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Studies On The Adsorption Of Cu^{2+} Ions Using Strong Cation Exchanger Resinex^{TM} K-8H.

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ABSTRACT

In the present work the adsorption processes of copper (Cu^{2+}) ions on Resinex^{TM} K-8H strong acid cation exchange resin in the H^+ form, was investigated it is used in this study under different conditions. The amount of copper (Cu^{2+}) metal ion adsorbed on the exchange resins increases with increasing it is initial concentrations. The adsorption of metal ion (Cu^{2+}) has been found to increase with an increase in temperature from 29^0C to 51^0C . The increase in adsorption capacity of the adsorbent with temperature indicates an endothermic process. The thermodynamic parameters, the Gibbs free energy change(ΔG), Enthalpy change (ΔH) and Entropy change (ΔS)are calculated and show that the adsorption of copper (Cu^{2+}) is spontaneous and endothermic in nature.

Key words: Cation exchange resin; Copper; Adsorption kinetics; Adsorption mechanism.

Introductin

The adsorption behavior of metal ions on a new inorganic cation exchanger titanium Ti(IV) molybdosilicate in different solvent systems namely acetic acid, formic acid, dimethylsulfoxide, phenol, triton, formamide and dimineralized water has been studied (Nabi *et al*, 2007). In order to demonstrate analytical utility of titanium Ti(IV) molybdosilicate, quantitative separation of Fe^{3+} and Cu^{2+} contents of a commercially available pharmaceutical sample viz Fefol-Z has been performed on its column (Nabi *et al*, 2007).

The equilibrium data for the adsorption of Cu(II) and Pb(II) on PS-EDTA resin were tested with three adsorption isotherm models which were found to be suitable for the two ions adsorptions. In addition, the kinetic adsorption fitted well to the pseudo-second-order model and the corresponding rate constants were obtained. Furthermore a higher desorption efficiency of Cu(II) and Pb(II) from the PS-EDTA resin using acid treatment was available (Wanga *et al*, 2010).

The maximum adsorption capacity in single system for Cu(II), Pb(II) and Cd(II) was calculated to be 2.27 mmol/g, 1.27 mmol/g and 0.65 mmol/g individually. The initial adsorption rate followed the order as Cu(II) > Pb(II) > Cd(II) at the fixed initial concentration, and for each metal the initial adsorption rate increased as the initial concentration increased. In addition, the modified Langmuir model could describe the binary competitive adsorption behavior successfully, with which the interaction coefficient was obtained to follow the order as Cu(II) < Pb(II) < Cd(II) (Li *et al*, 2011).

The use of the strongly basic polystyrene and polyacrylate anion exchangers to remove heavy metal ions Cu(II), Zn(II), Co(II) and Pb(II) in the presence ofa new generation chelating agent from wastewaters was evaluated (Kołodyńska, 2011).

The heavy metal ion adsorption reached up to 56.67 mg/g for Cu(II) and 38.39 mg/g for Zn(II) on Amberlite IRA 402 and up to 51.10 mg/g for Cu(II) and 43.09 mg/g for Zn(II) on Amberlite IRA 458. The equilibrium adsorption studies of Cu(II) and Zn(II) complexes with GLDA have been described by the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models (Kołodyńska, 2011).

The maximum adsorption capacities and isotherm parameters were found from the Langmuir and Freundlich equations. The characteristics of Ni(II) and Cu(II) metal bindings were interpreted by using Scatchard plot graphics, and it was showed that in different concentrations multi-type and/or nonspecific interactions among metal ions and modified silica gel structures were the prevailing effects causing the Ni(II) and Cu(II) adsorptions. Conclusively, probable benefit of each specific binding type in adsorptions of Ni(II) and Cu(II) from aqueous media has been discussed in detail (Dumrul *et al*, 2011).

A comparative study on adsorption of copper Cu(II) ion over NH2-SBA-15 silica and TCPP-SBA-15 was performed. The results show that TCPP-SBA-15 material has higher adsorption capacity thanNH_2-SBA-15 silica and it reaches the adsorption maxima around 13mmolg^{-1}(Jeong *et al*, 2011).

Adsorption reactions of Cd(II) and Cu(II) with nanoparticle agglomerates of titanium(IV) oxide (NHTO) were investigated from single and bi-component systems at optimized pH 5.0. Kinetic data of metal ion removal reactions described the pseudo-second order equation very well (Debnath and Ghosh, 2011).

The concentrations of metal ions Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) on Amberlite IR-120 have been measured by batch techniques and with AAS analysis. Adsorption analysis results obtained at various

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concentrations showed that the adsorption pattern on the resin followed Freundlich isotherms (Demirbas *et al*, 2005).

Experimental:

(1)- Resin and material:

A commercial synthetic, strongly acidic cation exchange resin in the H- form of resinex^{TM} K-8H of gyl type structure supported from Jacobi (Swedish company). All chemicals used were of analytical reagent grade and obtained from commercial suppliers without further purification. The certified stock solution of lead Cu(II) was purchased from merck.

(2)- Methods:

For the kinetic studies, 50 mL Cu(II) solution at a respective initial Cu(II) concentrations (282, 394, 525, 663, 2892, 5849, 8413 and 11206 mg/L) was introduced into a 100 mL conical flask containing 1.0 g of the dried cation exchanger. The flasks were capped joint-stopper and agitated at a desired temperature (19, 37 and 51°C) in separate. After different contact time intervals, aliquots of metal ion solution were withdrawn and centrifuged to obtain the supernatants.

The supernatants were then kept to determine the Cu(II) concentrations using AAS varion 6 (Analytik Jena AG Konrad-Zuse-StraBe 1 07745 Jena). The amount of metal ion adsorbed q_t (mg/g), at time t (min), was calculated by equation:

[$q_t = (C_i - C_t)V/m$] where C_i and C_t (mg/L) are initial and equilibrium concentrations of metal ion, respectively, V (L) is the volume of metal ion solution, and m (g) is the mass of the adsorbent.

Results And Discussions

(A)- Studies Of Adsorption Processes:

The adsorption data of the metal complexes $[Cu(IOA)]^{n+}$ on Resinex^{TM} K-8H were analyzed according to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) models (Langmuir, 1918), (Freundlich,1918), (Temkin and Pyzhev, 1940) and (Dubinin and Radushkevich, 1047).

In the case of Freundlich isotherm (Fig. 1. a, b, c and d), the higher values of the K_F indicate the higher affinity of the cation exchange resin for the metal complexes. The values of *n* between zero and one indicate favourable adsorption. The results obtained (Table 1) with the Freudlich isotherm model show that the adsorption capacities are lower than the experimental data ($qe_{,exp}$). The parameter K_F related to the adsorption density is higher in the case of adsorption on Resinex^{TM} K-8H. The R^2 values in the case of Freundlich isotherm ranged from 0.986 to 0.992.

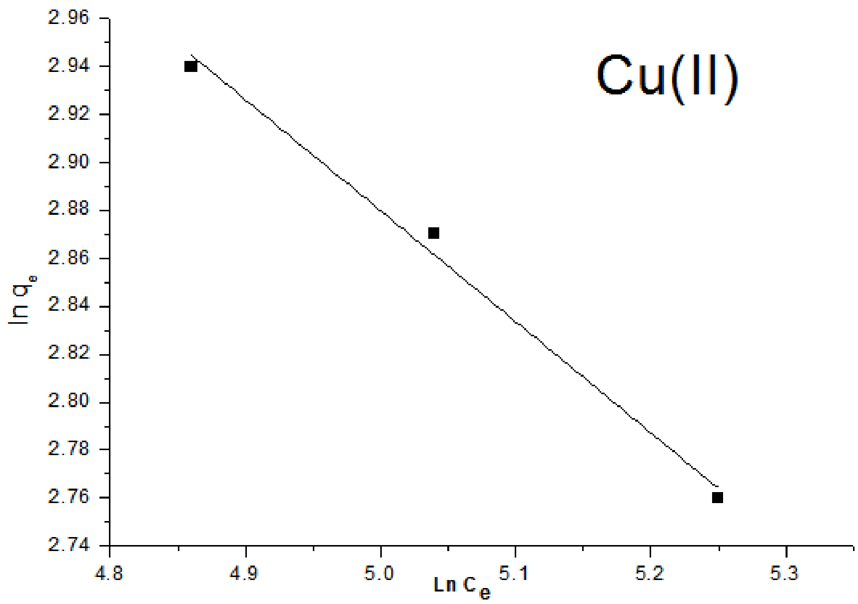

Fig. 1.a: Freundlich plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of H_3PO_4 0.1M

