Effect of Extracts from Rhatany Roots *(*Krameria ramosissima) on Heavy Metals *in* Jordanian Industrial Wastewater

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ABSTRACT

Much concentration was directed towards different types of adsorbents used in adsorbing heavy metals from the industrial waste water by using the availables chemical, physical and biological techniques. The present study is designed to use less-cost and more available adsorbents to eliminate heavy metals in the industrial waste water. An alcoholic essence from the natural material Rhatany is used in this research (with concentrations 100,200, 300, 400, 500, 600 milligram/liter) as a primary material with adsorbing Cadmium, Cobalt, Chrome, and Copper, from the lab prepared mixture. The research investigated a number of variables as the acid pointer pH, time of mixing, primary concentration, lightening, temperature, and their various effects on the absorbing process to define the ideal circumstances to get the best adsorbing of materials by using this material. Equilibrium Isotherm experiences were conducted and the findings were analyzed by using Freundlich model and Langmuir model. It is found that Langmuir model is the better mathematical model to represent the results of adsorbing all the ions than Freundlich model where Langmuir constant factor was (0.967,0.962,0.976,and 0.965 milligram/gram)for Cadmium, Cobalt, Chrome, and Copper.(Kinetic) experiments were conducted where the findings were used to analyze the effect of the stratum   surrounds the particles of the adsorbing material. There was good harmony between the practical and theoretical findings taken from the absorbing model in Kinetic experiments when mobile interaction model of the second degree Pseudo Second Order Kinetic is used where more than 95% of Cadmium, Cobalt, Chrome, and Copper, were adsorbed. The findings showed the possibility of eliminating Cd(II), with 100% , Co(II), with 100%, Cr(VI), with 100%, Cu(II),   with 100% with a capacity of adsorption of Cadmium, Cobalt, Chrome, and Copper, with 25 milligram for each gram from the roots of Rhatany. Comparisons between the findings of the present study and other studies showed the high efficiency of this cheap type of these adsorbed and available materials to eliminate the pollution of Cadmium, Cobalt , Chrome, and Copper, (as heavy poisonous metals) from industrial water before releasing it to sewage water.

1. Introduction

Many practical studies affirmed the ability of the plant in helping to clean the polluted water of pools and waste water of factories and sewage .The plant was used economically and effectively in treating the waste water of rubber and palm oil factories[1]. The plant also reduced the biological and organic load especially COD and TN with about 60% of olive oil factories in Italy[2].The pollutants in pools of waste water of plant extracts factory in Sri Lanka were reduced by using the plant. The plant with Chloral and jungle were used to clean waste water in three tanks in oil refinery in Vietnam where petrol was purified with 97-98%; which also helps in eliminating many of mineral elements [3].

By using the plant it was possible to produce a system able of treating water polluted with big amounts of sulfate without producing undesired smells or insects. The treated water was equal to its counterpart which was produced by advanced minor treatment, USA [4].

The plant was efficient in removing nitrates and aluminum with non-toxic amount in the waste water of Oxalic acid factory and the waste water in India where the plant was able of removing 66% and 95% respectively of the nitrogen content[5].The plant removed mercury from the waste water chloride acids (concentration to 1 milligram/liter) and showed its ability in removing the element from the polluted water[6]. The plant is used in treating the waste water of tanning factory where accumulation was found for most of the Chromium to be 38 portion in million)followed by water lentil with great accumulation in roots [7].

The small plants (10g weight, 10cm length, and two leaves) in plastic containers (10 liters) could remove the heavy elements from waste water symbols of a factory in Lawanj region in Indonesia; the growth of the plants increased with the little concentration of those elements[8].

The plant with other water herbs like water lentil could remove many pollutants from the waste water tanks in a Chinese hospital with increasing the content of the plants of the pollutants[9].Within one year ,the plant removed 58%of TN, 46%of IN, 80%of TP, 56%of IP in waste water in Aukayama in Japan. The plant was better than 10 kinds of grasses among them a type of Typha , Elodea and Jungle[10].Near a small town in Alabama ,USA, the plant was

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under study as a cheap and easy treatment for waste water (for a year and a half) in the department of civil engineering in south Carolina state. It was found that at the rate of hydraulic loads of 1870cubic meter/hectare /day it is possible to keep the level of BCOD5 and TSS under the level of 10milligram/liter and the NH4-N under the level of 5milligram/liter, whereas at the rate of load of 1170cubic meter the NH4-N reduced to less than 2 milligram/liter[11].

High-efficiency liquid–liquid extractions also extensively used. Separation, which is achieved by selecting the solvent used with a determinate species, is employed to remove heavy metals ions such as Cadmium, Copper, Nickel, Lead, Tin, and Zinc. One disadvantage of this method is its use of an organic solvent that is harmful for human health and the environment[12,13]. Another alternative approach is chemical precipitation, where an insoluble solid is obtained from species initially dissolved by changing their solubility equilibrium. A number of applications of the technique are possible because they are based on the formation of flakes in the dissolved metal. During the process, small dispersed particles are observed initially. The separticles soon aggregate, form flakes that increase in volume, and then decant, thus facilitating their removal. Therefore, this technique is important in metal ion removal and can be usedto remove Chrome, Copper, Nickel, Lead, Tin, and Zinc [14-16].

2. Materials and Methods
2.1. Preparation of Adsorbent Rhatany roots
Adsorbent mass was collected from the local market. The adsorbent mass was dried in sun for ten days. The buds were removed and further dried in sun for another ten days. This adsorbent mass was washed with tap water to remove any dust or foreign particles attached to adsorbent mass and thoroughly rinsed with distilled water. The washed adsorbent mass was dried at 50 C° and ground to a powder with kitchen grinder. Grinded adsorbent mass was further thoroughly washed with distilled water till the color of washing water clear. The powdered adsorbent mass was dried in an oven at 50°C to a constant weight. The following operating condition such as pH, adsorbent amount, contact time, and metal ion concentration were investigated.

2. 2. Ethanol extracts preparation
Extract of rhatany has been Prepared by five different methods or processes.By alcohol.(Ethanol), diluted alcohol, decoction in water, infusion in warm water.and lastly; by displacement with cold water. Rhatany, when treated with alcohol(ethanol), yields larger amount of extract than by any other means

3. Methodology
The extraction of the Rathany Roots was obtained by methodology based on [17,18,19, 20]. Hundred gram of powdered Rhatany roots were kept in 1000 ml conical flask and added 500 ml of a solvent such ethanol 95%. the solution was continuously stirred by shaker for 24 hours at room temperature 25 ° C and at the same time was also dredged for 24 hours (within 24 hours, the target compounds were extracted from the plant materials by solvent). The extraction was filtered using a muslin cloth and then Whatman no. 1 filter paper. Then centrifuge using a Hettich Universal device at 3000 RPM for 10 minutes, The solvent from the extract was removed by using rotary vacuum evaporator RE52 with the water bath temperature of 50°C. Finally, the residues were collected and used.

3.1. Preparation of extract dilutions
A stock solution of plant aqueous extract was prepared by dissolving 6.0 g of extract in 1000 ml of ethanol to produce extract solutions of 6.0 mg/ml. six concentrations of each extract (36 mg/ml , 72 mg/ml, 108 mg/ml ,144 mg/ml,180 mg/ml and 201 mg/ml) were prepared by dilution and placed in sterile bottles and stored in the refrigerator until use.

3.2. Preparation of synthetic wastewater.
A special mixture of Cadmium, Cobalt, Chrome, and Copper ions was prepared from the analytical stock standard at quite a concentration of 1000 ppm to each ion. Another solution was prepared to get a concentration of (100 ppm, 200 ppm, 300 ppm, 400 ppm,500 ppm and 600 ppm)to each ion by using serial dilution method with constant pH. the pH of the synthetic wastewater was adjusted by using HNO_3 1%(v/v) and or NaOH.The final concentration of metal ions in synthetic wastewater was analyzed by atomic absorption (ICP-MS).

3.3. ICP-MS operating parameters
The ICP-MS operating parameters were as follows: high frequency transmission power 1200 W; sampling depth 6.4 mm; auxiliary air flow 1.0 L/min; cooling air flow 16.0 L/min; atomization gas flow 1.02 L/min; ascension 1.1 mL/min; atomization temperature 5[degrees]C; analysis time of one sample 3 min.

3.4. ICP-MS measurement
The ICP-MS system was calibrated by the method of external standards with Rh, Re as the internal standard. The reagent blank solution contained 1% of concentrated HNO3 . Mixed standard solutions containing 4 elements, Cadmium, Cobalt , Chrome, and Copper, were prepared in reagent blank solutions. The back ground interferences from the plasma gases, air entrainment and solvent were corrected by subtraction of reagent blank signals. The isobaric spectral interferences originating from the polyatomic ion species involving the sample matrix elements maybe eliminated by selecting a suitable isotope, corrected or reduced by applying interference correction equations.

4. Adsorption Experiment Bach mode
Adsorption experiments conducted to investigate the effects of process such as initial metal concentration, PH, Temperature and contact time on the adsorption of Cadmium, Cobalt , Chrome, and Copper. at six conical flasks(250 ml) containing 100 ml of these ions of known PH Concentration and adsorbent dose were prepared To study the effect of pH, pHs (2, 4, 6, 8, 10 and 12) and adsorbent dose of 6 ml, 9 ml, 12ml, 15ml, 18ml , and 21ml (1 ml= 6mg/l) respectively. for a contact time of 30 min .For each 100 ml of metal Cadmium, Cobalt , Chrome, and Copper of 6 ml, 12ml, 18ml, 24ml , 30ml and 36ml (1 ml= 6mg/l) respectively used and pH adjusted before adding adsorbent . The Mixture was agitated on a rotary shaker at 200 rpm for 1 h . The pH was adjusted to the required value using 0.1M NaOH and /or 0.1 M HNO3 before the addition of the sorbent. After that the mixture was centrifuged for 10 minutes at a speed of 300 rpm using an impact-5 Centrifuge to separate the supernatant from the adsorbent. The residual concentration of metals in the supernatant was determined using ICP.

All the experiments were done in replicated and results averaged. The percentage removal and metal uptake efficiencies of all adsorbents were determined with following expressions:

$$q = V(C_0 – C_e)/ m*1000 \tag{1}$$

where q is the quantity of metal uptake by adsorbent mass(the amount of ions unit Volume of Rhatany Extraction) in mg.g-1 C_o and C_e are the initial and final(after sorption

at equilibrium) metal respectively 100 v is the volume of solution in ml and m is the dry weight of the Rhatany Roots add in grams. The adsorption efficiency was measured by the following equation:

$$E= (C_0 – C_e / C_0) \times 100 \qquad (2)$$

4.1. Study of Process Parameter

The effect of four parameters heavy metals concentration, contact time, pH and temperature were studied. To study the effect of certain parameter, that parameter has been changed progressively keeping the other three constant. After adsorption content of flasks werefilteredandfiltratewere subjected to add suitable reagent for adsorption of ICP- MS

4.2. Adsorption Kinetics

Adsorption Kinetics Experiments were carried out in 250 ml flasks containing 100 ml of the metals ions solution using a known amount of Rhatany Roots . the flasks were agitated for various time intervals(10-120 min) on rotary shaker at 100 rpm under constant temperature (202 K) .The samples were taken at different time intervals centrifuged and analyzed for remaining concentrations. The kinetic data was analyzed using Pseudo-first order and Pseudo-second order and Pseudo- third order models.

4.3. Study of Adsorption

Isotherm varying metal ion solution with concentration 100 mgL^{-1}, 200 mgL^{-1} ,300 mgL^{-1} ,400 mgL^{-1} ,500 mgL^{-1} and 600 mgL^{-1} Were made by proper dilution of stock solution of syntheses wastewater of (Cadmium, Cobalt, Chrome, and Copper) ions .PH was adjusted to 4-8. 6ml of adsorbent was added to 100 ml of each metal solution and was agitated for half an hour .At the end it is filtered and the filtrate was analyzed for metal ion by (ICP-MS) .

% removal =[Co-Ci /Co] x 100 %,

where Ci and Co are the initial and final concentration of metal solution(mg/L) respectively.

5. Adsorption Thermodynamics

Adsorption of Cadmium, Cobalt , Chrome, and Copper onto Rhatany Roots were investigated at different temperatures((40,55,and70°C) in the orbital shaking incubator under preoptmized conditions.

