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Isotherm, Kinetic and Thermodynamic of Adsorption of Heavy Metal Ions onto Local Activated Carbon

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Abstract

In this work, the adsorption isotherm, Kinetic and thermodynamic of removal of Fe^{3+}, Cu^{2+}, Pb^{2+} and Zn^{2+}) ions by activated carbon produced from rice husk were studied. The results shown that the Freundlich isotherm model achieved best fit with the equilibrium adsorption data for adsorption of (Fe^{3+}, Cu^{2+} and Pb^{2+}) ions, it is indicates to multilayer adsorption nature of these metal ions on RHAC. The adsorption capacity (K_f) of the adsorbent have a value of (312.1, 628.93 and 162.66 mg/g) for (Fe^{3+}, Cu^{2+} and Pb^{2+}), respectively. The Langmuir isotherm model gives best fit with the equilibrium adsorption data, it is instated to monolayer adsorption nature of (Zn^{2+}) ions on RHAC. The monolayer adsorption capacity (Q) have a value of (714.285 mg/g). The adsorption kinetics were followed the pseudo-second-order model, this model gives the best- fit to experimental data for all heavy metal ions which studied in this work. which have highest correlation coefficient values of (0.988 ,0.996 ,0.999 and 0.9232) for (Cu^{2+}, Fe^{3+}, Pb^{2+} and Zn^{2+}), respectively. Also, the adsorption thermodynamic showed that the adsorption of heavy metal ions becomes more feasibility with increasing in temperature due to negative values of ΔG. The adsorption process is endothermicdue to positive values of ΔH.

Keyword: Activated carbon, Adsorption, Isotherm, kinetic, Thermodynamic, Heavy metal ions, Rice husk

1. Introduction

The contamination of water by heavy metal ions has increased over the last few decades due to industrial processes such as petroleum refinery process and the development of new technology in refining of petroleum (Ambursa et al., 2011). Commonly encountered metals of concern include Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} etc. These metals are toxic in both their chemically combined forms as well as the elemental form. Exposure to these contaminants present even in low concentrations in the environment can prove to be harmful to the human health. In order to solve heavy metal pollution in the environment, it is important to bring applicable solutions. Some in place treatment technologies available for the removal of heavy metal ions from aqueous solutions are chemical precipitation, ion exchange, coagulation, and bioremediation and sorption/ adsorption. Of all these techniques adsorption at solid substrate is preferred because of its high efficiency, easy handling and cost effectiveness as well as availability of different adsorbents (Baskaranet al., 2010). Activated carbon (AC) is still the main noted adsorbent for the removal of pollutants from polluted gaseous and liquid streams. The high adsorption capacity is mainly due to the high surface area and the existence of functional groups on its active sites. The challenge in utilizing AC is, however, to cater to the demands with reasonable costs for end-users. AC production costs can be reduced by either choosing a cheap raw material and/or by applying a proper production method (Alkhatib et al., 2011). Rice husk is an agricultural waste material, This is in accordance with the increase in world population since paddy is the staple food in many countries, a hard protecting coverings of grains of rice obtained from the threshing of the rice and constitutes about 20% of 650 million tons of rice produced annually in the world (Lau et al., 2011; Dada et al., 2012).

In this work. The adsorption isotherm, Kinetic and thermodynamic of heavy metal ions onto activated carbon produced from rice husk were studied.

The study of adsorption kinetics is significant as it provides valuable insights into the reaction pathways and the mechanism of the reactions. Several kinetic models are used to explain the mechanism of the adsorption processes (Mohammadi et al., 2010).Therefore, it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate adsorption treatment plants. To develop adsorption kinetics, a knowledge of the rate law describing the sorption system is required. The rate law is determined by experimentation (Ho, 2006; Ho & McKay, 1998). In this manner, the zero, first, second (FOGLER, 2006), third order (Ho et al., 2000), pseudo first, pseudo second order (Panneerselvam et al., 2009), Intraparticle diffusion (Safa & Bhatti, 2011), Elovich (Srihari & Das, 2008) and the First order reversible (Al-Jomaa, 2011), Kinetic equations were used to describe the experimental data.

Adsorption isotherm is a functional expression that correlates the amount of solute adsorbed per unit weight of the adsorbent and the concentration of adsorbate in bulk solution at a given temperature under equilibrium conditions. It is important to establish the most appropriate correlations for the batch equilibrium data using empirical or theoretical equations as it plays a functional role in predictive modeling procedures for analysis and design for adsorption systems. Several equilibrium models have been developed and employed for such analysis. However, no general model has been found to fit the experimental data accurately under any given condition (Somasundaram et al., 2013). For this purpose, the Langmuir (Safa & Bhatti, 2011), the Freundlich (Kumagai et al., 2010), Temkin (Dada et al., 2012) and the D-R (Katal et al., 2012), isotherm equations were used to describe the experimental data.

2. Experimental Section

2.1 Materials

Zinc Chloride with purity (97%), Phosphoric acid purity (85 %) and Sodium Hydroxide with purity (97.5%) was supplied from THOMAS BAKER (Chemicals) Company. Copper chloride anhydrous with purity (99%) was supplied from BDH (Chemicals) Company . Iron nitrate (ferric nitrate) with purity (99%) was supplied from MERCK Company. Hydrogen chloride with purity (37 %) was supplied from Scharlab.S.L Company. Nitrogen gas with purity (90%) and Carbon Dioxide gas with purity (95 - 99 %) was supplied from Basrah Factory. Rice Husks were collected from Almshgab City Al-najafALashraf, Iraq, which had been discarded as waste from rice cultivation. Thousands of tonnes were disposal in the above place causing a big problem to environment.

2.2 Adsorbent

Activated carbon produced from rice husk (RH) by physical method was used as an adsorbent material in this study , the preparation method was described following :

Initially, the (RH) were well washed with distilled water and dried in electrical oven for 24 hours. The carbonization step was carried out in electrical furnace for 2hr at 500Ċ and heating rate of 30 ºC/min in absence air using nitrogen (N_2) at flow rate is 200 L/min.

In the activation step, the product from carbonization step was activated by passing carbon dioxide (CO_2) instead of nitrogen for 2hr at 700Ċ.

Table 1. Characteristics of the adsorbent

BET surface area m^2/g	Bulk density g/cm^3	Particle density g/cm^3	Porosity	Pore Volume cm^3/g	pH
201.1518	0.2553	1.4369	0.8223	3.6876	9.3

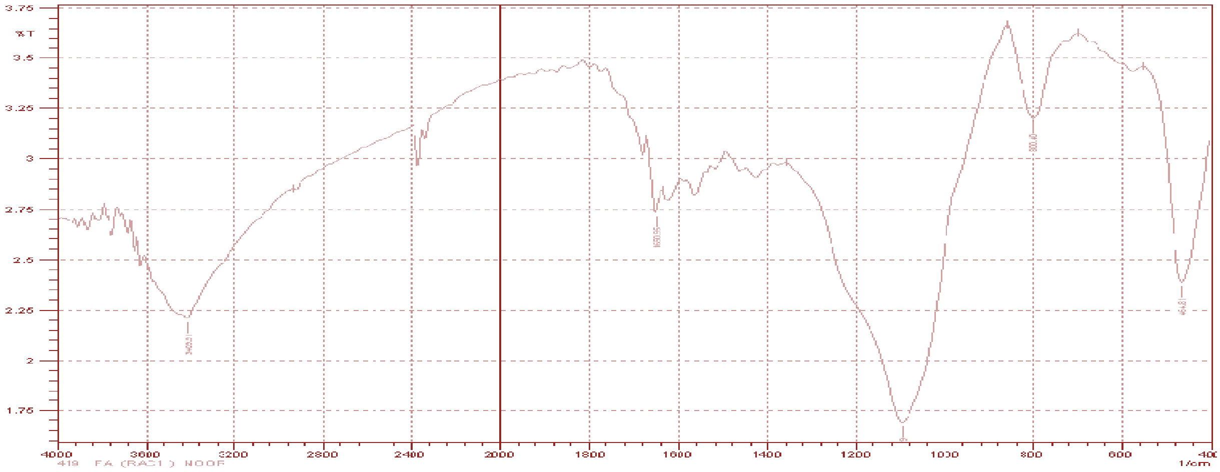

Figure 1. FTIR spectra of adsorbents

2.3 Adsorbate

After measuring the concentrations of heavy metal ions in waste oil water from different locations (West Qurna, Nahran Bin Umer, Barjessia) by using atomic absorption , were found that different concentrations as shown in Table 2.

