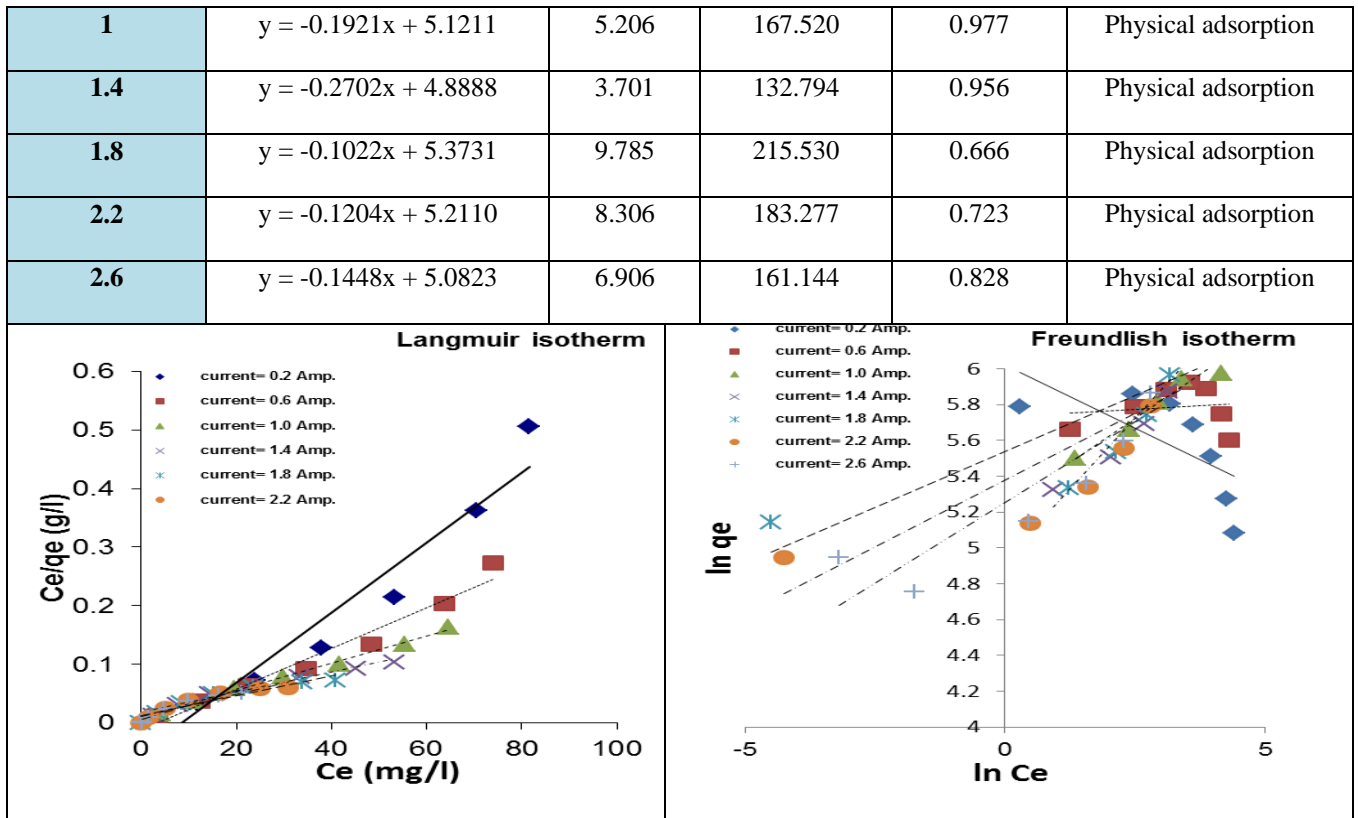


Fig. 9. Langmuir and Freundlich models at different values of applied current and contact time, 150 ppm initial metal concentration and mean values of pH and stirring speed

Table 10. Constants values and determination coefficients for Langmuir and Freundlich models at different values of applied current and contact time, 200 ppm initial metal concentration and mean values of pH and stirring speed