Thermodynamic Study Thermodynamic parameters such as the free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) changes during adsorption can be evaluated from the following Equations (3,4 and 5)

$$Kc=CAe/Ce \qquad (3)$$
$$\Delta Go=-RTlnKc \qquad (4)$$
$$logK_c=(\Delta S^o/2.303RT)–(\Delta H^o/2.303RT) \qquad (5)$$

where Kc is the equilibrium constant C_e is theequilibrium concentration in solution (mg/L) and C_{Ae} is the Liquid -phase concentration at equilibrium (mg/L). ΔG^o, ΔH^o and ΔS^o are changes in Gibbs free energy (Kj/mol), enthalpy (KJ/mol) and entropy(J/mol/K) , respectively. R is the gas constant (8.314 J/mol/K) and T is the temperature (K).

6. Results and Discussion

6.1 Effect of initial Cd(II) Co(II) Cr(VI) and Cu(II) Concentration on adsorption

The initial Cadmium, Cobalt , Chrome, and Copper concentration servers as an important driving force for overcoming mass transfer resistance of Cadmium, Cobalt, Chrome, and Copper between the Rhatany aqueous and the metals aqueous . The effects of different initial concentrations Cadmium, Cobalt , Chrome, and Copper on the rhatany roots adsorption capacity are shown in fig(1) and table(1). The adsorption capacity of the rhatany roots toward Cadmium, Cobalt, Chrome, and Copper first increased and then remained constant with increasing initial Cadmium, Cobalt , Chrome, and Copper concentration. This result was observed because higher Cadmium, Cobalt, Chrome, and Copper concentrations result in an increased concentration gradient, which, leads to a higher probability of collision among Cadmium, Cobalt, Chrome, and Copper ions and the active adsorption sites on the rhatany roots, thereby increasing adsorption capacity. With further increase in Cadmium, Cobalt, Chrome, and Copper concentration, the adsorption capacity remained constant because the active adsorption sites became saturated [21]. Therefore Cadmium, Cobalt, Chrome, and Copper with an initial concentration of (6ml/L = 36mg/L)was chosen as the ideal initial concentration for all subsequent experiments .
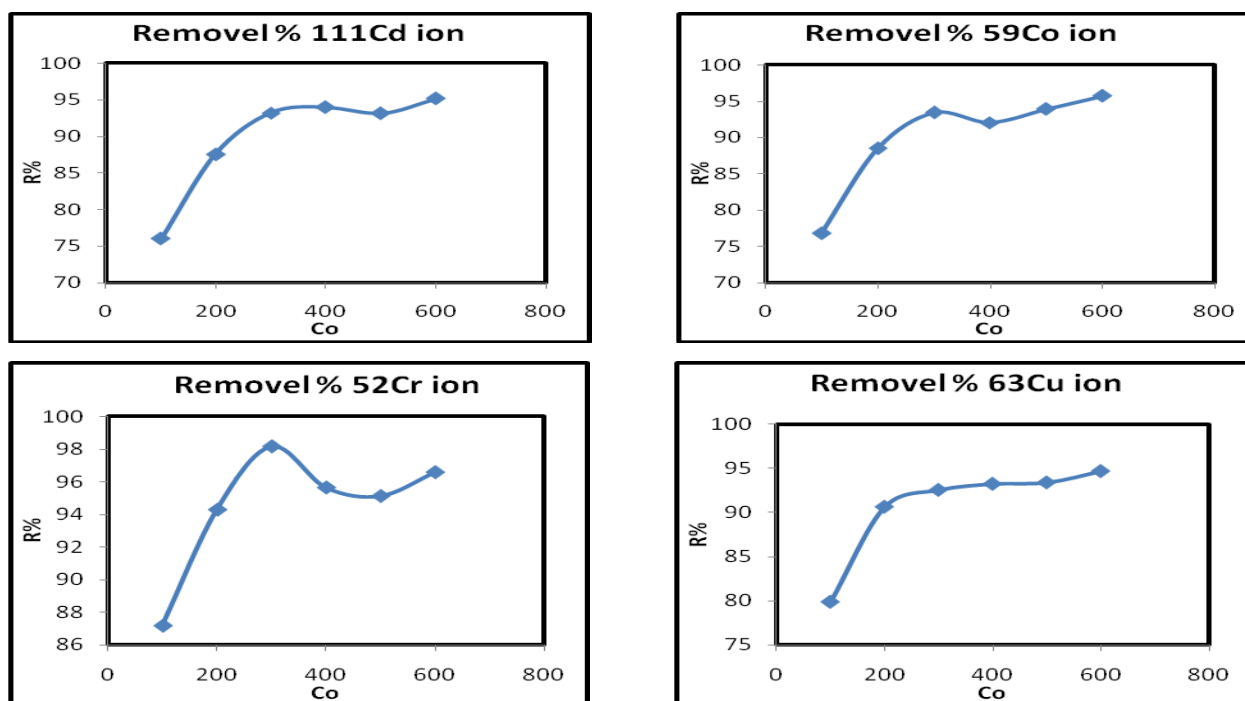

Fig 1. Effect of Volume of adsorbent on the adsorption of Cadmium, Cobalt, Chrome, and Copper ions with concentration of 6 ml – 21 ml Rhatany Roots.

Table 1 .The calculated parameters of the Removal of ions from Rhatany Roots surfaces.

Volume Adsorbent	6ml	9 ml	12 ml	15 ml%	18 ml	21 ml
Cd^{+2}	75.966%	87.544%	93.206%	93.993%	93.162%	95.151%
Co^{+2}	76.816%	88.481%	93.449%	92.083%	93.957%	95.739%
Cr^{+3}	87.188%	94.281%	98.153%	95.635%	95.118%	96.573%
Cu^{+2}	79.834%	90.609%	92.527%	93.215%	93.375%	94.685%
pH Adsorbent	2	4	6	8	10	12
Cd^{+2}	85.166%	87.23%	99.691%	99.945%	99.999%	89.050%
Co^{+2}	84.617%	88.234%	99.864%	99.928%	99.987%	88.05%
Cr^{+3}	87.804%	90.862%	91.908%	91.242%	92.289%	93.083%
Cu^{+2}	82.28%	85.784%	99.665%	99.695%	99.865%	99.924%
TC⁰ Adsorbent	25 °C	40 °C	55 °C	70 °C	85 °C	100 °C
Cd^{+2}	71.561%	92.081%	99.537%	99.853%	99.975%	99.997%
Co^{+2}	75.011%	92.333%	99.702%	99.864%	99.099%	99.991%
Cr^{+3}	79.150%	93.763%	91.564%	89.414%	90.654%	91.427%
Cu^{+2}	68.427%	91.128%	99.625%	99.649%	99.921	99.934%
time min Adsorbent	20 min	40 min	60 min	80 min	100 min	120 min
Cd^{+2}	83.796%	86.050%	99.417%	99.853%	99.987%	99.94%
Co^{+2}	84.267%	87.758%	99.540%	99.847%	99.987%	99.941%
Cr^{+3}	86.609%	89.380%	91.228%	89.578%	90.634%	91.710%
Cu^{+2}	81.925%	84.634%	99.586%	99.657%	99.928%	99.877%

6.2. Effect of pH on adsorption.

The PH of Cadmium, Cobalt , Chrome, and Copper solution is an important factor for determining the adsorption of Cadmium, Cobalt , Chrome, and Copper on the surface of the rhatany roots .The effects of PH on the adsorption capacity are shown in fig(2) and table(1). These results indicate that the adsorption capacity of Cadmium, Cobalt, Chrome, and Copper first increased and then became constant with increasing PH .A pronounced dependence of Cadmium, Cobalt, Chrome, and Copper adsorption on the solution PH was observed. This adsorption behavior may result from the strong electrostatic repulsion, between the positively charged rhatany roots surface and the Cadmium, Cobalt, Chrome, and Copper ions in solution, which hinders the metal-binding process. With increasing pH, the repulsive interaction decreased and the extent of Cadmium, Cobalt, Chrome, and Copper adsorption increased, presumably because of an ion-exchange mechanism between the surface protons and the Cadmium, Cobalt, Chrome, and Copper ions[22]. The optimum pH value for adsorption was determined to be 6.8, and this pH was used in subsequent studies.
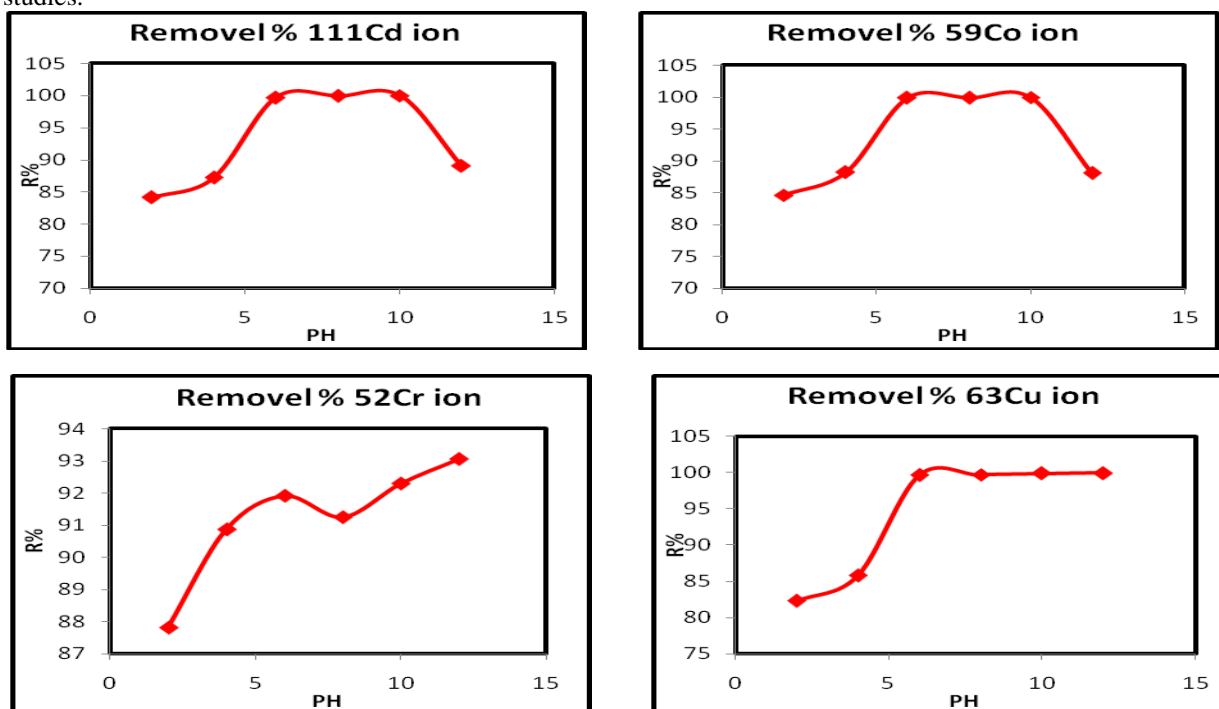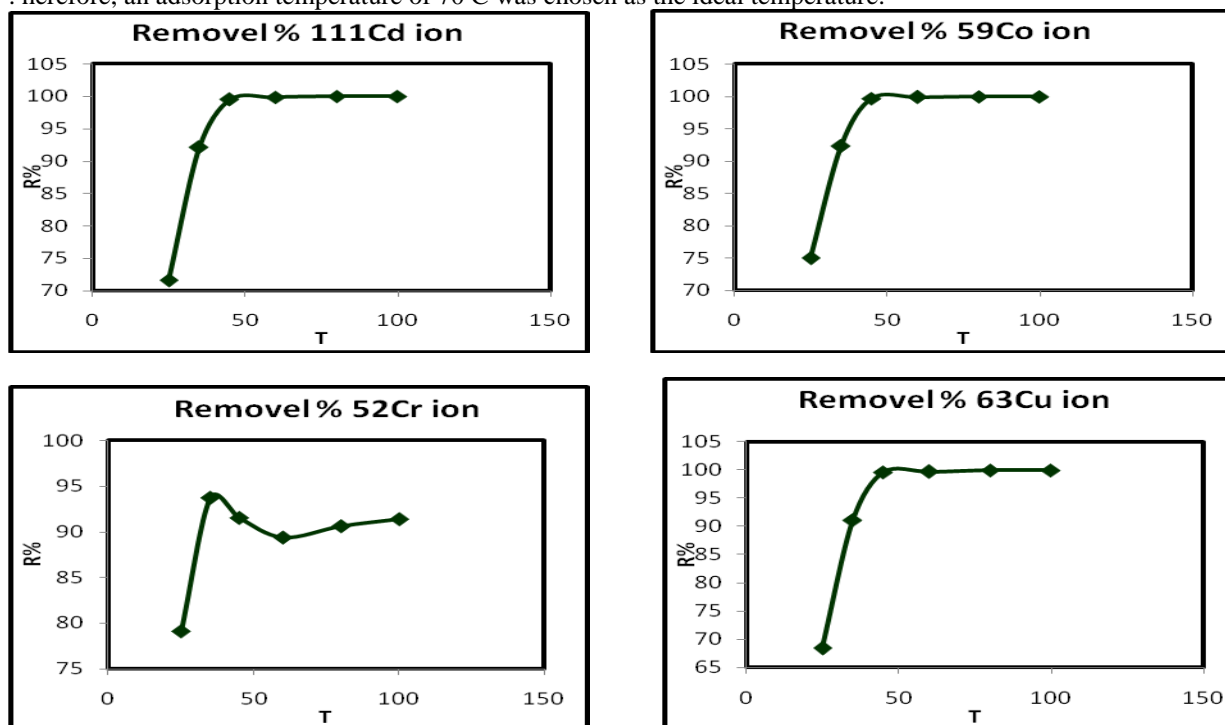