Table 2. Heavy metal ions concentration in different oil location in Basrah city

Location	Cu^{2+}	Fe^{3+}	Pb^{2+}	Zn^{2+}
Nahran Bin Umer	**2.3**	**7.2**	**4**	**42**
West Qurna	**0.5**	**2.4**	**3**	**7.4**
Barjessia	**4**	**3.6**	**4.5**	**16.2**

For simulated waste oil water, solutions were prepared with lower and higher concentrations of these four heavy metal ions in the locations mentioned above.

2.4 Preparation of Standard Solutions

The stock solutions of 1000 mg/L (ppm) of Cu^{2+}, Fe^{3+}, Pb^{2+} and Zn^{2+} were prepared by dissolving 2.1368 g of $CuCl_2$, 7.3073 g of $Fe(NO_3)_3$, 1.3557 g of $PbCl_2$ and 2.1273 g of $ZnCl_2$ in 1000 ml volumetric flasks and fill up to the mark with distilled water. And then a certain volume (10 ml) of oil has been added to all above solution with efficient agitation.

2.5 Analyze a Sample of Heavy Metal Ions by Using Atomic Absorptions Pectrophotometer (AAS)

The concentration of metal ions was measured by using atomic absorption spectrophotometer (BUCK Scientific, Model 210 VGP). In atomic absorption spectroscopy, metal atoms were vaporized into a flame, and the metal vapor absorbed radiation from the specific hollow cathode lamp in proportion to the number of atoms present. Beer's Law was followed in the part-per-million range (remember that ppm means mg of metal/liter of solution).

2.6 Saturation Time

The saturation time are determined for adsorption of heavy metal ions on the RHAC with different dosage while the other operational parameters were kept constant at initial concentration (50 ppm), pH (3), rotation speed (600 rpm), particle size (0.3 mm), temperature (25 Ċ). The experimental data are presented in Figure 2 and Table 3.

2.7 Adsorption Studies

Batch equilibrium studies were carried out in (125 ml) flaskusing 100 mL of (50 ppm) of metal bearing solution with a certain dosage of the AC. The flasks were agitated in an isothermal water-bath (MemmertGmbh Type WMB 22) at 25Ċ until equilibrium was reached. The pH values were controlling by adding 0.1 N NaOH or 0.1 N HCl. And mixed at 600 rpm using Variable-Speed Benchtop, model 5850, Eberbach. Before the metal solution analyzed using AAS was filtered through filter paper.

The amount of equilibrium adsorption, Q_e and Q_t (mg/g) were calculated by:

$$Q_t = \frac{(C_i - C_t)V}{W} \quad (1)$$

$$Q_e = \frac{(C_i - C_e)V}{W} \quad (2)$$

Where:

Q_e and Q_t (mg/g) are the adsorption capacities at equilibrium and at time t (min), respectively. C_i and C_e are the liquid-phase concentrations of metal ions at initial and equilibrium (mg/L) respectively. V is the volume of the solution (L), W is the weight of adsorbent (g).

3. Results and Discussion

3.1 Adsorption Isotherm

Adsorption equilibrium is the set of conditions at which the number of molecules arriving on the surface of the adsorbent equals the number of molecules that are leaving.

The relation between the amount of substance adsorbed by an adsorbent (solid) and the equilibrium concentration of the substance at constant temperature is called the adsorption isotherm (Theodore and Ricci, 2010).

For determining the adsorption isotherm several models have been suggested such as the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models.

The applicability of the isotherm equation to the adsorption study done was compared by judging the correlation coefficients (R^2) (Tan, 2008).

3.1.1 The Langmuir Isotherm

This isotherm describes adsorbate–adsorbent systems in which the extent of adsorbate coverage is limited to one molecular layer. Although the isotherm, proposed originally by Langmuir (1918).

The Langmuir model was assumed each adsorbate molecule occupies only one site, surface is homogeneous, a single molecule occupies a single surface site and adsorption on surface is localized (Do, 1998).

The linear form of the Langmuir isotherm equation is given as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_\circ K_l} + \frac{1}{Q_\circ} C_e \qquad (3)$$

Where:

$Q_\circ$ and K_l are Langmuir constants related to the monolayer adsorption capacity of the adsorbent (mg/g) it is the maximum amount adsorbed and the rate of adsorption (L/mg), respectively.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L). This parameter is defined by (Tan, 2008; Surchi, 2011):

$$R_L = \frac{1}{1+K_l C_\circ} \qquad (4)$$

If $R_L > 1$ unfavorable adsorption, $R_L = 1$ linear adsorption, $0 < R_L < 1$ favorable adsorption and $R_L = 0$ irreversible adsorption.

3.1.2 The Freundlich Isotherm

The Freundlich equation is very popularly used in the description of adsorption of organics from aqueous streams onto activated carbon[Do, 1998].

This equation takes the following form:

$\mathrm{C} = KP^{1/n}$ **(5)**

The well-known logarithmic form of the Freundlich isotherm is given by the following equation:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \qquad (6)$$

where *:*

K_f and n are Freundlich constants with n giving an indication of how favorable the adsorption process is. K_f is the adsorption capacity of the adsorbent which can be defined as the adsorption or distribution coefficient and represents the quantity of adsorbed onto adsorbent for a unit equilibrium concentration.

3.1.3 Dubinin-Radushkevich (D-R) Isotherm

Dubinin, Polanyi, and Radushkevich suggested about 1947 a simple but very useful empirical theory allowing one to calculate the amount of gas adsorbed in a microporous sorbent. The theory was based on a pore filling model (Keller & Staudt, 2005).

The linear form of the ***(D-R)*** isotherm equation is given as (Chowdhury et al., 2010):

$$\ln Q_e = \ln Q_\circ - K_{DR}\varepsilon^2 \qquad (7)$$

The ε parameter is calculated from:

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \qquad (8)$$

Where: K_{DR} is D-R constant ($mmol^2/J^2$), ε is Polanyi potential (J $mmol^{-1}$), R is universal gas constant (8.314 J/mol^1K^1) and T is temperature (K).

3.1.4 Temkin Isotherm

Another empirical equation is the Temkin equation proposed originally by Temkin (1935) Temkin and Pyzhevwere considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions (Tan, 2008; Surchi , 2011).

The linear form of the Temkin isotherm equation is given as (Chowdhury et al., 2010):

$$Q_e = B_T\ln K_T + B_T\ln C_e \qquad (9)$$

$$b_T = \frac{RT}{B_T} \qquad (10)$$

Where :K_T is Temkin adsorption potential(L/g), $B_T\&b_T$ are Temkin constant.

3.1.5 Saturation Time

The adsorption reached to equilibrium state at saturation time, the equilibrium time indicated to the maximum adsorption capacity of the adsorbent under identified operating conditions, no more H.M.I. was further removed from the solution.

Table 3. The saturation time of adsorption of H.M.I. on RHAC

Dose H.M.I.	1g/100ml Time min	2g/100ml Time min	3g/100ml Time min	4g/100ml Time min
Cu^{2+}	75	30	45	30
Fe^{3+}	45	25	25	30
Pb^{2+}	45	15	15	20
Zn^{2+}	30	15	15	15