Applied current (Amps)	Langmuir model: $C_e/q_e = (1/b q_{max}) + (C_e/q_{max})$					
	correlation	q_{max}	b	R^2	R_L	Case
0.2	$y = 0.0038x + 0.0326$	263.158	0.117	0.958	0.041	favorable
0.6	$y = 0.0028x + 0.0106$	357.143	0.264	0.979	0.019	favorable
1	$y = 0.0023x + 0.0023$	434.783	1.000	0.997	0.005	favorable
1.4	$y = 0.0021x + 0.0085$	476.190	0.247	0.991	0.020	favorable
1.8	$y = 0.0022x + 0.0100$	454.545	0.220	0.979	0.022	favorable
2.2	$y = 0.0026x + 0.0082$	384.615	0.317	0.976	0.016	favorable
2.6	$y = 0.0031x + 0.0044$	322.581	0.705	0.984	0.007	favorable

Applied current (Amps)	Freundlich model: $\ln q_e = \ln K_f + (1/n) \ln C_e$				
	correlation	n	K_f	R^2	Case
0.2	$y = -0.0372x + 6.0368$	26.882	418.552	0.234	Physical adsorption

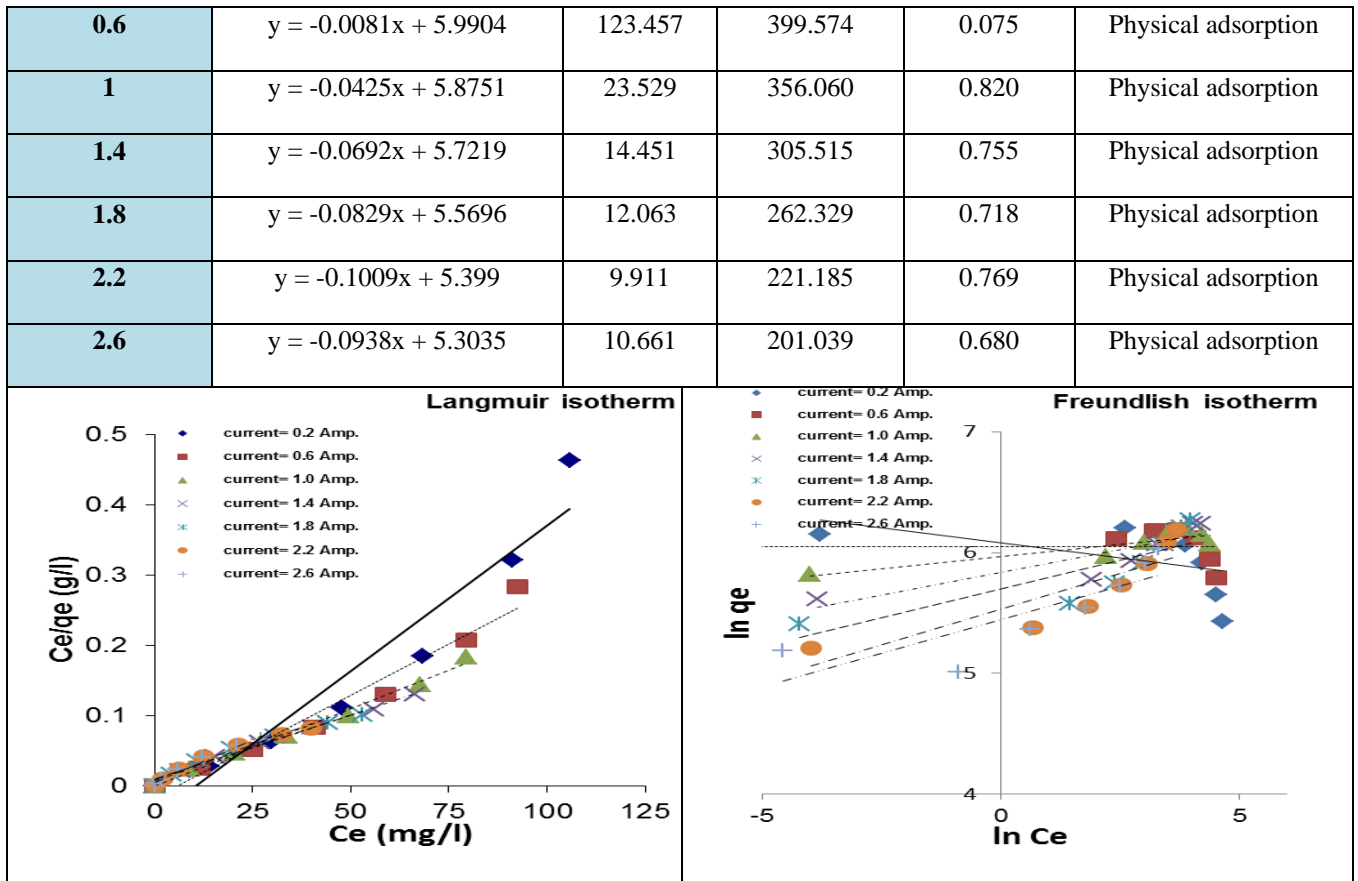


Fig. 10. Langmuir and Freundlich models at different values of applied current and contact time, 200 ppm initial metal concentration and mean values of pH and stirring speed

Table 11. Constants values and determination coefficients for Langmuir and Freundlich models at different values of applied current and contact time, 250 ppm initial metal concentration and mean values of pH and stirring speed

Applied current (Amps)	Langmuir model: $C_e/q_e = (1/b q_{max}) + (C_e/q_{max})$					
	correlation	q_{max}	b	R^2	R_L	Case
0.2	$y = 0.0034x + 0.042$	294.118	0.081	0.937	0.047	favorable
0.6	$y = 0.0027x + 0.0173$	370.370	0.156	0.971	0.025	favorable
1	$y = 0.0023x + 0.0032$	434.783	0.719	0.993	0.006	favorable
1.4	$y = 0.0022x + 0.0043$	454.545	0.512	0.998	0.008	favorable
1.8	$y = 0.0023x + 0.008$	434.783	0.288	0.995	0.014	favorable
2.2	$y = 0.0026x + 0.0062$	384.615	0.419	0.991	0.009	favorable
2.6	$y = 0.003x + 0.0038$	333.333	0.789	0.993	0.005	favorable