Fig.2 .Effect of PH on the adsorption of Cadmium, Cobalt , Chrome, and Copper ions with PH of 2 – 12 Rhatany Roots.

6.3. Effect of temperature on adsorption.

The plot of rhatany roots Cadmium, Cobalt, Chrome, and Copper adsorption capacity vs. Temperature is shown in fig(3) and table(1). The Cadmium, Cobalt, Chrome, and Copper adsorption capacity increases as the temperature was increased from 40 to

75 C because of the increased diffusion rate of Cadmium, Cobalt , Chrome, and Copper ions across the external boundary layer and within the pores of the rhatany roots and because of decrease in the thickness of the boundary layer surrounding the adsorbent. Consequently, the mass transfer resistance of ions in the boundary layer decreased. Furthermore, at higher temperature, the energy of the system facilitated the binding of Cadmium, Cobalt, Chrome, and Copper to the surface of the rhatany roots, indicating that the adsorption of Cadmium, Cobalt, Chrome, and Copper ions on the rhatany roots surface was controlled by an endothermic process[23]. herefore, an adsorption temperature of 70 C was chosen as the ideal temperature.

Fig.3. Effect of Temperature on the adsorption of Cadmium, Cobalt , Chrome, and Copper ions with concentration of 2 – 12 Rhatany Roots.

6.4. Effect of time on adsorption

The effects of different adsorption times on the rhatany roots adsorption capacity towered Cadmium, Cobalt, Chrome, and Copper are shown in fig(4) and Table(1). At prolonged adsorption times, the Cadmium, Cobalt , Chrome, and Copper   adsorption capacity of the rhatany roots initial increased rapidly and then decreased slowly because the surface of the rhatany composite was covered with a large quantity unsaturated functional groups. Cadmium, Cobalt , Chrome, and Copper ions were adsorbed by diffusing into the microporous adsorbent ; a complex was formed within the active sites of the adsorbent, thus resulting in a sharp adsorption equilibrium that decreased with the saturation of the functional groups on the rhatany roots surface [24]. Therefore, the optimum adsorption time of 40 min was selected for all further experiments.
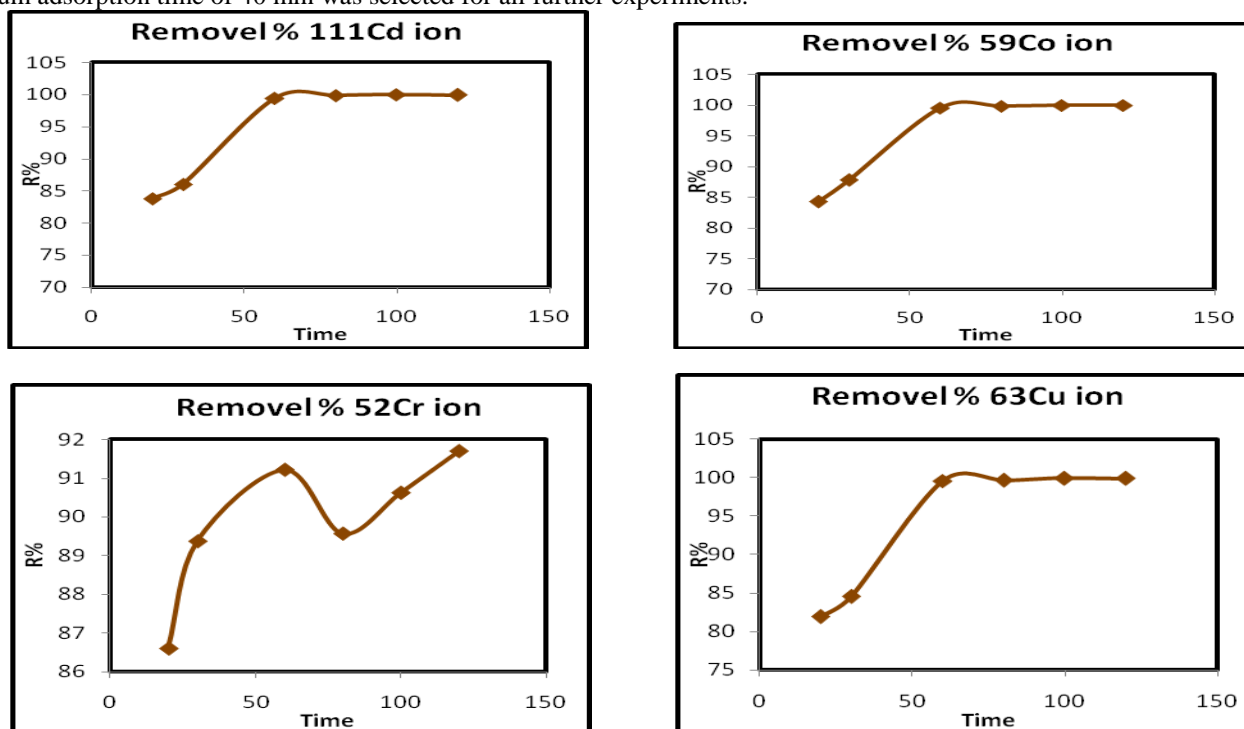

Fig.4. Effect of Time on the adsorption of Cadmium, Cobalt , Chrome, and Copper ions with Time of 20 – 120 min Rhatany Roots.

7. 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)(liquid) and the equilibrium concentration of the substance at constant temperature is called the adsorption isotherm [25]. For determining the adsorption isotherm several models have been suggested such as the Langmuir, Freundlich, isotherm models. The applicability of the isotherm equation to the adsorption study done was compared by judging the correlation coefficients [26].

7.1. 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[27] 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[28].The linear form of the Langmuir isotherm equation is given as:

$$C_e/q_e = 1/Q_o \, K_l + (1/Q_o) \, C_e \qquad (6)$$

Where, C_e = equilibrium concentration (mg/L), q_e = the equilibrium amount at time per unit adsorbent (mg/g). Q_o 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

7.2. The Freundlich Isotherm

The Freundlich equation is very popularly used in the description of adsorption of organics from aqueous streams onto activated carbon[28] .

This equation takes the following form:

$$C = KP^{1/n}. \qquad (7)$$

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

$$\log Q_e = \log K_f + 1/n \log C_e \qquad (8)$$

where : K_f and n are Freundlich constants with n giving an indication of how favorable the adsorption process is. K_f (mg/g) 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. Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

For this study the following Figures and tables are showing the isotherm models of adsorption of heavy metal ions on the Rhatany Roots From the calculated parameters of the Freundlich and Langmuir isotherms models of ions from Rhatany Roots surfaces,the results shown the Langmuir isotherm model achieved best fit with the equilibrium adsorption data, which have highest correlation coefficient values (R^2) of (0.967, 0.962 , 0.976 , 0 .965) for Cadmium, Cobalt, Chrome, and Copper, respectively. It indicates to monolayer adsorption adsorption nature of these metal ions on Rhatany Roots.

The adsorption capacity (Qo) of the adsorbent have a value of (333.33, 294.985, 588.235, 288.184 mg/g) for Cadmium, Cobalt , Chrome, and Copper , respectively.

8. Isotherm studies

The study of equilibrium curves is very important for understanding the design of an adsorption system. In this study, tow adsorption isotherms, the Langmuir and Freundluch adsorption isotherm models, were used to describe the obtained equilibrium data fig(5) and table(2)shows the adsorption capacity of the rhatany roots at different initial Cadmium, Cobalt, Chrome, and Copper concentration at adsorption temperature of 298°C. Isothermal adsorption curves were plotted using the equilibrium adsorption amount qe and the adsorption equilibrium concentration C_e. As shown in figures (5-8) and table(2), the adsorption equilibrium amount on the rhatany roots surface was enhanced by increasing the initial Cadmium, Cobalt, Chrome, and Copper concentration. Moreover, the degree of increase was higher at lower concentration and decreased with increasing initial Cadmium, Cobalt, Chrome, and Copper concentration .At an allow initial Cadmium, Cobalt, Chrome, and Copper concentration, the rhatany roots would have sufficient active adsorption sites to interact with all Cadmium, Cobalt , Chrome, and Copper ions, however, at initial concentrations beyond a critical saturation level, the active adsorption sites on the adsorbent surface were mostly occupied by Cadmium, Cobalt , Chrome, and Copper ions, further limiting the adsorption. The isothermal adsorption curves were plotted and fitted employing the Langmuir and Freundlich [29.30].

Table 2 .The calculated parameters of the Freundlich and Langmuir isotherms models of ions from Rhatany Roots surfaces.