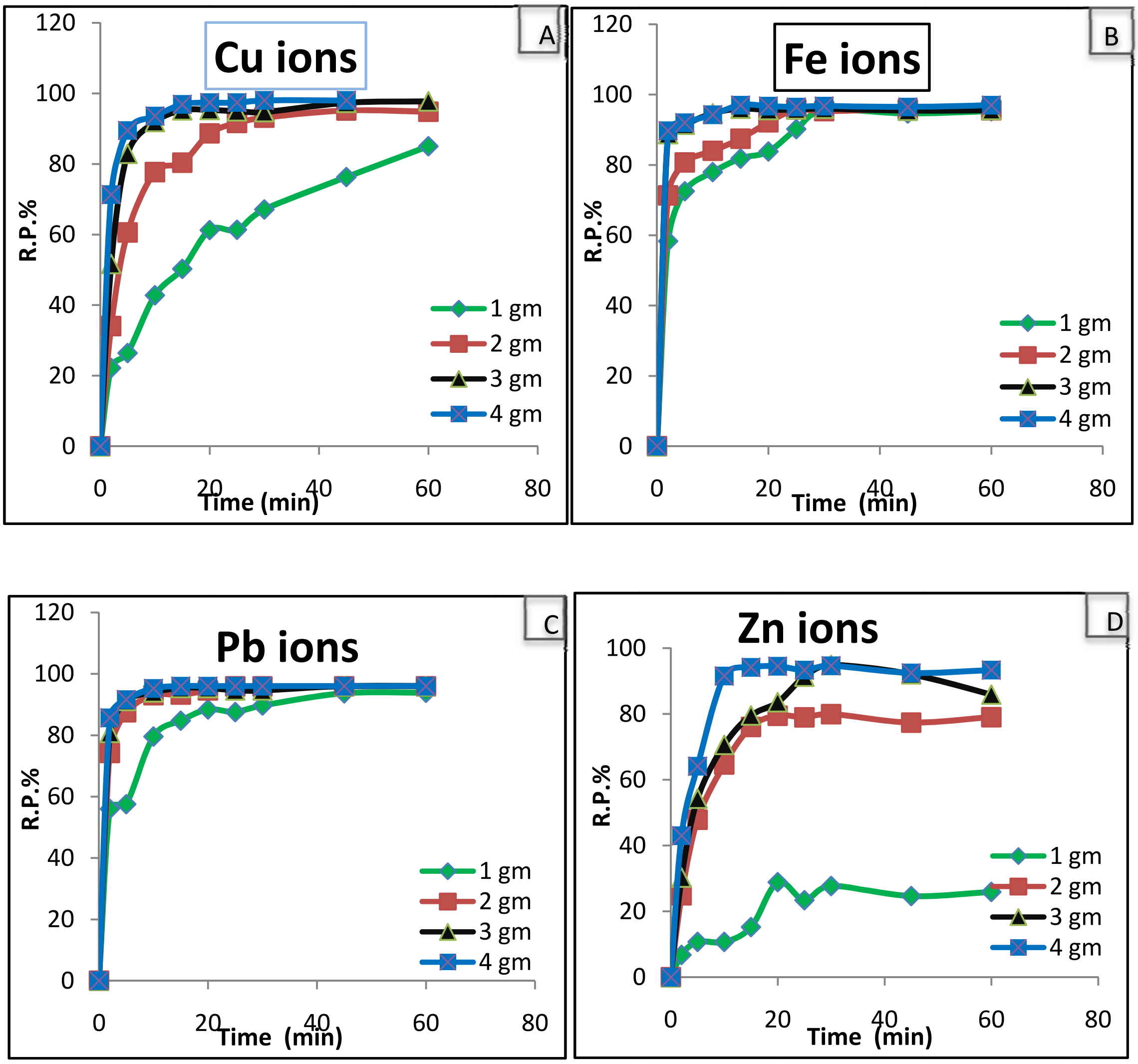

Figure 2. (A-D) The saturation time of adsorption of H.M.I. on RHAC

For this study the following curves are showing the isotherm models of adsorption of heavy metal ions on the RHAC.

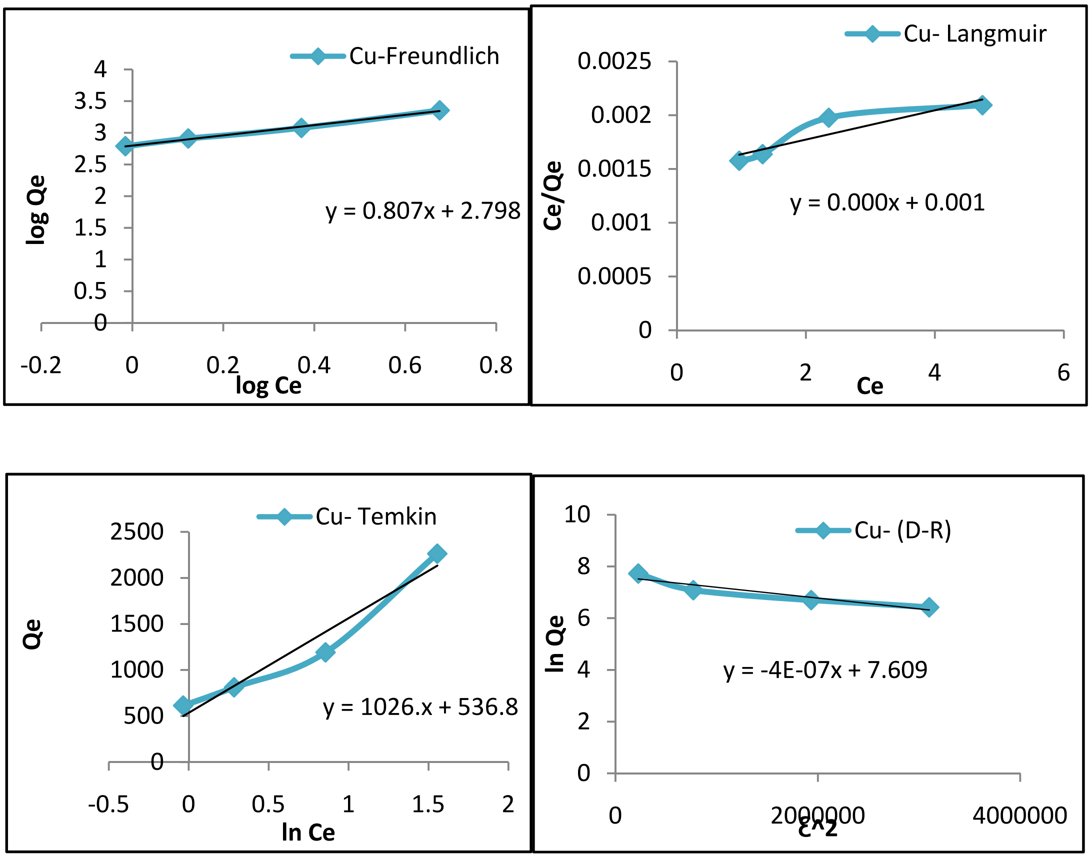

Figure 3. Cu^{2+} Adsorption Isotherm on RHAC fitted to Freundlich, Langmuir, Temkin and Dubinin–Radushkevich Equations

Table 4. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of Cu^{2+} ion by RHAC

Freundlich isotherm				*Langmuir* isotherm			
$1/n$	**n**	**K_f mg/g**	**R^2**	**Q mg/g**	**K_l L/mg**	**R_L**	**R^2**
0.8076	**1.2382**	**628.93**	**0.9958**	**666.6667**	**15**	**0.00133**	**0.8341**
Temkin isotherm				Dubinin–Radushkevich isotherm			
K_T L/mg	**b_T**	**B_T**	**R^2**	**Q mg/g**	**K_{DR} mol^2/KJ^2**		**R^2**
1.6867	**2.41290**	**1026.8**	**0.9508**	**2016.462**	**4*10^-7**		**0.8882**