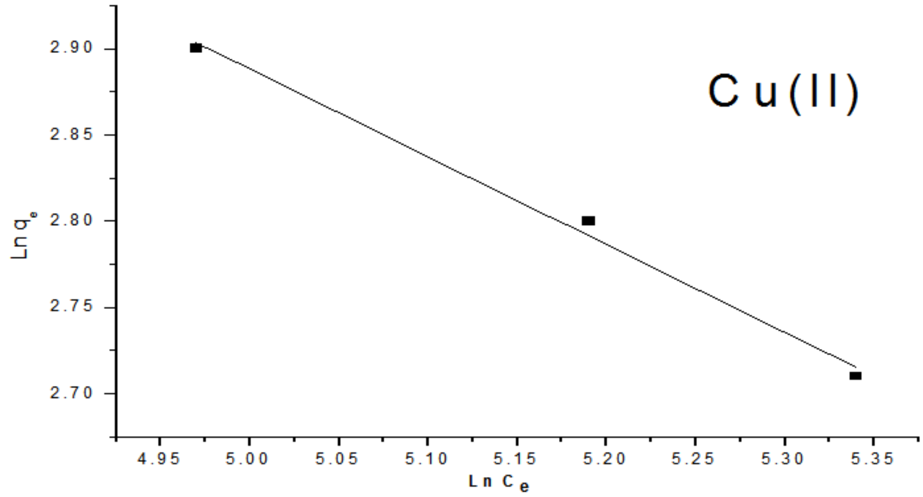

Fig. 1.b: Freundlich plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of H_2SO_4 0.1M

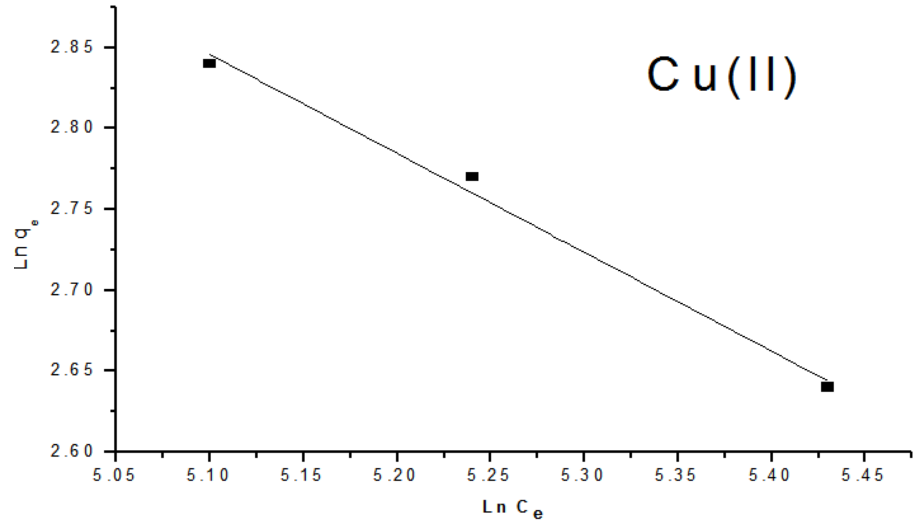

Fig. 1.c: Freundlich plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of HNO_3 0.1M

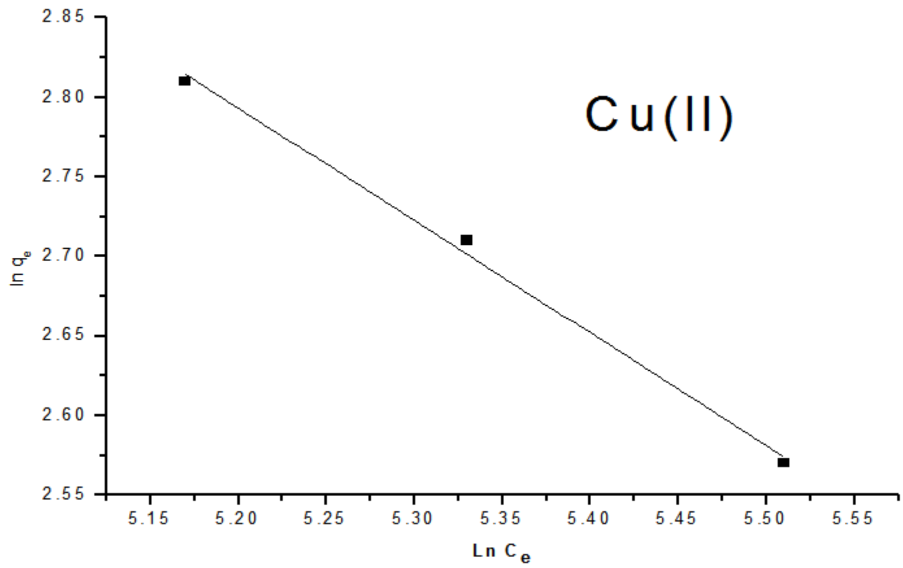

Fig. 1.d: Freundlich plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of HCl 0.1M

Table 1: Parameters of Freundlich, Langmuir isotherms of Cu(II) in presence of inorganic acids and at different temperatures (19^{0}C, 37^{0}C and 51^{0}C), M = 8.0 mmol/L.

$H_3PO_4H_2SO_4HNO_3HCl$				
Freundlich Cu n k_f R^2	 2.16 180.57 0.986	 1.96 229.04 0.988	 1.64 387.44 0.986	 1.41 646.57 0.992
Langmuir Cu Q_o b R_L R^2	 11.77 0.24 8.27×10^{-3} 0.996	 10.77 0.18 0.01 0.994	 9.4 0.12 0.02 0.995	 8.5 0.1 0.02 0.992

Table 2: Parameters of Temkin and Dubinin-Radushkevich (D-R) isotherms of Cu(II) in presence of inorganic acids and at different temperatures (19^{0}C, 37^{0}C and 51^{0}C), M=8.0 mmol/L.

$H_3PO_4H_2SO_4HNO_3HCl$				
Temkin Cu B_T K_t R^2	 7.99213 7.18×10^{-4} 0.995	 8.57218 8.28×10^{-4} 0.994	 9.74484 1.04×10^{-3} 0.994	 10.34101 1.14×10^{-3} 0.995
D-R Cu X_m β R^2	 14.43 6.45816×10^{-4} 0.905	 13.51 8.7211×10^{-4} 0.949	 12.28 0.00128 0.922	 11.19 0.00174 0.941

Based on Langmuir model (Fig. 2. a, b, c and d) for $[Cu(IOA)]^{n+}$ complexes adsorption on Resinex^{TM} K-8H, the calculated values of adsorption capacities ($qe_{,cal}$) are comparable with those obtained experimentally ($qe_{,exp}$). Moreover, the second Langmuir constant (K_L) values for Cu-phosphate, Cu-sulfate, Cu-nitrate and Cu-chloride media are as follows; 0.24, 0.18, 0.12 and 0.10, respectively (Table 1). The high values of K_L were obtained for the Resinex^{TM} K-8H. Generally, these values follow the order: Cu-phosphate > Cu-sulfate > Cu-nitrate > Cu-chloride media. This trend is consistent with the results presented earlier.