| Parametres	Freundlich isotherm				Langmuir isotherm			
	Kf	1/n	n	R^2	Q_o	Kl	R^2	Rl
Adsorbent								
111Cd	55.719	0.573	1.745	0.129	1428.571	0.013	0.025	0.441
59Co	48.529	0.631	1.585	0.099	1851.852	0.010	0.008	0.507
52Cr	73.451	0.586	1.706	0.508	1000.000	0.039	0.341	0.206
63Cu	26.002	0.819	1.221	0.555	2702.703	0.006	0.031	0.619
pH								
111Cd	397.192	-0.043	-23.256	0.196	500	0.222	0.923	0.043
59Co	396.278	-0.04	-25	0.183	476.191	0.226	0.940	0.042
52Cr	87.096	0.441	2.268	0.928	1000.000	0.037	0.983	0.213
63Cu	428.549	-0.144	-6.944	0.793	288.1840	6.298	0.962	0.002
TC°								
111Cd	371.535	-0.093	-10.753	0.661	250.000	-1.333	0.951	-0.008
59Co	373.250	-9.099	-10.101	0.722	226.244	1.573	0.951	0.006
52Cr	146.555	0.263	3.802	0.337	1000.000	0.033	0.775	0.231
63Cu	425.643	-0.163	-6.135	0.786	203.353	-8.995	0.9 87	-0.001
time min								
111Cd	394.457	-0.101	-9.901	0.710	333.333	3.750	0.967	0.003
59Co	394.457	-0.102	-9.804	0.715	294.985	**5.947**	**0.962**	**0.002**
52Cr	85.901	0.420	2.381	0.939	588.235	0.054	0.976	0.156
63Cu	429.536	-0.141	-7.092	0.776	288.184	5.689	0.965	0.002
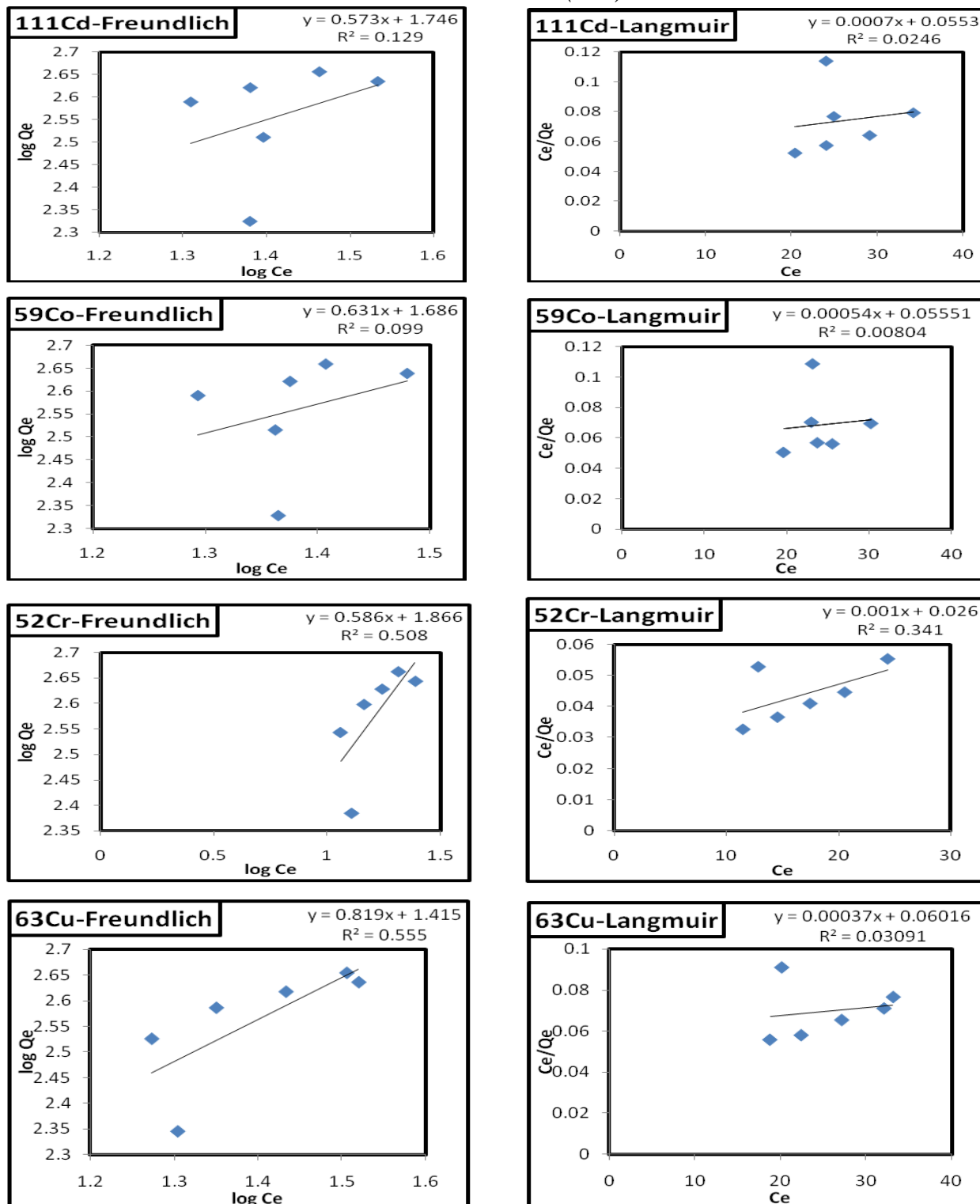
Figure 5. Adsorption isotherm of Cadmium, Cobalt , Chrome, and Copper ions on Rhatany Roots surface at different initial Concentration.
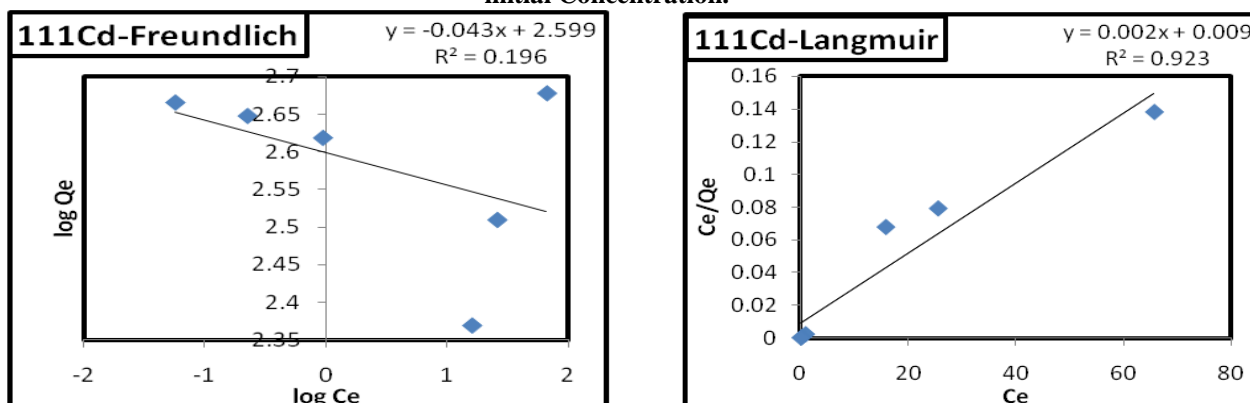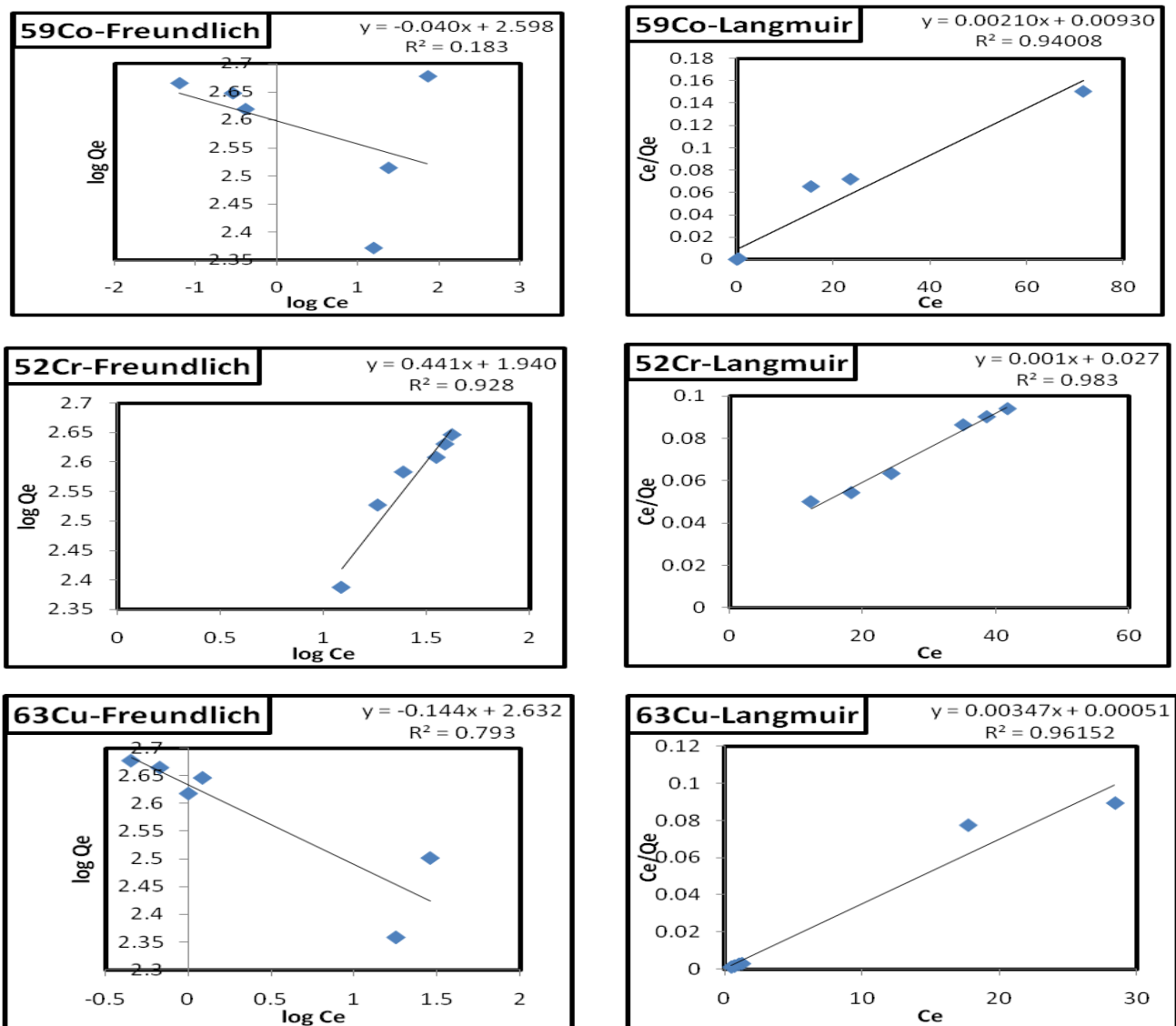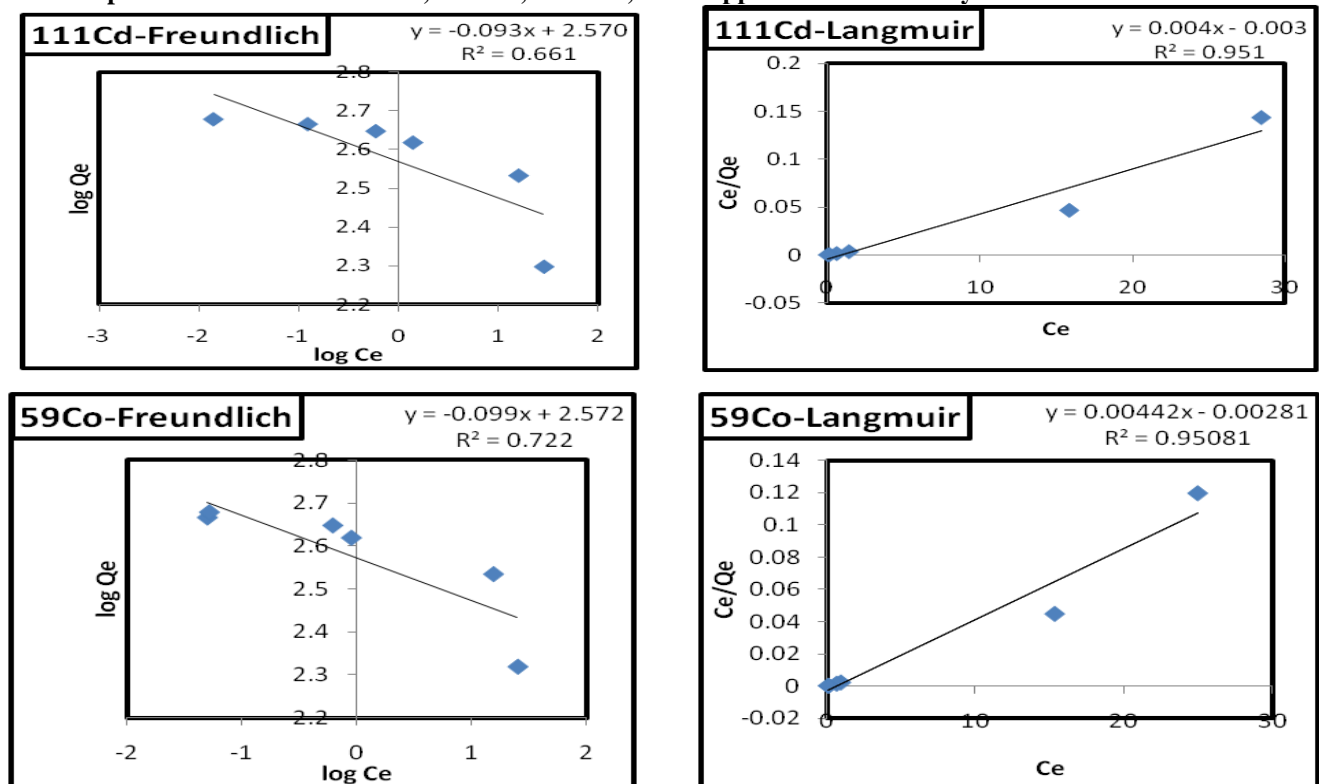
Figure 6. Adsorption isotherm of Cadmium, Cobalt , Chrome, and Copper ions on Rhatany Roots surface at different PH.
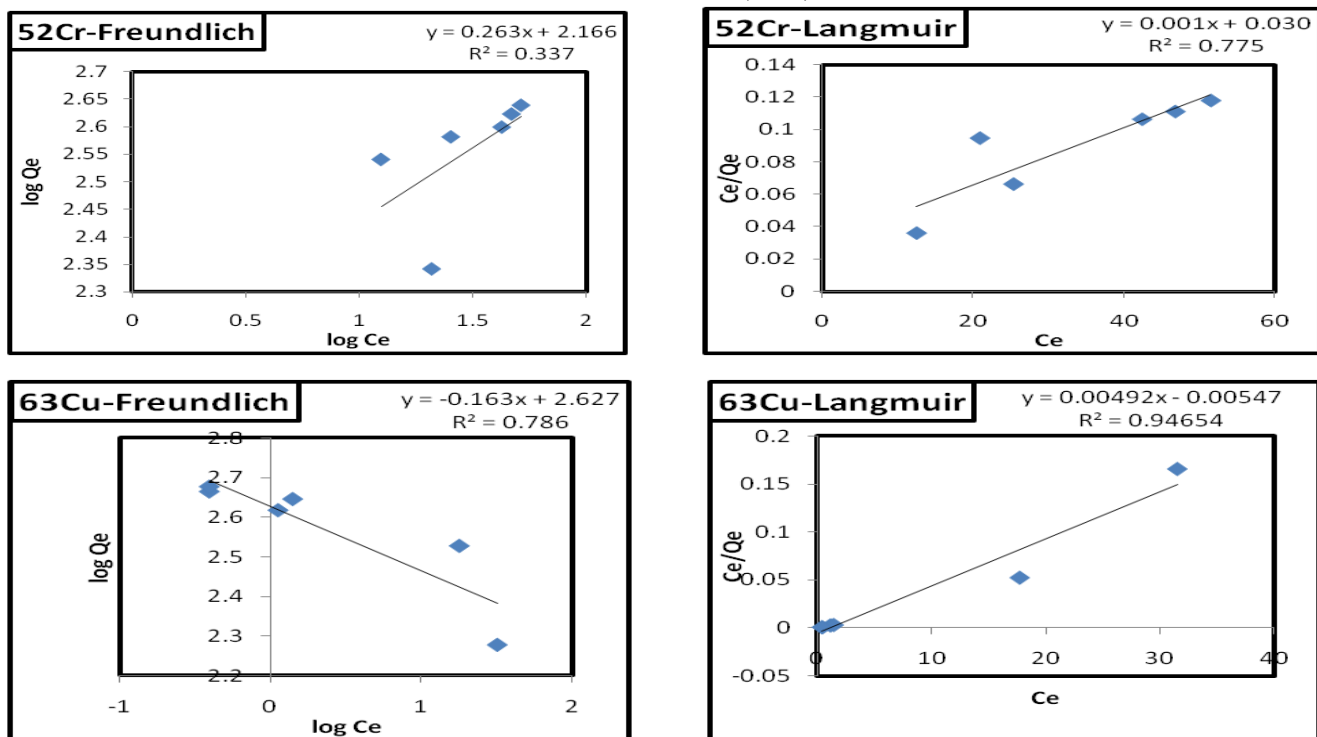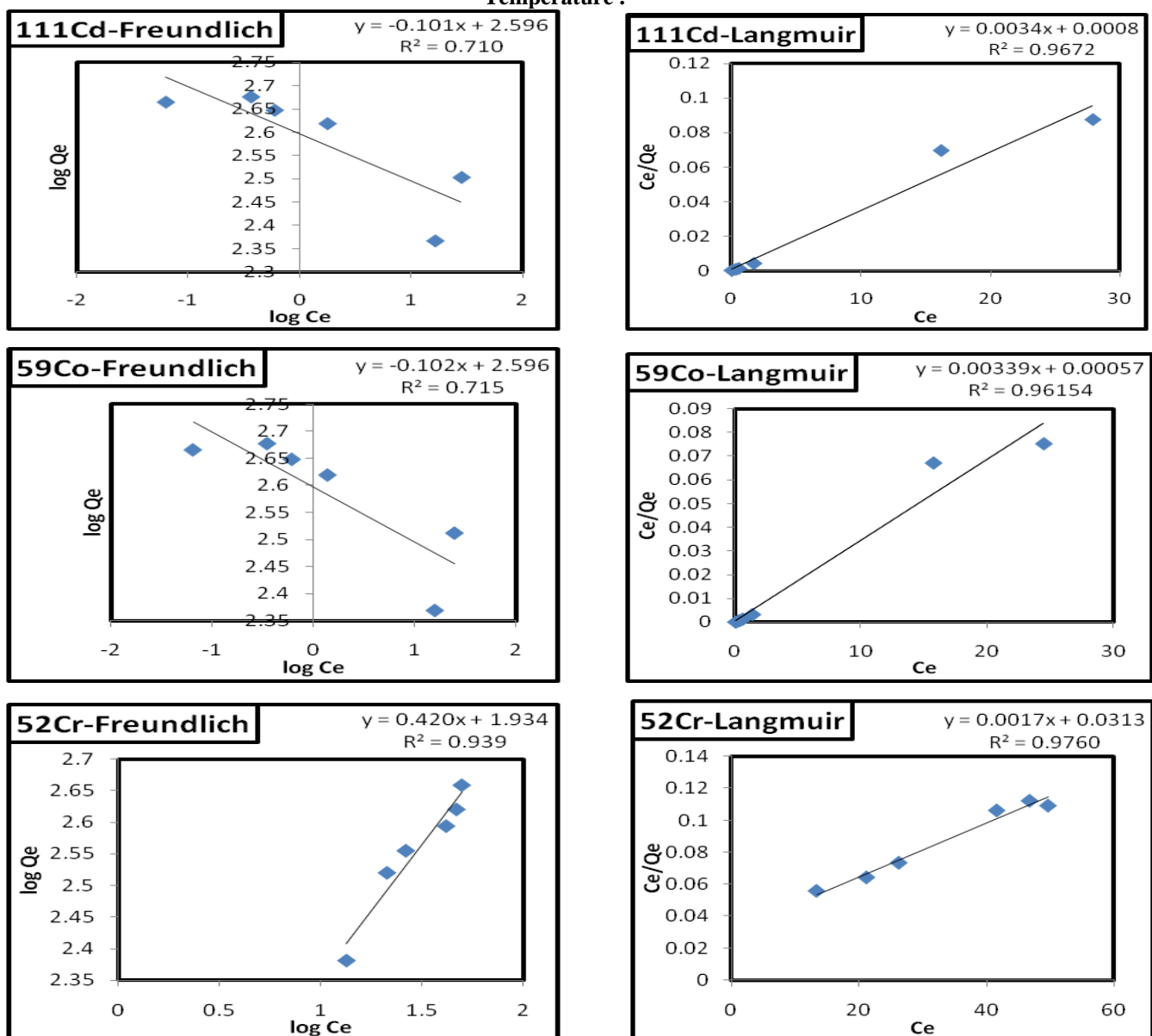
Figure 7. Adsorption isotherm of Cadmium, Cobalt , Chrome, and Copper ions on Rhatany Roots surface at different Temperature .
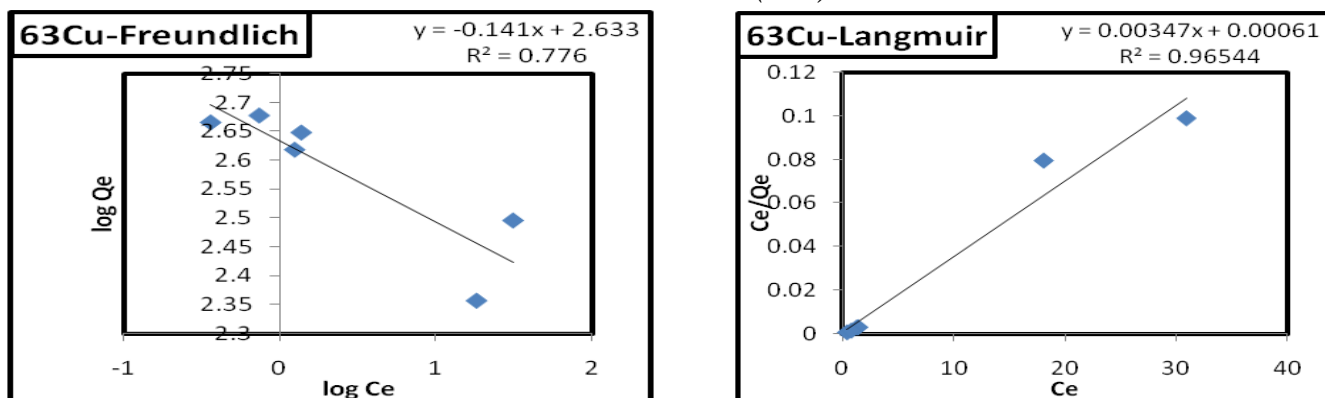
Figure 8. Adsorption isotherm of Cadmium, Cobalt , Chrome, and Copper ions on Rhatany Roots surface at different Time.