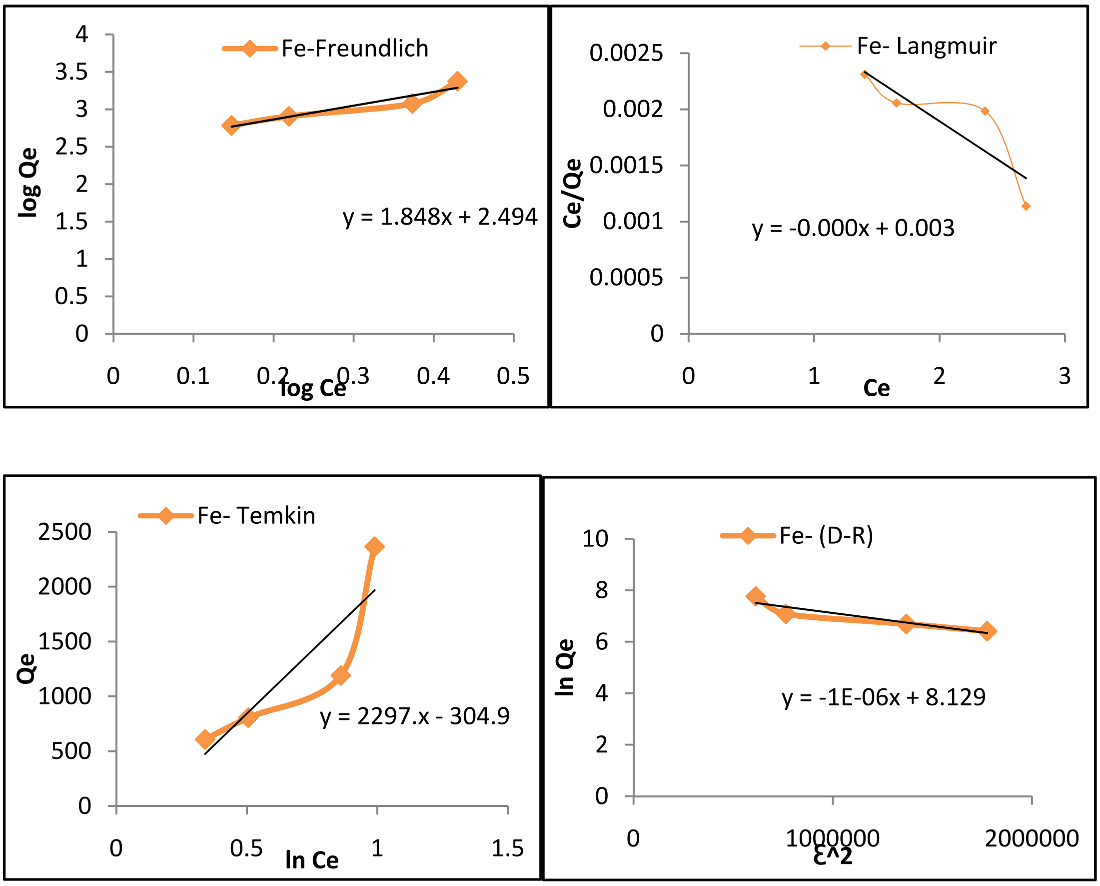

Figure 4. Fe^{3+} Adsorption Isotherm on RHAC fitted to Freundlich, Langmuir, Temkin and Dubinin–Radushkevich Equations

Table 5. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of Fe^{3+} ion by RHAC

Freundlich isotherm				*Langmuir* isotherm			
$1/n$	**n**	**K_f mg/g**	**R^2**	**Q mg/g**	**K_l L/mg**	**R_L**	**R^2**
1.8482	**0.54167**	**312.1045**	**0.9012**	**294.1176**	**4.857143**	**0.004101**	**0.7457**
Temkin isotherm				Dubinin–Radushkevich isotherm			
K_T L/mg	**b_T**	B_T	**R^2**	**Q mg/g**	**K_{DR} mol^2/KJ^2**		**R^2**
0.875704	**1.07823**	**2297.8**	**0.7806**	**3392.424**	**1*10^-6**		**0.8553**

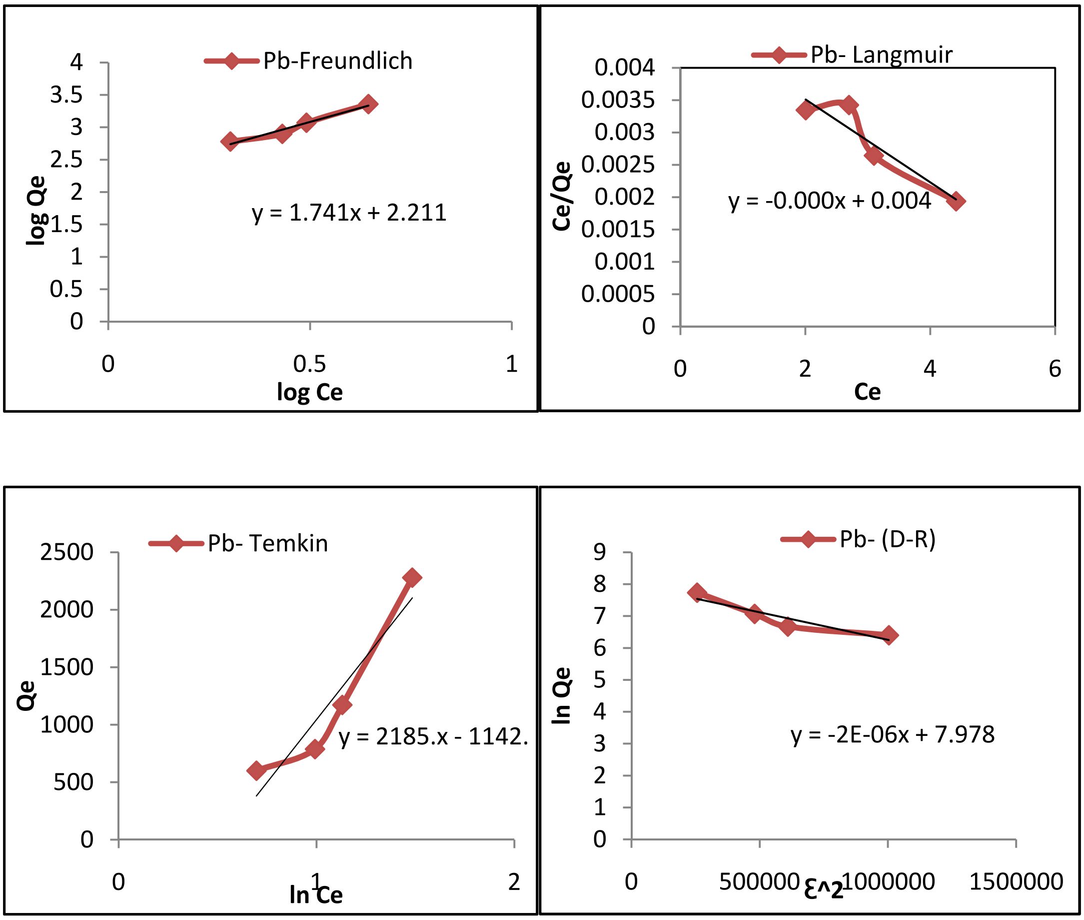

Figure 5. Pb^{+2} Adsorption Isotherm on RHAC fitted to Freundlich, Langmuir, Temkin and Dubinin–Radushkevich Equations.

Table 6. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of Pb^{+2} ion by RHAC

Freundlich isotherm				*Langmuir* isotherm			
$1/n$	n	K_f mg/g	R^2	Q mg/g	K_l L/mg	R_L	R^2
1.7419	**0.574**	**162.667**	**0.966**	**208.3333**	**8**	**0.002494**	**0.8731**
Temkin isotherm				*Dubinin–Radushkevich isotherm*			
K_T L/mg	b_T	B_T	R^2	Q mg/g	$K_{DR}\ mol^2/KJ^2$		R^2
1.68628	**1.1334**	**2185.9**	**0.9047**	**2916.093**	**2*10^-6**		**0.868**

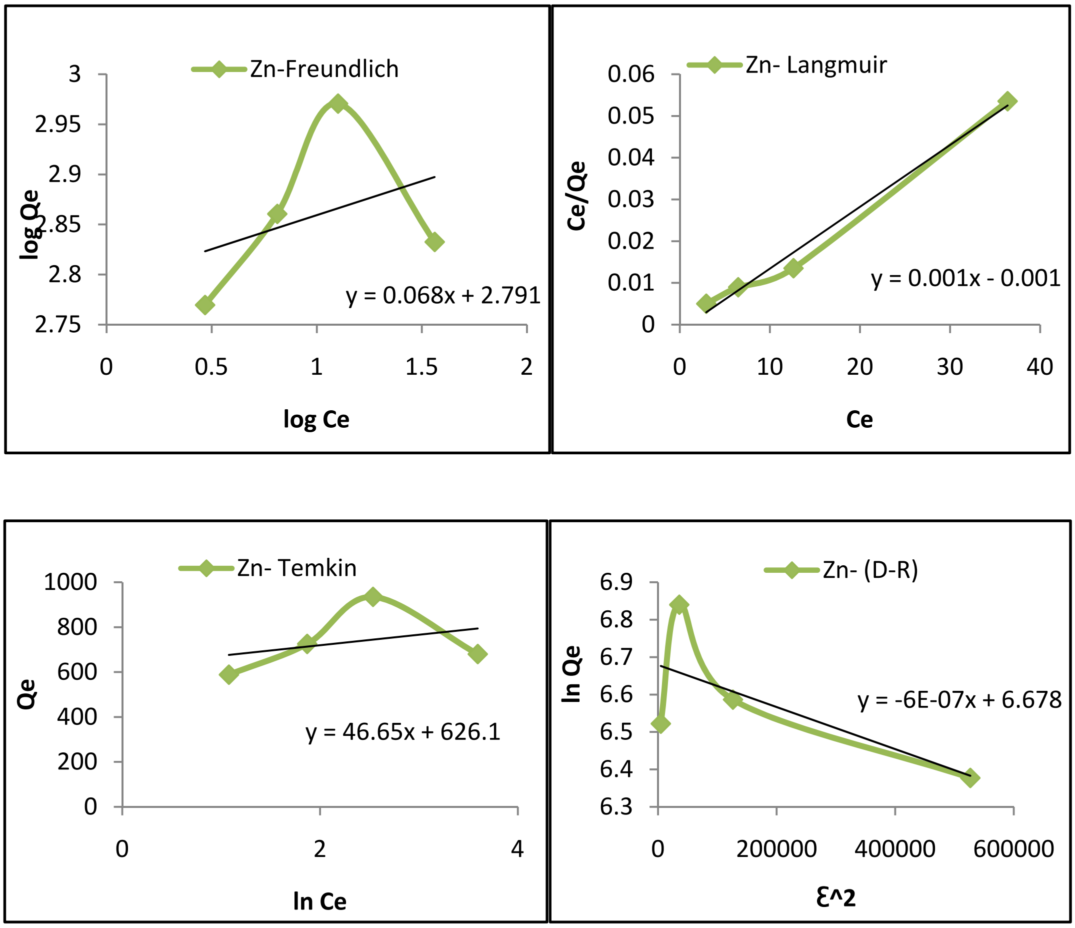

Figure 6. Zn^{+2} Adsorption Isotherm on RHAC fitted to Freundlich, Langmuir, Temkin and Dubinin–Radushkevich Equations