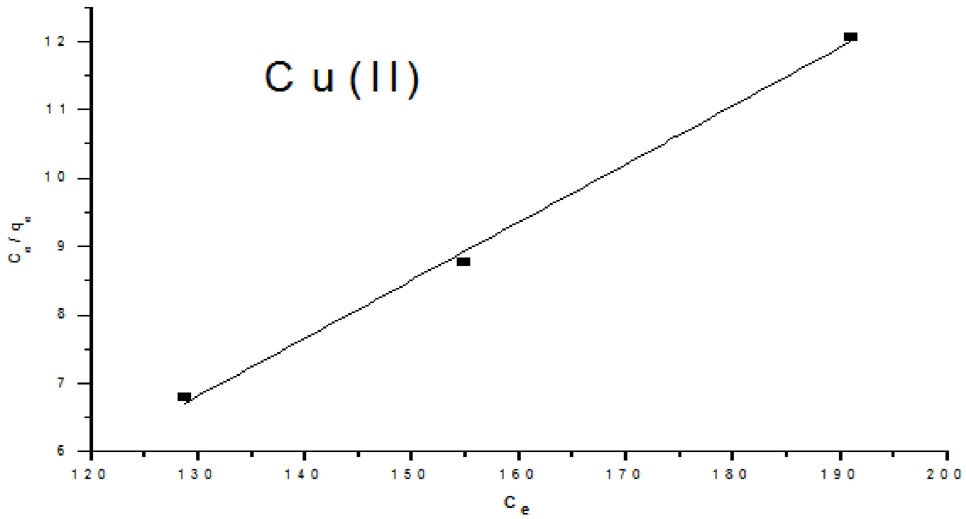

Fig. 2.a: Langmiur plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of H_3 PO_4 0.1M

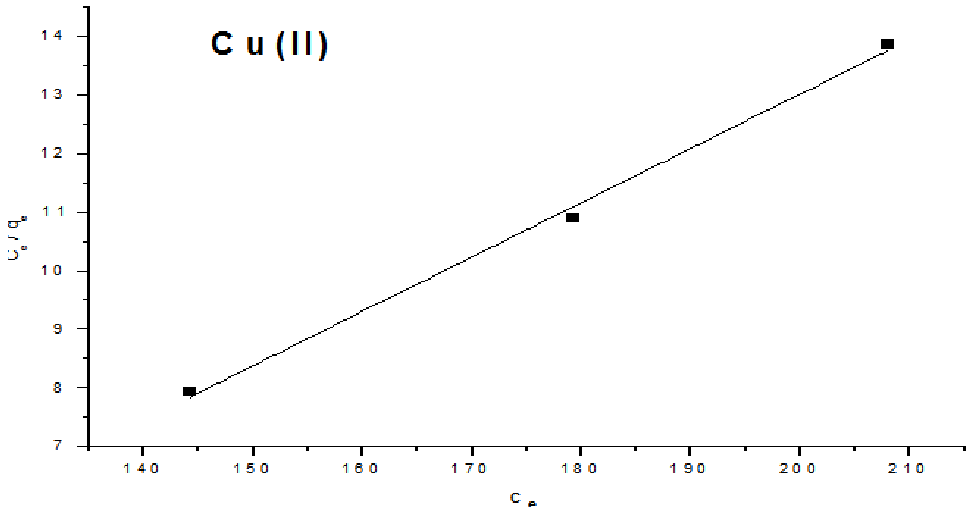

Fig. 2.b: Langmiur plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of H_2 SO_4 0.1M

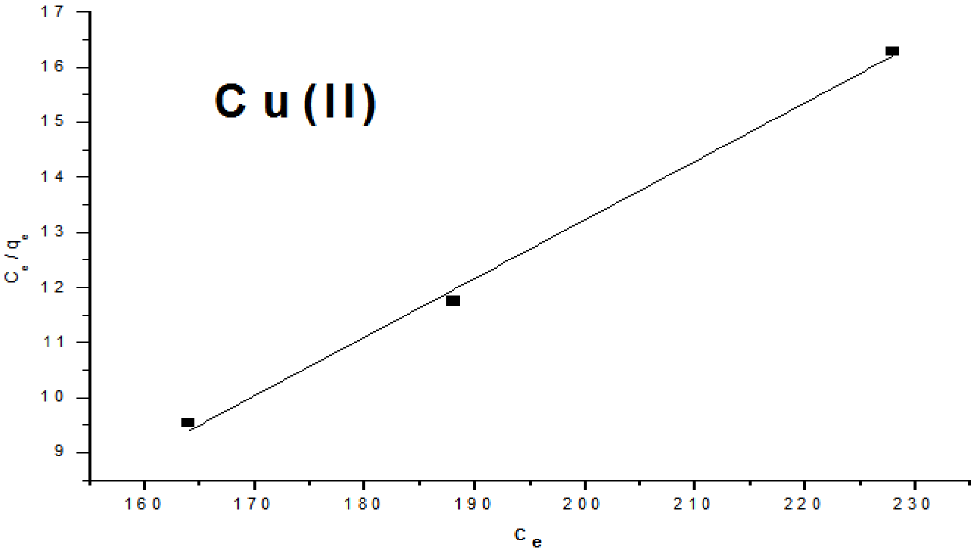

Fig. 2.c: Langmiur plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of HNO_3 0.1M

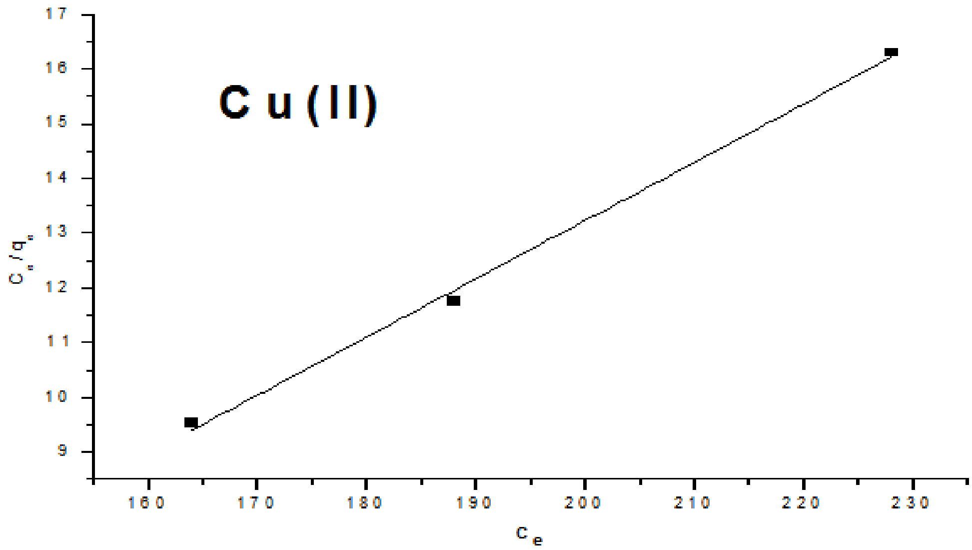

Fig. 2.d: Langmiur plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of HCl 0.1M

However, it is not consistent with the sequence of the stability constants (ln *K*) of these metal complexes with inorganic acids but rather their biodegradability. The degree of suitability of cation exchanger for the adsorption of metal complexes under investigations was also estimated from the values of the separation factor constant (R_L) according to the relation [9]. The R_L values for the studied $[Cu(IOA)]^{n+}$ complexes on Resinex^{TM} K-8Hare presented in(Table 1).

The Temkin and Pyzhev isotherm (Eq.1) for Cu(II) is shown in (Fig. 3. a, b, c and d) the related parameters are given in (Table 2) b_T related to heat of adsorption. Values lower than 8 indicate weak interaction between metal and the adsorbent. However, lower value of B_T for Cu(II) indicates presence of relatively weaker cohesive forces in between the adsorbent and copper ions. Process, as indicated by B_T values can be expressed as physical adsorption (Fritz and Pietrzyk, 1961).

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (1)$$

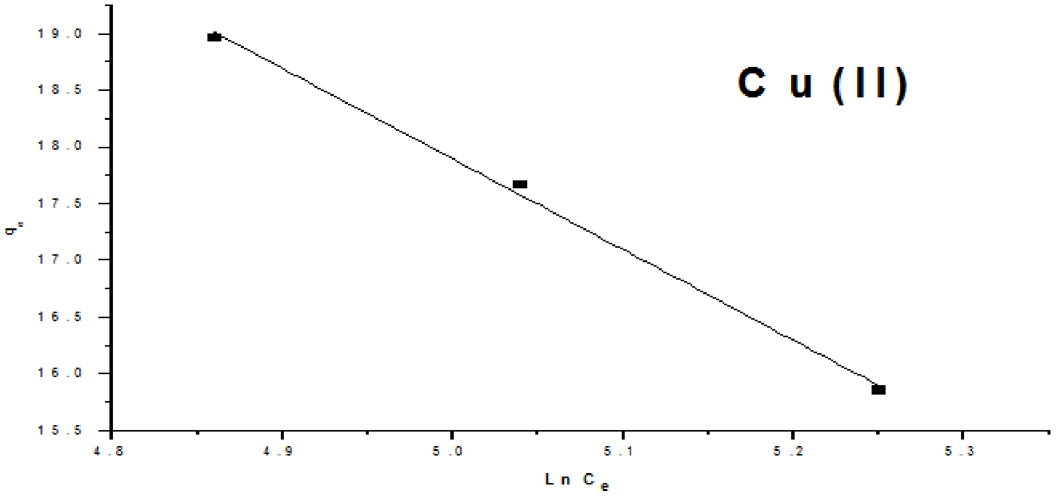

Fig. 3.a: Temkin plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of H_3PO_4 0.1M