9. Adsorption Thermodynamics

Thermodynamic parameters helps to evaluate the orientation and the feasibility of the physicochemical adsorption process and provides vital information on the inherent energy and the structural changes due to metal ion adsorption, it also provides information on the mechanism of the adsorption process. The thermodynamic parameters such as changes in free energy ΔG^o, Enthalpy ΔH^o and the Entropy ΔS^o were calculated from (6)-(8).

$$Kc=C_{ad}/C_e \tag{9}$$
$$\Delta G^o=-RT\ln K_c \tag{10}$$
$$\Delta G^o=\Delta H^o-T\Delta S^o \tag{11}$$

Where Kc is the equilibrium constant of adsorption, C_{ad} (mg/l) is the concentration of Cadmium, Cobalt , Chrome, and Copper ions adsorbed by the Rhatany Roots at equilibrium, Ce (mg/l) is the concentration of Cadmium, Cobalt, Chrome,and Copper ions remaining in solution at equilibrium, R is the universal gas constant (8.314J/mol/K) and T (K) is the absolutetemperature.

Table 3. Thermodynamic parameters of Cadmium, Cobalt , Chrome, and Copper ions)on Rhatany Roots at initial metal ion concentration 100 mg/L , pH=4.0 , pH=6.0 , pH=8.0 and pH=10.0 and Temperature 40 ,55, and 70 ^{o}C .