Table 7. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of Zn^{2+} ion by RHAC

Freundlich isotherm				*Langmuir* isotherm			
$1/n$	**n**	**K_f mg/g**	**R^2**	**Q mg/g**	**K_l L/mg**	**R_L**	**R^2**
0.068	**14.70588**	**618.4434**	**0.1404**	**714.2857**	**0.933333**	**0.020979**	**0.9867**
Temkin isotherm				Dubinin–Radushkevich isotherm			
K_T L/mg	**b_T**	**B_T**	**R^2**	**Q mg/g**	**K_{DR} mol^2/KJ^2**		**R^2**
673042	**53.10069**	**46.658**	**0.1151**	**0.999994**	**6.6787**		**0.4907**

From above figures ,the results shown the Freundlich isotherm model achieved best fit with the equilibrium adsorption data, which have highest correlation coefficient values (R^2) of (0.9012, 0.9958 and 0.966) for (Fe^{3+}, Cu^{2+} and Pb^{2+}), respectively. It is indicates to multilayer adsorption nature of these metal ions on RHAC. The adsorption capacity (K_f)of the adsorbent have a value of (312.1, 628.93 and 162.66 mg/g) for (Fe^{3+}, Cu^{2+} and Pb^{2+}), respectively.

The Langmuir isotherm model gives best fit with the equilibrium adsorption data, which have highest correlation coefficient values of (0.9867) for (Zn^{2+}). It is instated to monolayer adsorption nature of (Zn^{2+}) ions on RHAC. The monolayer adsorption capacity ($Q_{\circ}$) have a value of (714.285 mg/g).

3.2 Kinetic Model of Heavy Metal Ions Adsorption

There are different differential equations were used for finding kinetic model in the batch system, these equations were solved by using integral method. If the kinetic model was assumed correct, the appropriate plot of the concentration-time data should be linear.

In this study, kinetic models were studied with different models to describe the kinetic of adsorption. These include Zero order, First order, Second order , Third order, Pseudo First order, Pseudo Second order, Parabolic Diffusion and Elovich –Type.

3.2.1 Zero Order

Differential equation which describes zero order is (FOGLER, 2006):

$$\frac{dC}{dt} = -K \tag{11}$$

Integrating with $C = C_i$ at $t = 0$, yield

$$C_t = C_i - kt \tag{12}$$

Where:

k is the rate constant of zero order adsorption (mg·L^{-1}·min^{-1}).

C_i and C_t are the liquid-phase concentrations of metal ions at initial and at time t, respectively (mg/L).

3.2.2 First Order

Differential equation which describes first order is (FOGLER, 2006):

$$-\frac{dc}{dt} = K_1 C \tag{13}$$

With the limit $C = C_i$ at $t = 0$ gives

$$\ln\frac{C_i}{C_t} = K_1 t \tag{14}$$

The linear form of firs order equation is:

$$\ln C = \ln C_i - K_1 t \tag{15}$$

Where:

K_1 is the rate constant of first order adsorption (min^{-1}).

3.2.3 Second Order

Differential equation which describes second order is (FOGLER, 2006; Ho et al., 2000):

$$-\frac{dC}{dt} = K_2 C^2 \tag{16}$$

With the limit $C = C_I$ initially, yields

$$\frac{1}{C_t} = \frac{1}{C_i} + K_2 t \tag{17}$$

Where:

K_2 is the rate constant of Second order adsorption ($L \cdot mg^{-1} \cdot min^{-1}$).

3.2.4 Third Order

The third order equation is given by the following (Ho et al., 2000):

$$\frac{1}{{C_t}^2} - \frac{1}{{C_i}^2} = K_3\, t \tag{18}$$

Where:

$K_3$the rate constant of third order adsorption ($mg^2/L^2 min$)

3.2.5 Pseudo First Order (Lagergren's Equation)

Lagergren's first-order rate equation is the earliest known one describing the adsorption rate based on the adsorption capacity, Lagergren described liquid–solid phase adsorption systems. In order to distinguish kinetics equations based on concentrations of solution from adsorption capacities of solids, Lagergren's first-order rate equation has been called pseudo-first-order, It is summarized as follows (Radniaet al., 2011; Ho & McKay, 1998):

$$\frac{dQ_t}{dt} = K_{1p}(Q_e - Q_t) \tag{19}$$

Where:

K_{1p} is the rate constant of the pseudo first-order adsorption (1/min).

Eq. (19) was integrated with the boundary conditions from t=0 to t=t and from Q_t=0 to Q_t=Q_t yield

$$\ln\left(\frac{Q_e}{Q_e - Q_t}\right) = K_{1p} t \tag{20}$$

Eq. (20) may be rearranged to a linear form:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_{1p}}{2.303} t \tag{21}$$

3.2.6 Pseudo Second Order (Lagergren's Equation)

The pseudo-second-order expression can be derived from (Ho & McKay, 1998; chowdhury & Saha, 2010):

$$\frac{dQ_t}{dt} = K_{2p}(Q_e - Q_t)^2 \tag{22}$$

Where: K_{2p} is the rate constant of adsorption ($g \cdot g^{-1} \cdot min^{-1}$).

Separating the variables in Eq. (22) and integrating this for the boundary conditions t = 0 to t = t and Q_t =0 to Q_t= Q_t gives:

$$Q_t = \frac{K_{2p}Q_e^2}{1+Q_eK_{2p}t} \quad \text{or} \quad Q_t = \frac{t}{\frac{1}{K_{2p}Q_e^2}+\frac{t}{Q_e}} \tag{23}$$

Eq. (23) can be rearranged to obtain a linear form :

$$\frac{t}{Q_t} = \frac{1}{K_{2p}Q_e^2} + \frac{1}{Q_e}t \tag{24}$$

3.2.7 The Intraparticle Diffusion Model

Intraparticle diffusion is a transport process involving movement of species from the bulk of the solution to the solid phase. In a well stirred batch adsorption system, the intraparticle diffusion model has been used to describe the adsorption process occurring on a porous adsorbent (Itodo, 2010).

The diffusion model can be expressed by following equation (BADMUS et al., 2007; Itodo, 2010; Ahn et al., 2008):

$$C_t = \emptyset + K_{ip}\sqrt{t} \tag{25}$$

K_{ip} is intraparticle diffusion rate constant (mg/$gmin^{0.5}$) ,$\emptyset$ is intraparticle diffusion constant i.e.intercept of the line (mg/g), It is directly proportional to the boundary layer thickness.

3.2.8 Elovich –Model

The Elovich equation was developed for describing the kinetics of heterogeneous Chemisorption, the equation assumes a heterogeneous distribution of adsorption (In other words the active sites of the adsorbent are heterogeneous) or activation energies that vary continuously with surface coverage and its widely used in liquid –solid adsorption .

The Elovich equation is generally expressed as (HO & MCKAY 2004; Perez-Marın et al., 2006; CHEUNG et al., 2011):

$$\frac{dC_t}{dt} = \alpha\exp(-\beta C_t) \tag{26}$$

where :α and β are constants of Elovich –type equation .

The parameter α represents the rate of chemisorption and the parameter β is related to the extent of surface coverage and the activation energy of chemisorption.

To simplify the Elovich equation (Chien & Clayton, 1980; Renugadevi et al., 2011) assumed αβ>>1 and applying the boundary conditions C_t= 0 at t = 0 and C_t= $C_t$at t = t, equation (26) becomes:

$$C_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{27}$$

Where: C_t is concentration of adsorbate in solid phase at time (t).