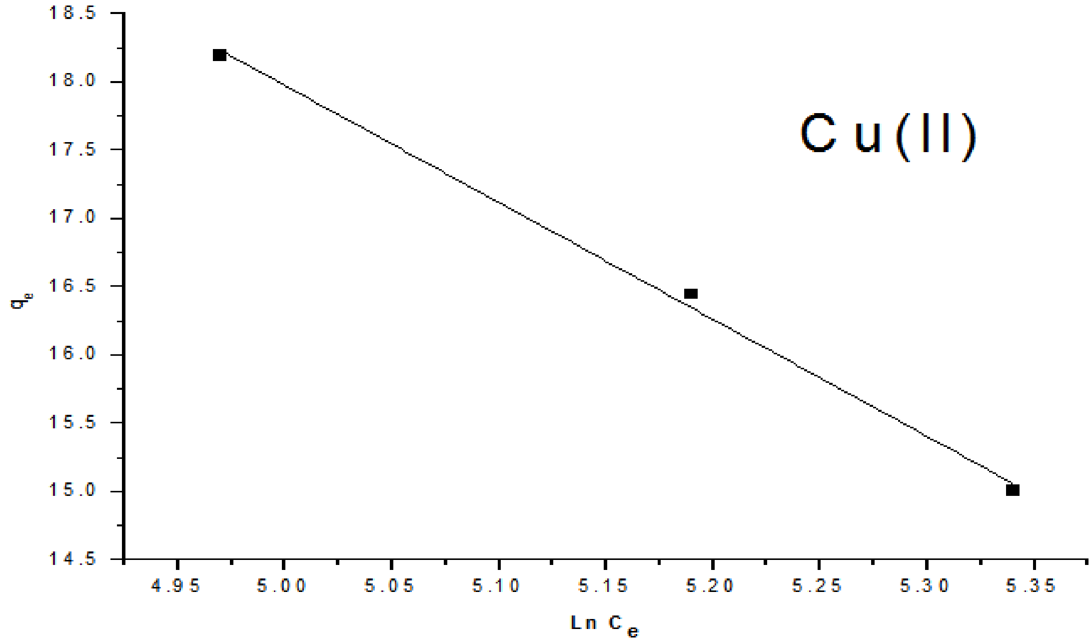

Fig. 3.b: Temkin plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of H_2SO_4 0.1M

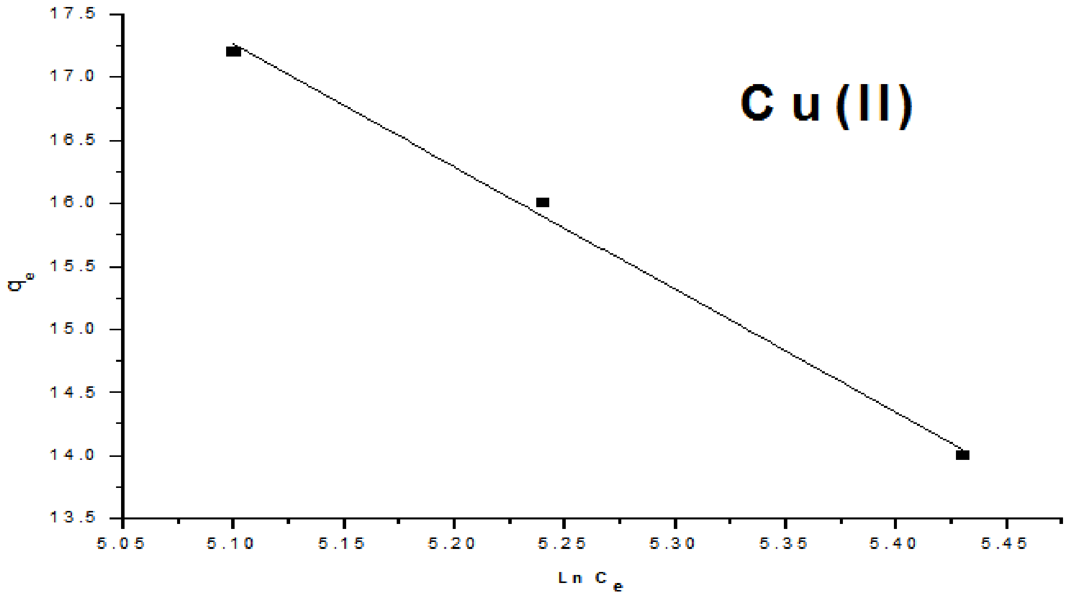

Fig. 3.c: Temkin plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of HNO_3 0.1M

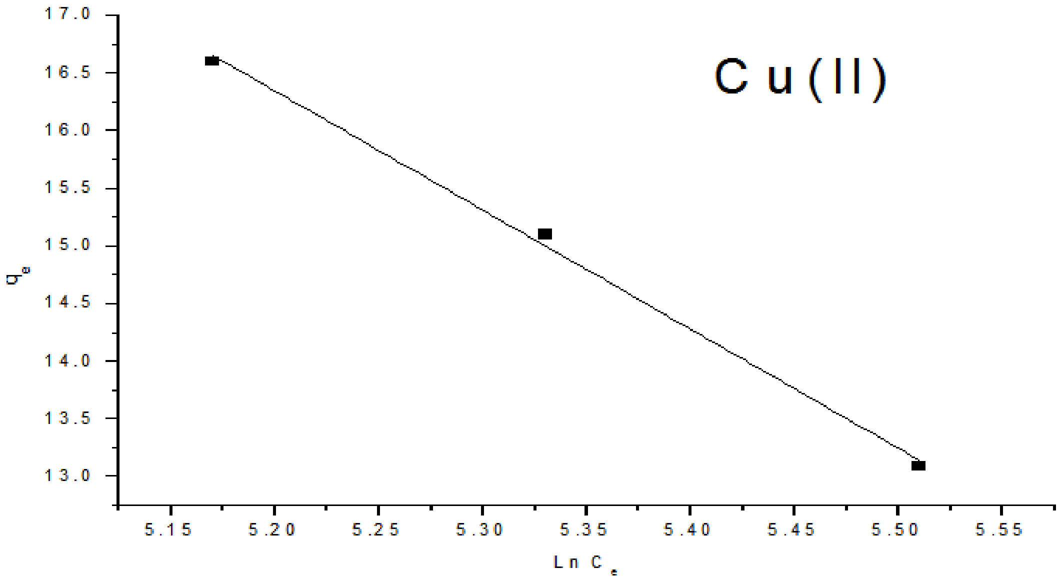

Fig. 3.d: Temkin plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of HCl 0.1M

In the present study, Dubinin-Radushkevich (D-R) isotherm constants (Eq. 2), monolayer capacity (X_m) and adsorption energy (β) are represented in (Fig. 4. a, b, c and d) and tabulated in (Table 2). The magnitude of β is used to determine the type of adsorption mechanism. When one mole of ions is transferred to adsorbent surface, its value is higher than 8.0 kJ/mol which indicates chemical adsorption. However, at lower 8.0 KJ/mol the adsorption processes are physical in nature (Li*et al*, 2008).

$$\log q_e = \log X_m - \beta \varepsilon^2 \qquad (2)$$

Where X_m is the Dubinin-Radushkevich monolayer capacity (mg/g), β is a constant related to adsorption energy, and $\mathcal{E}$ is the Polanyi potential [15].