Heavy Metals		Thermodynamic parameters			
	pH	ΔH_o (kJ/mol)	ΔS^o (J/mol.K)	ΔG^o (kJ/mol)	R^2
111Cd	4	-2.134	0.009	-5.003	0.992
	6	-10.388	0.033	-22.272	0.841
	8	-3.062	0.013	-8.195	0.903
	10	-7.798	-0.004	-18.513	0.998
59Co	4	-2.181	0.009	-5.159	0.999
	6	-11.288	0.039	-24.187	0.831
	8	-0.679	0.008	-3.377	0.845
	10	-8.514	0.034	-19.606	0.791
52Cr	4	-2.197	0.009	-5.268	0.996
	6	6.291	-0.017	11.877	0.998
	8	0.493	-0.001	0.582	0.896
	10	0.156	0.001	0.001	0.66
63Cu	4	-2.705	0.010	-6.112	0.938
	6	-9.521	0.034	-20.524	0.711
	8	-1.426	0.010	-4.818	0.999
	10	-1.301	0.010	-4.721	0.767
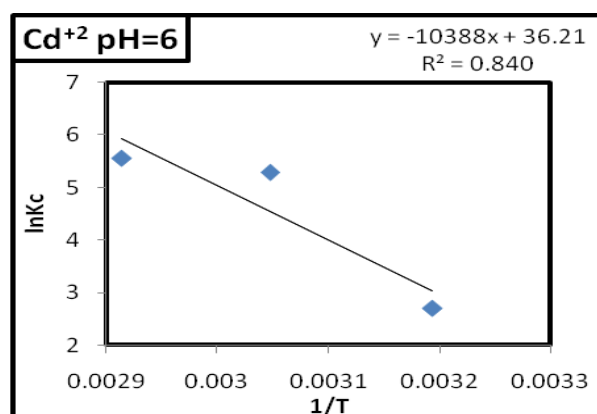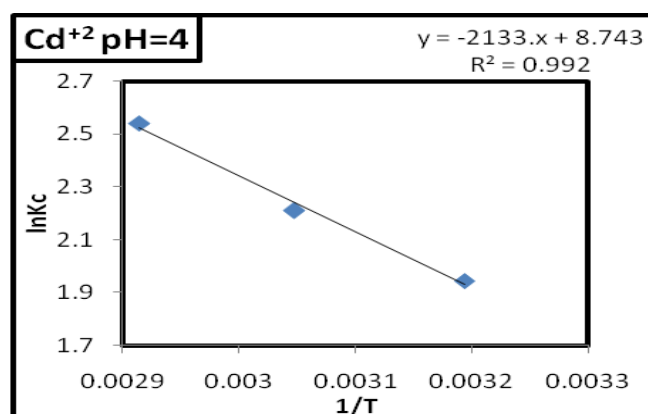
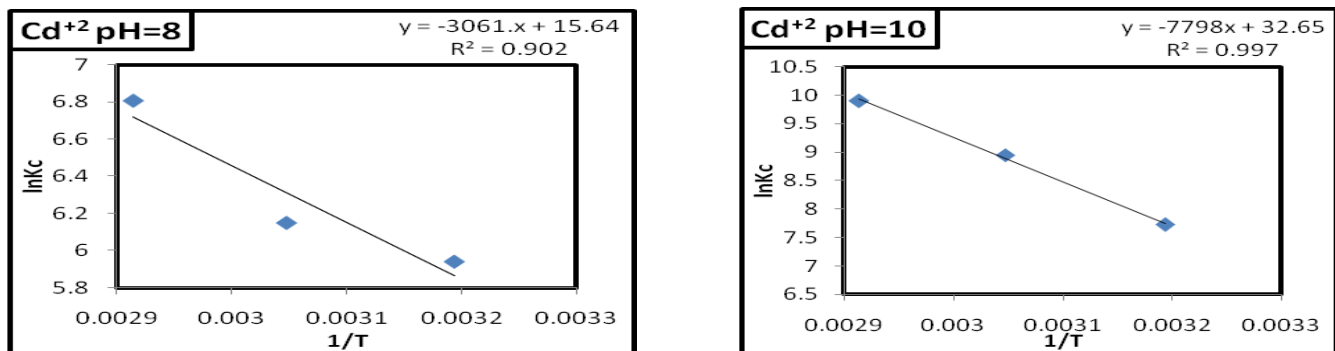**Figure 9. Plots lnKc Vs 1/T for the determination of thermodynamic parameters for adsorption of (Co^{+2})ions on the Rhatany Roots at   pH=4.0 , pH=6.0 , pH=8.0 and pH=10.0.**
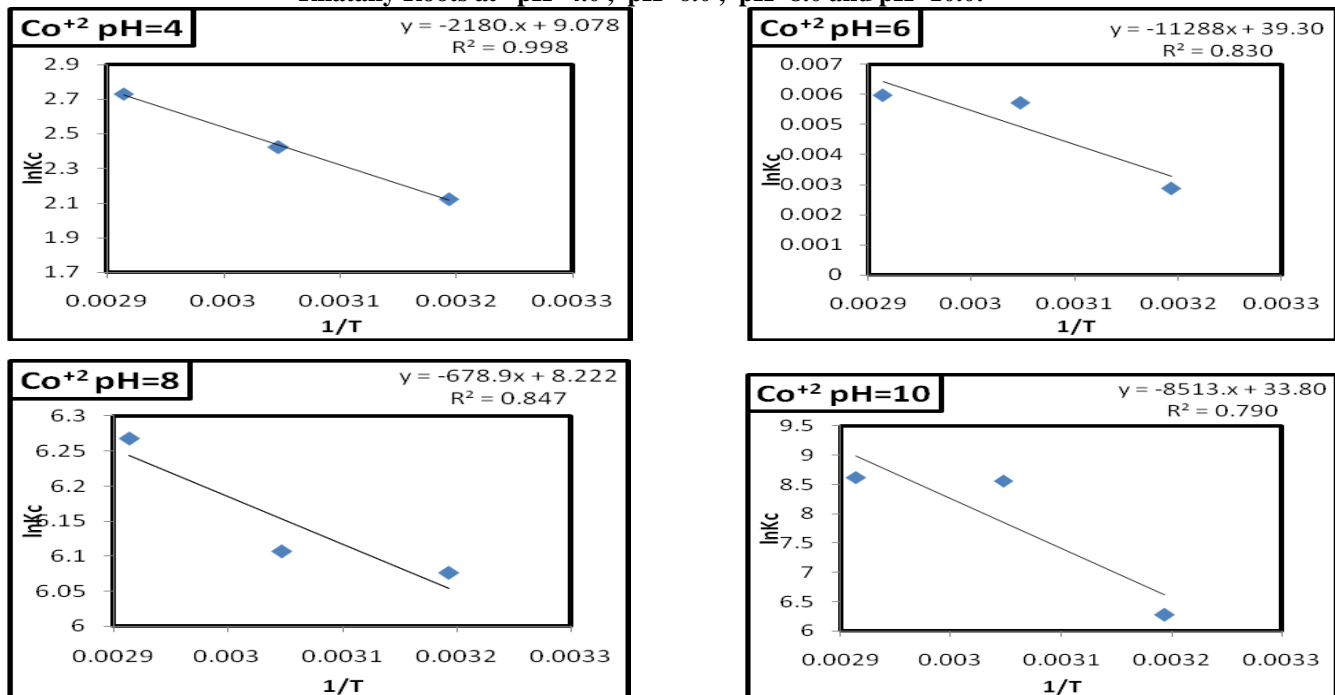

Figure 10. Plots lnKc Vs 1/T for the determination of thermodynamic parameters for adsorption of $\overline{(Co^{+2})}$ions on the Rhatany Roots at   pH=4.0 , pH=6.0 , pH=8.0 and pH=10.0.

Figure 11. Plots lnKc Vs 1/T for the determination of thermodynamic parameters for adsorption of (Cr^{+6})ions on the Rhatany Roots at   pH=4.0 , pH=6.0 , pH=8.0 and pH=10.0.

Figure 12. Plots lnKc Vs 1/T for the determination of thermodynamic parameters for adsorption of (Cu^{+2})ions on the Rhatany Roots at pH=4.0 , pH=6.0 , pH=8.0 and pH=10.0.
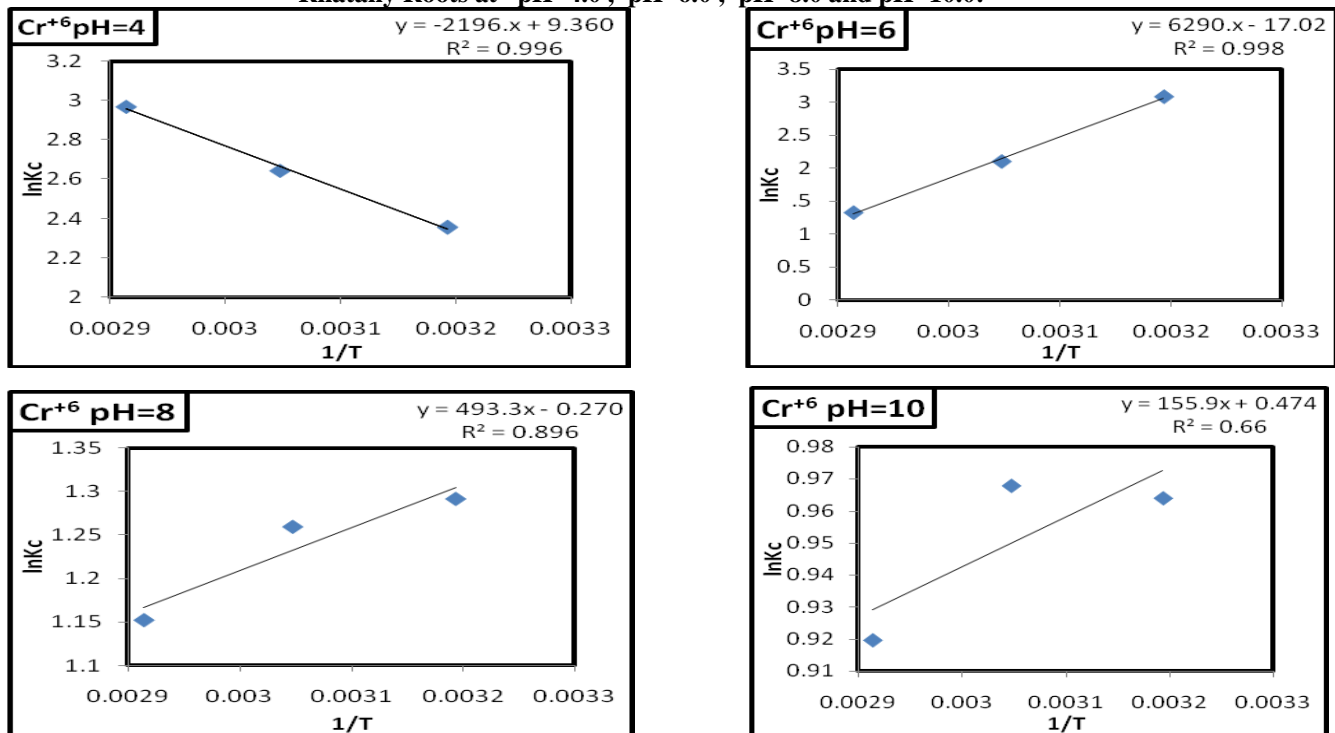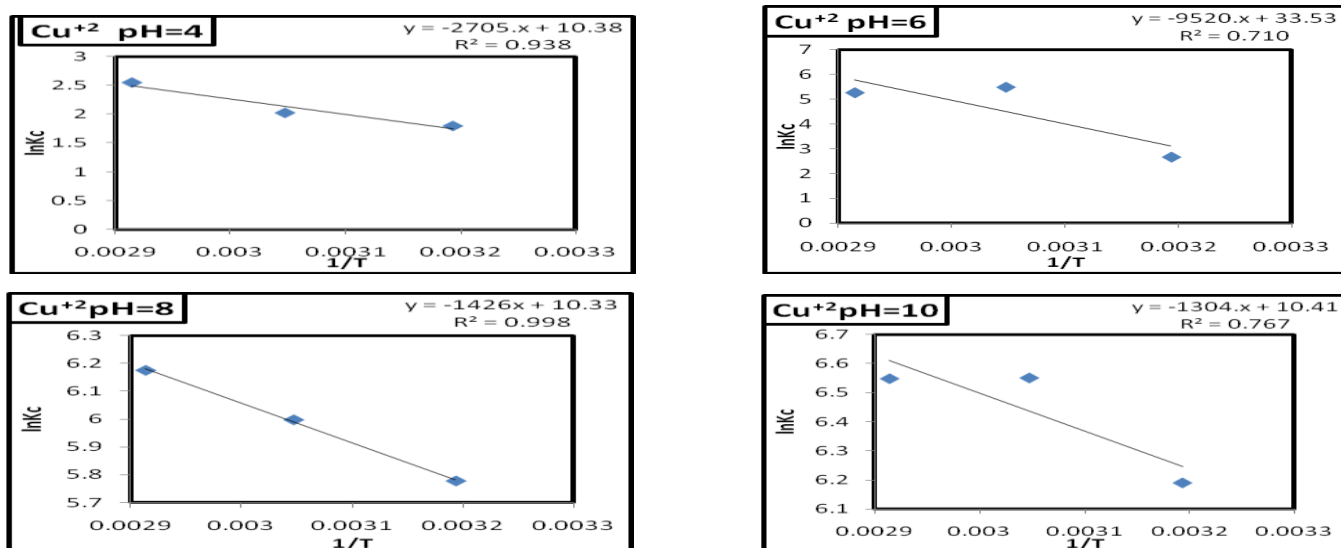
The plot of the changes in free energy against temperature is shown in figures (9-12). ΔS^o and ΔH^o were obtained from the slope and intercept respectively. Thermodynamic parameters obtained are presented in table (3). The value of the regression coefficient R^2 of 0.9755 showed a good agreement between free energy changes and temperature. It is clear that the reaction is spontaneous in nature as negative values of ΔG^o were obtained at all temperatures. Also, the positive value of $\Delta S°$ reflected the affinity of the adsorbent for particular of heavy metal ions and confirms the increased randomness at the solid–solution interface during adsorption. An exothermic adsorption process was indicated by the negative enthalpy ΔH^o obtained. This sorption process can be explained better by the magnitude of ΔH^o . The heat evolved during physisorption lies generally in the range of 2.1 – 20.9 KJ/mol [32,33]. This implies that the sorption of Cadmium, Cobalt , Chrome, and Copper ions unto Rhatany Roots may be attributed to a physical adsorption process.