For this study the following curves are showing the kinetic models of adsorption heavy metal ions on the RHAC.

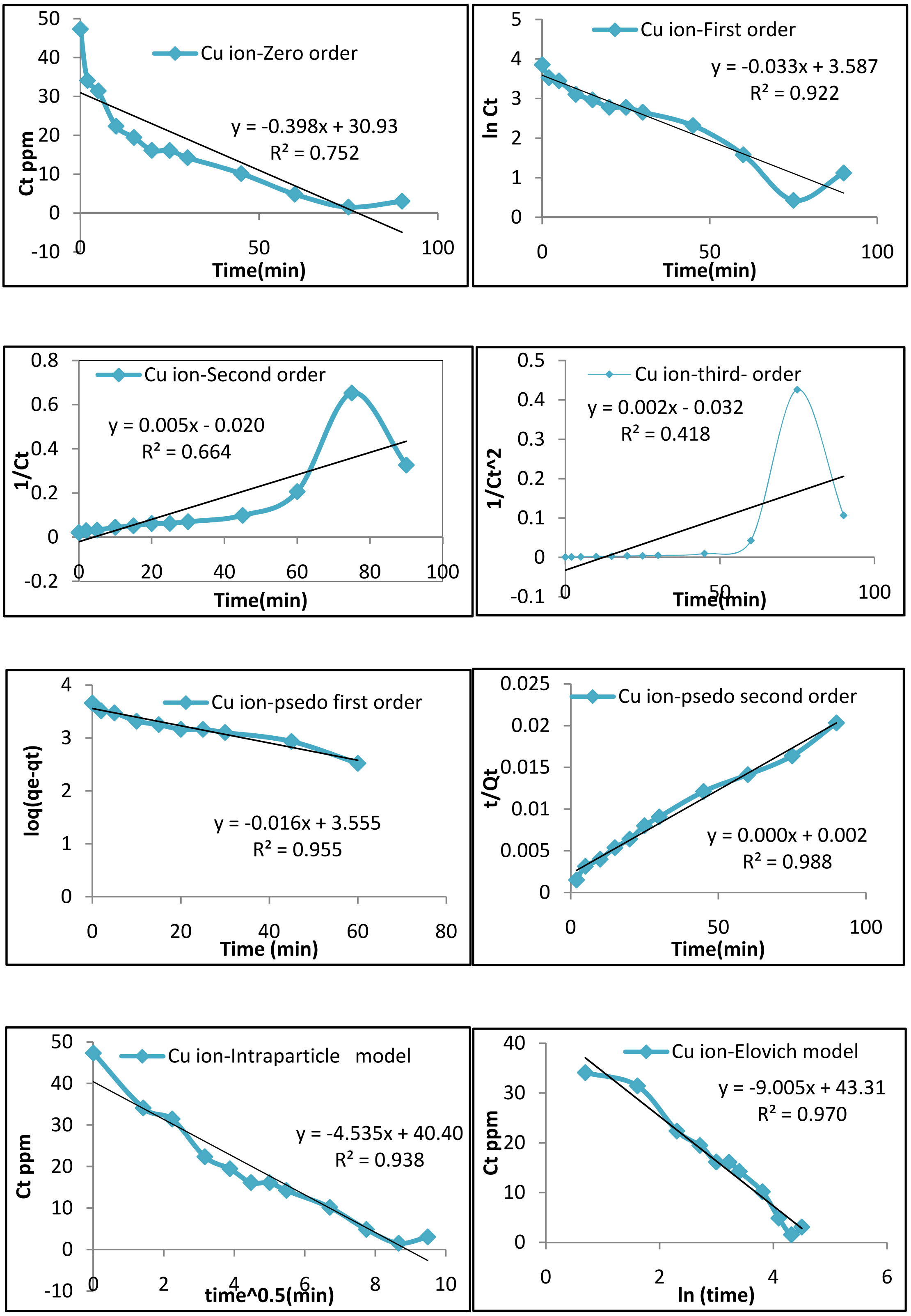

Figure 7. The kinetic models of adsorption of Cu^{+2}ions on the RHAC

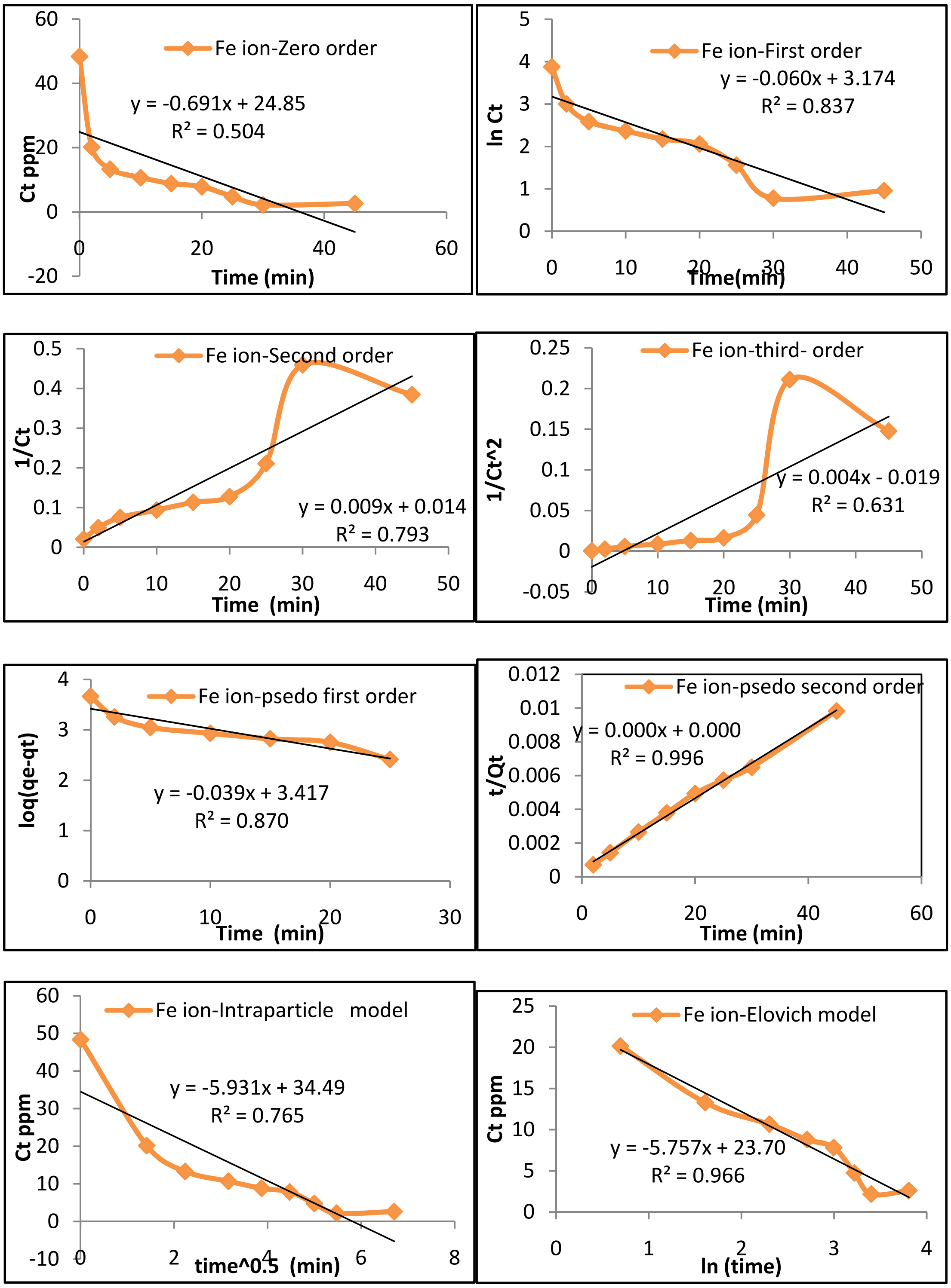