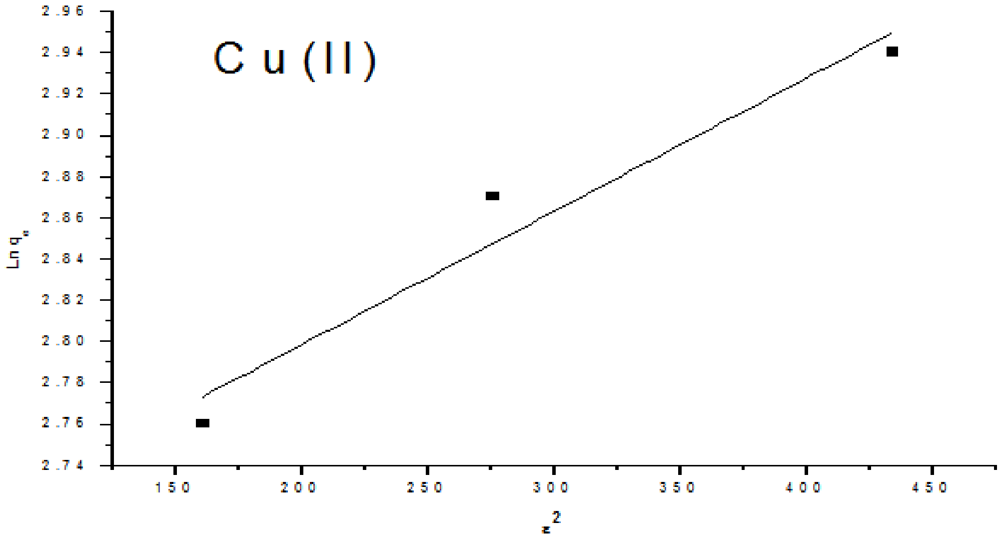

Fig. 4.a: D-R plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of $H_3 PO_4$ 0.1M

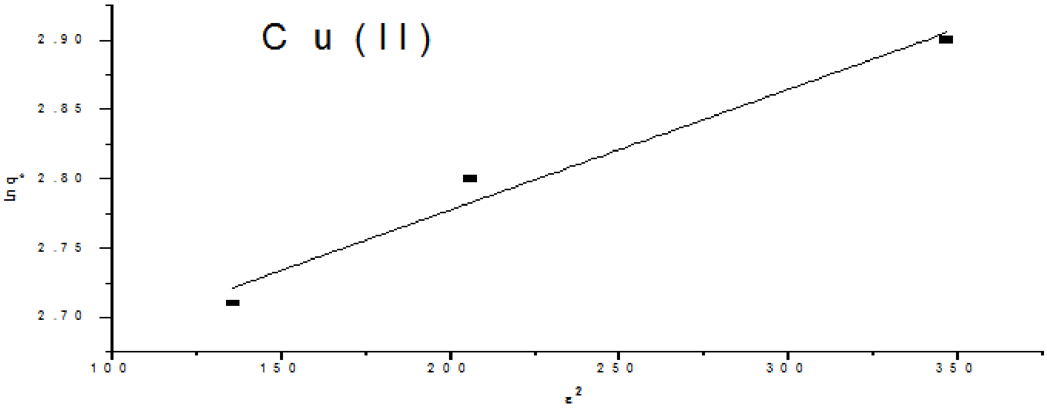

Fig. 4.b: D-R plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of $H_2 SO_4$ 0.1M

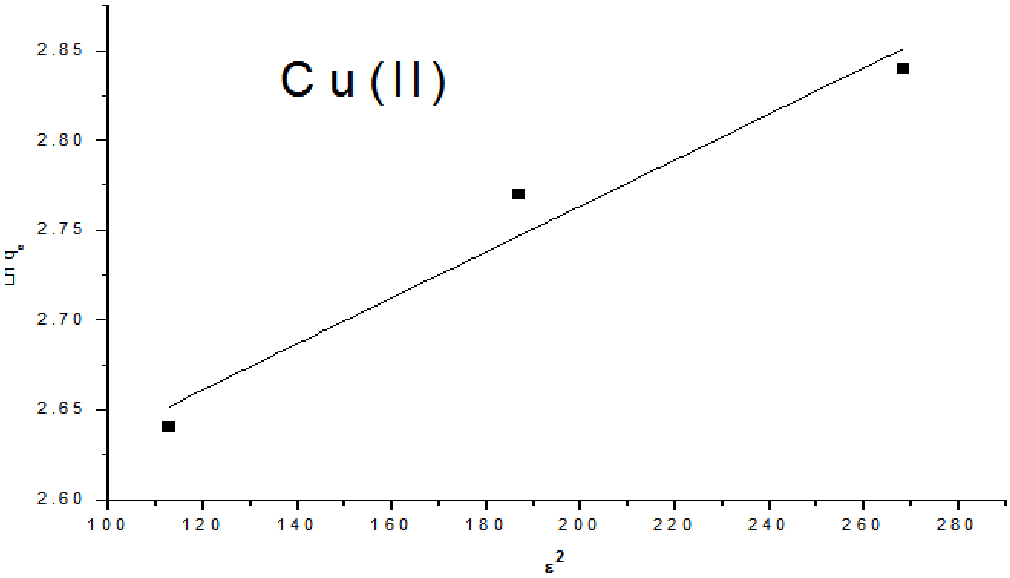

Fig. 4.c: D-R plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of HNO_3 0.1M

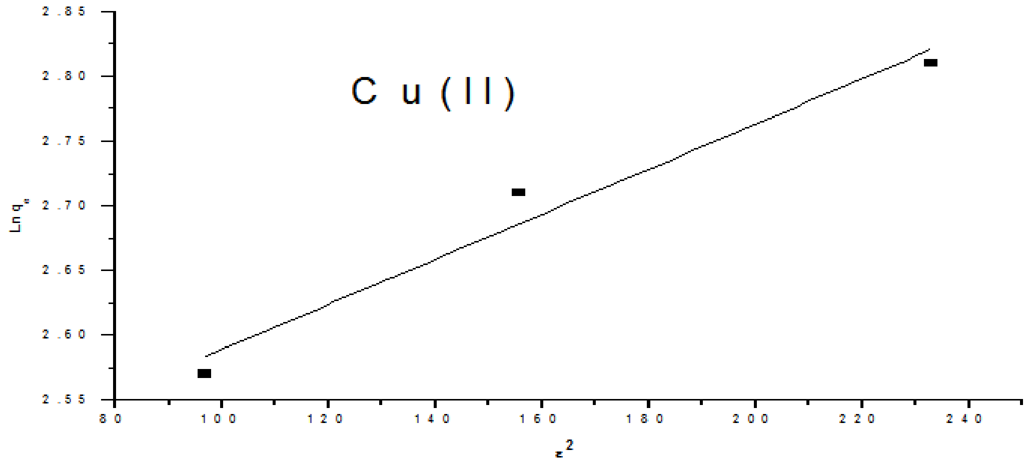

Fig. 4.d: D-R plot for the Cu(II) adsorption (8mm ol/L) by resinx K-8 in the presence of HCl 0.1M

(B)- Kinetics Modeling On Adsorption [16]:

In order to characterize the adsorption kinetics of the studied Resinex™ K-8H, adsorption experiments were carried out with single metal ion in inorganic acid solutions. According to the above presented assumption of complexation conditions, the cation exchange process of Cu(II) complexes in the Cu(II)–inorganic acid (phosphoric, sulfuric, nitric and hydrochloric acid) systems on Resinex™ K-8H strong acid cation exchange resin, can be as follows in (Eq. 3).

$$RSO_3^- H^+ \text{ (exchange)} + M^{2+} \text{ (aqueous)} \rightleftharpoons (RSO_3)_2^{2-}M + 2H^+ \quad (3)$$

Based on Eqs. (4) and (5) for the pseudo first-order and the pseudo second-order kinetic models (Figs. 5. a, b, c and d&6. a, b, c and d) it was also found in (Tables 1 and 2) that the values of k_1 were greater than k_2 values of the adsorption of $[Cu(IOA)]^{n+}$ on Resinex™ K-8H.

$$\text{Log } (q_e - q_t) = \log q_e - \frac{k1}{2.303} t \quad (4)$$

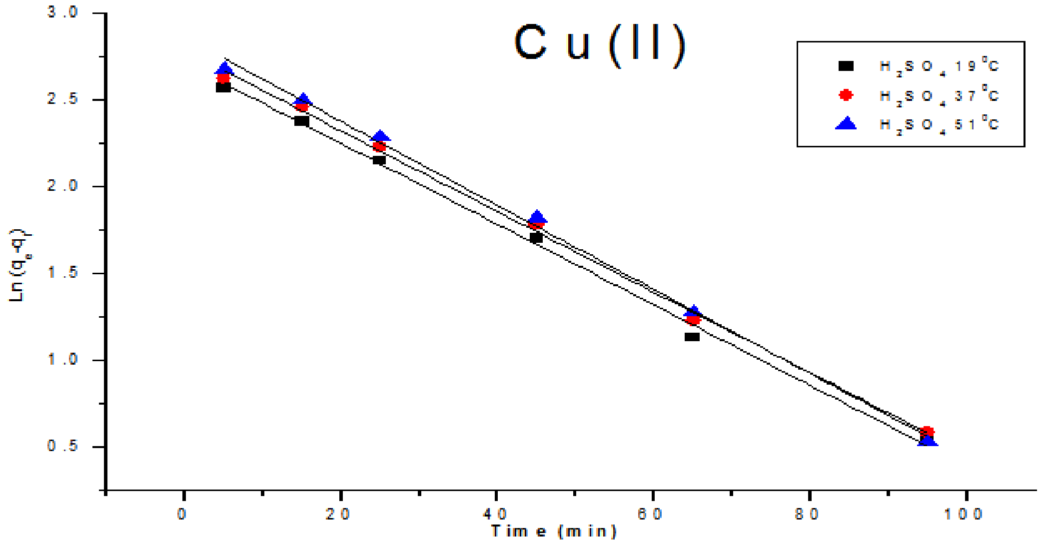

Fig. 5.a: Pseudo first order plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of H_3PO_4 0.1M at different temperatures.