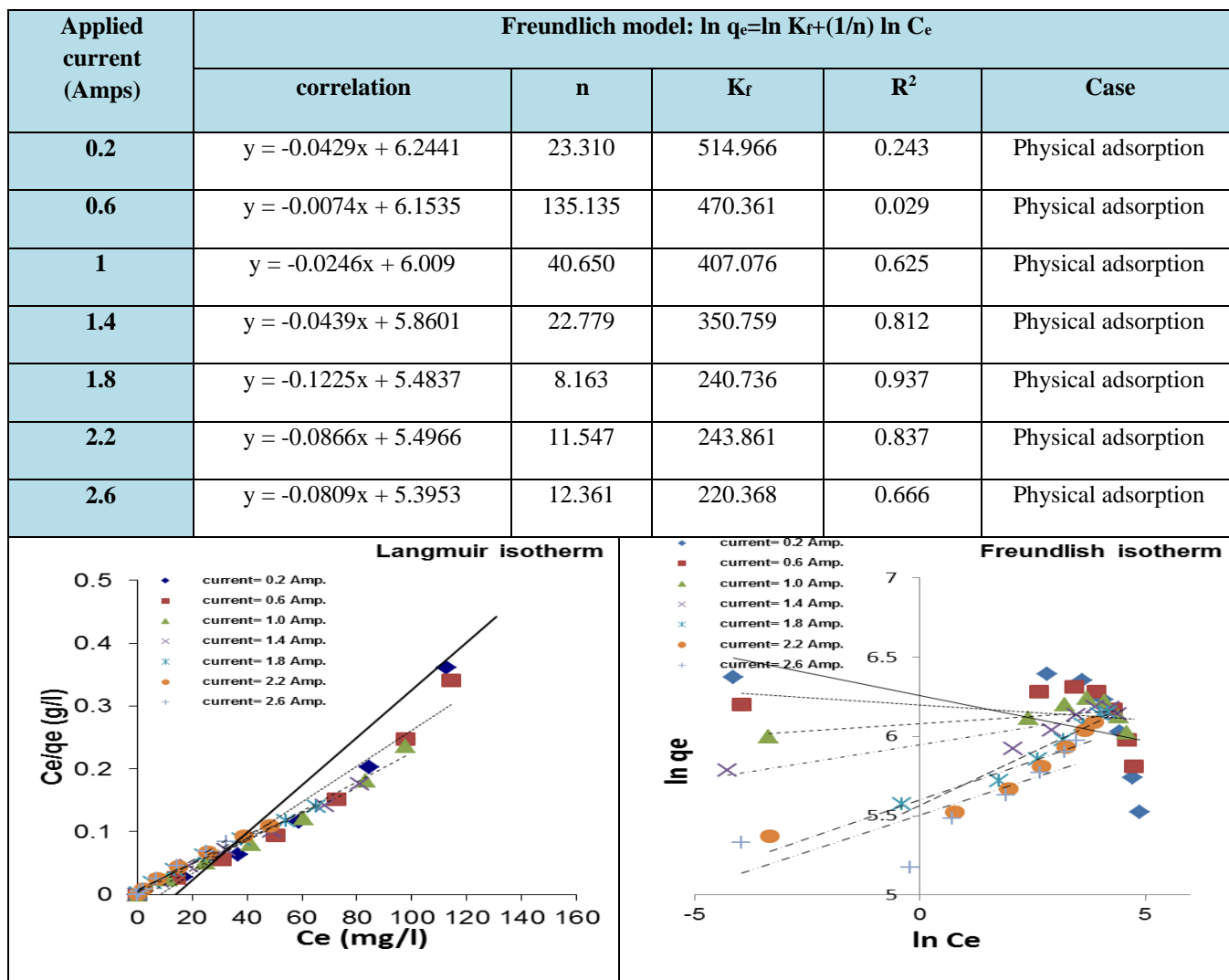


Fig. 11. Langmuir and Freundlich models at different values of applied current and contact time, 250 ppm initial metal concentration and mean values of pH and stirring speed

Table 12. Constants values and determination coefficients for Langmuir and Freundlich models at different values of applied current and contact time, 300 ppm initial metal concentration and mean values of pH and stirring speed

Applied current (Amps)	Langmuir model: $C_e/q_e = (1/b q_{max}) + (C_e/q_{max})$					
	correlation	q_{max}	b	R^2	R_L	Case
0.2	$y = 0.0033x + 0.0541$	303.030	0.061	0.929	0.052	favorable
0.6	$y = 0.0028x + 0.0252$	357.143	0.111	0.966	0.029	favorable
1	$y = 0.0025x + 0.0093$	400.000	0.269	0.988	0.012	favorable
1.4	$y = 0.0024x + 0.0001$	416.667	24.000	0.998	0.0001	favorable
1.8	$y = 0.0025x + 0.0105$	400.000	0.238	1.000	0.014	favorable
2.2	$y = 0.0026x + 0.0211$	384.615	0.123	1.000	0.026	favorable