Figure 8. The kinetic models of adsorption of Fe^{+3} ions on the RHAC

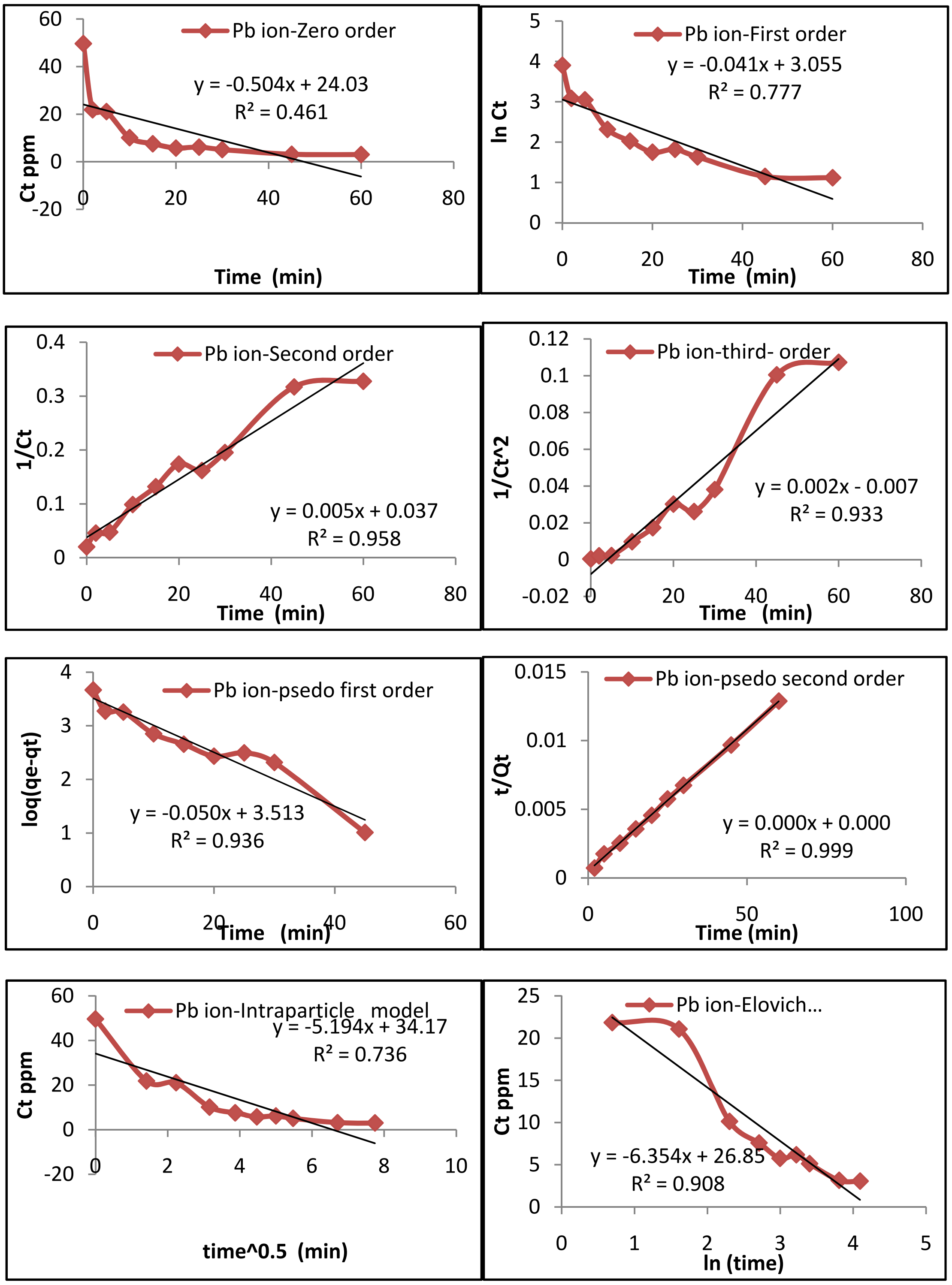

Figure 9. The kinetic models of adsorption of Pb^{+2} ions on the RHAC

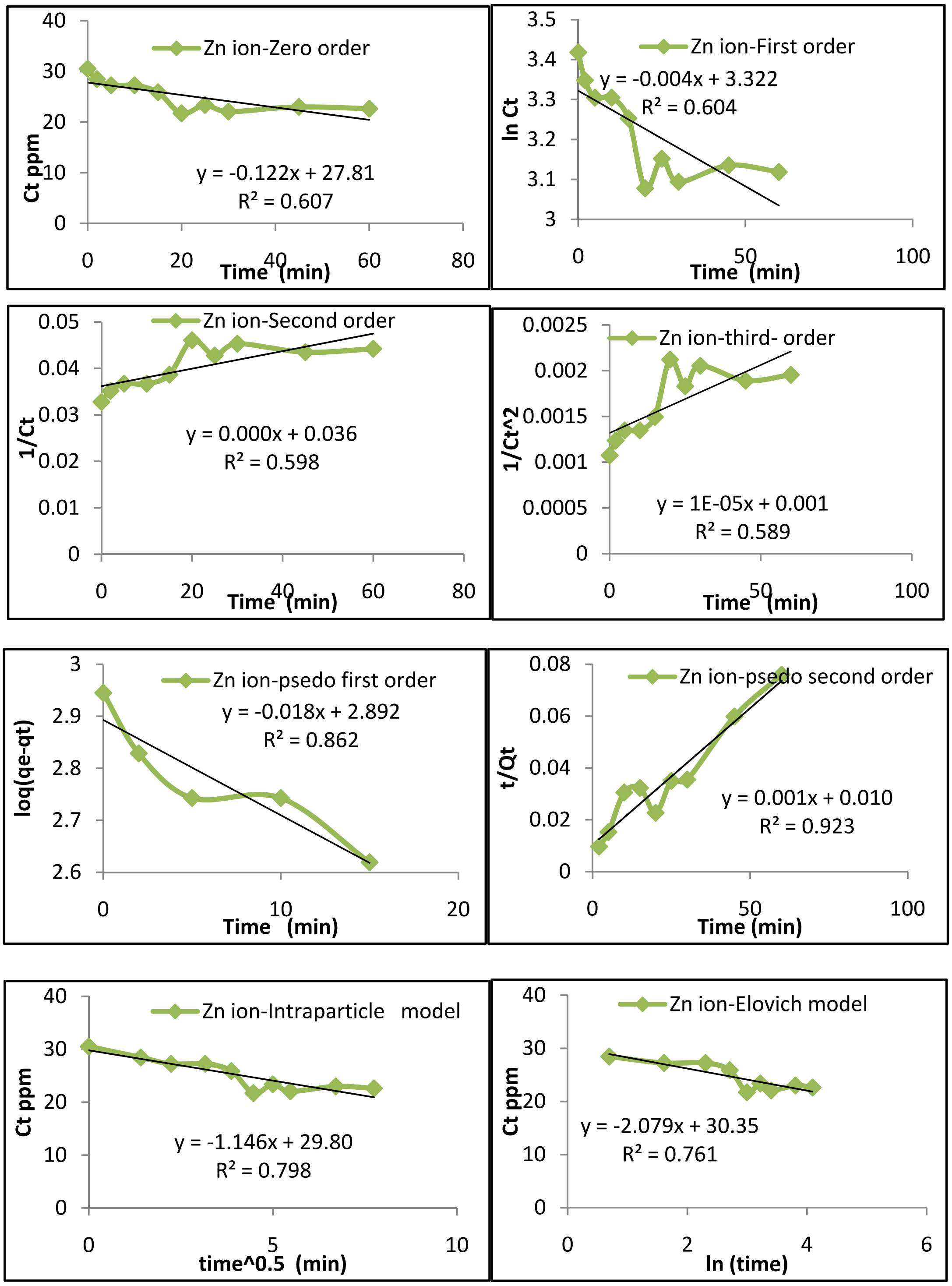

Figure 10. The kinetic models of adsorption of Zn^{+2} ions on the RHAC.