10. 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.

10.1. Zero Order

Differential equation which describes zero order is[36]

$$dc/dt=-K \tag{12}$$

Integrating with C=Ci at t = 0

$$C_t=C_i–Kt \tag{13}$$

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).

10.2. First Order

Differential equation which describes first order is[36]

$$-dc/dt=K_1C \tag{14}$$

With the limit C =Ci at *t* = 0 gives

$$lnC_i/C_t=K_1t \tag{15}$$

The linear form of firs order equation is:

$$lnC=lnC_i-K_1 \tag{16}$$

Where:$K_1$is the rate constant of first order adsorption (min-1).

10.3. Second Order

Differential equation which describes second order is :

$$-dc/dt=K_2C_2 \tag{17}$$

With the limit = C_i initially, yields

$$1/C_t=1/C_i+K_2t \tag{18}$$

Where:K_2 is the rate constant of Second order adsorption (L·mg-1·min-1).

10.4.Third Order

The third order equation is given by the following[37]

$$1/C_t^2=1/C_i^2+K_3t \tag{19}$$

Where: K_3 the rate constant of third order adsorption **.**

10.5. 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[38]

$$dQ_t/dt=K_{1p}(Q_e-Q_t) \tag{20}$$

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 and from Q_t=0

$Q_t=Q_t$

$$ln(Q_e/Qe-Qt)=K_{1p}t \tag{21}$$

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

$$log(Q_e-Q_t)=logQe–(K_{1p}/20303)t \tag{22}$$

10.6.Pseudo Second Order (Lagergren's Equation)

The pseudo-second-order expression can be derived from, [39,40].

$$dQ_t/dt=K_{2p}(Q_e-Q_t)^2 \tag{23}$$

Where: K is the rate constant of adsorption (g·g-1·min-1).Separating the variables in Eq. (22) and integrating this for the boundary conditions t = 0 to t

$$Qt=logQe–(K2pQe2/1+QeK2pt \tag{24}$$

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

$$t/Q_t=1/K_{2p}Q_e^2+(1/Q_e)t \tag{25}$$

10.7. The Intraparticle Diffusion Model

Intraparticle diffusion is a transport process involving movement of species from the bulk of the solution to the solid phase.

Table 4. The calculated parameters of the Pseudo-First order & Pseudo-Second order kinetic models of (ions from Rhatany Roots surfaces).

	Zero order		1st order		2nd order		3rd order	
Heavy metals	K_0	R^2	K_1	R^2	K_2	R^2	K_3	R^2
111Cd	0.234	0.565	0.055	0.774	-0.09	0.289	1.173	0.173
59Co	0.215	0.595	0.054	0.776	-0.087	0.300	1.075	0.176
52Cr	0.391	0.961	0.013	0.934	0.001	0.853	0.001	0.738
63Cu	0.391	0.961	0.042	0.749	-0.021	0.591	-0.045	0.335
Heavy metals	Pseudo 1st order		Pseudo 2nd order		Intraparticlediffusion model			
	K_{1p}	R^2	K_{2p}	R^2	K_{ip}	θ	R^2	
111Cd	0.668	0.791	$1.88679*10^{-5}$	0.993	-3.669	37.43	0.573	
59Co	0.067	0.787	$1.96078*10^{-5}$	0.995	-3.399	34.55	0.611	
52Cr	0.059	0.626	0.00002	0.992	6.083	-15.90	0.959	
63Cu	0.067	0.791	$1.8181*10^{-5}$	0.991	-3.999	41..07	0.573	

In a well stirred batch adsorption system, the intraparticle diffusion model has been used to describe the adsorption process occurring on a porous adsorbent[41].The diffusion model can be expressed by following equation [42,43].

$$C_t = \theta + K_{jp}\sqrt{t} \tag{26}$$

11.Kinetic Studies.