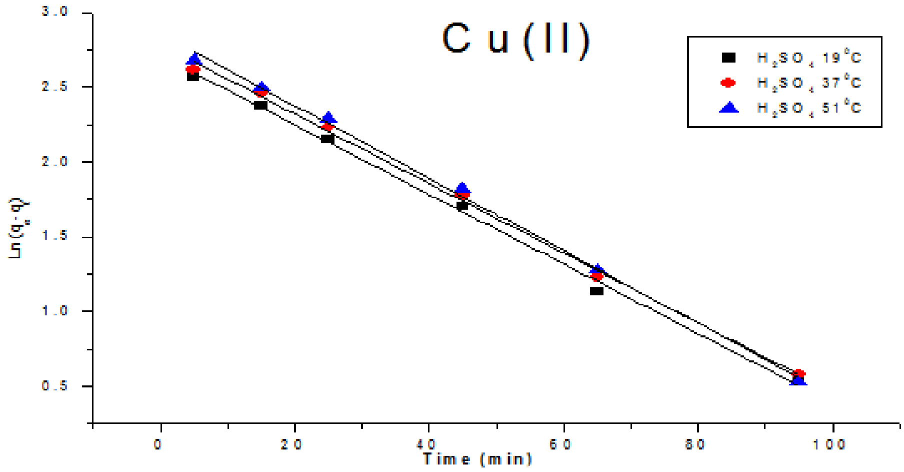

Fig. 5.b: Pseudo first order plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of H_2SO_4 0.1M at different temperatures.

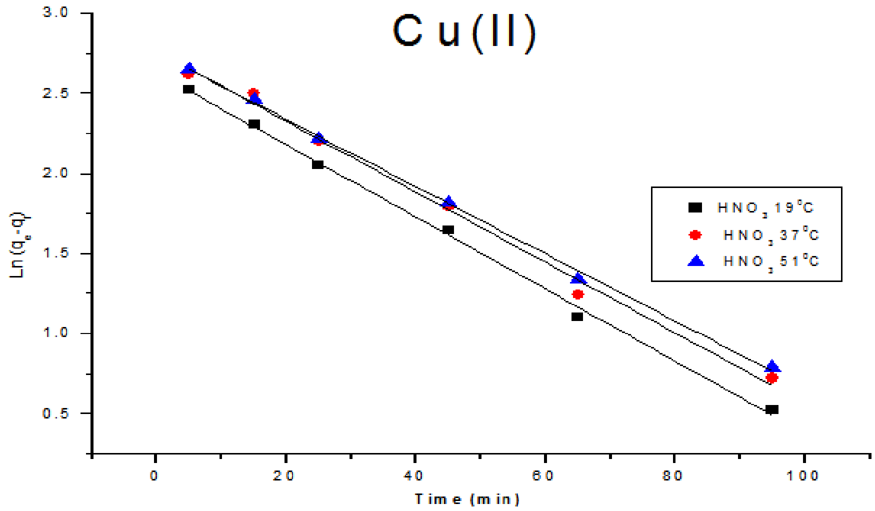

Fig. 5.c: Pseudo first order plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of HNO_3 0.1M at different temperatures.

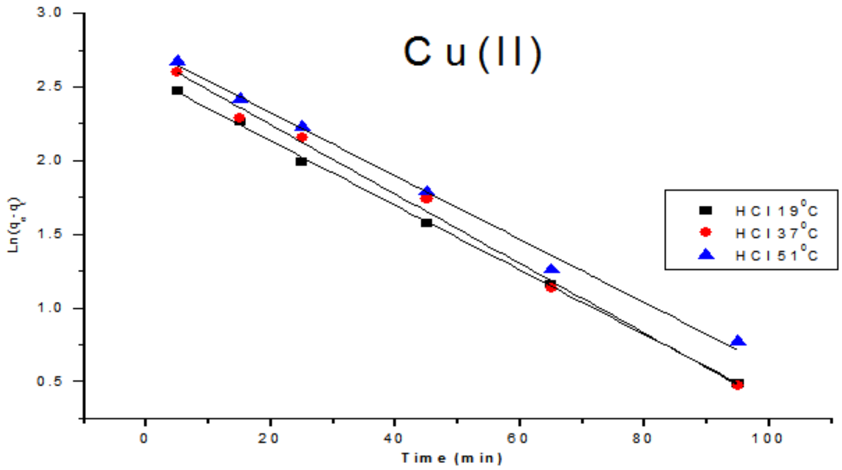

Fig. 5.d: Pseudo first order plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of HCl 0.1M at different temperatures.

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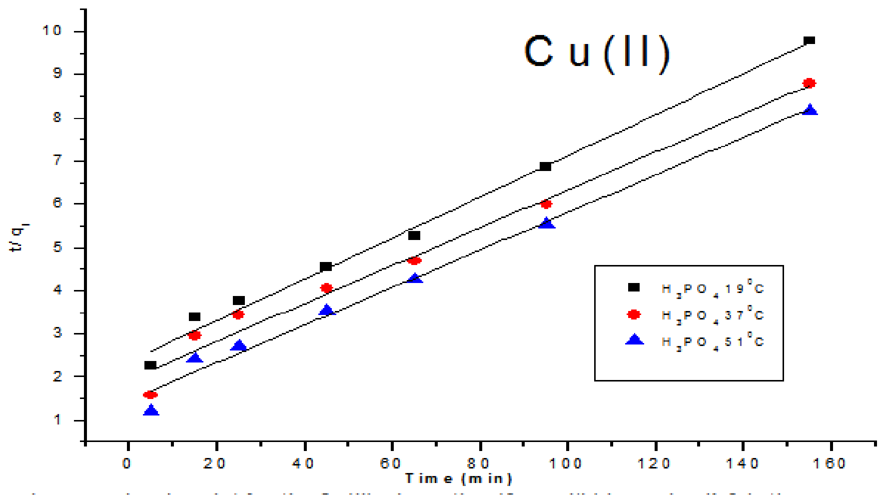

Fig. 6.a: Pseudo second order plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of H_3PO_4 0.1M at different temperatures.

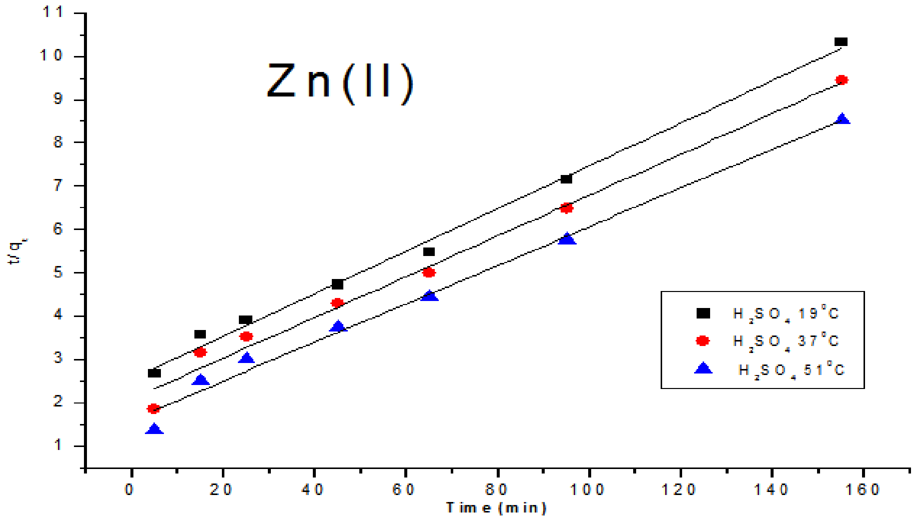

Fig. 6.b: Pseudo second order plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of H_2SO_4 0.1M at different temperatures.