2.6	$y = 0.0027x + 0.0234$	370.370	0.115	0.991	0.028	favorable
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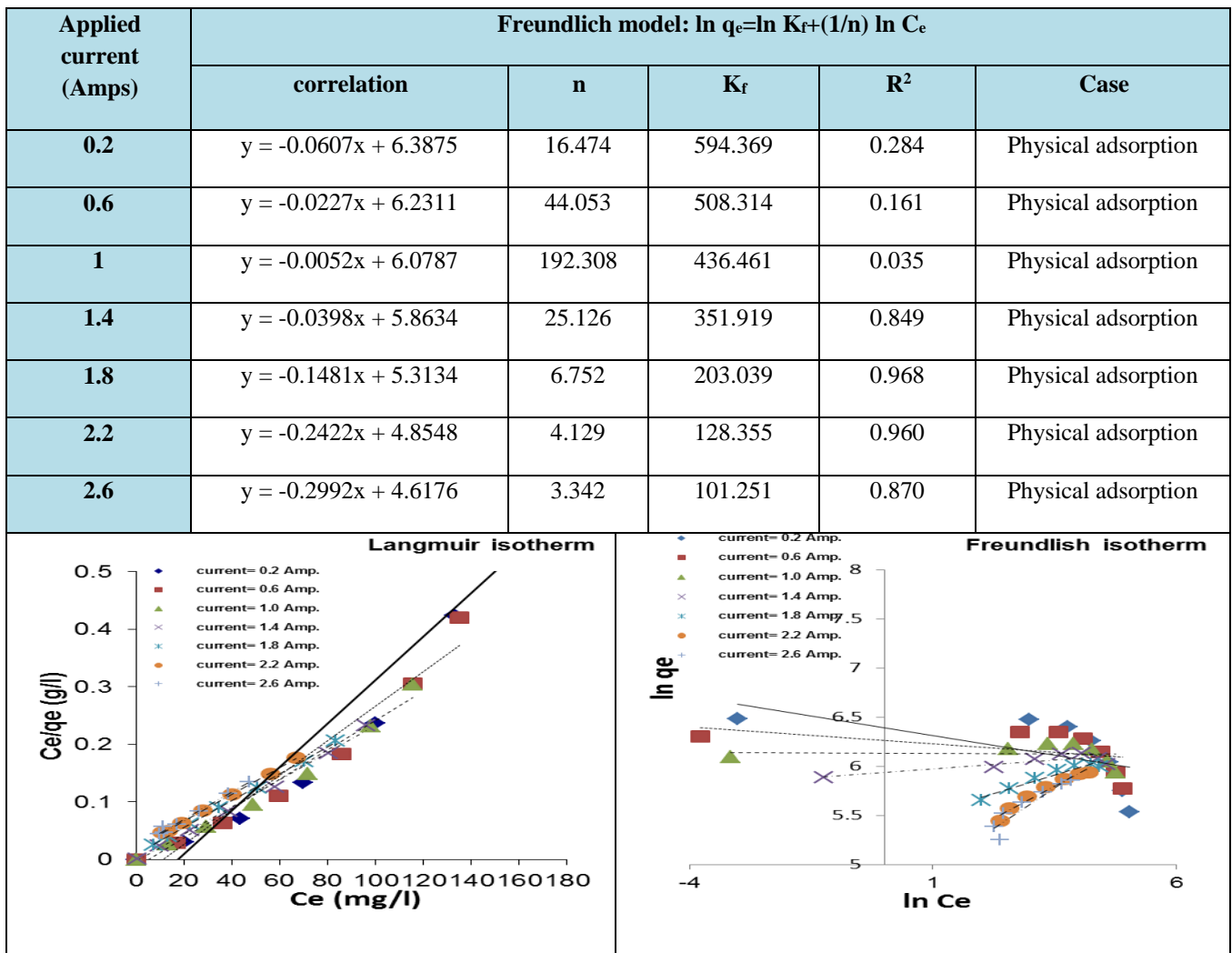


Fig. 12. Langmuir and Freundlich models at different values of applied current and contact time, 300 ppm initial metal concentration and mean values of pH and stirring speed

Adsorption kinetics modeling

Numerous kinetic models were suggested to describe the reaction order of any adsorption systems based on solution concentration. Kinetic models based on the capacity of the adsorbent have also been presented, such as the Lagergren's first-order equation and Ho's second-order expression[21].

In the present batch design, the adsorption kinetic models are required to predict in the process of heavy metals removal from the simulated wastewater electrocoagulation.

1. Pseudo-first order model:

The pseudo-first order model is widely used for the adsorption of a solute from an aqueous solution [22]. The pseudo-first-order equation is expressed as follows:

$$\text{Log}(q_e - q_t) = \text{log } q_e - (k_1 / 2.303) t \tag{12}$$

where the rate constant (k_1) is calculated from the slope of the straight line in the following result figure.