Table 8. The kinetic models of adsorption of heavy metal ions on the RHAC

Heavy metal ions	Zero order		1st order		2nd order		3nd order	
	K□	R^2	K_1	R^2	K_2	R^2	K_3	R^2
$\mathbf{Cu^{+2}}$	0.3989	0.7527	0.0331	0.9221	0.0051	0.664	0.0026	0.418
$\mathbf{Fe^{+3}}$	0.6912	0.5045	0.0606	0.8371	0.0093	0.7933	0.0041	0.6314
$\mathbf{Pb^{+2}}$	0.504	0.461	0.0411	0.777	0.0054	0.9589	0.002	0.9334
$\mathbf{Zn^{+2}}$	0.1227	0.6074	0.0048	0.6049	0.0002	0.5988	0.00001	0.5893

Heavy metal ions	Pseudo 1st order		Pseudo 2nd order	
	K_{1p}	R^2	K_{2p}	R^2
$\mathbf{Cu^{+2}}$	0.0735	0.9555	$1.739 * 10^{-5}$	0.9883
$\mathbf{Fe^{+3}}$	0.0909	0.8709	$8 * 10^{-5}$	0.9963
$\mathbf{Pb^{+2}}$	0.11607	0.9368	$8 * 10^{-5}$	0.9991
$\mathbf{Zn^{+2}}$	0.04214	0.8626	$1.163 * 10^{-4}$	0.9232

Heavy metal ions	Intraparticle diffusion			Elovich model		
	Kip	∅	R^2	β	α	R^2
$\mathbf{Cu^{+2}}$	-4.5353	40.708	0.9384	-0.11104	-0.073399	0.9706
$\mathbf{Fe^{+3}}$	-5.9318	34.498	0.7651	-0.17367	-0.09378	0.9661
$\mathbf{Pb^{+2}}$	-5.1941	34.176	0.7365	-0.15736	-0.092858	0.9081
$\mathbf{Zn^{+2}}$	-1.1468	29.808	0.7985	-0.48095	$-9.4 * 10^{-7}$	0.7612

From the above figures and results, the kinetics of adsorption was followed the pseudo-second-order model, this model gives the best- fit to experimental data for all heavy metal ions which studied in this work. which have highest correlation coefficient values of (0.988, 0.996, 0.999 and 0.9232) for (Cu^{2+}, Fe^{3+}, Pb^{2+} and Zn^{2+}), respectively. That means the rate of occupation of adsorption sites is proportional to the square number of unoccupied sites, because the pseudo-second order model is based on a second order mechanism (Al-Jomaa, 2011; John, 1998).

3.3 Thermodynamic of Heavy Metal Ions Adsorption

The Gibbs free energy change (ΔG°) of the adsorption process can be calculated from classic Van't Hoff equation (Deosarkar & Hangirgekar, 2012; Somasundaram et al., 2013):

$$\Delta G^{\circ} = -2.303 RT \log K_d \tag{28}$$

$$K_d = \frac{C_{e,solid}}{C_e} \tag{29}$$

The Enthalpy change (ΔH°) (i.e. heat of adsorption) and Entropy change (ΔS°) are related with the Gibbs free energy by the equation :

$$\log K_d = \frac{\Delta S^{\circ}}{2.303R} - \frac{\Delta H^{\circ}}{2.303R\,T} \tag{30}$$

Where:

K_d is equilibrium constant of Van't Hoff equation, $C_{e,solid}$ is solid phase concentration of metal ions at equilibrium(mg/L), ΔG° is Gibbs free energy change (KJ/mol), ΔH° is Enthalpy change (KJ/mol) and ΔS° is entropy change (KJ/mol K).

A plot $\log K_d$ Vs. (1/T) is given straight line, ΔH° and ΔS° can be determined from intercept and slope, respectively.

In this study the following curves are showing the thermodynamic of adsorption heavy metal ions on the RHAC.

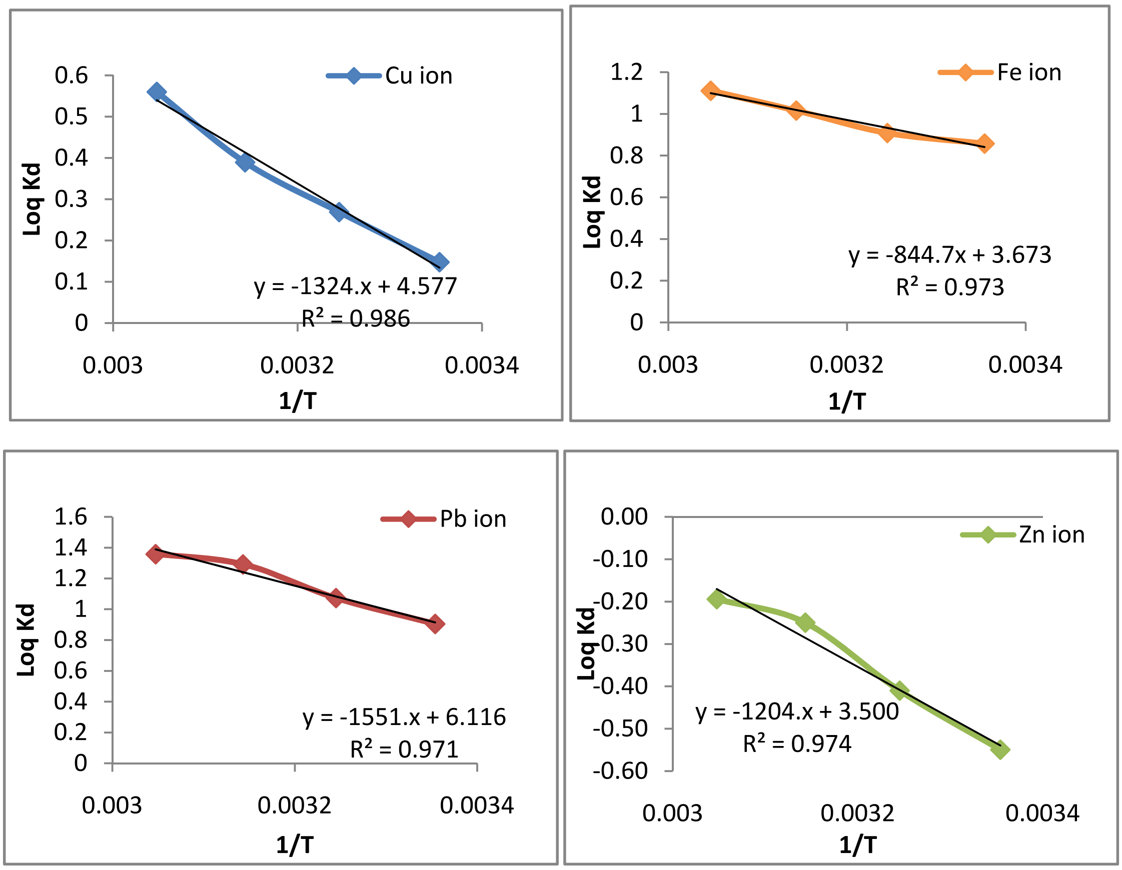

Figure 11. Thermodynamic Of Heavy Metal Ions Adsorption on the RHAC

Table 9. Thermodynamic Of Heavy Metal Ions Adsorption on the RHAC

Heavy	ΔG°(KJ/mol)				K_d				ΔH°	ΔS°
metal ions	25 Ċ	35Ċ	45 Ċ	55 Ċ	25 Ċ	35Ċ	45 Ċ	55 Ċ	KJ/mol	KJ/mol.K
Cu^{+2}	-0.84	-1.59	-2.37	-3.52	1.40	1.86	2.45	3.63	25.2	0.087
Fe^{+3}	-4.89	-5.36	-6.19	-6.98	7.20	8.09	10.3	12.8	16.1	0.070
Pb^{+2}	-5.16	-6.33	-7.87	-8.53	8.03	11.8	19.8	22.8	29.7	0.117
Zn^{+2}	-3.14	-2.42	-1.52	-1.22	0.28	0.39	0.56	0.64	23.0	0.067

The negative value of ΔG° indicates the feasibility and spontaneous nature of the adsorption process and more negative which indicates that the adsorption process becomes more spontaneous with rise in temperature, which favors the adsorption process (Gayathri & Kumar, 2009; Sharma et al., 2011), in the other word that the adsorption process is spontaneous and the degree of spontaneity increases with increasing the temperature (Surchi, 2011).

The value of ΔS° can be used to describe the randomness during adsorption process, the positive value of ΔS° reflected the affinity of the adsorbent for particular of heavy metal ions and confirms the increased randomness at the solid–solution interface during adsorption (Gayathri & Kumar, 2009; Hameed et al., 2011).

The positive value of ΔH° confirms the endothermic nature of the adsorption process. This result also supports the suggestion that the adsorption capacity of adsorbent increases with increasing temperature (Surchi, 2011).

4. Conclusion

The adsorption of (Fe^{3+}, Cu^{2+} and Pb^{2+}) ions followed the Freundlich isotherm model which indicated to multilayer adsorption nature. While the adsorption of Zn^{2+} (ions followed the Langmuir isotherm model which indicated to monolayer adsorption nature of (Zn^{2+})) ions on RHAC. The adsorption kinetics of H.M.I. on the RHAC was followed the pseudo-second-order model. Also, the adsorption thermodynamic showed that the adsorption becomes more feasibility & randomness with increasing in temperature, the adsorption process on the RHAC is endothermic.

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