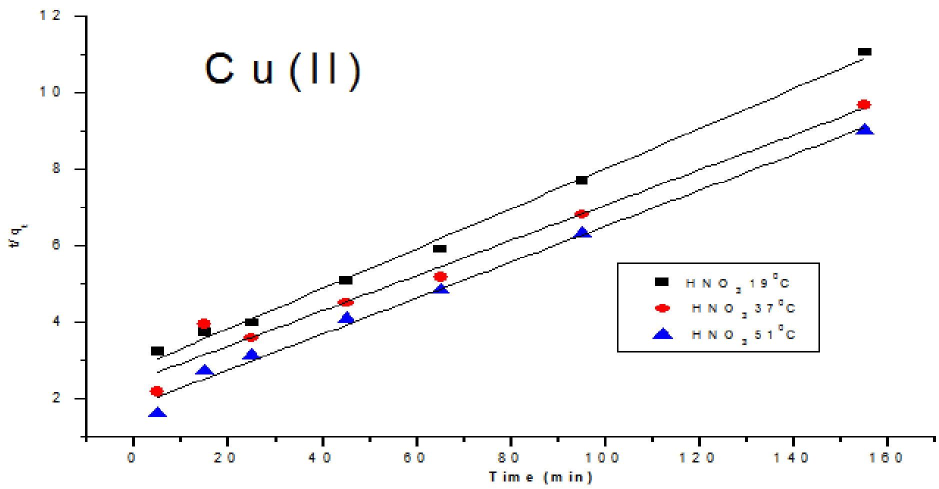

Fig. 6.c: Pseudo second order plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of HNO_3 0.1M at different temperatures.

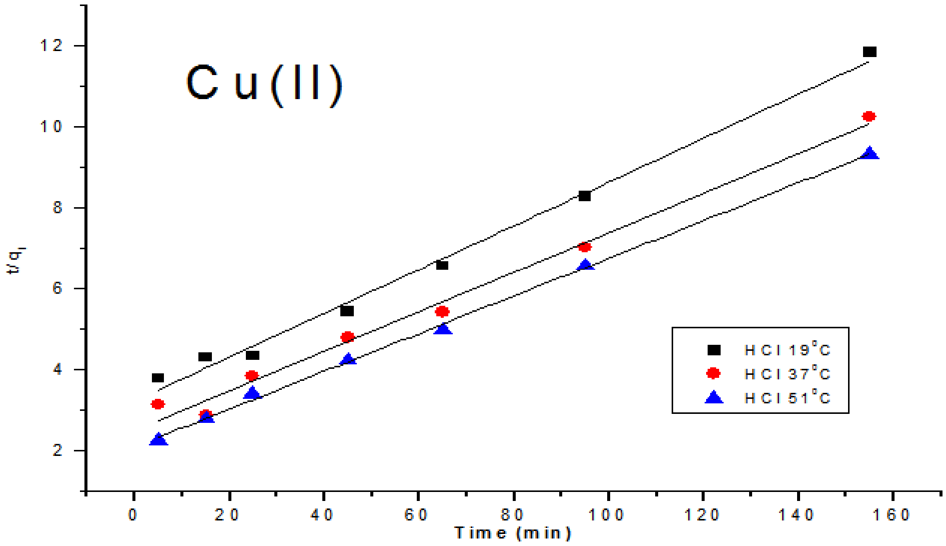

Fig. 6.d: Pseudo second order plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of HCl 0.1M at different temperatures.

The values of correlation coefficients (R^2) for the adsorption of $[Cu(IOA)]^{n+}$ complexes were equal to 0.997, 0.997, 0.997 and 0.999 for the pseudo first-order kinetic model and 0.991, 0.993, 0.995 and 0.991 for the pseudo first-order kinetic model, respectively as in (Figs. 6 a, b, c and d). The calculated data from the first-order equation are close to the experimental results (Table 1). Consequently, the pseudo first-order equation was selected as the most adequate to the model adsorption of Cu(II) complexes with inorganic acids.

As follows from the literature data other researchers also proposed the pseudo second-order kinetic model for describing the adsorption of toxic metal ions on the ion exchangers (Li*et al*, 2008), (Bulut and Tez, 2007), (Kołodyn, 2011) and (Saraswat *et al*, 1979).

According to the Weber and Morris model(Weber and Morris, 1963).It is possible to establish whether the adsorption is intraparticle diffusion or not. For this aim the Weber and Morris equation is used (Eq. 5).

$$q_t=k_{id}t^{0.5}+C \quad (5)$$

Where q_t is the amount adsorbed (mg/g) at time t.

In the presented study the k_{id} values were determined by the slopes of the straight-line portion of plots (Fig. 7. a, b, c and d). From these values, the contribution of the surface adsorption in the rate controlling step can be established. Moreover, the intercept of the plot reflects the boundary layer effect. Large values of the intercept indicate the contribution of the surface adsorption in the rate controlling step. It can be explained by low stable or degradable of these complexes.

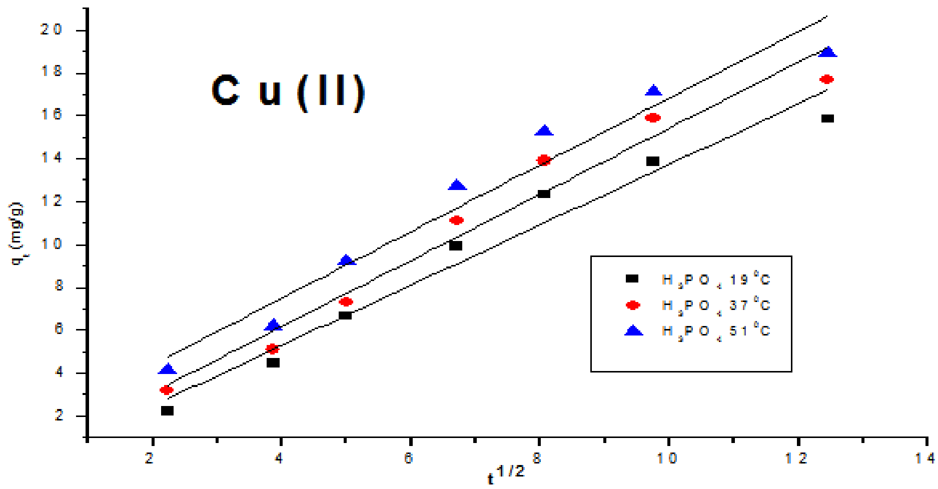

Fig. 7.a: Weber plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of H_3PO_4 0.11M at different temperatures.

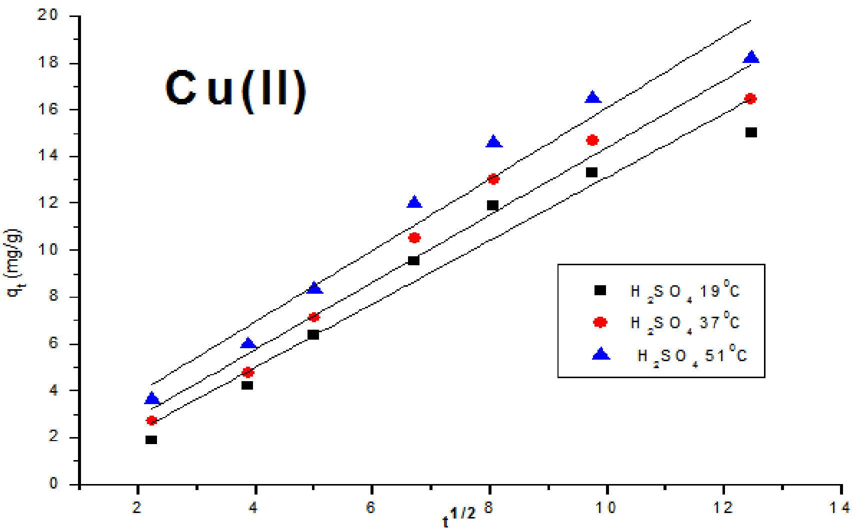

Fig. 7.b: Weber plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of H_2SO_4 0.1M at different temperatures.