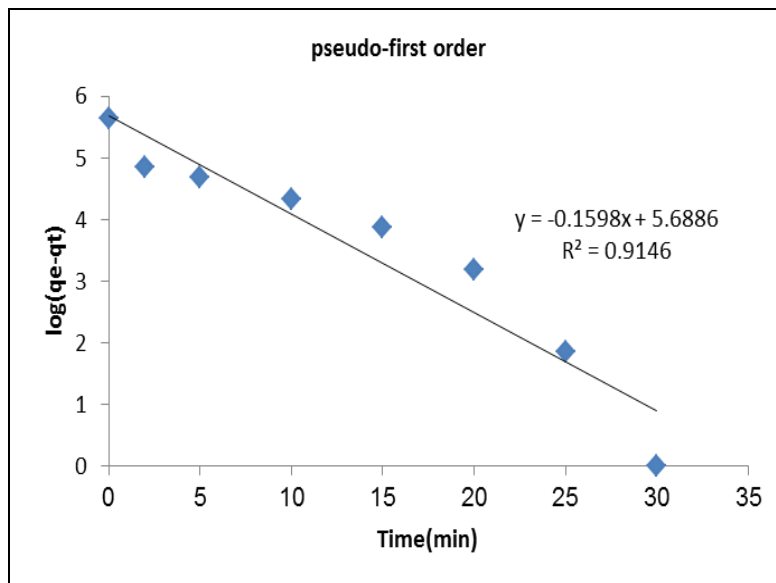


Fig. 13.: Pseudo-first order model plot of adsorption of lead on flocs by electrocoagulation

2. Pseudo-second order model:

The pseudo-second-order equation predicts the behavior over the whole range of adsorption which based on the equilibrium adsorption capacity on the adsorption capacity of the adsorbent. The following equation is the form of that model.

$$(t/q_t) = (1/k_2'q_e^2) + (1/q_e) t \tag{13}$$

where k_2' ($g\ mg^{-1}\ min^{-1}$) is the rate constant of pseudo-second order adsorption. The following plot shows the result of that model.

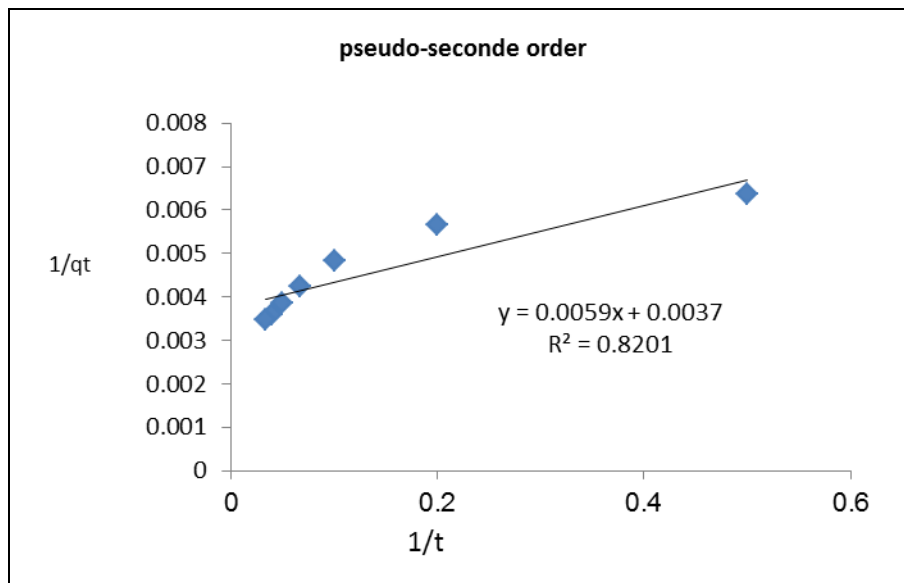


Fig. 14.: Pseudo-second order model plot for the adsorption of lead on flocs by electrocoagulation

Intra-particle diffusion

The intra-particle diffusion model is used to explore the intra-particle diffusion as follows:

$$q_t = K_{dif} t^{1/2} \tag{14}$$

where K_{dif} is the intra-particle diffusion rate constant which is estimated from the slope of the following figure. Moreover, intra-particle diffusion is the rate-controlling step if the line passes through the origin [22].