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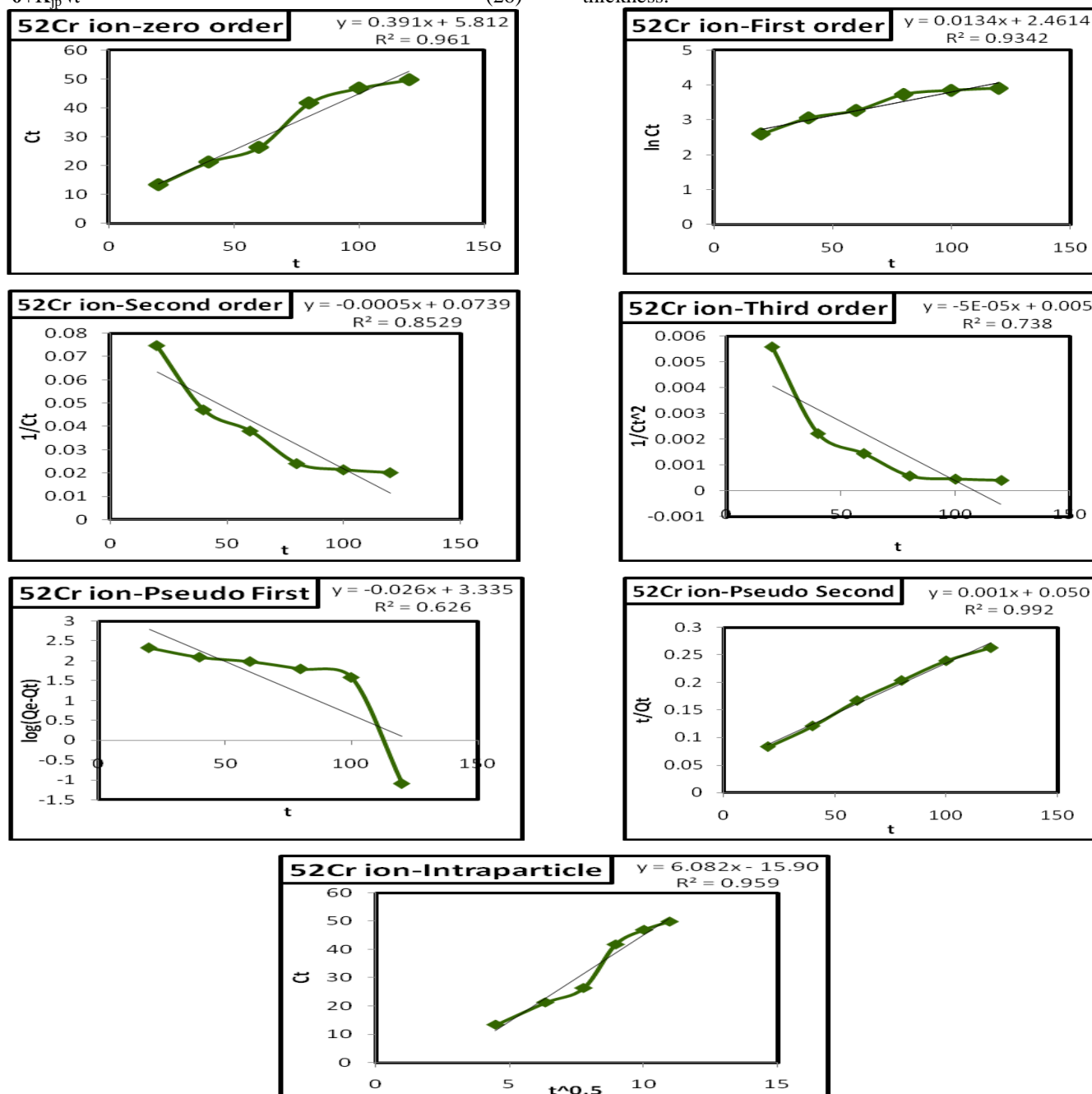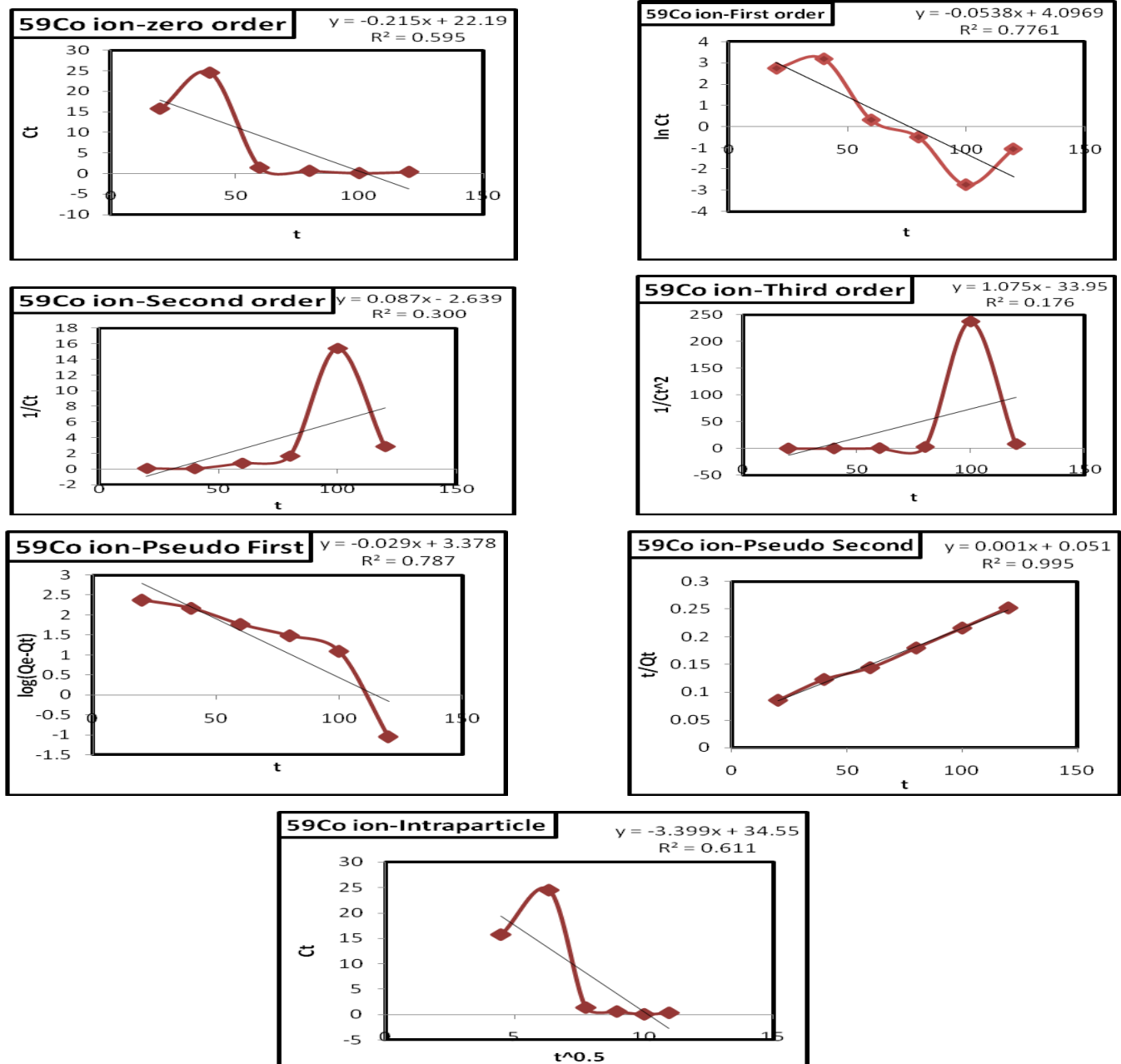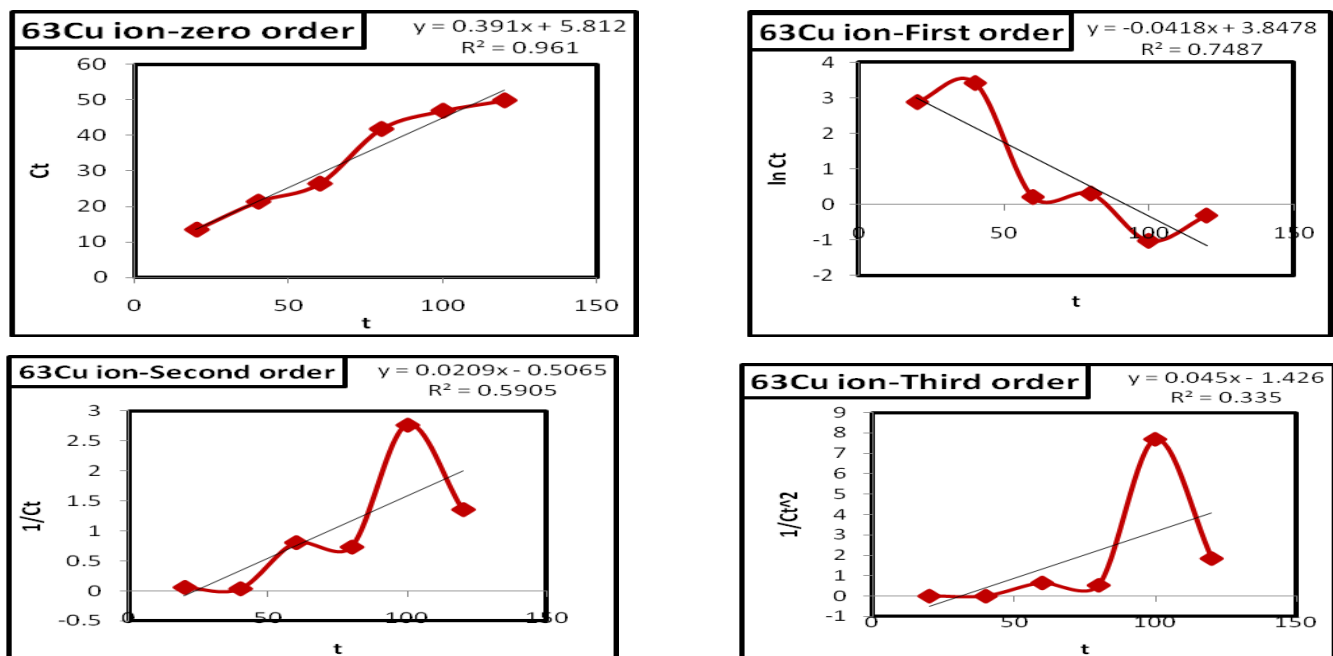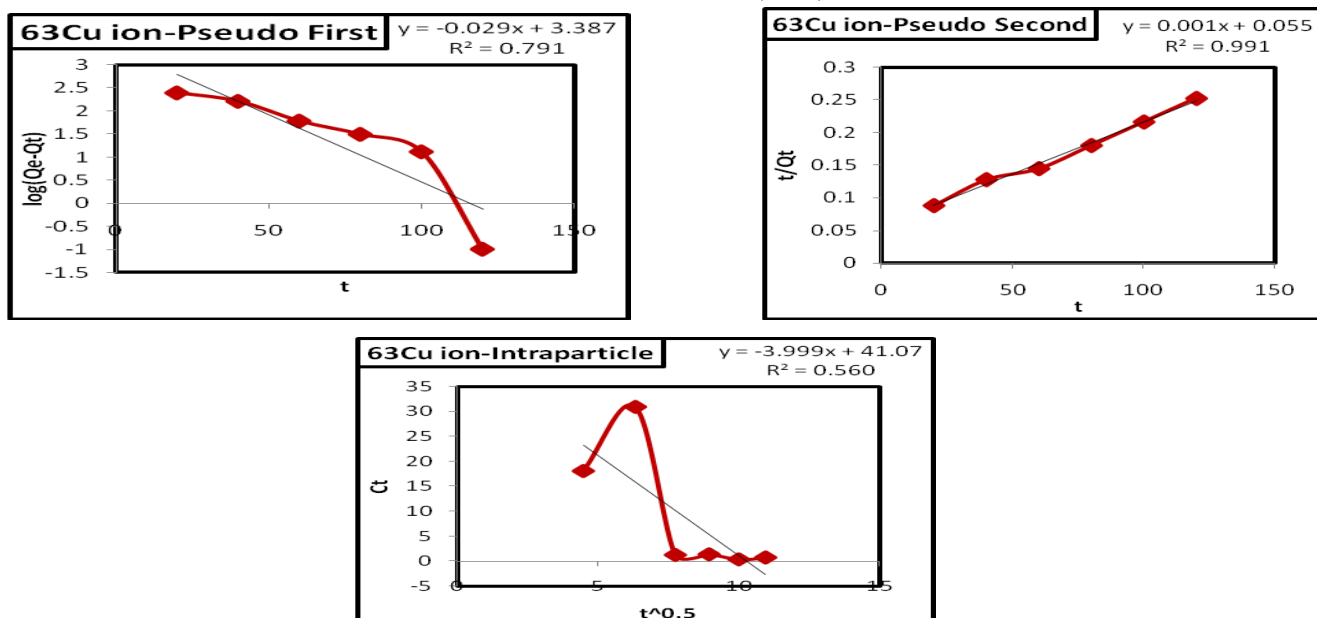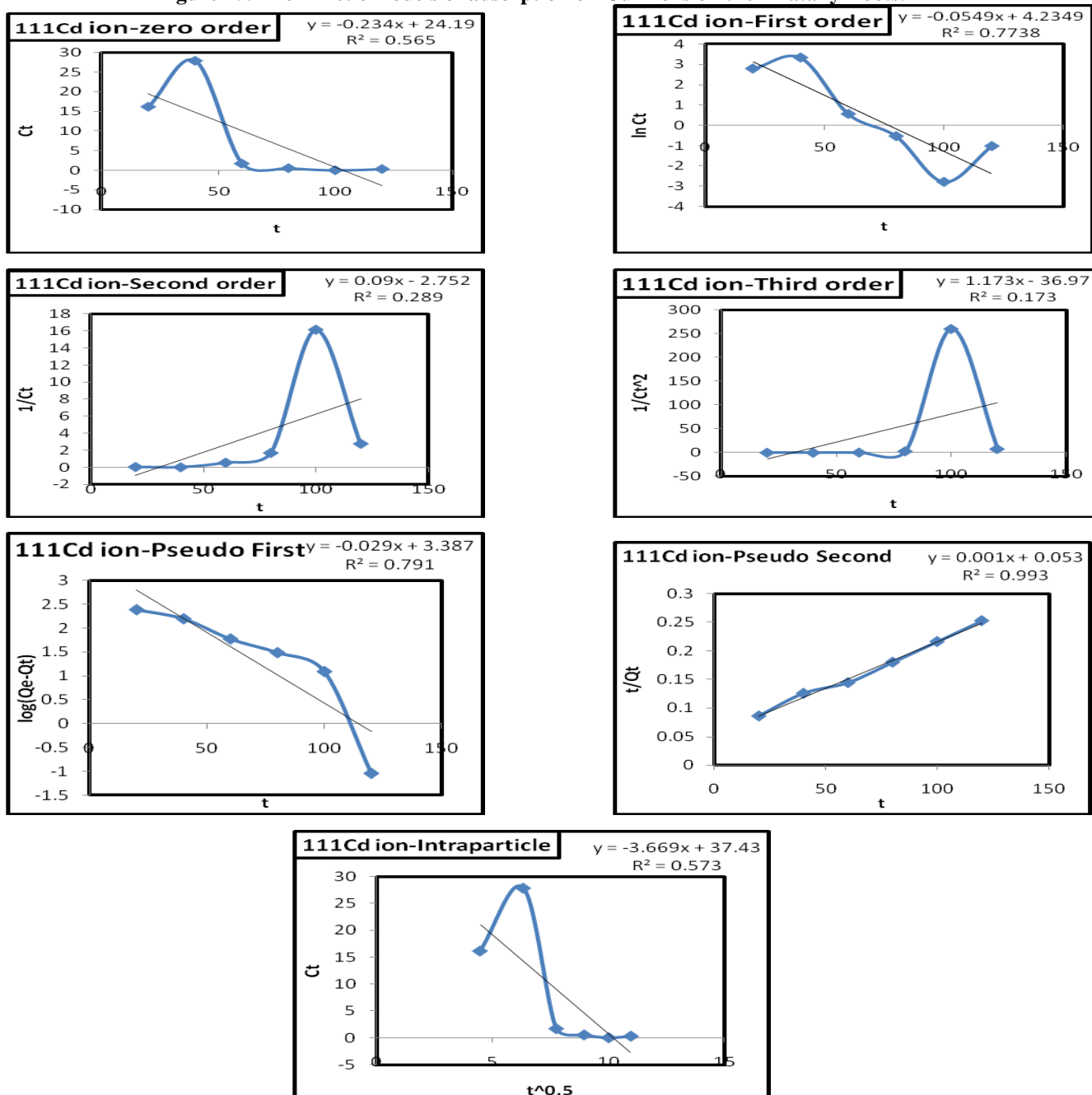

Figure 13. The Kinetic models of adsorption of Cr^{+6} ions on the Rhatany Roots.

Figure14.The Kinetic models of adsorption of Co^{+2} ions on the Rhatany Roots.

Figure 15. The Kinetic models of adsorption of Cu^{+2} ions on the Rhatany Roots.

Figure 16.The Kinetic models of adsorption of Cd^{+2} ions on the Rhatany Roots.

From above figures(13-16),and results, the dependence of the reaction rate on the initial concentration Cadmium, Cobalt , Chrome, and Copper ions was investigated by assuming pseudo-first–order and pseudo-second-order models fig(13) showed the effect of time on the rhatany roots adsorption capacities at various initial of Cadmium, Cobalt, Chrome, and Copper ions concentrations. As evident in the figure(13), qt increases significantly with increasing time t (min) during the initial stage and then slowly decreased, followed by a continuous increase at time(min).After 40 min at adsorption equilibrium, the rhatany roots reached the maximum adsorption value of 94.86 mg/g. The adsorption of Cadmium, Cobalt**,** Chrome, and Copper ions onto the rhatany involves the following steps. First, the Cadmium, Cobalt**,** Chrome, and Copper ions adsorb onto the surface of the rhatany roots, were it reacts with active functional groups, thus accelerating the adsorption rate. Second, the Cadmium, Cobalt**,** Chrome, and Copper ions diffuse into the interior through microporous surface channels on the rhatany roots decreasing the adsorption rate. Finally, adsorption equilibrium is reached. The adsorption kinetic curve of the rhatany roots was modeled by fitting the pseudo first-order equation (15) and the pseudo-second-order adsorption kinetic equation (18) [44] where qe mg/g is the amount of Cd(II) Co(II) Cr(VI) and Cu(II) ions adsorbed at time upon reaching equilibrium, qt (mg/g) is the amount of Cd(II) Co(II) Cr(VI) and Cu(II) ions adsorbed at time (min), and k_1(min-1) and k_2[g_(mg/min)-1] are the rate constants of the pseudo-first – order and pseudo-second-order adsorption kinetic equation, respectively. The result of the adsorption kinetics and fitting models are listed in table (4)and figures(13-16).

12. Conclusions

This study that extraction Rhatany roots which is widely available at law cost can be used as an efficient adsorption material for removal of Cadmium, Cobalt, Chrome, and Copper from Synthetic Wastewater solution was carried out in batch shake flasks experiment . The operational parameters like Ph has significant effect on the removal efficiency. Kinetics data were best modeled by a pseudo Second order kinetics equation.

The adsorption isotherms at different temperatures could be well described by Langmuir and Freundlich isotherm models were used for the study and equilibrium data well fitted Langmuir model. The thermodynamic study shows that the adsorption of Cadmium, Cobalt**,** Chrome, and Copper were exothermic nature. The negative values of ΔG^o reveal the feasibility and spontaneous nature of the process.

Acknowledgement

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