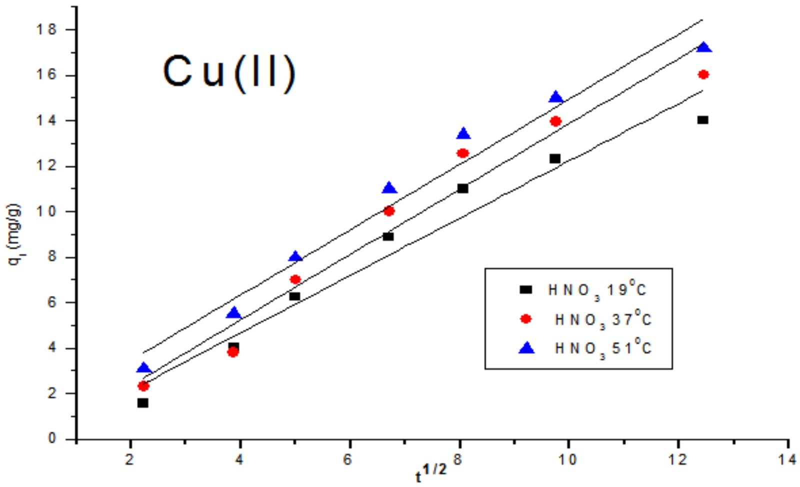

Fig. 7.c: Weber plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of HNO_3 0.1M at different temperatures.

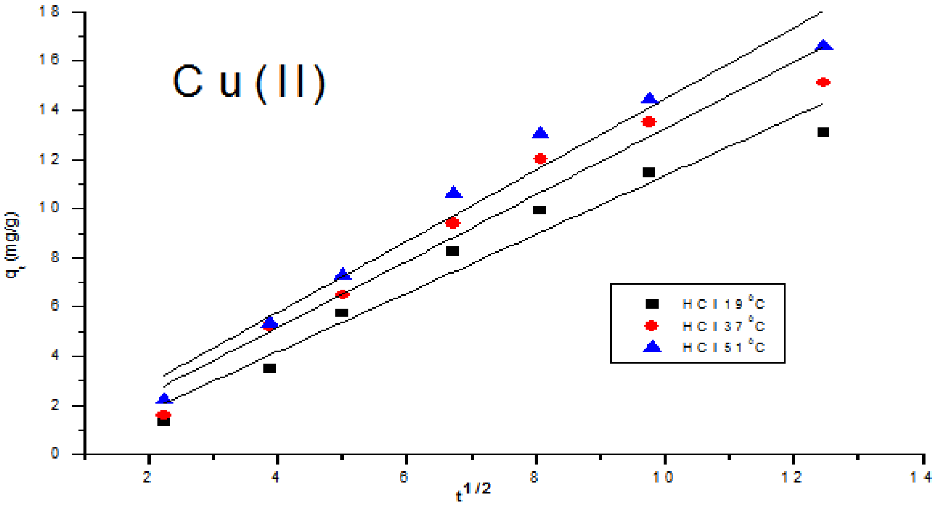

Fig. 7.d: Weber plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of HCl 0.1M at different temperatures.

(C)- Study The Effect Of Tempreture (19^0C, 37^0C and 51^0C).

The thermodynamic parameters(Enthalpy change (ΔH),Entropy change (ΔS)and Gibbs free energy change(ΔG)) for $[Cu(IOA)]^{n+}$complexes adsorption on (Fig. 48) can be calculated from Eqs. (1) and (6).

$$Ln(k)=ln(A) - (E_a/RT) \quad (6)$$

Where *(E_a)* is the activation energy of adsorption.

The increase in adsorption capacity of Resinex™ K-8H may be attributed to the enlargement of pore size or activation of the adsorbent surfaces (Fig. 8). The values of qe/ce (K_D) are also high at all temperatures and increase with the increase of temperature showing endothermic process.

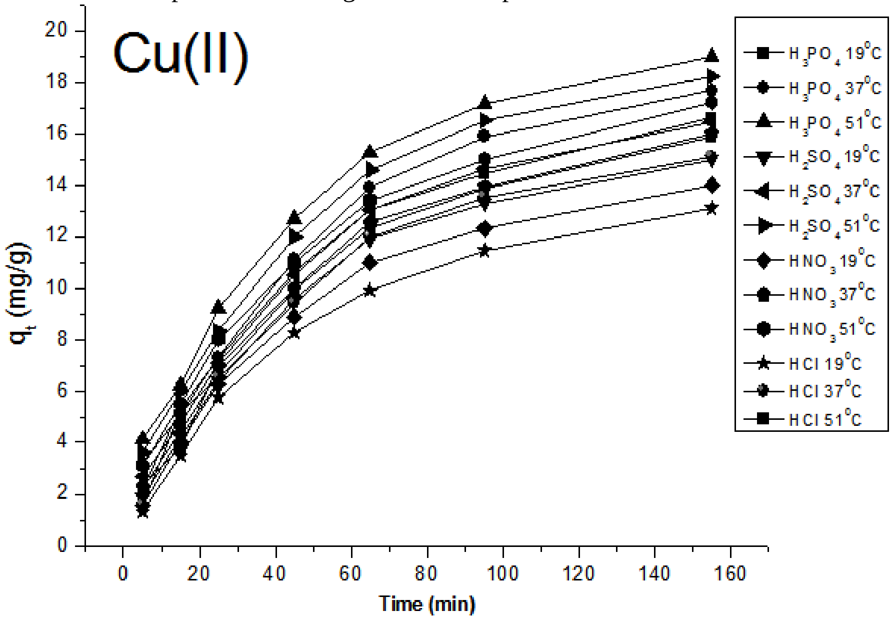

Fig. 8: Effect of different temperatures on the adsorption of Cu (II) 8mmol/L in the presence of Some inorganic acids.

The negativeGibbs free energy change(ΔG) values indicated that the adsorption of Cd(II) complexes on Resinex™ K-8H was thermodynamically spontaneous. In addition, the decrease in (ΔG) values with the increase in temperature shows that the adsorption was favourable at higher temperatures.The enthalpy and the entropy changesfor the adsorption process were obtained from the Van't Hoff equation (from ln K_D vs. $1/T$ plots) as shown in (Fig.9).

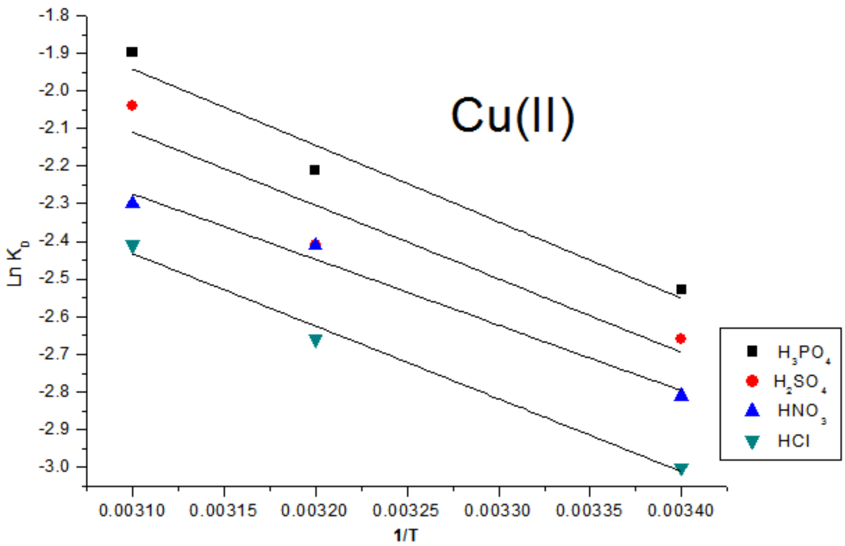

Fig. 9: Van't Hoff plot for the Cu (II) adsorption (8mmol/L) by resinx K-8 in the presence of inorganic acids at different temperatures.

The enthalpychanges (ΔH) for Resinex[TM] K-8H were 16.87, 16.21, 14.49 and 16.03 kJ/mol in presence of phosphoric, sulfuric, nitric and hydrochloric acid, respectively.

These values suggest that physical adsorption is predominant. The positive value indicates the endothermic nature of the adsorption process. The positive values of the entropy change (ΔS) show the affinity for $[M(IOA)]^{n+}$ complexes with the Resinex[TM] K-8H.

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