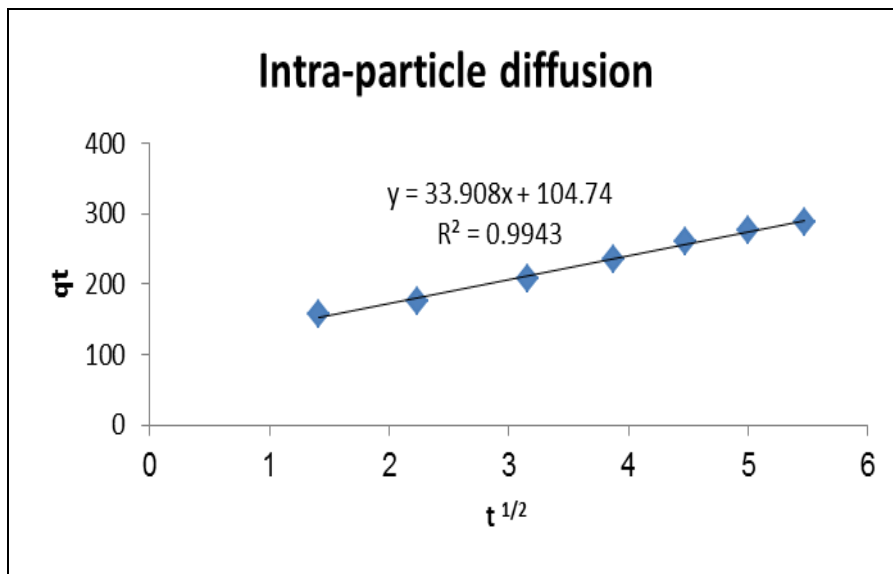


Fig. 15.: The intra-particle diffusion model plot for the adsorption of lead on flocs by electrocoagulation

The following table explains the summary of adsorption kinetics models and the intra-particle diffusion equation.

Table 13. Summary of adsorption kinetics modeling

Kinetics type	Model	constants	R ²
Pseudo-first order	Y= -0.1598 x + 5.6886	k ₁ ' = 0.368(1/min)	0.9146
Pseudo-second order	Y= 0.0059 x + 0.0037	k ₂ ' = 0.797(g/mg.min)	0.8201
Intra-particle diffusion	Y= 33.908 x +104.74		0.9943

Thermodynamics study:

To estimate the values of the basic heat adsorption (ΔH), thermodynamic functions Gibbs energy (ΔG), and the change in entropy (ΔS) of the adsorption process. At mean values of other parameters, temperature variation with time had been studied as shown its behavior and correlation in Fig. 1.

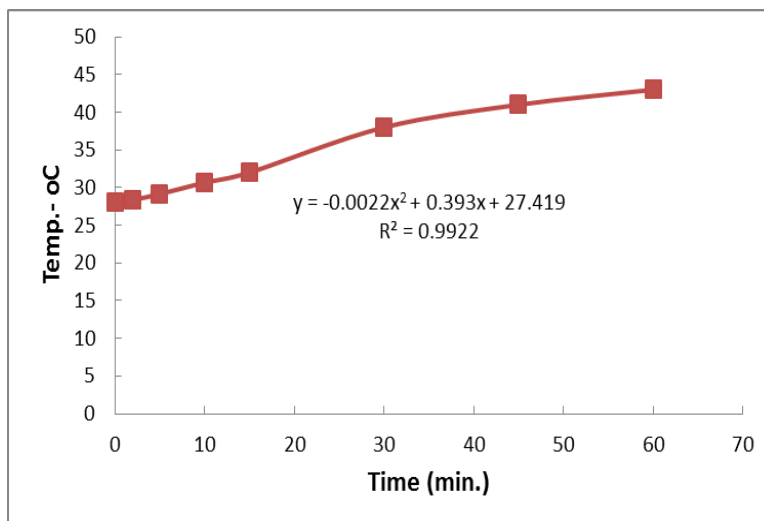


Fig. 16.: Temperature variation vs. time at mean other parameters in the electrocoagulation cell

The correlation that relates the temperature with time is shown in equation (1) as follows:

$$\text{Temp.}(^{\circ}\text{C}) = -0.0022(\text{time})^2 + 0.393(\text{time}) + 27.419 \quad (15)$$

The equilibrium constant (K_d) at each temperature is [17]:

$$K_d = \frac{q_e V}{C_e m} \quad (16)$$

Where

q_e : the magnitude adsorbate in (mg/g),

C_e : the concentration of the adsorbate at the equilibrium (mg/L).

V : volume of liquid phase (0.5 liter)

W : weight of adsorbent (i.e. flocs) (g)

The heat of adsorption (ΔH) estimated by using the *Van't Hoff* equation:

$$\text{Log } K_d = -(\Delta H/2.303 RT) + \text{constant} \quad (17)$$

The values of ($\log K_d$) are plotted versus ($1/T$) as listed their values in (Table 14) to produce a straight line with slop ($-\Delta H/2.303R$) as shown in Fig. 17.

Table 14. Calculations of Van't Hoff equation to estimate the value of ΔH at mean other parameters

Time (min.)	Temp. °C	Temp. K	q_e/C_e	m(g)	K_d	1/T	Log K_d
2	28.196	301.196	3.257	0.310	5.262	0.0033	0.721
5	29.329	302.329	4.285	0.300	7.149	0.0033	0.854
10	31.129	304.129	6.821	0.286	11.915	0.0033	1.076
15	32.819	305.819	11.222	0.277	20.290	0.0033	1.307
20	34.399	307.399	19.912	0.271	36.795	0.0033	1.566
25	35.869	308.869	42.158	0.268	78.540	0.0032	1.895
30	37.229	310.229	166.841	0.270	309.031	0.0032	2.490

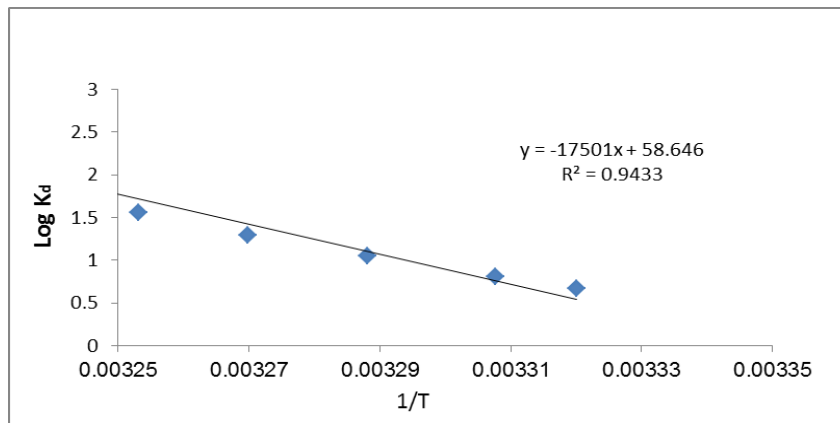


Fig. 17. Estimation of ΔH at mean other parameters

The value of ΔH could be calculated from the slope of Fig. 17, where the value of gas constant R is 8.314 J/K.mol . Other values of Gibbs energy ΔG and the change in entropy ΔS could be estimated according to the following equations [21]:

$$\Delta G = -RT \ln K_d \tag{18}$$

$$\Delta G = \Delta H - T\Delta S \tag{19}$$

Table explain the estimated values of ΔG and ΔS for different values of temperature.

Table 15. Values of thermodynamics parameters

Temp. °C	Temp. K	ΔH (J/mol)	ΔG (J/mol)	ΔS (J/mol)
28.196	301.196	335094.1	-4158.105	1125.310
29.329	302.329		-4944.167	1123.843
31.129	304.129		-6265.283	1121.789
32.819	305.819		-7653.527	1120.377
34.399	307.399		-9214.293	1119.927
35.869	308.869		-11205.475	1121.246
37.229	310.229		-14787.943	1128.039

The positive sign of ΔH refers that operation is endothermic which requires a perceivable energy that can be added by the electricity as in the electrocoagulation process. While the negative sign of ΔG refers to the process to be considered as spontaneous nature, where more negative values reflect a more energetically favorable adsorption process. Moreover, the positive value of ΔS is attributed to random of irregularity at the liquid- solid interaction [17 ; 24; 25].

Conclusions

The results showed that adsorption phenomenon via electrocoagulation technique is more effective and give high removal efficiency for several values of applied current along periods of experiments. At mean values of parameters for different period of time, the isotherm models of Langmuir and Freundlich are:

Langmuir: $q_e = \frac{39.206 C_e}{1+0.247 C_e}$

Freundlich: $q_e = 354.82 C_e^{0.168}$

Moreover, for other conditions, both isotherm models can be applied according to the specified conditions. The adsorption process follows pseudo-first order kinetics and the intra-particle diffusion studied graphically. The result shows that the adsorption process of lead was spontaneous and endothermic in nature.

It is confirmed that electrocoagulation cell is more efficient to generate aluminum hydroxide which adsorbed lead presented in the simulated wastewater.

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